

UNIVERSITÉ D'ORLÉANS

ÉCOLE DOCTORALE ÉNERGIE, MATÉRIAUX, SCIENCES DE LA TERRE ET DE L'UNIVERS

Institut des Sciences de la Terre d'Orléans - ISTO

THÈSE présentée par :

Héctor Ricardo CAMPOS RODRÍGUEZ

soutenue le : 16 décembre 2024

pour obtenir le grade de : **Docteur de l'Université d'Orléans**

Discipline/ Spécialité : Sciences de la Terre / Métallogénie

Doctoral thesis in Economic Geology

Mafic magmatism and metasediments in the Central Iberian Zone, Spain: Towards a better understanding of the sources and mechanisms of Sb mineralization?

THÈSE dirigée par :

IACONO-MARZIANO Giada
TUDURI Johann
SIZARET Stanislas
POCHON Anthony

Chargée de recherche, CNRS
Ingénieur-géologue, HDR, BRGM
Professeur des Universités, Université d'Orléans
Co-encadrant, Ingénieur-chercheur, BRGM

RAPPORTEURS :

Sophie DECRÉE
Philippe BOULVAIS

Permanent Researcher, RBINS / Université Libre de Bruxelles (ULB)
Maître de Conférences, Université de Rennes 1

JURY :

DECREE Sophie
BOULVAIS Philippe
IACONO-MARZIANO Giada
HIGUERAS Pablo
PROUTEAU Gaëlle
SIZARET Stanislas

Présidente du jury, Permanent Researcher, RBINS / ULB
Maître de Conférences, Université de Rennes 1
Chargée de recherche, CNRS
Professor, Universidad de Castilla - La Mancha (UCLM)
Maître de Conférences, Université d'Orléans
Professeur des Universités, Université d'Orléans

INVITÉS :

TUDURI Johann
POCHON Anthony

Ingénieur-géologue, HDR, BRGM
Ingénieur-chercheur, BRGM

UNIVERSITÉ D'ORLÉANS

ÉCOLE DOCTORALE ÉNERGIE, MATÉRIAUX, SCIENCES DE LA TERRE ET DE L'UNIVERS

Institut des Sciences de la Terre d'Orléans - ISTO

THÈSE présentée par :

Héctor Ricardo CAMPOS RODRÍGUEZ

soutenue le : 16 décembre 2024

pour obtenir le grade de : **Docteur de l'Université d'Orléans**

Discipline/ Spécialité : Sciences de la Terre / Métallogénie

**Magmatisme mafique et métasédiments
dans la Zone-Centro-Ibérique, Espagne :
vers une meilleure compréhension des sources
et des mécanismes des minéralisations à Sb?**

THÈSE dirigée par :

IACONO-MARZIANO Giada
TUDURI Johann
SIZARET Stanislas
POCHON Anthony

Chargée de recherche, CNRS
Ingénieur-géologue, HDR, BRGM
Professeur des Universités, Université d'Orléans
Co-encadrant, Ingénieur-chercheur, BRGM

RAPPORTEURS :

Sophie DECRÉE
Philippe BOULVAIS

Permanent Researcher, RBINS / Université Libre de Bruxelles (ULB)
Maître de Conférences, Université de Rennes 1

JURY :

DECRÉE Sophie
BOULVAIS Philippe
IACONO-MARZIANO Giada
HIGUERAS Pablo
PROUTEAU Gaëlle
SIZARET Stanislas

Présidente du jury, Permanent Researcher, RBINS / ULB
Maître de Conférences, Université de Rennes 1
Chargée de recherche, CNRS
Professor, Universidad de Castilla - La Mancha (UCLM)
Maître de Conférences, Université d'Orléans
Professeur des Universités, Université d'Orléans

INVITÉS :

TUDURI Johann
POCHON Anthony

Ingénieur-géologue, HDR, BRGM
Ingénieur-chercheur, BRGM

**MAFIC MAGMATISM AND METASEDIMENTS IN THE
CENTRAL IBERIAN ZONE, SPAIN: TOWARDS A BETTER
UNDERSTANDING OF THE SOURCES AND MECHANISMS
OF Sb MINERALIZATION?**

This PhD thesis is respectfully dedicated to the memory of Dr. Eric Gloaguen (BRGM), who directed this work and the AUREOLE project from its outset. He provided invaluable guidance and support until his untimely passing in September 2024.

A mi Madre y a mi Padre, Mariela y Héctor Aníbal.

A Camille Ferrand.

ACKNOWLEDGEMENTS

Y así acaba todo, desaparecimos en una efímera danza en un mar de ilusiones, desaparecimos en un añorado mar de sueños que quedaran grabados en los rincones más profundos del alma.

A whole adventure and odyssey just ended, these years of PhD were a great journey of professional and personal growth. I have been very fortunate to have many invaluable people involved in this process, to all of them my most sincere gratitude.

First of all, I would like to thank my PhD thesis directors starting with Eric Gloaguen, to whom this work is respectfully dedicated. Eric was one of the masterminds behind the AUREOLE project and, despite all of the difficulties in his life, he stayed and worked hardly from the very beginning until his last breath. It was an honor to work with him, with such a curious and passionate mind to whom geology was one of his main motivations. To Eric and his family, to his memory, to his scientific and human legacy.

Grazie mille to my PhD thesis director Giada Iacono-Marziano for her invaluable support, for giving me a reason to believe in this work at the hardest moments, for her advices and her humanism. Mi ritengo fortunato per aver avuto l'opportunità di lavorare con una persona così eccezionale e grande scienziata. Le parole non bastano per esprimere la mia riconoscenza. Ti sono e sarò eternamente grato. Grazie Giada.

Un grand merci to my PhD thesis director Johann Tuduri, a brilliant geologist. In spite of the difficulties, he always managed to steer this project in the right direction by giving invaluable advice that helped this thesis to see a proper end. Thank you for all of the effort and the patience that you put into this project.

Thanks to Stanislas Sizaret (PhD thesis director) and to Anthony Pochon (PhD co-supervisor) for guiding this work from the beginning to the end and beyond. Thank you for your advices, invaluable discussions and for helping me along the way.

Je tiens à exprimer ma profonde gratitude et mon respect le plus sincère à tous ceux qui ont dirigé cette thèse. Le succès de ce projet est indubitablement lié à vos efforts incommensurables.

To the members of the jury-Sophie Decrée, Philippe Boulvais, Giada Iacono-Marziano, Pablo Higuera, Gaëlle Prouteau and Stanislas Sizaret- I extend my profound gratitude for your

meticulous review of this work. Your insightful observations and constructive feedback have significantly enhanced the quality of this thesis.

Mi más profundo agradecimiento al equipo español del proyecto AUREOLE. Gracias a Pablo Higuera, Saturnino Lorenzo y José María Esbri por todos los consejos, discusiones y por haber coordinado una campaña de muestreo y exploración en España que ha sido todo un éxito. Gracias por haber sido parte de esta tesis doctoral.

Kiitos totales to my close friend and the very definition of “Sisu” Ville Virtanen. Kiitos for your interest and commitment in this thesis, for always supporting me, for your advices, for all the motivation, the good moments and for giving me the opportunity to discover the geology of Suomi (Finland). Kippis to you, always remembering “Pelikaani lens turbiiniin Punaselle kaikki puhelin kii”. Looking forward to having a good kalja in Piano or Tinatuoppi. Gracias Ville y Milla por haber estado presentes en este camino de vida.

Gracias a mi Madre Mariela, a mi Padre Héctor Aníbal, a mis hermanas Adriana y Juliana, a toda mi familia, gracias a ti Camille Ferrand. A ustedes, mi eterno agradecimiento por el apoyo incondicional durante todos estos años, por haber sido mi motor, mi motivación y mi paz. Este Doctorado también es de ustedes.

A Gabriel (que pasa mi rey), Malcom (¡el sobreviviente con Yandel!), a los hijos de Orléans (Tania “Campix, no me da la vida”, Federica x 2-the goulash revenge, Elena, Monica-Claudio’s Carbonara is the best, costeño, Viktor-Slatkiću, PY, Matejta-el deseo de la vida, Alessandra and Nastassja-questa vita è troppo corta, Diletta, Kristijan-Slatkiću, Miles). A todos ustedes gracias por estar siempre ahí, por todos los buenos momentos, las risas, los bailes, las tristezas, las locuras, por el buen chisme y por toda la alegría que han traído a mi vida.

To the band Matices. As we all know, music is life. It makes us feel and breathe. It is a delicate and peaceful path where we can connect with the deepest parts of our souls. Thanks to Julie, Khadija, Yann, Mika, Claudio and Alex. The music sounds better with you!

To friends and colleagues at ISTO-BRGM and ADSO! Camille (c’est ton tour!), Bryan (Breizh!), FX, Nathan, Francois, Bence, el comandante, Gina, Fabien, Tom, Vivi, Walid, Audrey, Gaetan, Jack, Mathieu, Cordula, Carolina, Benjamin, Pauline, and those I forgot to mention. This journey was easier and funnier because you were part of it. Remember Mont Fuji!

To Olivier, Marie-France, Ida, Patricia, Philippe, Sylvain, Fabienne, Carole, Nathalie (x2), Marlène, Samira. Merci pour toute votre aide durant cette thèse.

Many thanks to all of those who were directly/indirectly involved in this process since my BSc and MSc at the Universidad Nacional de Colombia and the Université de Rennes: Professor Thomas Cramer, members of the Research Group in Economic Geology and Applied Mineralogy (GEGEMA), members of the SGA Student Chapter Colombia-Bogotá, Philippe Boulvais, Yannick Branquet, Pierre Gautier, Marc Poujol and Rémi Coltat.

Gracias a mi gente “porque un amigo es una luz...” haha: Aziz, Andrés, Nicolás, Mache, Martha, Joshe, David, Chucho, Fabio. Amistad pura y sincera, siempre dando la vida. Todos ustedes han estado presentes desde siempre y desde mucho antes que este viaje comenzara.

Un grand merci à toute la team des Enfants Terribles et du Kaprice ! Elenita et Lisa vous êtes le soleil d’Orléans. Al parcerito Felipe (¡el desorden incondicional!), a Alex (¡que tonto eres!), Houssene, Amelie, Marine, Jules, Maina, Maëna, Chris, Océane, Tandi, Elise, Margot, Benito del Barrio...

"No sólo no hubiéramos sido nada sin ustedes, sino con toda la gente que estuvo a nuestro alrededor desde el comienzo. Algunos siguen hasta hoy... **¡GRACIAS TOTALES!**"

Gustavo Cerati, último concierto de Soda Stereo-20 de septiembre de 1997.

This work was funded by the ANR (ANR-19-MIN2-0002-01), the AEI (MICIU/AEI/REF.: PCI2019-103779) and author's institutions in the framework of the ERA-MIN2 AUREOLE project (<https://aureole.brgm.fr>), as well as by LabEx VOLTAIRE (ANR-10-LABX-100-01), EquipEx PLANEX (ANR-11-EQPX- 0036) and Project SBPLY/17/180501/000273, Consejería de Educación, Regional Government of Castilla-La Mancha, Spain. We thank the company Villar del Rey Natural Stones in the Extremadura Region for their support by letting us work and sample in their quarries. We appreciate the valuable discussions with Dr. David Orejana García (Universidad Complutense de Madrid, Spain) Dr. Jérémie Melleton (BRGM, France) and Dr. Bryan Cochelin (ISTO, France).

ABSTRACT

This work studies the possible sources and mechanisms responsible for the formation of Sb deposits in the Central Iberian Zone (CIZ) by using the mineral systems concept. This approach sees the mineral deposits as a combination of several geological processes occurring at different time and space, offering more predictivity power compared to the classic ore deposit models (McCuaig et al., 2010; McCuaig & Hronsky, 2014).

The thesis focuses on the geochemical and geochronological characterization of mafic intrusions, along with the geochemical and paleothermal characterization of metasediments in the CIZ. Five areas within the CIZ are covered: the Guadalmez syncline (GS), the Almadén syncline (AS), the Codosera syncline (CS), La Susana Mine (SUM) and La Nazarena Mine (NZM).

The geochronological data show that the mafic rocks from the NZM were emplaced during the Lower Ordovician. The alkaline dolerites from the GS, AS and SUM were emplaced during at least two events, the first one at the end of the Silurian, and the second one during the upper Devonian to Carboniferous. The mafic rocks from the CS present a transitional affinity and were emplaced during the Carboniferous, either as a single major event around 350Ma or as a series of discrete events between 359 ± 22 Ma and 332 ± 17 Ma. The mafic suites of the AS, GS, SUM and NZM show no evidence of crustal contamination, whereas the rocks from the CS may have experienced slight crustal contamination. All studied rocks show an enrichment in LREE, high $Gd/Yb > 2.9$ and $Ti/Y > 554$ ratios, suggesting the presence of residual garnet in the mantle source. The source of these mafic rocks is therefore likely to be a hydrous metasomatized mantle bearing garnet. A temporal link between the mafic rocks from the CIZ and those from the Armorican Massif is proposed, suggesting a major mafic magmatic event at *ca.* 360 Ma.

Abstract

The study of the metasedimentary sequences of the CS shows that the thermal changes are dependent on the age of the metasediments and their sampling location within the structure. The measured temperatures of $\approx 210\text{-}370^{\circ}\text{C}$, suggest low-grade metamorphism. The geochemical data show large heterogeneities in terms of major elements, S and Sb contents, with significant enrichment in Sb within the Lower Carboniferous rocks of the Gévora Formation (up to >250 ppm Sb).

Two main possible sources and mechanisms could be related to the formation of Sb deposits in the CIZ, these include the (i) magmatic degassing of mafic intrusions and the (ii) devolatilization of the metasedimentary sequences. (i) Sb deposits in the CIZ are spatially associated to mafic rocks, these mafic rocks are synchronous with mafic intrusions and Sb deposits in the Armorican Massif. In this case, primary fluid inclusions in ilmenite, bearing Sb, Cu, Sn, Mo, W and Pb, would suggest the occurrence of a metal and metalloid-enriched fluid phase in the mafic magma at the time of the ilmenite crystallization. (ii) On the other hand, geochemical data indicate Sb enrichment within the metasedimentary rocks, suggesting that Sb may have been mobilized within the contact aureoles of the mafic sills, during thermal devolatilization.

More detailed studies are needed to quantify the contribution of these two sources and processes to the formation of Sb-mineralization in the CIZ.

RÉSUMÉ ÉTENDU

Le concept de systèmes minéraux a été développé au cours des vingt dernières années pour comprendre la formation des gisements minéraux comme étant une combinaison de plusieurs processus géologiques se produisant à différents moments et dans différents espaces (Goldfarb et al., 2010; Groves et al., 2005; Kerrich et al., 2005; Knox-Robinson & Wyborn, 1997; McCuaig et al., 2010; McCuaig & Hronsky, 2014; Wyborn et al., 1994). Cette approche conçoit les gisements minéraux comme des systèmes critiques auto-organisés et le point de convergence de régimes de masse et d'énergie de grande ampleur (McCuaig & Hronsky, 2014). Afin de créer l'un de ces systèmes complexes, il est nécessaire de concentrer des grandes quantités de métaux dans des volumes réduits de roche par des flux advectifs de masse, d'énergie et de fluides à grande échelle, avec l'implication de barrières de seuil pour empêcher l'énergie de se dissiper (Kerrich, 1983; McCuaig et al., 2010; McCuaig & Hronsky, 2014). Cela implique la prise en compte d'un grand nombre de processus à une échelle régionale, du camp et de gisement (McCuaig & Hronsky, 2014). La notion de système minéraux repose sur quatre éléments clés indispensables à la formation et à l'évolution des gisements minéraux, à savoir l'architecture de la lithosphère, une géodynamique favorable, la fertilité et la préservation des gisements (McCuaig et al., 2010; McCuaig & Hronsky, 2014). Cette approche holistique et multi-échelle offre une meilleure capacité prédictive comparée aux modèles classiques de gisements minéraux (McCuaig et al., 2010; McCuaig & Hronsky, 2014). La plupart de ces modèles classiques ont été conçus pour l'étude de la minéralisation à l'échelle du gisement (McCuaig et al., 2010; McCuaig & Hronsky, 2014). Ils sont toutefois soumis à certaines limites représentées par une diminution constatée de l'efficacité des processus d'exploration, qui a

entraîné une diminution correspondante de la découverte de nouveaux gisements minéraux (McCuaig & Hronsky, 2014; McKeith et al., 2010).

En ce qui concerne les gisements à Sb dans des domaines équivalents des grands orogènes (tels que l'Arc Ibéro-Armoricain de la Chaîne Varisque), l'approche des systèmes minéraux semble très appropriée pour étudier les sources et les processus impliqués dans leur formation à l'échelle continentale, à l'échelle du camp et à l'échelle des différents gisements. L'Arc ibéro-armoricain héberge plusieurs gisements à Sb (généralement associés au $\text{Au}\pm\text{Hg}\pm\text{W}\pm\text{As}\pm\text{Pb}$) et constitue la plus importante macrostructure varisque, incluant les Massifs Armoricaïn et Ibérique (Weil et al., 2010). En termes d'antimoine, le Massif Armoricaïn et la Zone-Centro-Ibérique (CIZ) du Massif Ibérique ont été les provinces métallogéniques à Sb les plus importantes en France, en Espagne et au Portugal au cours du 20^{ème} siècle (Guilloard, 2009; Gumiel, 1982; Gumiel & Arribas, 1987).

Différents modèles génétiques ont été proposés afin d'expliquer la formation des gisements à Sb dans l'Arc Ibéro-Armoricain (Massif Armoricaïn et CIZ). Parmi ces modèles, certains proposent une source crustale métamorphique des fluides minéralisateurs (*e.g.* 'Or 300 event'-Orogenic gold model, see Chapter 1: Bouchot et al., 2005; Munoz et al., 1992) alors que d'autres favorisent des sources magmatiques associées à des grandes intrusions felsiques (Chauris & Marcoux, 1994; Couto et al., 1990; Fouquet, 1980; Marcoux et al., 1984; Ortega et al., 1996; Ortega & Vindel, 1995; Serment, 1978). Les deux types de modèles sont associés à des événements extensionnels ayant eu lieu à la fin de l'orogénèse Varisque vers 300 Ma (Bouchot et al., 2005; Chauris & Marcoux, 1994; Couto et al., 1990; Fouquet, 1980; Marcoux et al., 1984; Munoz et al., 1992; Ortega et al., 1996; Ortega & Vindel, 1995; Serment, 1978). La participation d'une activité exhalative hydrothermale liée au volcanisme mafique a aussi été proposée afin d'expliquer la formation des gisements à Hg de classe mondiale de la région d'Almadén (Higueras, 1995; Higueras et al., 2000, 2013; Higueras & Oyarzun, 2005; Palero-

Fernández et al., 2015) et de certains gisements à Sb dans le CIZ (Arribas & Gumiel, 1984; Gumiel, 1982; Gumiel & Arribas, 1987). Des études plus récentes ont suggéré un lien spatial, temporel et potentiellement génétique entre des gisements à Sb et un magmatisme mafique à 360Ma dans le Massif armoricain (Pochon, 2018; Pochon et al., 2016 a, b, 2018, 2019, 2023, 2024).

A partir de l'approche des systèmes minéraux, qui perçoit les gisements minéraux comme une petite pièce d'un ensemble plus vaste de processus géologiques (McCuaig & Hronsky, 2014) et, les corrélations entre le Massif Ibérique et Armoricain (Arc Ibéro-Armoricain), peut-on transposer dans la CIZ certains des processus géologiques et des sources proposés pour la formation des gisements à Sb dans le Massif Armoricain ? Pour cela, il faut répondre aux questions suivantes :

- 1- Existe-t-il un lien entre le magmatisme mafique et des minéralisations à Sb dans la CIZ à 360Ma ?
- 2- Existe-t-il un lien entre Sb et métasédiments, impliquant une source métamorphique (modèle Or orogénique) dans la CIZ ?
- 3- A échelle régionale et du camp, quelles sont les sources possibles responsables de la formation des gisements à Sb dans la CIZ ?

L'objectif de cette thèse est de présenter de nouvelles perspectives sur les processus et les sources potentielles d'antimoine (Sb) dans la CIZ à échelle continentale (Arc Ibéro-Armoricain), de province (CIZ) et de district (zones d'étude). Ce travail emploie le concept de Systèmes Minéraux pour permettre une compréhension plus complète des critères cartographiques permettant de cibler des gisements à Sb. Cette étude se focalise sur cinq zones de la CIZ : le synclinal de Codosera (CS), le synclinal d'Almadén (AS), le synclinal de Guadalmez, la mine de la Susana (SUM) et la mine de Nazarena (NZM). Le CS comprend une

séquence métasédimentaire paléozoïque hébergeant le plus grand essaim de sills mafiques signalé dans le Massif Ibérique (López-Moro et al., 2007, 2020a) et le plus grand district à Sb d'Espagne (Gumiel & Arribas, 1987). L'AS abrite le gisement de classe mondiale à Hg d'Almadén (Hall et al., 1997; Higuera et al., 1995, 2013; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009) tandis que le GS abrite plusieurs occurrences et minéralisations à Sb (Barquero et al., 2022; Lorenzo Álvarez et al., 1995). Ainsi que le CS, l'AS et le GS sont constitués d'une séquence métasédimentaire paléozoïque (Lorenzo Álvarez et al., 1995). Les deux autres sites, correspondant au SUM et au NZM, présentent des occurrences à Sb et des corps mafiques encaissés dans des séquences métasédimentaires précambriennes-cambriennes et paléozoïques (Gumiel, 1982).

MAGMATISME MAFIQUE DANS LA CIZ

La mise en place des sills mafiques du GS, de l'AS, du CS, de la NZM et de la SUM s'échelonne sur plus de 200 Ma. Les données géochronologiques de cette étude identifient au moins quatre événements magmatiques distincts : i) le premier a eu lieu vers 480 Ma dans la NZM, et coïncide avec le début de l'ouverture de l'océan Rhéique signalé à l'Ordovicien inférieur (ca. 477 Ma; Orejana et al., 2017 and references therein); ii) le deuxième a eu lieu à environ 420 Ma dans le GS, et coïncide avec la phase finale de l'ouverture de l'océan Rhéique pendant le Silurien au Dévonien inférieur (ca. 430-415 Ma; Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012); iii) le troisième, survenu entre 387 ± 18 Ma et 360 ± 22 Ma au SUM, GS et AS ; iv) et le dernier au CS se produisant entre 359 ± 21 Ma et 332 ± 17 Ma. Les troisième et quatrième événements (du Dévonien inférieur au Carbonifère) sont synchrones avec la subduction/fermeture de l'océan Rhéique et le début de l'orogénie Varisque, les deux événements étant signalés entre 415 Ma- 360 Ma (Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012). Au cours du Dévonien supérieur et du début du Carbonifère, un cadre géodynamique extensionnel a été mis en place dans la CIZ au début de l'orogénie Varisque.

Durant cette période, la zone de cisaillement de Badajoz-Córdoba a accommodé la déformation Varisque par une cinématique transtensionnelle latérale gauche conduisant à un événement extensionnel documenté dans la partie sud de la CIZ (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016).

Le magmatisme mafique dans les GS, AS, SUM et CS est synchrone avec le magmatisme mafique dans le Massif Armoricaire (Pochon et al., 2016b), nous permettant de proposer l'occurrence d'événement mafique à l'échelle de la chaîne Varisque mis en place à la fois dans la CIZ et dans le Massif armoricaire à environ 360-350 Ma.

Deux types majeurs de magmatisme ont été identifiés dans cette étude, l'un d'affinité alcaline (GS, AS, NZM, SUM) et le deuxième d'affinité transitionnelle dans le CS.

En ce qui concerne les roches des AS, GS, SUM et NZM, les anomalies positives en Pb, l'enrichissement en LREE, les rapports Nb/Yb -Th/Yb - Gd/Yb suggèrent (i) l'implication d'une source mantellique métasomatisée contenant du grenat, potentiellement associée à la dévolatilisation d'un slab cadomien/rhéique, et (ii) à un faible degré de fusion partielle. Ces roches ne présentent aucun signe de recyclage ou de contamination crustale.

En ce qui concerne le magmatisme mafique du Dévonien supérieur au Carbonifère dans le CS, les légers enrichissements en LREE pourraient impliquer une source métasomatisée plus hydrique avec du grenat similaire à celle des suites mafiques du Massif Armoricaire (Pochon et al., 2016). Par conséquent, le magmatisme mafique observé dans le Massif armoricaire est similaire à celui du CIZ en termes d'âge de mise en place et de géochimie. Les données présentées dans cette thèse sont compatibles avec un degré élevé de fusion partielle et l'absence de contamination crustale. La source mantellique métasomatisée de la CS pourrait être liée à la dévolatilisation d'un slab Rheic lors des premiers stades de l'orogénie Varisque.

Implications du magmatisme mafique sur les minéralisations à Sb

Une éventuelle corrélation entre des minéralisations à Sb et du magmatisme mafique a été suggérée dans le Massif armoricain et dans la CIZ (Campos Rodríguez et al., 2023; Chatelin, 2022; Pochon et al., 2016; Pochon, 2018; Pochon et al., 2018, 2019, 2023, 2024). Dans le Massif Armoricain, les gisements à Sb et les roches mafiques sont spatialement et temporellement corrélés à environ 360 Ma, ce qui suggère un forte lien génétique entre des gisements à Sb et des roches mafiques à 360 Ma (Pochon, 2018; Pochon et al., 2016 a, b; 2018, 2019). Dans la CIZ, le magmatisme mafique au sein du CS, du GS, de la SUM et de la NZM est spatialement associé à des minéralisations à Sb. D'après les résultats présentés ci-dessus, le magmatisme mafique et les séquences métasédimentaires qui l'encaissent auraient pu apporter des fluides minéralisateurs qui auraient pu contribuer à la formation des gisements à Sb dans la CIZ. Le magmatisme mafique peut apporter des fluides contenant du Sb par dégazage magmatique pendant la cristallisation de roches mafiques (Pochon et al., 2023, 2024). Dans le CS, le volcanisme mafique a déjà été suggéré comme étant une source possible des fluides minéralisateurs responsables de la formation du gisement à Sb±W de San Antonio (Arribas & Gumiel, 1984). Selon Arribas & Gumiel (1984), ce processus s'est déroulé au Dévonien sur une plate-forme continentale externe affectée par une tectonique extensive pertinente générant un système de failles qui a permis la formation des brèches intraformationnelles ainsi qu'une activité exhalative hydrothermale liée au volcanisme basique.

CARACTÉRISATION GÉOCHIMIQUE ET PALÉOTHERMIQUE DES SÉDIMENTS ET DES MÉTASÉDIMENTS AU CS.

Les roches sédimentaires/métasédimentaires (contenant de la matière organique) telles que les schistes noirs, les ardoises et les greywackes sont considérées comme étant des sources potentielles d'antimoine et d'autres éléments associés (Au, As, Cu; *e.g.* Bloomstein & Clark, 1989; Pitcairn et al., 2006; Pohl, 2011; Ridley, 2013). L'un des paramètres les plus critiques influençant la mobilisation de l'antimoine et d'autres éléments au cours des processus métamorphiques est la température. Pitcairn et al. (2006), ont déterminé que la diminution la plus importante de la teneur en Sb se produit à 450°C et 600°C dans des roches métamorphiques quartzo-feldspathiques (jusqu'au faciès amphibolite) et leurs protolithes. En dessous de 450°C, le Sb est redistribué parmi des phases sulfurées (Pitcairn et al., 2006). Dans ce contexte, une caractérisation géochimique (géochimie en roche totale) et paléothermique (Raman Spectroscopy of Carbonaceous Material, RSCM) des sédiments et des métasédiments a été réalisée afin de (i) comprendre la température maximale du métamorphisme régional qui aurait pu affecter la datation U-Pb sur apatite des sills mafiques, et (ii) leurs possibles implications sur la formation des gisements à Sb.

Températures RSCM dans le CS

Les changements thermiques dans le CS dépendent, selon l'étude Raman, de l'âge des métasédiments et de leur lieu d'échantillonnage au sein de la structure.

Les températures maximales atteintes par le Schist Greywacke Complex d'âge précambrien et l'unité ordovicienne-silurienne Sierra Fría sont de 365-390°C. Les températures de la formation carbonifère de Gévora (GF) semblent être plus élevées dans la partie sud-est de la structure (370°C) et plus basses dans la partie ouest de la CS (210-340°C, augmentant du S au N).

Bien que l'unité Sierra Fría d'âge Ordovicien au Silurien présente des températures relativement plus élevées que la formation Gévora d'âge Carbonifère, la gamme de température globale est cohérente avec le faible degré de métamorphisme précédemment documenté pour le synclinal CS et dans cette partie de la CIZ (*e.g.* López-Moro et al., 2007)

Seules deux valeurs anormales (575°C et 557°C) ont été observées dans les roches de SFU et ont été attribuées à un effet de métamorphisme de contact, en raison de la proximité spatiale avec le granite d'Albuquerque et d'un corps mafique (d'environ 1 km de large).

Distribution du Sb dans le CS

Dans le CS, les valeurs en Sb les plus élevées se trouvent dans la GF dans les parties ouest et est de la structure. Les échantillons à fortes valeurs en Sb prélevés dans la partie occidentale proviennent de la mine San Antonio ($Sb \pm W$), les teneurs en Sb pourraient donc être liées à la présence de sulfures ou d'oxydes de Sb. Dans la partie orientale, les échantillons à forte teneur en Sb proviennent de la carrière Villar del Rey, où aucune minéralisation en Sb n'a été signalée et où aucun sulfure ou oxyde de Sb n'a été observé. Ces échantillons présentent les plus grandes quantités de soufre, ce qui pourrait être lié à une corrélation Sb-S observée pour les roches GF. Aucune phase contenant du Sb n'a été identifiée par les observations et les analyses MEB. Les microanalyses par sonde électronique indiquent que les teneurs en Sb en pyrite et dans ses inclusions de sphalérite sont inférieures à 300 ppm dans ces échantillons, ce qui suggère que la pyrite ne peut pas être le principal minéral contenant du Sb. Le carbone organique dans cette partie de la structure est également élevé, mais aucune hypothèse ne peut être proposée dans ce cas puisqu'il n'y a pas de corrélation claire entre le Sb et le carbone organique.

Comparaison entre les teneurs en Sb dans les CS et les teneurs globales en Sb dans des schistes noirs

Globalement, les roches du CS, en particulier celles provenant de la GF, sembleraient être légèrement plus enrichies en Sb par rapport aux données globales des schistes précambriens et post-cambriens (Fig. 4.13). Ces données comprennent des schistes du Canada, de la Chine, des États-Unis et de l'Inde, et proviennent de 8 publications (Fan et al., 2004; Goodfellow et al., 2009; Manikyamba et al., 2008; Manikyamba & Kerrich, 2006; Orberger et al., 2007; Pašava et al., 2008; Turner & Kamber, 2012; Xu et al., 2013). La valeur médiane des roches GF (Med=2,85) est plus élevée que celle des SGC-SFU (Med=2,02) et des schistes noirs globaux (Med=2,01). Les teneurs en Sb plus élevées mesurées dans les échantillons du GF sont comparables aux valeurs les plus élevées observées dans le monde. Ces valeurs extrêmement élevées ont été mesurées dans les schistes noirs du Cambrien inférieur de la formation de Niutitang dans le sud et le sud-ouest de la Chine, dans lesquels le Sb se trouve dans des croisements complexes de sulfures et de matières carbonées (Orberger et al., 2007; Pašava et al., 2008; Xu et al., 2013). Dans ces schistes noirs, l'enrichissement en Sb est syn-sédimentaire et provient d'une eau de mer anoxique, éventuellement mélangée à des fluides hydrothermaux (Orberger et al., 2007 and references therein).

Du fait qu'aucun minéral contenant du Sb ne soit identifié dans les échantillons de la Codosera, il est impossible de déterminer si l'enrichissement en Sb de ces roches est primitif et donc antérieur à la mise en place du magma ou s'il est dû à des processus métamorphiques qui se sont produits après l'intrusion des magmas.

Implications des températures RSCM dans la datation U-Pb sur apatite des roches mafiques de la CIZ

Les températures de fermeture classiques de l'apatite se situent entre 375 et 550°C (Dodson, 1973; Webster & Piccoli, 2015). Néanmoins, des études plus récentes ont montré que la température de fermeture pouvait être plus élevée (770-870°C) en se basant sur la vitesse de refroidissement et l'épaisseur de plusieurs sills mafiques dans le Massif Armoricaïn (Pochon et al., 2016). Considérant que l'épaisseur de chaque sill étudié dans cette thèse est relativement faible et le fait que ces corps mafiques ont subi un refroidissement et une solidification très rapides, nous pouvons utiliser la gamme de température d'apatite de fermeture plus élevée de 770-870°C de Pochon et al. (2016). Sur cette base, les températures RSCM trouvées pour la plupart des roches métasédimentaires du CS (comprises entre 212-370°C) ainsi que le métamorphisme de faible degré rapporté dans la zone étudiée, appuient l'hypothèse selon laquelle le système isotopique des apatites datées n'a pas été réinitialisé après l'intrusion des sills mafiques.

Implications pour les minéralisations à Sb : Dévolatilisation thermique pendant la mise en place des magmas

Les séquences métasédimentaires du CS montrent une gamme de températures entre 210-370°C, ce qui impliquerait que le Sb a été redistribué dans les phases sulfurées de la roche, sans le mobiliser efficacement. Des températures plus élevées, comme celles atteintes dans les auréoles de contact des sills mafiques, amélioreraient la mobilisation du Sb. Un échantillonnage adéquat des métasédiments perpendiculaires au contact avec les sills serait essentiel en vue d'évaluer cet effet de dévolatilisation. De ce fait, un tel échantillonnage devrait être réalisé dans le même horizon stratigraphique, afin d'éviter les différences dues aux variations stratigraphiques initiales (Svensen et al., 2023). L'échantillonnage utilisé dans cette thèse avait

pour objectif d'étudier les températures maximales atteintes lors du métamorphisme régional et n'a considéré qu'occasionnellement les auréoles de contact.

L'APPROCHE DES SYSTÈMES MINÉRAUX APPLIQUÉE À L'ÉTUDE DES GISEMENTS À Sb DANS L'ARC IBÉRO-ARMORICAIN ET LA CIZ

L'Arc Ibéro-Armoricain représente un cas d'étude idéal pour l'application du concept de systèmes minéraux aux minéralisations à Sb. Cette macrostructure comprend des domaines équivalents au sein des massifs Armoricaïn et Ibérique, qui se sont formés au cours de l'orogénèse Varisque (Ballèvre et al., 1992; Dias & Ribeiro, 1995). Plusieurs éléments critiques pour la formation de gisements de Sb ont été identifiés à l'échelle continentale, de la province, du camp et des gisements. La géodynamique et l'architecture favorables sont représentées par l'ouverture de l'océan Rhéique à l'échelle continentale (Arc Ibéro-Armoricain), qui a provoqué des processus extensionnels, la fusion du manteau, la sédimentation dans des bassins et la mise en place des magmas mafiques à l'intérieur de ceux-ci, à l'échelle de la province (CIZ ou Massif Armoricaïn). L'orogénèse Varisque et les événements postérieurs ont aidé à la préservation des minéralisations à Sb dans la Chaîne.

En ce qui concerne la fertilité, l'existence d'une source mantellique enrichie en Sb n'a pas été attestée dans cette étude, mais il s'agit d'un élément possible qui devrait être étudié à l'échelle continentale ou de la province. À l'échelle du camp, deux éléments critiques ont été identifiés : (i) l'enrichissement en Sb des roches métasédimentaires du CS suggérant un possible enrichissement primaire des roches sédimentaires dans lesquelles le magma mafique s'est mis en place, et (ii) l'enrichissement en Sb des phases magmatiques volatiles exsolues pendant les derniers stades de cristallisation de ces magmas mafiques (observé au CS, mais aussi au Massif armoricaïn).

Résumé Étendu

Des études plus détaillées doivent être menées afin de déterminer les contributions respectives de ces processus à la formation de minéralisations à Sb dans l'Arc Ibéro-Armoricain.

CONTENTS

ABSTRACT	1
RÉSUMÉ ÉTENDU	3
INTRODUCTION	23
CHAPTER 1: ANTIMONY-USSES, GEOCHEMISTRY AND ORE DEPOSITS	31
1.1. Uses of antimony	32
1.2. Antimony criticality, reserves and market.....	33
1.3. Chemistry and geochemistry of antimony.....	36
1.4. Possible fluid and metal sources of antimony	38
1.5. Antimony ore deposits and mineral systems	46
1.5.1-Epithermal deposits	47
1.5.2. Reduced magmatic/intrusion related	49
1.5.3. Polymetallic veins associated to magmatic centers	49
1.5.4. Carbonate replacement deposits.....	50
1.5.5. Greenstone belts-hosted deposits	52
1.5.6. Sb deposits associated with mafic rocks	54
CHAPTER 2: THE PLACE OF THE VARISCAN OROGEN IN THE EUROPEAN BASEMENT AND THE EVOLUTION OF THE CENTRAL IBERIAN ZONE.....	56
2.1. The European geological basement	57
2.2. The Variscan orogen	58
2.2.1. The Northern Variscan Domain	58

2.2.2. The Central Variscan Domain (CVD)	60
2.2.2.1. The Armorican Massif	60
2.2.3. The southern Variscan Domain (SVD)	62
2.2.3.1. The Iberian Massif	62
2.3. Correlations among the Iberian and French units-The Ibero-Armorican Arc	70
2.4. The Central Iberian Zone (CIZ)-Main study domain	72
2.4.1 Sedimentation: From Cadomian to Variscan times	73
2.4.2. Deformation and metamorphism: From Pre-Variscan to Variscan times	76
<i>Pre-Variscan deformation</i>	76
<i>Variscan deformation</i>	77
<i>Variscan metamorphism</i>	80
2.4.3. Mafic magmatic stages in the CIZ: Pre-Variscan and Variscan times.	84
<i>Cadomian (Panafrican).</i>	84
<i>Ordovician.</i>	86
<i>Silurian.</i>	87
<i>Middle to late Devonian.</i>	88
<i>Late Devonian to early Carboniferous-Onset of the Variscan orogeny</i>	89
<i>Last stages of the Variscan orogeny</i>	91
2.5. Main study area #1: La Codosera syncline	93
2.6. Main study areas #2 and #3: The Almaden and Guadalmez synclines	97
2.7. The Susana and Nazarena mines	102

2.8. Antimony mineralization in the Ibero-Armorican arc	102
2.8.1. Sb in the Armorican Massif.....	102
Possible origin of the Sb in the Armorican Massif	107
2.8.2. Sb in the Iberian Massif.....	109
2.9.2.1. Antimony mineralization in the Central Iberian Zone.....	113
<i>Main Sb mineralization in the studied areas.....</i>	<i>113</i>
<i>Synthesis of the relevant Sb deposits in the CIZ</i>	<i>117</i>
 CHAPTER 3: Evolution of the mafic magmatism in the Central Iberian Zone, Spain.	
Insights from: La Susana Mine, La Nazarena Mine, La Codosera, Almadén and	
Guadalmez synclines.....	120
3.1-Introduction.....	121
3.2-Analytical methods.....	124
3.2.1- Sampling	124
3.2.2-Whole rock geochemistry analyses.....	128
3.2.3-Electro probe micro analyses.....	128
3.2.4-U-Pb dating on apatite.....	129
3.2.5- Laser ablation inductively coupled plasma mass spectrometry	131
3.4-Results	131
3.4.1-Relationships between dolerites and C1 Variscan schistosity cleavage	131
3.4.2-Dolerite petrography	133
4.3-Dolerites geochemistry.....	137
4.4-Dolerite geochronology	146

<i>Apatite features</i>	146
<i>U-Pb dating on apatite</i>	149
3.4.5-Fluid inclusion bearing ilmenite	152
3.5-Discussion	153
3.5.1-Interpretation of the apatite dating and significance of the ages	153
3.5.2-Temporal relationship between dolerites and their host rocks	154
3.5.2.1-Guadalmaz syncline	154
3.5.2.2-Almaden syncline	155
3.5.2.3-Codosera syncline	155
3.5.2.4-Susana Mine	156
3.5.2.5-Nazarena Mine	156
3.5.3-Magmatic events in the GS, AS and CS over ≈ 200 Ma	158
3.5.4-Major geological events, evolution and geochemistry of the mafic magmatism in the CIZ	158
5.4.1-Neoproterozoic to Ordovician	159
5.4.2-Silurian to Lower Devonian	159
5.4.3-Lower Devonian to Carboniferous	160
5.5-Concordance with local geological events in the Variscan belt: The Armorican Massif and the AS	168
6-Link between mafic magmatism and Sb mineralization-Armorican Massif and CIZ.	169
Conclusions	170

CHAPTER 4: GEOCHEMICAL AND PALEOTHERMAL CHARACTERIZATION OF SEDIMENTS AND METASEDIMENTS AT THE CODOSERA SYNCLINE, CENTRAL IBERIAN ZONE, SPAIN	174
4.1-INTRODUCTION.....	175
4.2-STUDY AREA AND SAMPLING	177
4.2.1-La Codosera Syncline	177
4.2.2-Sampling	179
4.3-ANALYTICAL METHODS AND DATA PROCESSING	181
4.3.1-Petrography	181
4.3.2-Scanning Electronic Microscope (SEM)	181
4.3.3-Raman spectroscopy of carbonaceous material (RSCM).....	181
4.3.4-Whole rock geochemistry analyses.....	183
4.3.5- Electro probe micro analyses	184
4.4-RESULTS	184
4.4.1-Petrography and phase identification	184
4.4.2-Whole rock geochemistry analyses-Sb distribution in the CS	189
4.4.2.1- Antimony in the SGC, SFU and the GF.....	193
4.4.3-Sb contents of sulfide minerals	196
4.4.4-RSCM-TEMPERATURES	197
4.4.4.1-Schist Greywacke Complex (Precambrian-Cambrian) and Unidad de Sierra Fría (Ordovician).....	199
4.4.4.2-Gévora Formation.....	199

4.5-DISCUSSION	201
4.5.1-Geochemistry of the CS sequences	201
4.5.1.1- Sb distribution in the CS	202
4.5.1.2-Comparison between Sb values in the CS and Sb global contents in black shales.....	202
4.5.2-RSCM temperatures in the CS	204
4.5.3-Implications of the RSCM metamorphic temperatures in the apatite dating of mafic rocks in the CIZ	205
4.5.4- Metamorphism in the CIZ and in the CS	207
4.5.5- Temperatures and Sb mineralization in the CS.....	208
4.6-CONCLUSIONS	209
CHAPTER 5: SYNTHESIS.....	212
5.1-Mafic magmatism, metasediments and Sb mineralization in the mineral systems framework: the CIZ and the Armorican Massif	213
5.2.-Evolution of the mafic magmatism in the CIZ.....	213
<i>5.2.1.-Geochronology of the mafic intrusions at the GS, AS, CS, NZM and SUM</i>	213
<i>5.2.2.-Geochemistry and possible sources of the mafic intrusions at the GS, AS, CS, NZM and SUM</i>	214
5.3-Geochemical and paleothermal characterization of sediments and metasediments at the CS	215
<i>5.3.1- Maximum metamorphic temperatures in the CS.....</i>	215
5.3.1.1-Thermal implications in the U-Pb apatite dating of mafic sills	216

5.3.2.-Geochemistry of the CS metasedimentary rocks	216
5.4- Implications for Sb mineralization: mafic magmatism and metasediments as possible Sb sources in the CIZ.	218
5.4.1-Exsolution of magmatic volatile phases	219
5.4.2-Thermal devolatilization of sedimentary rocks during magma emplacement..	221
5.5- Simplified model considering the possible sources of Sb deposits in the CS.....	224
5.6-The mineral systems approach applied to the study of Sb deposits in the Ibero-Armorican Arc and the CIZ.....	225
5.7-Perspectives	227
5.7.1-Short term-CIZ	227
5.7.2-Long term-Moroccan Sb deposits.....	228
CONCLUSIONS.....	234
REFERENCES	241
LIST OF FIGURES	287
LIST OF TABLES	305
ANNEXES.....	308
<i>PUBLICATIONS AND INTERNATIONAL CONFERENCES</i>	337

INTRODUCTION

Introduction

The study of mineral deposits has evolved significantly over time. Initially focused on the simple description of ore samples on a small scale, it has progressively integrated the study of structural parameters, favorable host rocks, metasomatic and fluid processes, among others (Conolly, 1936; McKinstry, 1941, 1955). These main features are basically studied in order to (Agricola, 1556; Loughlin & Behre, 1933): **i)** improve the exploitation of mineral deposits by considering their geometry and nature; and **ii)** predict and target prospective zones by understanding all of the mechanisms involved in the formation of mineral deposits. All of these studies and factors have led to the creation of the ore deposit models that we know today in which mineral deposits are classified into different categories (Hedenquist et al., 2005). These models are mostly focused on the study of the mineralization at deposit scale and, despite their high utility, they present some limitations represented by the decrease in the efficiency of exploration processes and, therefore, the decrease in the discovery of new mineral deposits (McCuaig & Hronsky, 2014; McKeith et al., 2010).

In the last two decades, the above limitations and facts have led to the development of the concept of "mineral systems", which no longer considers the formation of mineral deposits on a local scale, but rather as a combination of several geological processes occurring in different time and space (Goldfarb et al., 2010; Groves et al., 2005; Kerrich et al., 2005; Knox-Robinson & Wyborn, 1997; McCuaig et al., 2010; McCuaig & Hronsky, 2014; Wyborn et al., 1994). Here the mineral deposits are seen as self-organized critical systems and the convergence point of vast regimes of mass and energy (Fig. 1: McCuaig & Hronsky, 2014). To form one of these complex systems, it is necessary to concentrate large amounts of metals in small volumes of rock by large-scale advective mass, energy, and fluid flows with the involvement of threshold barriers to prevent the energy from dissipating into the sink (Fig. 1: Kerrich, 1983; McCuaig et

Introduction

al., 2010; McCuaig & Hronsky, 2014). This requires consideration of a large number of processes at regional, camp and deposit scale (Fig. 1: McCuaig & Hronsky, 2014).

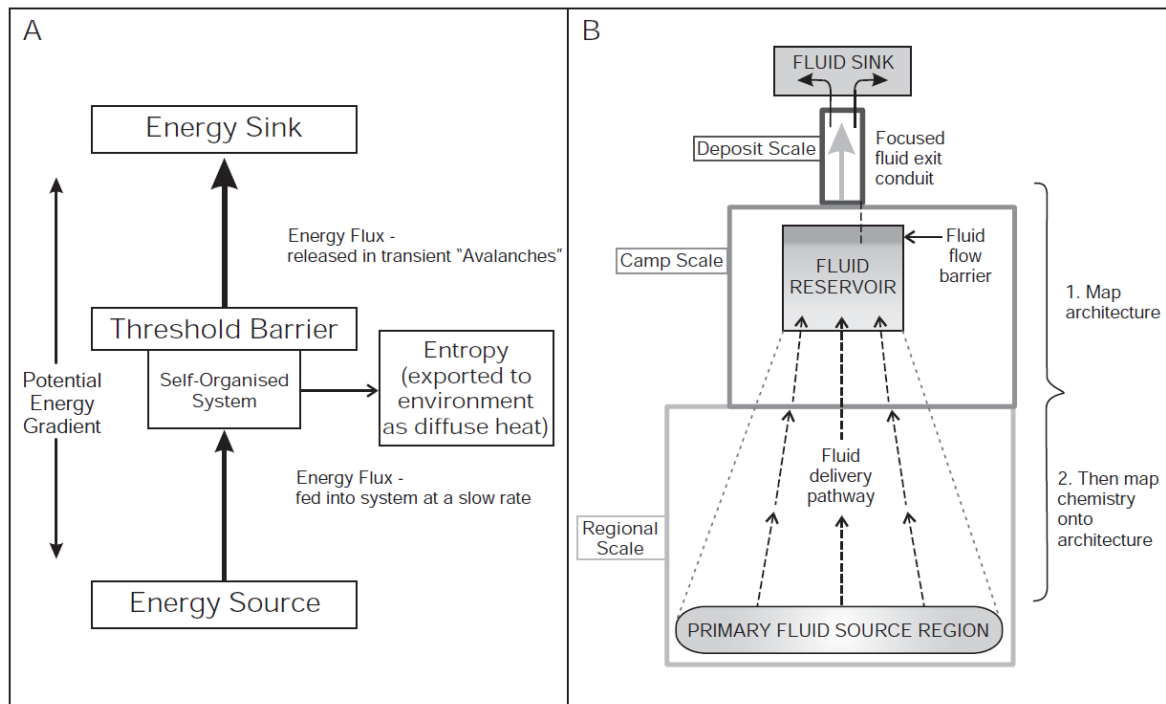


Figure 1. Basic model for a self-organized system. Keys to the generation of self-organized critical behavior are that the energy is continually added to the system and that a threshold barrier is present that prevents the energy from dissipating to the sink. The energy is added continually and slowly over long time frames, whereas the energy release is via transient dynamic “avalanches” of much shorter duration; B. Translation of the self-organized critical system concept to ore genesis as the focus of a scale-hierarchical mass concentrative fluid (including magma) advection system. Different sets of processes are important at different scales, an aspect that must be considered in research and exploration strategy.

The holistic and multiscale mineral systems concept has been increasingly used for studying mineral deposits, offering a more substantial predictivity power compared to the classic ore deposit models (McCuaig et al., 2010; McCuaig & Hronsky, 2014). This approach relies on the interaction of four key-elements for the formation of a mineral deposit (Fig. 2: McCuaig et al., 2010; McCuaig & Hronsky, 2014): **i)** Favorable lithosphere architecture: the structure of the lithosphere is essential for the mobilization of mineralizing fluids; **ii)** Favorable (transient)

Introduction

geodynamics: Compressive or extensive events are able to create threshold barriers which are essential for the accumulation of critical elements in specific areas; **iii) Fertility:** This term is referred to the potential of an specific area to promote the formation of ore-deposits; **iv)**

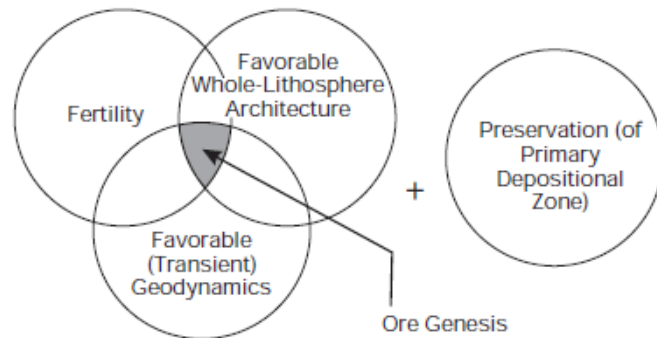


Figure 2. Main critical elements composing the mineral systems approach, necessary for the formation and discovery of an ore-deposit.

Preservation of (primary) depositional zone: For a mineral deposit to be discovered and exploited it is necessary that this object remains well-preserved during any geological events (erosion, orogeny).

In the case of the understanding of Sb prospectivity in equivalent domains of large orogens (such as the Ibero-Armorican Arc of the Variscan Belt), the mineral systems approach seems to be very convenient to study the sources and processes involved in their formation at regional, camp and, deposit scales (Fig. 1). The Ibero-Armorican Arc hosts several Sb deposits (usually associated with $\text{Au}\pm\text{Hg}\pm\text{W}\pm\text{As}\pm\text{Pb}$) and represents the most important Variscan macrostructure, starting from the Armorican Massif in Brittany (France), crossing the Cantabrian Sea and ending at the Iberian Massif in southern Spain at the Betic Alpine Front (Weil et al., 2010). The existence of this macrostructure was proposed on the basis of several geological equivalences between some of the domains of the Armorican and the Iberian Massif (*e.g.* Central Iberian Zone-Central Armorican Domain; Galicia Tras-Os Montes Zone-South Armorican Domain: Ballèvre et al., 1992; Días & Ribeiro, 1995). In terms of Sb, the Armorican Massif and the Central Iberian Zone (CIZ) were the most important Sb metallogenic provinces in France, Spain and Portugal during the 20th century (Guilloard, 2009; Gumiel, 1982; Gumiel & Arribas, 1987).

Introduction

Different genetic models have been proposed to explain the formation of Sb deposits in the Ibero-Armorican Arc (Armorican Massif and CIZ). Some of the models propose a metamorphic crustal source for the mineralizing fluids (*e.g.* 'Au 300 Ma'-Orogenic gold model, see Chapter 1: Bouchot et al., 2005; Munoz et al., 1992) while others prefer magmatic sources associated with large felsic intrusions (see Chapter 1: Chauris & Marcoux, 1994; Couto et al., 1990; Fouquet, 1980; Marcoux et al., 1984; Ortega et al., 1996; Ortega & Vindel, 1995; Serment, 1978). Both types of models are associated with extensional events that occurred at the end of the Variscan orogeny between *ca.* 300 Ma (Bouchot et al., 2005; Chauris & Marcoux, 1994; Couto et al., 1990; Fouquet, 1980; Marcoux et al., 1984; Munoz et al., 1992; L. Ortega et al., 1996; L. Ortega & Vindel, 1995; Serment, 1978). The involvement of hydrothermal exhalative activity related to mafic volcanism was also proposed to explain the formation of the world class Hg deposits of Almadén (Higueras, 1995; Higueras et al., 2000, 2013; Higueras & Oyarzun, 2005; Palero-Fernández et al., 2015) and some of Sb deposits in the CIZ (Arribas & Gumiel, 1984; Gumiel, 1982; Gumiel & Arribas, 1987). More recent studies have suggested a spatial, temporal and a possible genetical link between Sb deposits and mafic magmatism at 360Ma in the Armorican Massif (Pochon, 2018; Pochon et al., 2016 a, b, 2018, 2019, 2023, 2024).

Based on the Mineral system approach, which sees the mineral deposits as a small part of a larger group of geological processes (McCuaig & Hronsky, 2014) and the correlations among the Iberian and Armorican Massif (Ibero-Armorican Arc), is it possible to transpose into the CIZ some of the geological processes and sources proposed for the formation of Sb deposits in the Armorican Massif? To test this, the following questions must be answered:

- 1- Is there a link between mafic magmatism and Sb mineralization in the CIZ at 360Ma?

Introduction

- 2- Is there a link between Sb and metasediments, possibly implying a metamorphic source (orogenic gold model) in the CIZ?
- 3- At regional and camp scale, which are the possible sources responsible for the formation of Sb deposits in the CIZ?

The objective of this thesis is to present new insights into the processes and potential sources of antimony (Sb) in the CIZ at the continental (Ibero-Armorican Arc), province (CIZ) and camp scales (study areas). This work employs the Mineral Systems approach to facilitate a more comprehensive understanding of the mapping criteria for targeting Sb deposits. This study focuses on five areas within the CIZ: the Codosera syncline (CS), the Almadén syncline (AS), the Guadalmez syncline, la Susana Mine (SUM) and the Nazarena Mine (NZM). The CS, includes a Paleozoic metasedimentary sequence hosting the biggest swarm of mafic sills reported in the Iberian Massif (López-Moro et al., 2007, 2020a) and the largest Sb-W district in Spain (Gumiel & Arribas, 1987). The AS hosts the world class Hg Almadén deposit (Hall et al., 1997; Higuera et al., 1995, 2013; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009), whereas the GS hosts several Sb occurrences and mineralization (Barquero et al., 2022; Lorenzo Álvarez et al., 1995). Like the CS, the AS and GS are composed by a Paleozoic metasedimentary sequence (Lorenzo Álvarez et al., 1995). The two other locations, corresponding to the SUM and NZM, present Sb occurrences and mafic bodies hosted in Precambrian-Cambrian (SUM) and Paleozoic (NZM) metasedimentary sequences (Gumiel, 1982).

This manuscript is organized into 5 Chapters with a preamble and a general conclusion:

Chapter 1 covers the basics of antimony, including its importance, geochemistry, and market. It also reviews the established metallogenic models for explaining the formation of Sb deposits around the globe.

Chapter 2 presents the geological setting of the Ibero-Armorican arc and a comparative analysis between the Armorican Massif and the CIZ. This comparison will concentrate on the mafic magmatism, deformation, structure, and sedimentation in the CIZ from the Cambrian to the late Carboniferous periods.

Chapter 3 presents new petrological and geochemical data for some of the mafic intrusions in the CS, AS, GS, SUM and NZM. The emplacement ages of these bodies are constrained by U-Pb dating of apatite. We analyze the geochemical evolution and the potential mantle sources of the Ordovician to Carboniferous mafic magmatism in the CIZ. Furthermore, the timing of the magmatism in the CS, AS, GS, SUM, and NZM is discussed, with the latter being situated within the Variscan geodynamic setting. Additionally, the role of magmatism in the formation of Sb mineralization is explored.

Chapter 4 presents a geochemical and thermal characterization of the sedimentary/metasedimentary sequences of the CS, which hosts the San Antonio Sb-W deposit and several mafic sills (studied in Chapter 3). The thermal data help to understand the influence of the mafic intrusions and regional metamorphism in the CS metasedimentary rocks as well as to assess the thermal potential of the CS sequences for mobilizing Sb-bearing fluids. The geochemical data contribute to an understanding of the potential of the CS metasedimentary rocks as a possible source for the Sb in the CS.

Chapter 5 provides a synthesis of all findings, evaluating the possible sources and processes, at regional and camp scale, involved in the formation of Sb±Hg±W±Au deposits in the study areas of the CIZ and conclude with an overview of the mineral systems concept applied to the formation of Sb deposits in the CIZ.

CHAPTER 1: ANTIMONY-USES, GEOCHEMISTRY AND ORE DEPOSITS

1.1. Uses of antimony

Antimony is an important semi metal that has been used along human history. Antimony sulfide or stibnite (Sb_2S_3) has been known since 3100B.C, when it was used as makeup by the Egyptians and antient Hindus. At medieval times

this mineral was unsuccessfully used by alchemists that tried to transform lead into gold (Carlin, 2013; Gibson, 1998; Seal II et al., 2017).

(Carlin, 2013; Gibson, 1998; Seal II et al., 2017).

During World War II, antimony was used as fire proofing in the form of antimony trichloride (SbCl_3) in vehicles and tents covers: in case of fire

antimony and chlorine form unstable compounds capable of removing oxygen from the air (Gibson,

1998). Antimony compounds were also employed in the pharmaceutical industry, nowadays abandoned given the toxicity of the components (Hellgren et al., 1995; Seal II et al., 2017).

Nowadays, this metalloid has a widely range of uses (Fig.1.1), two of the most important of which corresponds to (i) flame retardants (in the form of antimony trioxide, Sb_2O_3) in safety equipment, and (ii) lead acid storage batteries, containing up to 4 to 6% of antimony-lead alloy, in order to make battery terminals more resistant to corrosion (Gibson, 1998; Seal II et al., 2017). Other uses include chemicals, catalysts and stabilizers in plastic manufacture, glass/ceramics, electronics, clothing, rubber, among others. (Brobst & Pratt, 1981; European Commission, 2020; Seal II et al., 2017). Antimony is also used in the military industry as combustion material in ammunition, tracer bullets, detonators (Gibson, 1998; Seal II et al., 2017).

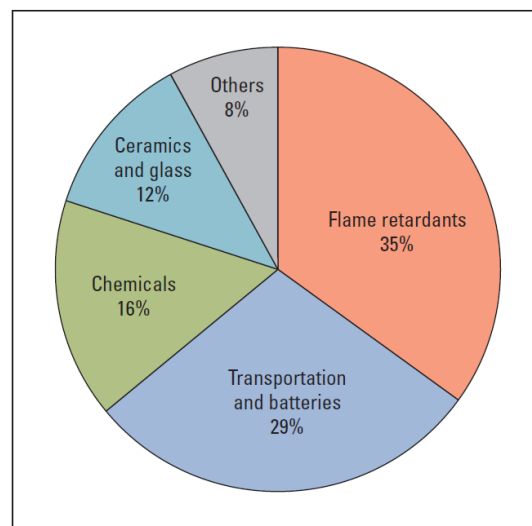


Figure 1. 1. Current major uses of antimony (Carlin, 2013).

1.2. Antimony criticality, reserves and market

In the light of the monopolistic production of antimony by China and Tajikistan ($\approx 73\%$ of global production), and in view of the sanctions imposed on Russia in the context of the Ukraine conflict, the European Commission and the U.S. government have identified this element as critical for the functioning of several sectors, including the production of flame retardants, lead-acid batteries, in the military industry, among others (European Commission, 2020, 2023; Seal II et al., 2017; U.S. Geological Survey, 2023). Both, the U.S. and the EU, import 100% of their antimony supply, none of them is currently mining any marketable Sb in their territories. The U.S. imports 46% of antimony ore and concentrates from China, whereas 63% of the EU's imports come from Turkey (European Commission, 2023; U.S. Geological Survey, 2023). Regarding the processing of this substance, the EU processes 18% of the global supply mainly in Belgium, France and Spain (European Commission, 2023).

The global antimony mine production is dominated by China (40000 tons) followed by Tajikistan (21000 tons), Turkey (5800 tons), Burma (4600 tons), Russia (4300 tons), Bolivia (3000 tons), among others (Table 1.1; U.S. Geological Survey, 2024). The world total production and reserves of Sb were estimated at 83kt and $\approx 2,000,000$ tons in 2023, respectively (U.S. Geological Survey, 2024).

Chapter 1

Table 1. 1. World mine production and reserves of antimony. (U.S. Geological Survey, 2024).

	Mine production		Reserves ⁷
	2022	2023 ^e	
United States	—	—	⁸ 60,000
Australia	2,290	2,300	⁹ 140,000
Bolivia	3,000	3,000	310,000
Burma	^e 4,600	4,600	140,000
Canada	^e 2	2	78,000
China	^e 40,000	40,000	640,000
Guatemala	24	24	NA
Iran	^e 500	500	NA
Kazakhstan	^e 300	300	NA
Kyrgyzstan	40	40	260,000
Laos	^e 220	220	NA
Mexico	^e 700	700	18,000
Pakistan	^e 79	80	26,000
Russia	4,300	4,300	350,000
Tajikistan	21,000	21,000	50,000
Turkey	^e 5,800	6,000	99,000
Vietnam	250	250	NA
World total (rounded) ¹⁰	83,100	83,000	>2,000,000

The price of the antimony ton has varied from less than USD 6174 in 1994 to more than USD 14000 in 2011 (highest peak, Fig.1.2; Carlin, 1994, 2011), these values decreased drastically from USD 12458 per ton in 2012 to USD 7.385 per ton in 2016 (Fig. 1.2; (Carlin, 2012; European Commission, 2020; Klochko, 2016). Since then, the price per ton of Sb has gradually increased to almost USD 13624 nowadays (European Commission, 2020, 2023; Klochko, 2024; Research and Markets, 2023).

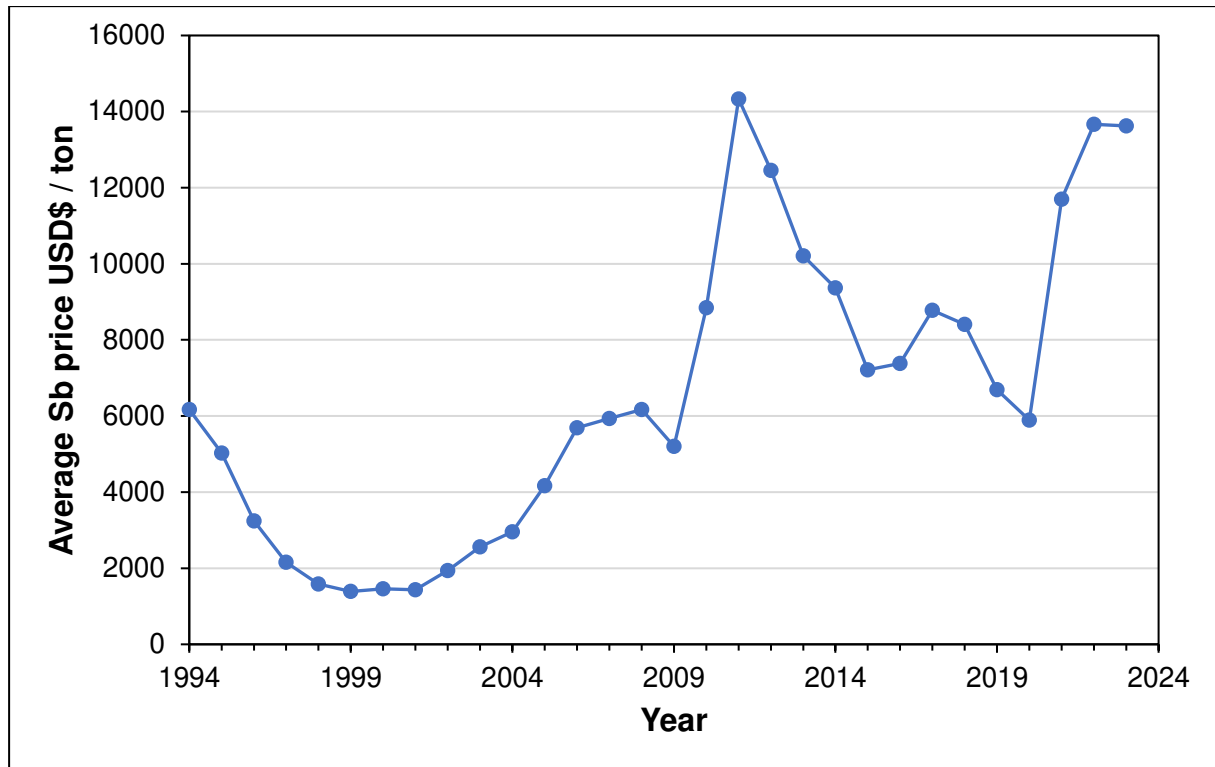


Figure 1. 2. Average antimony prices per ton from 1994-2024 in USD\$. All values were taken from the Minerals Yearbook and the Mineral Commodities Summary from the US Geological Survey (Carlin, 1994, 1995, 2004, 2005, 2006, 2007, 2009, 2010, 2011, 2012, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003; Guberman, 2013, 2014; Klochko, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2024; Sangine, 2023)

The size of the world market for antimony (Fig. 1.3) reached USD 2 Billion in 2022, compared to USD 1.77 million in 2018, the global consumption is expected to increase in the next years and the value of the market is expected to reach 3 Billion by 2028 (European Commission, 2020; Research and Markets, 2023).

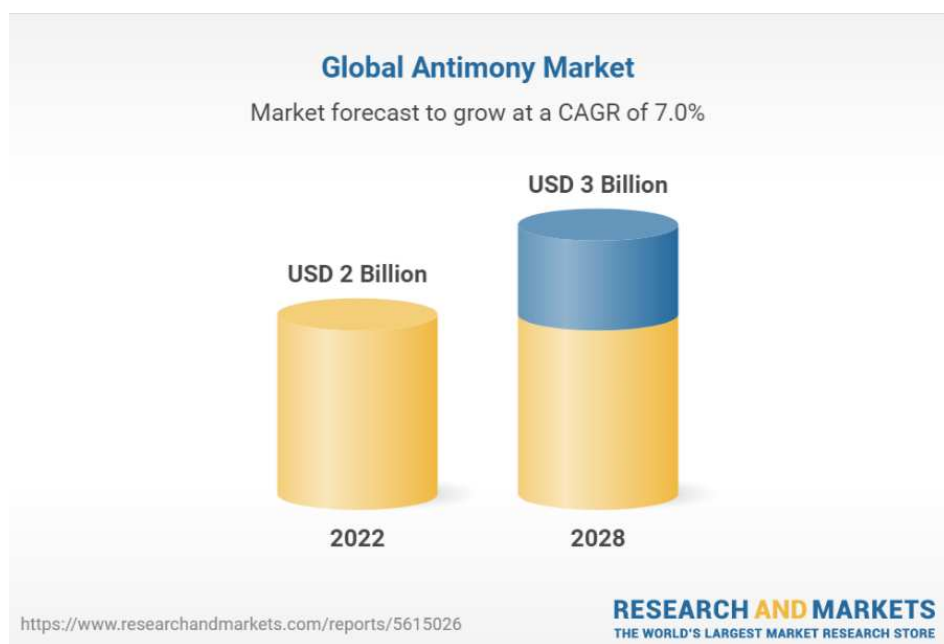


Figure 1. 3. Global antimony market forecast, 2022-2028. CAGR: Compound Annual Growth Rate. (Research and Markets, 2023)

1.3. Chemistry and geochemistry of antimony.

Antimony (Sb) is a silver to white, brittle semi metal, which possess a hardness of 3 to 3.5 and specific gravity of 6.68. This semi-metal (atomic number 51, atomic weight 121,760) shows poor conductivity of electricity and heat, it presents a melting point of 630.5 °C, and a boiling point of 1587°C. It has several oxidation states (Sb^{5+} , Sb^{3+} , Sb^0), the most common one is Sb^{3+} (Schwarz-Schampera, 2014). This Sb (III) is usually transported in neutral pH solutions as hydroxocomplexes ($\text{Sb}(\text{OH})_3$) (Obolensky et al., 2007; Zotov et al., 2003). In alkaline solutions antimony can be present as sulfide ($\text{Sb}_2\text{S}_4^{2-}$ and HSb_2S_4) and hydroxide ($\text{Sb}_2(\text{OH})_6$) complexes (Zotov et al., 2003). Hydrothermal fluids with high acidity (pH 2-3) present the highest Sb-bearing capacity compared to alkaline (pH 7-8) and sulfide depleted fluids (Obolensky et al., 2007). Low-sulfide/high-chloride acid fluids can contain up to 120g/kg H_2O of Sb, whereas low-sulfide/low chloride fluids present less than 94.7g/kg H_2O (Obolensky et al., 2007).

The antimony is a chalcophile element, strongly related to arsenic, lead and mercury. Its geochemical behavior is found between the one of the Pb and Hg. This element is present in more than 264 mineral phases. Due to its strong affinity to sulfur, it is commonly found as (Boyle & Jonasson, 1984): sulfides (stibnite-Sb₂S₃), sulfosalts (berthierite-FeSb₂S₄; tetrahedrite-(Cu,Fe)₁₂Sb₄S₁₃; boulangerite-Pb₅Sb₄S₁₁; stephanite-Ag₅SbS₃; jamesonite (Pb₄FeSb₆S₁₄), freibergite-(Ag, Cu, Fe)₁₂(Sb, As)₄S₁₃; bournonite-PbCuSbS₃; gudmundite-FeSbS; among others) but also oxides (valentinite-Sb₂O₃; cervantite-Sb³⁺Sb⁵⁺O₄; etc.). Regarding the abundance of Sb, its average content in chondrite has been estimated at 0.142ppm (Schwarz-Schampera, 2014). The Earth's crust presents an abundance of 0.2ppm whereas in oceanic basalts the average content ranges from 0.02ppm to 0.8ppm (Jochum et al., 1993). Maximum concentrations in granites, sandstones and carbonates are 0.2ppm, 0.6ppm, and 0.2ppm respectively, whereas schists and pelitic sediments can contain up to 1.5ppm and 2ppm (Pohl, 2011). In order to produce a mineral deposit with an economic potential of 3% Sb (30kg per tonne), it is necessary to have an enrichment of 150000 times its Clarke (Schwarz-Schampera, 2014).

Antimony also belongs to the group of Fluid Mobile Elements (B, Li, Cl, As, Sb, Pb, U, Cs, Sr, Ba), which are known for being volatile elements that are especially enriched in fluids coming from dehydration of the lithosphere in subduction zones at mantle depth (Bonatti et al., 1984; Deschamps et al., 2010, 2012; Scambelluri et al., 2001; Vils et al., 2011). In low temperature hydrothermal fluids (300-100°C), Sb behaves as a highly volatile element (Obolensky et al., 2007). The precipitation occurs when the temperature and pH changes, this could be related to several processes such a sudden decreasing of pressure, an adiabatic cooling or due to the interaction of Sb-bearing fluids with highly sulfidized rocks (Obolensky et al., 2007; Pohl, 2011; Schwarz-Schampera, 2014)

In ore deposits, it usually found mainly as sulfide in association with arsenic, mercury, copper, lead, among others. Considering its strong affinity to Au and Ag, the antimony represents a useful pathfinder for exploring these metals (Schwarz-Schampera, 2014).

1.4. Possible fluid and metal sources of antimony

Several studies have been carried out in order to understand the possible processes and sources of the Sb deposits, most of them sharing two main features, shallow depths (less than 5km) and low formation temperatures, ranging from 150 to 350°C (Obolensky et al., 2007). The wide range of geological settings and distribution of Sb deposits have led to propose several models and sources in order to explain the origin of the mineralizing fluids.

- i) A magmatic source of the fluid coming from intrusions of granitic magmas was proposed considering the strong spatial relationship between Sb deposits and granitoid bodies. In this model the type of mineralization will change depending on the distance from the felsic intrusions: in the farthest parts the assemblage is marked by $Pb \pm Zn \pm Ba \pm Ag \pm F$ mineralization, the intermediate parts host the main $Sb \pm Au \pm As$ deposits and the closest parts present $W \pm Sn \pm Au$ mineralizations (Hart, 2007; Schwarz-Schampera, 2014).

This model has been suggested for Sb deposits in France in the Quimper and the Vendée districts considering the possible coeval formation of the Sb mineralization and the emplacement of felsic magmatism (Chauris & Marcoux, 1994; Fouquet, 1980; Marcoux et al., 1984; Serment, 1978). Nevertheless, this hypothesis lacks constraints from fluid inclusions and geochronological data. In Canada, Burrows & Spooner (1988) suggested a source of the mineralizing fluids coming from TTG intrusions. The fluids show low salinity (5.6 ± 1.2 equiv wt% NaCl), high contents of

pure CO₂ and $\delta^{18}\text{O}$ values that matches with magmatic signatures (Burrows & Spooner, 1988)

- ii) A fluid metamorphic source related to the orogenic gold model, where the Sb deposits are located at the epizonal (Fig. 1.4; Sb $\pm$ Hg, <200°C, prehnite pumpellyite facies) and mesozonal (Sb $\pm$ Au, >250°C, up to greenschists facies) range (Goldfarb & Groves, 2015). The fluids show a deep metamorphic crustal origin with a low salinity (2-10 wt %), a near neutral pH (5.5), high CO₂ concentrations, an oxidation state similar to the host rocks and an isotopic data ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{34}\text{S}$) that varies depending on the age of the mineralization and the host rock (Goldfarb & Groves, 2015; Ridley, 2013b).

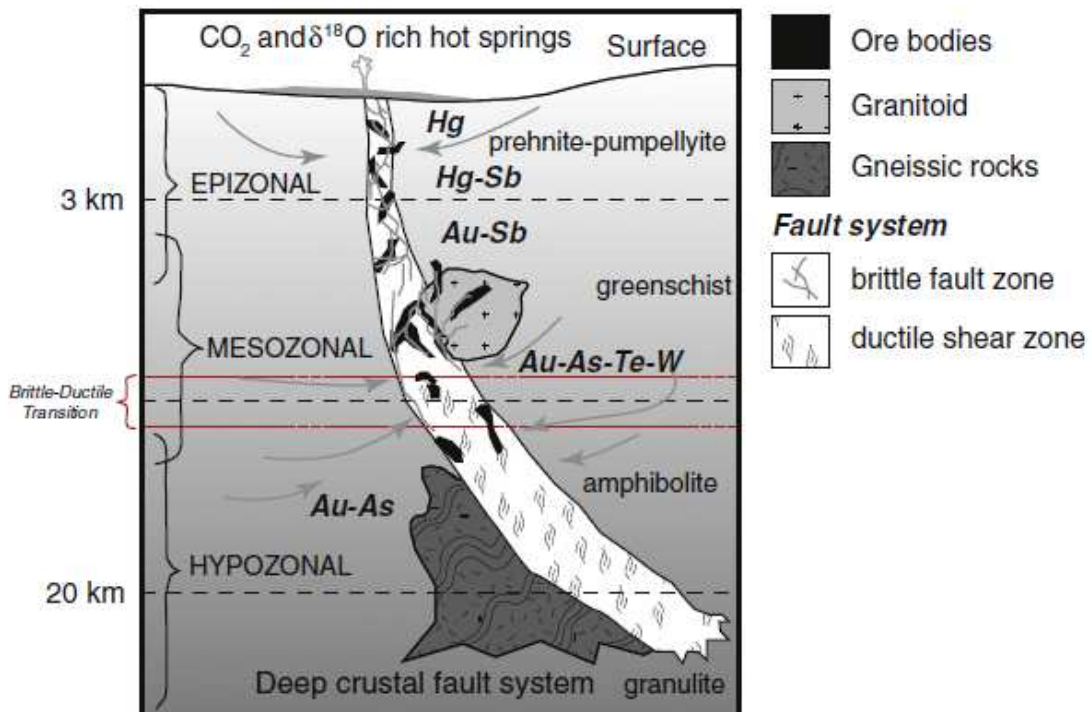


Figure 1. 4. Ore variation of orogenic-gold deposits based on depth. (Goldfarb & Groves, 2015).

In this model, the metamorphic dehydration reactions during a prograde metamorphism setting (chlorite breakdown, greenschist-amphibolite facies transition, 500-550°C) are responsible for the formation of the mineralizing fluids (Beaudoin & Pitre, 2005; Goldfarb et al., 2001; Goldfarb & Groves, 2015; Phillips & Powell, 2009; Pitcairn et al., 2005, 2014b, 2014a; Tomkins, 2010, 2013). This can be triggered by several processes such as magmatic intrusions, crustal thickening, slab-rollback, mantle plume, asthenosphere upwelling or oceanic ridge-subduction (Fig. 1.5; Goldfarb & Groves, 2015).

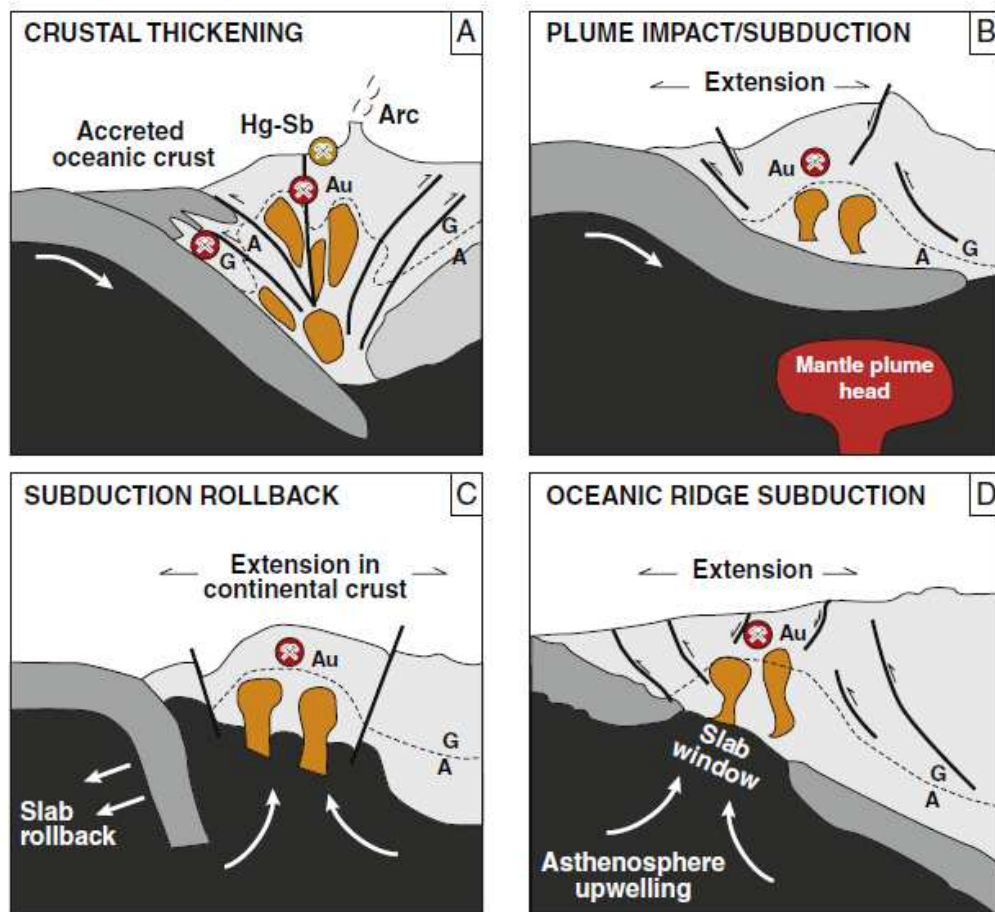


Figure 1. 5. Processes and scenarios in subduction settings that could lead to the mobilization and formation of Sb deposits (Goldfarb & Groves, 2015). These scenarios are related to the devolatilization of oceanic rocks accreted along a continental margin in regions where the crust has been thickened (A); the generation of extensional structures related to the ascension of a mantellic plume (B), subduction roll back (C) and the subduction of an oceanic ridge (D).

In this scenario, sedimentary/ metasedimentary rocks such as black shales/schists, slates and greywackes are the likely source of antimony and other associated elements (Au, As). In these lithologies the diagenetic pyrite is considered to be the main Sb-Au-As bearing mineral (Gregory et al., 2015; R. Large et al., 2012; Pitcairn et al., 2006). LA-ICP-MS trace element analyses performed for pyrite in black shales, showed that the Sb content in this mineral can vary from 0.04ppm to 2878ppm, more than 14000 its Clarke (Gregory et al., 2015). The Au in diagenetic pyrite shows various concentrations ranging from 16ppb and 0.42ppm (Gregory et al., 2015; Pitcairn et al., 2006). In the case of As its content ranges from 0.25ppm and 29597ppm, with an average concentration of 488pm (Gregory et al., 2015). The breakdown of pyrite into pyrrhotite is believed to be the main cause for Au, As and Sb mobilization (Tomkins, 2010). This pyrite-pyrrhotite transition can be driven by chlorite breakdown which is represented by the following reaction $2\text{H}_2\text{O} + \text{C} + 2\text{FeS}_2 = \text{CO}_2 + 2\text{H}_2\text{S} + 2\text{FeS}$. The Fe content can also affect the Py-Po transition $\text{FeS}_2 + \text{FeO} = 2\text{FeS} + 0.5\text{O}_2$ (Tomkins, 2010). The rocks enriched in Fe will help to preserve the S in the rock whereas the C-rich rocks will generate more H_2S , which is believed to be the Au-carrier (Goldfarb & Groves, 2015; Tomkins, 2010). The ore precipitation may be induced by a loss in H_2S (by fluid-wall rock interaction, generating a decreasing in the Au solubility), interactions with acidic or reductant fluids, a fluid phase separation (gas-rich and water rich) and changes of temperatures and pressures that could affect the pH (Goldfarb & Groves, 2015; Groves et al., 1998; Ridley, 2013b).

As mentioned above, the temperature represents one of the most important factors when mobilizing Sb and other elements during metamorphic processes (Fig. 1.6).

Pitcairn et al. (2006) explored the Sb contents of metamorphic rock that experienced variable temperatures and concluded that the highest Sb mobilization occurs between 300 and 600°C (Fig.1.6) whereas other associated elements can be mobilized at lower temperatures, starting from 200°C for Au, and from 100°C for Hg (Pitcairn et al., 2006, 2014b).

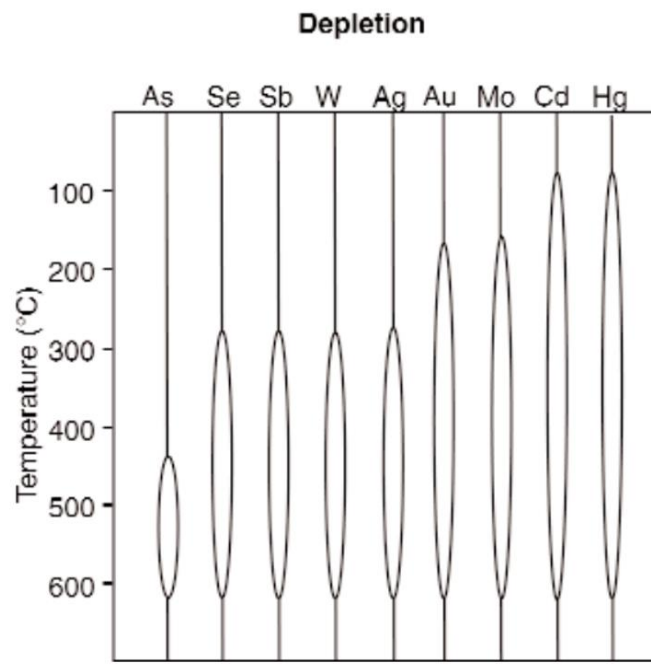


Figure 1. 6. Temperature zonation of the depletion of the ore-forming elements from the metamorphic rocks of the Otago and Alpine schists (Pitcairn et al., 2006)

- iii) The involvement of mafic magmatism as a possible participant in the formation of Sb mineralization been studied in recent years (Campos Rodríguez et al., 2023; Chatelin, 2022; Pochon, 2018; Pochon et al., 2016, 2018, 2019, 2023, 2024). This hypothesis has been developed on the basis of the spatial and temporal link between Sb deposits and mafic rocks found in the Armorican Massif at *ca.* 360 Ma (Pochon, 2018; Pochon et al., 2016, 2018, 2019). This mafic magmatism would be related to a slab roll back leading to the partial melting of the sub-continental lithospheric

mantle under the Armorica plate (Fig. 1.8; Pochon, 2018). This process would have generated important amounts of mafic magmas that contributed to the heating, rising and mobilization of crustal fluids that could have played a key role for the formation of several Sb deposits in the Armorican Massif (Pochon, 2018).

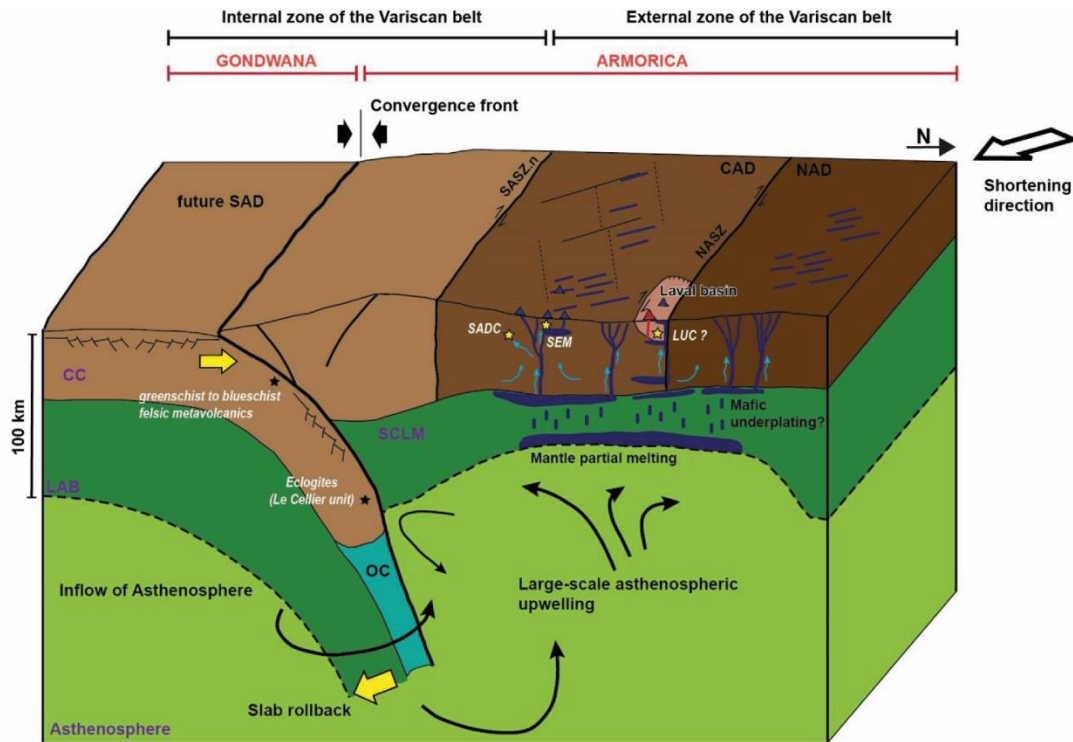


Figure 1. 7. Emplacement of the mafic magmatism in the Armorican Massif related to a slab roll back at ca. 360Ma. This event led to the partial melting of the sub-continental lithospheric mantle under the Armorica plate and the generation of important amounts of mafic magmas that contributed to the heating, rising and mobilization of several crustal fluids related to the Sb deposits in the Central Armorican Domain (Pochon, 2018).

- iv) A mixed source including metamorphic and meteoric fluids reported for Sb±Au deposits in the Armorican Massif and in the Variscan belt (Cheval-Garabédian et al., 2023). Fluid inclusion analyses performed for La Lucette Sb±Au deposit allowed to determine a primary low salinity aqueous-carbonic metamorphic fluid

related to the first W-base metal mineralizing stage showing trapping temperatures between 250°C-300°C and depths calculated at 5km-6km (Fig. 1.7; Cheval-Garabédian et al., 2023). The Sb±Au stage is represented by a cold aqueous meteoric fluid presenting trapping temperatures and depths estimated at 133°C-200°C and 3.5-6km (Cheval-Garabédian et al., 2023). Considering the similarities among several Sb±Au deposits and La lucette, this mixed source model has been suggested to be extended to the whole Sb±Au mineralization in the Variscan belt (Cheval-Garabédian et al., 2023). This model was latter questioned by Gloaguen et al. (2024), who asserted that the results presented by Cheval-Garabédian et al. (2023) are insufficient to support the idea of a generalized and unique metallogenic peak in the French Variscan belt at Carboniferous-Permian transition.

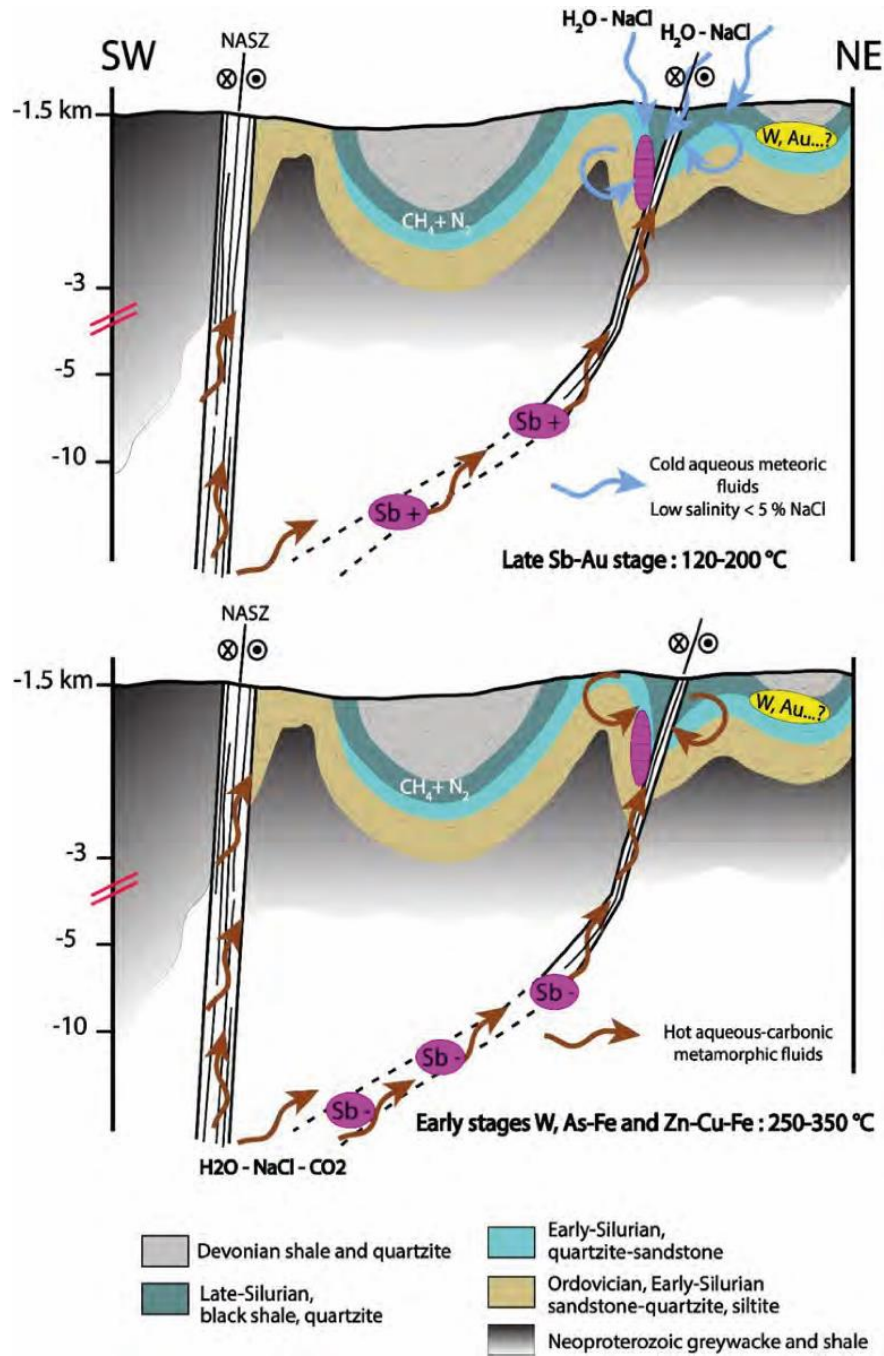


Figure 1. 8. Sb mineralization model for La Lucette deposit at late Variscan times (Cheval-Garabédian et al., 2023).

1.5. Antimony ore deposits and mineral systems

Most of the antimony deposits are formed in an epigenetic low temperature hydrothermal setting (150 to 350°C: Obolensky et al., 2007). Deposits can be found in both Archean terranes, associated to greenstone belts (South Africa or Canada); and in recent ones (Fig. 1.9), like the fumaroles related to active volcanoes in New Zealand (Schwarz-Schampera, 2014). It is less common to find Sb deposits in Archean terranes than in younger belts, due to the effect of erosion and the loss of significant concentrations of this element (Pohl, 2011).

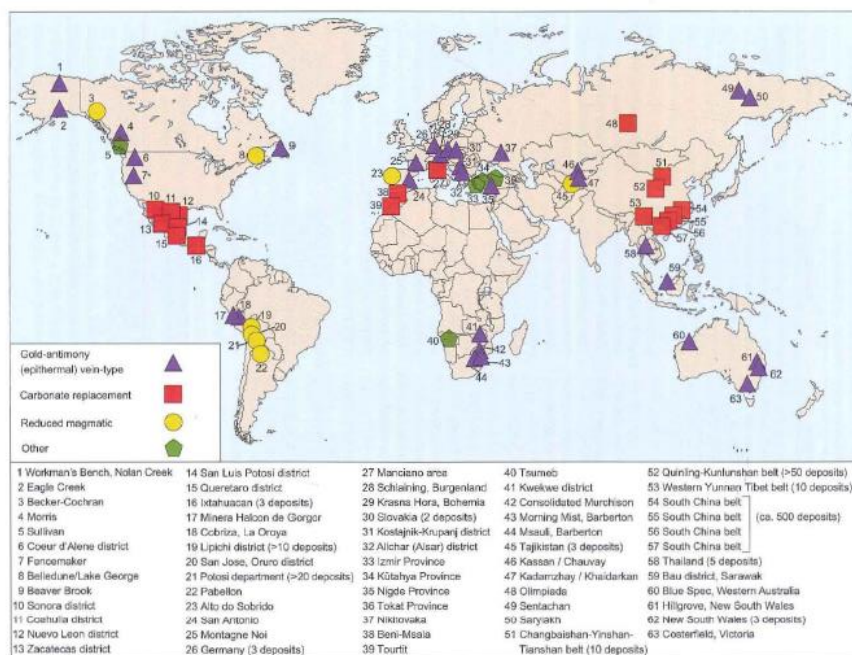


Figure 1. 9. Distribution of several Sb deposits, mines and occurrences. (Schwarz-Schampera, 2014).

The most relevant classifications or ore formation models where antimony deposits have been included are found within the hydrothermal ore deposits classification (Fig 1.10), among them the most common ones are: epithermal, reduced magmatic, polymetallic veins, carbonate replacement and orogenic gold (Pohl, 2011; Schwarz-Schampera, 2014):

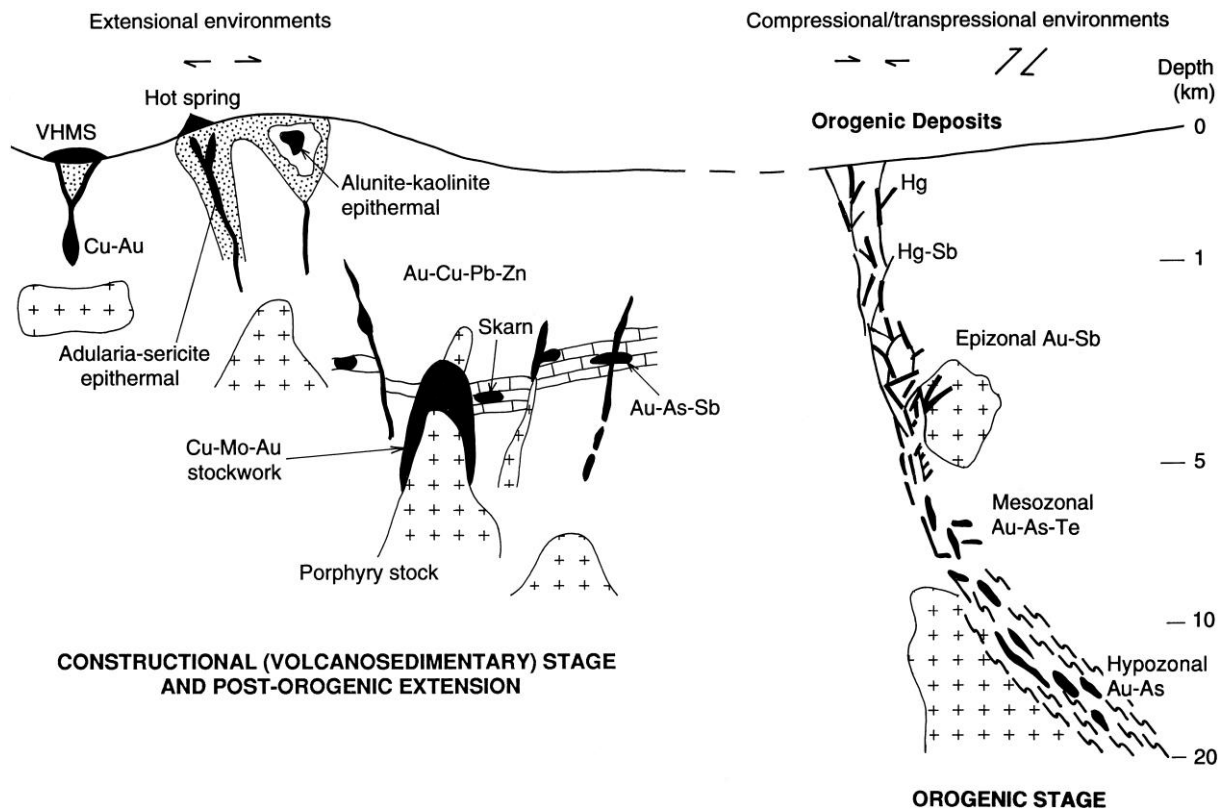


Figure 1. 10. Schematic representation of crustal environments of several hydrothermal deposits (where Sb is present) in terms of depth of formation and structural setting within a convergent plate margin. (Groves et al., 1998)

1.5.1-Epithermal deposits

These deposits are formed in subduction zones, and are temporary and spatially associated with volcanic and magmatic centers (Ridley, 2013b). The formation temperatures and depths of these deposits are generally low: $<300^{\circ}\text{C}$ and $<1.5\text{km}$ (Taylor, 2007). The most important metals exploited in the epithermal deposits are Au, Ag, as main products, Sb, Hg, Pb, Cu and Zn as by-products (Ridley, 2013b). Considering the sulfidation state and mineral assemblages, the epithermal deposits have been divided into three groups (Hedenquist et al., 2000; Sillitoe & Hedenquist, 2003) comprising (Figs. 1.10 and 1.11): a) high sulfidation (HS, oxidized with highly acidic fluids), with the most common assemblages represented by quartz, kaolinite, alunite, anhydrite, barite, together with gold-rich tennantite-tetrahedrite, pyrite-enargite, pyrite-famatinite and pyrite-luzonite (Einaudi et al., 2003); b) intermediate sulfidation

(IS), mainly composed by tetrahedrite, pyrite and chalcopyrite (Einaudi et al., 2003); and c) low sulfidation (LS, reduced), with adularia, sericite, pyrite-arsenopyrite, quartz, chalcedony, calcite, among others (Einaudi et al., 2003). Sb-ores are commonly found in the LS epithermal deposits classification (Fig 1.11) and are present in fractures or disseminated in enormous volumes of highly altered rocks (Ridley, 2013b)

Some of the most relevant Sb-bearing epithermal deposits in the world are located in Peru (e.g. Yanacocha, HS, Teal & Benavides, 2010), in Japan (e.g. Nansatsu, HS Hedenquist & Lowenstern, 1994), in Indonesia (e.g. Masupa Ria, IS, Thompson et al., 1994), in New Zealand in the Coromandel Peninsula (Hauraki, goldfield, LS, Simpson & Mauk, 2007), among others.

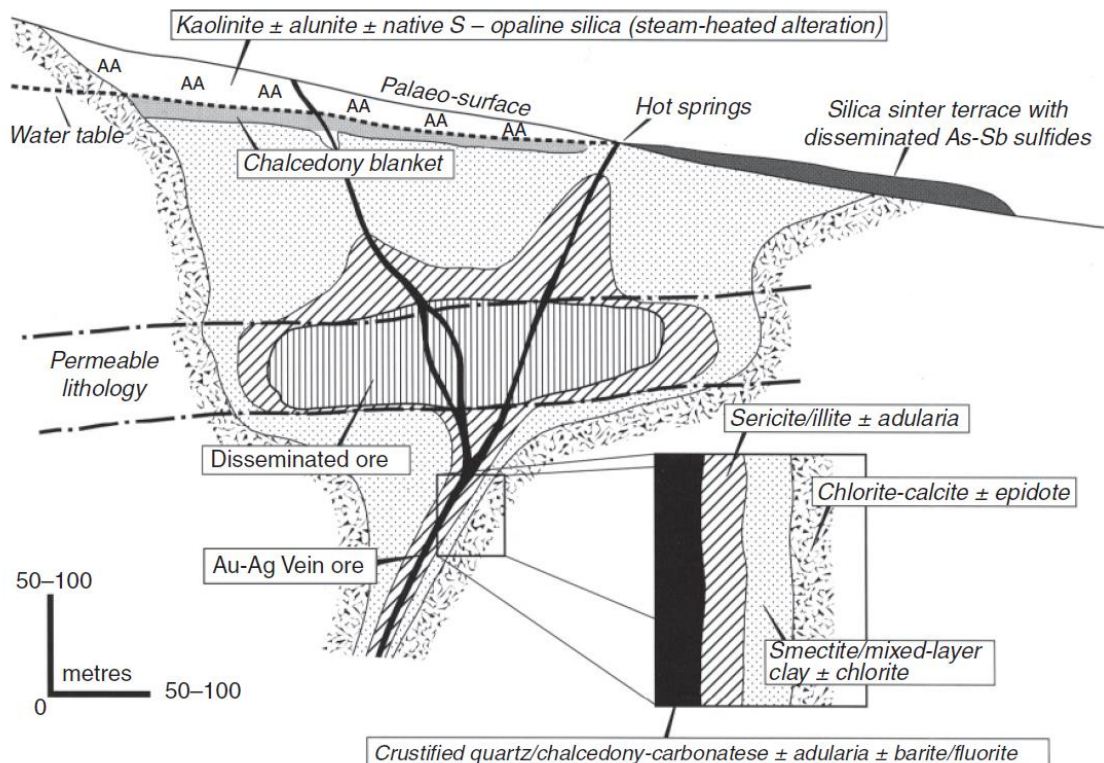


Figure 1. 11. Schematic cross section through a LS epithermal ore system showing a hypothetical composite system containing different styles of ore: vein ore, disseminated ore and hot spring ore, together with the distribution of alteration assemblages. (Einaudi et al., 2003; Hedenquist et al., 2000; Ridley, 2013b).

1.5.2. Reduced magmatic/intrusion related

The Sb mineralization in this type of deposit is strongly related to hydrothermal activity associated with the emplacement of reduced plutons (granitoids type I, A or S; Fig. 1.12) belonging to the ilmenite series (Hart, 2007; Schwarz-Schampera, 2014). The mineralized system is represented by veins and shows an important zonation starting with Au-W-As at the proximal parts of the intrusion; As-Sb-Au at the intermediate part; and Ag-Pb-Zn at the most distal part (Hart, 2007; Schwarz-Schampera, 2014). The main Sb ore consists of stibnite together with several sulfosalts possibly associated with lead, bismuth and tellurium (Schwarz-Schampera, 2014). The most relevant deposits are located in the Tombstone gold belt, in Central Yukon in Canada (related to intrusions of Cretaceous age; Hart, 2007).

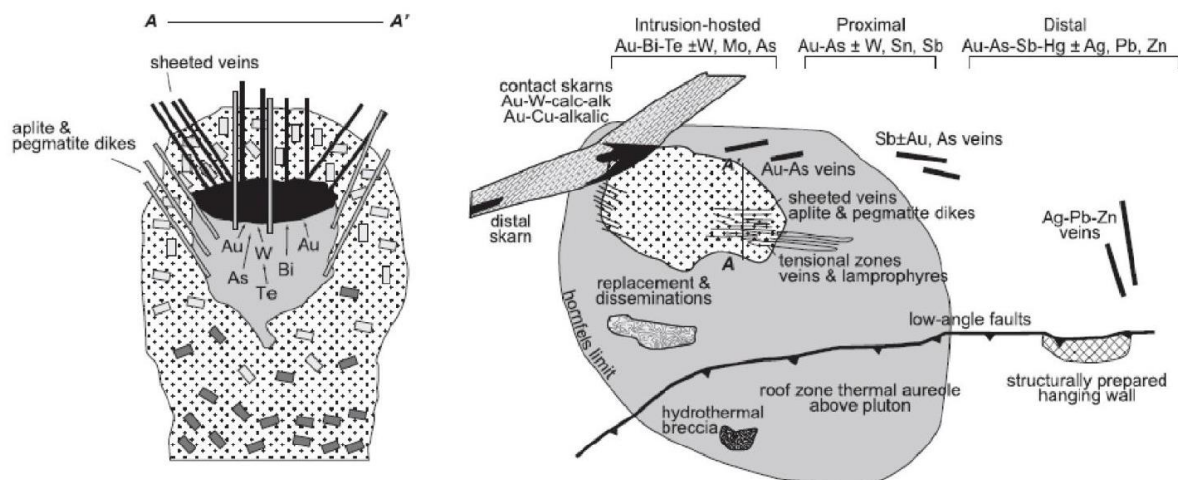


Figure 1. 12. Model of a reduced magmatic/intrusion related ore deposit. The mineralized system shows an important zonation starting with Au-W-As at the proximal parts of the intrusion; As-Sb-Au at the intermediate part; and Ag-Pb-Zn at the most distal part (Hart, 2007; Schwarz-Schampera, 2014).

1.5.3. Polymetallic veins associated to magmatic centers

These types of deposits show a strong structural control and are represented by large fields of veins or vein clusters where the mineralization is essentially composed by Sn, W, Mo, Bi, U, Au, Cu, Zn and Sb (Ridley, 2013b). The polymetallic veins can be found overprinting

porphyry ores (e.g. Morococha, Peru; Catchpole et al., 2011) or peripheral to porphyry and greisen deposits (Cornwall mining district, UK; Ridley, 2013); they can also be located in areas where none of these deposits have been reported, such as the vein fields in Idaho Springs, in Colorado, USA (Rice et al., 1985).

The mineralization is presented as small pods or disseminated sulfide in quartz/calcite veins whose thickness varies from some centimeters to 10m (Ridley, 2013b). The vein fields are zoned regarding both the metal content and the alteration features; for example, in the case of W-Sn deposits (e.g. Mole granite in Australia, Audétat et al., 2000) the distal parts of the field present chlorite-sericite alteration whereas the central part is associated to silicification and albite alteration (Audétat et al., 2000). The fluids show a magmatic-hydrothermal source with some involvement of meteoric waters in different proportions (Ridley, 2013b). The most relevant polymetallic vein deposits presenting Sb mineralization are located in the Bau district in Malaysia, in the Cobalt district in Canada and in the Bolivian antimony belt (Schwarz-Schampera, 2014).

1.5.4. Carbonate replacement deposits

They show several similarities with skarn deposits, as they are located within metasomatized carbonate rock. Nevertheless, the carbonate replacements deposits present a lack of calc-silicate gangue minerals and are usually found further from magmatic centers than the skarn-type deposits (Ridley, 2013b). The mineralization in the carbonate replacement ore deposits is represented by massive sulfides, presenting an assemblage mainly characterized by Pb-Zn-Ag, usually showing an irregular shape within the metasomatized carbonate host rocks. Often described as mantos, these deposits can also present chimneys shapes, that are affecting a part of the sedimentary sequence (Ridley, 2013b).

The Xikuangshan deposit, located in the Xiangzhing basin-Hunan Province in China, represents one of the most important carbonate replacement Sb mineralization and one of the biggest antimony reserves in the globe, containing up to 2110kt (Fan et al., 2004; Laznicka, 2014).

The orebodies are located within the Shetianqiao Formation of Upper Devonian age (Fig. 1.13), this unit is essentially composed of black shales as well as marls and limestones, with a mean of C_{org} of 0.97% (Fan et al., 2004). The mineralization is mainly composed by stibnite, located within highly silicified and carbonatized rocks (Fan et al., 2004; Yang et al., 2006). Considering the high Sb contents in the host rocks, the Shetianqiao Formation together with other sequences of pre-Devonian age have been proposed to be one of the main source of Sb (Fan et al., 2004).

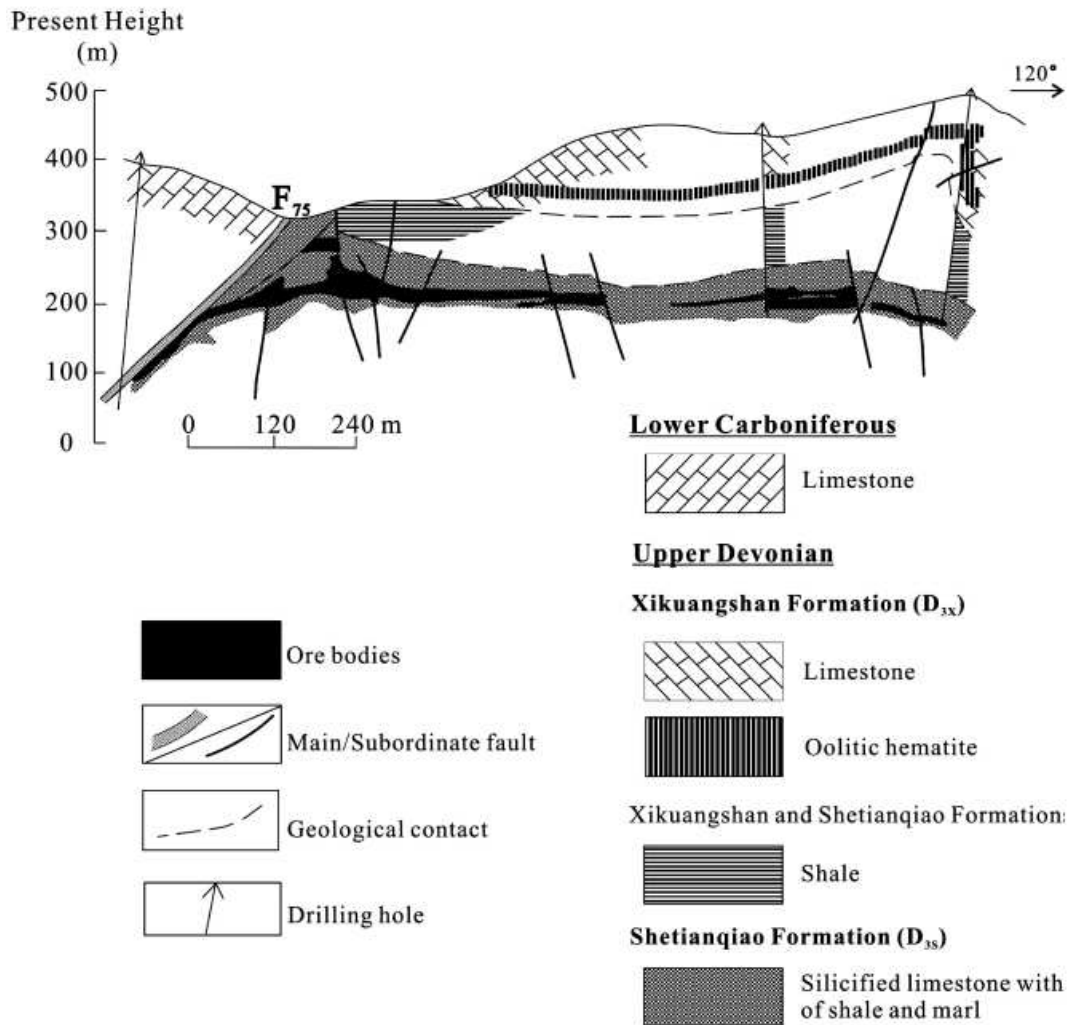


Figure 1. 13. Cross-section showing the ore bodies in the Xikuangshan deposit. The mineralization presents an important structural and stratigraphic control. (Yang et al., 2006).

1.5.5. Greenstone belts-hosted deposits

These are located within deformed terranes along large crustal scale fault zones, in compressional to transtensional settings and are believed to be syn to post orogenic (Goldfarb et al., 2001; Goldfarb & Groves, 2015). They are mainly mined for Au (main product) and As-Sb as by-products (Ridley, 2013b). The mineralization is usually present in gold-quartz-carbonate veins (Schwarz-Schampera, 2014), hosted in low grade metamorphic rocks (usually greenschist facies) and its formed in a wide range of pressure (between 1 and 5 kbars), depths (mesozonal-to epizonal, ≈ 3 -10 km, Figs. 1.4, 1.10 and 1.14) and temperatures around 200-

650°C (Goldfarb et al., 2001). Other lithologies associated with these types of deposits are intermediate to felsic intrusions, basalts as well as ultramafic intrusions (Dubé & Gosselin, 2007).

These deposits are widespread around the globe in greenstone belts of different ages (Ridley, 2013b). They are more commonly found in Archean-Proterozoic greenstone belts (e.g. Golden Mile-Yilgarn Craton-Australia, Vielreicher et al., 2016), than in Paleozoic Cordilleran Belts (e.g. Sierra Nevada Foothills-California). The most relevant Sb±Au±As deposits are located in Zimbabwe at the Kwekwe district of the Midland greenstone belt (Buchholz et al., 2007), and in South Africa at the Antimony line in the Murchinson greenstone belt (Poujol, 2001; Schwarz-Schampera et al., 2010; Vearncombe et al., 1992).

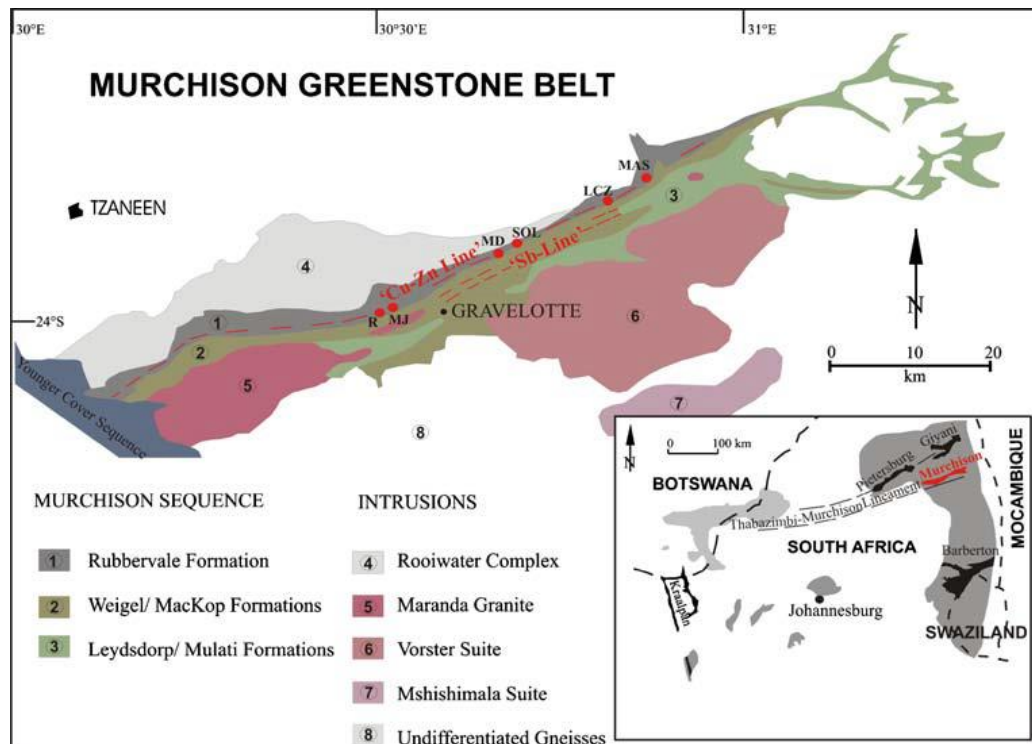


Figure 1. 14. Simplified geological map of the Murchinson greenstone belt showing the antimony line. (Poujol, 2001; Schwarz-Schampera et al., 2010)

1.5.6. Sb deposits associated with mafic rocks

Within the Armorican Massif, Sb deposits at surface are strongly associated with high magnetic and high-density zones, indicating mafic bodies at depth (Pochon et al., 2016). A temporal link was also demonstrated in this area by comparing the U-Pb dating in apatite of mafic sills and dykes with ^{40}Ar - ^{39}Ar dating in mica of several Sb deposits (*e.g.* Semnon; Saint-Aubin-des-Châteaux), both yielding an age at *ca.* 360 Ma (Pochon, 2018; Pochon et al., 2016b).

These deposits are represented by mineralized quartz-calcite veins associated with mafic rocks, they can be located in associated to shear zones (Dill, 2010). One of the main deposits belonging to this classification is Le Semnon in the Armorican Massif, which shows a shallow emplacement depth <2.5km and relatively high temperatures between 330 and 240°C (Pochon et al., 2018). Pochon et al. (2018) suggested that the shallow fluids responsible for the Sb mineralizing system were related to the emplacement of mafic dykes at *ca.* 360 Ma in the area (Fig. 1.15). The fluids were already Sb rich and were brought during the ascending of the mafic magma, the continuous circulation of fluids led to a pervasive alteration and to the precipitation of Sb-ores, that were accommodated by the regional deformation (Fig 1.15; Pochon et al., 2018). The mineral assemblage of this deposit includes Fe-As-(Au) as well as berthierite, native antimony and stibnite as main Sb-ore (Pochon et al., 2018).

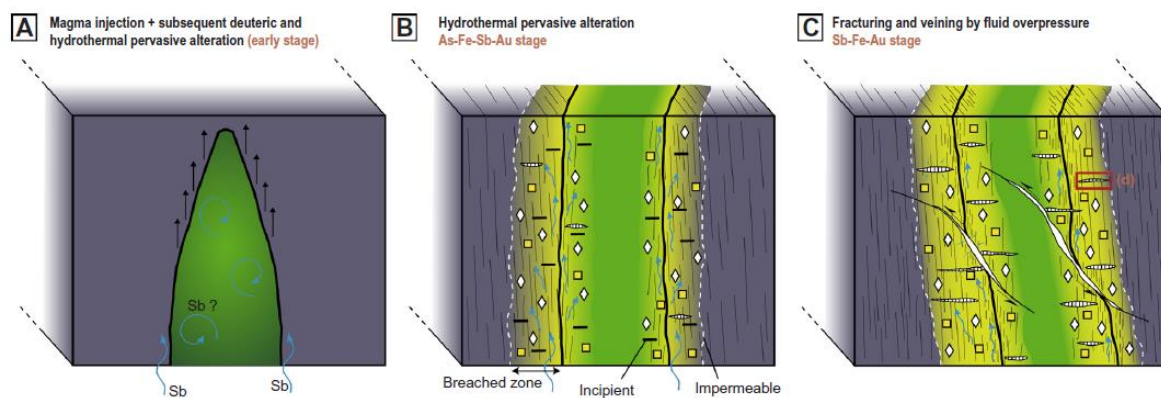


Figure 1. 15. Model proposed by Pochon et al. (2018) for explaining the main formation stages of the Le Semnon Sb-Au deposit in the Armorican Massif.

CHAPTER 2: THE PLACE OF THE VARISCAN OROGEN IN THE EUROPEAN BASEMENT AND THE EVOLUTION OF THE CENTRAL IBERIAN ZONE.

2.1. The European geological basement

The central and western European basement consist of several domains, representing the vestiges of ancient polyphased geological processes and orogenies. By far, the most important events reported in Europe correspond to the Cadomian orogeny (*ca.* 750-520 Ma, Murphy et al., 2002), the Cambro-Ordovician rift (related to the opening of the Rheic ocean; Arenas et al., 2007; Martínez Catalan et al., 2007; Matte, 2001; Nance et al., 2012), the formation of the Variscan belt (*ca.* 370-290 Ma; Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012; Paquette et al., 2017), the Triassic-Jurassic rifting associated to the opening of the Atlantic ocean (Stampfli & Borel, 2002) and the Alpine orogeny, starting at Middle Cretaceous times (Pfiffner, 2014).

The Pre-Variscan and Variscan basements represent the main study domains in this work (see parts 2.2-2.9 of this chapter). Indeed, both of them are well preserved in seven massifs across central and western Europe, including the Armorican (*e.g.* Icart gneiss, *ca.* 1.8-2.2 Ga.) and Central Massif (*e.g.* Lower Gneiss Unit; Lardeaux et al., 2014) in France ; The Iberian Massif domain in Spain and Portugal (*e.g.* Gévora Formation, early Carboniferous age, Central Iberian Zone; Rodríguez González, 2007); The Bohemian Massif (*e.g.* The Saxothuringian Zone; Franke, 2000); in Germany, Austria, Poland and Czech Republic; the Renish Massif in Germany (*e.g.* The Rhenohercynian Zone; Franke, 2000; Zeh & Gerdes, 2010); the Vosges-Schwarzwald massif (*e.g.* Gföhl unit Žák et al., 2011, 2014), located in the border between France and Germany; and finally, the Pyrenean Axial Zone between France and Spain (Martínez Catalán et al., 2021 and references therein).

2.2. The Variscan orogen

The Variscan Belt belongs to a Paleozoic orogen extending over 8000km long from the Ouachita, the Appalachians mountains to the Caucasus (Matte, 2001). It is the result of the total closing of the Rheic ocean followed by the collision between two main continental domains, Gondwana (to the south) and Laurussia (Laurentia-Baltica-Avalonia, to the north). This collisional event took place at the end of the Paleozoic era during late Devonian to Carboniferous times (Ballèvre et al., 2009, 2014; Franke et al., 2017; Kroner & Romer, 2013; Schulmann et al., 2022).

The European Variscan Belt shows a non-cylindrical geometry, modified by the Paleozoic evolution of the orogen presenting a NW-SE trending at lithospheric scale and transcurrent faults (Edel et al., 2018; Schulmann et al., 2022). Considering this, Edel et al. (2018) have divided the belt into three tectonic zones: The North, the Central and the South Variscan domains.

2.2.1. The Northern Variscan Domain

The North Variscan Domain (NVD, Fig. 2.1) includes the Renish Massif, The Bohemian Massif, the Vosges-Schwarzwald and some small outcrops (Spessart and Odenwald) at the North (Edel et al., 2018; Schulmann et al., 2022). It is bounded by the Sudetic Fault System (SFS, Schulmann et al., 2022) at the east and by the Bray Fault (Br (Schulmann et al., 2022) at the west. The NVD was first defined by Kossmat (1927) and its divided from south to north (Schulmann et al., 2022) into: The Moldanubian (MZ), the Teplá-Barradian (TPZ), the Saxothuringian (STZ), the Rhenohercynian (RHZ), and the Brunovistulian zones (Dudek, 1980; Edel et al., 2018; Martínez Catalán et al., 2021; Schulmann et al., 2022).

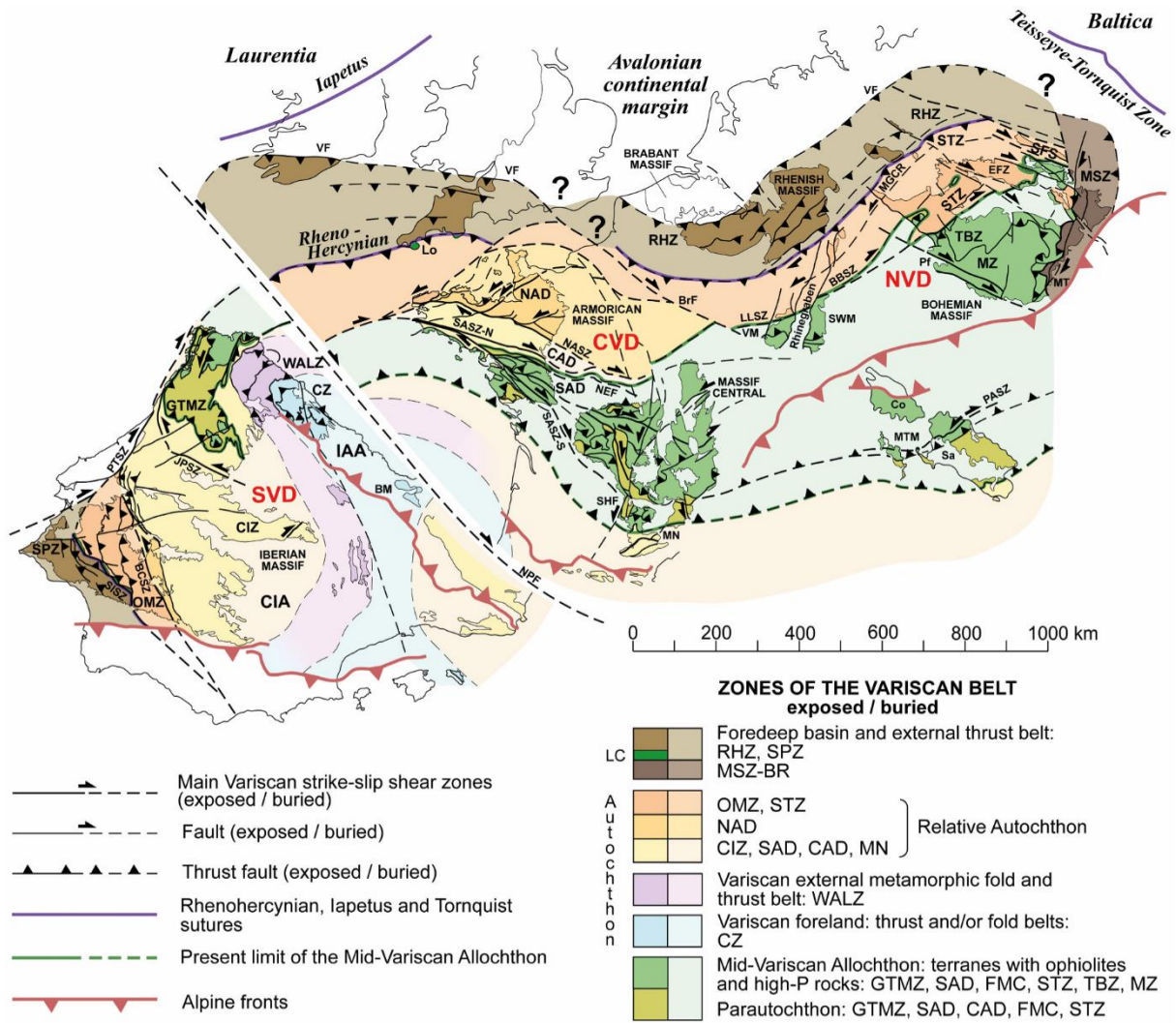


Figure 2. 1. Reconstruction of the European Variscan Belt from Late-Carboniferous-early Permian. **Variscan domains (VD):** CVD, Central; NVD, North-eastern; SVD, South-western. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Trás-os-Montes; MSZ, Moravo-Silesian Zone; MZ, Moldanubian; OMZ, Ossa-Morena; RHZ, Rhenohercynian; SPZ, South Portuguese; STZ, Saxothuringian; TBZ, Teplá-Barrandian; WALZ, West Asturian-Leonese. **Armorican Domains (AD):** CAD, Central; NAD, North; SAD, South. **Shear zones (SZ), faults (F) and fault zones (FZ):** BBSZ, Baden-Baden; BCSZ, Badajoz-Córdoba; BrF, Bray; EFZ, Elbe; JPSZ, Juzbado-Penalva; LLSZ, Lalaye-Lubine; MT, Moldanubian Thrust; NASZ, North Armorican; NEF, North-sur-Erdre; NPF, North Pyrenean; PASZ, Posada-Asinara; Pf, Pfahl-Danubian fault system; PTSZ, Porto-Tomar; SASZ, South Armorican (N and S, northern and southern branches); SHF, Sillon Houiller; SISZ, Southern Iberian; SFS, Sudetic fault system; VF, Variscan Front. **Other:** MT, Moldanubian thrust; BM, Basque Massifs; CIA, Central Iberian Arc; Co, Corsica; FMC, French Massif Central; IAA, Ibero-Armorican Arc; Lo, Lizard ophiolites; MTM, Maures-Tanneron Massif; MGCR, Mid-German Crystalline Rise; MN, Montagne Noire; Sa, Sardinia; SWM, Schwarzwald Massif; VM, Vosges Massif. Modified after (Martínez Catalán et al., 2021; Schulmann et al., 2022)

2.2.2. The Central Variscan Domain (CVD)

The CVD (Fig. 2.1) is bounded at the south by the Nort-sur Erdre fault and at the north by the North Armorican Shear Zone (Martínez Catalán et al., 2021). This domain includes: the French Massif Central, which comprises several metamorphic stacked nappes that belonged to the northern part of the Gondwana margin; and the Armorican Massif. The CVD presents some similarities with the NVD, these include an equivalent of the Saxothurugian Zone that has been reported at the Leon Unit (NW France, Ballèvre et al., 2009). Despite these similarities the geology and tectonics of the key units in both domains present important differences (Schulmann et al., 2022). Considering the importance of the Armorican Massif in this work, this domain will be overviewed in detail.

2.2.2.1. The Armorican Massif

Located in NW France (Fig 2.2), this unit is divided in three different domains separated by two main shear zones corresponding to the South Armorican Shear Zone (SASZ) and the North

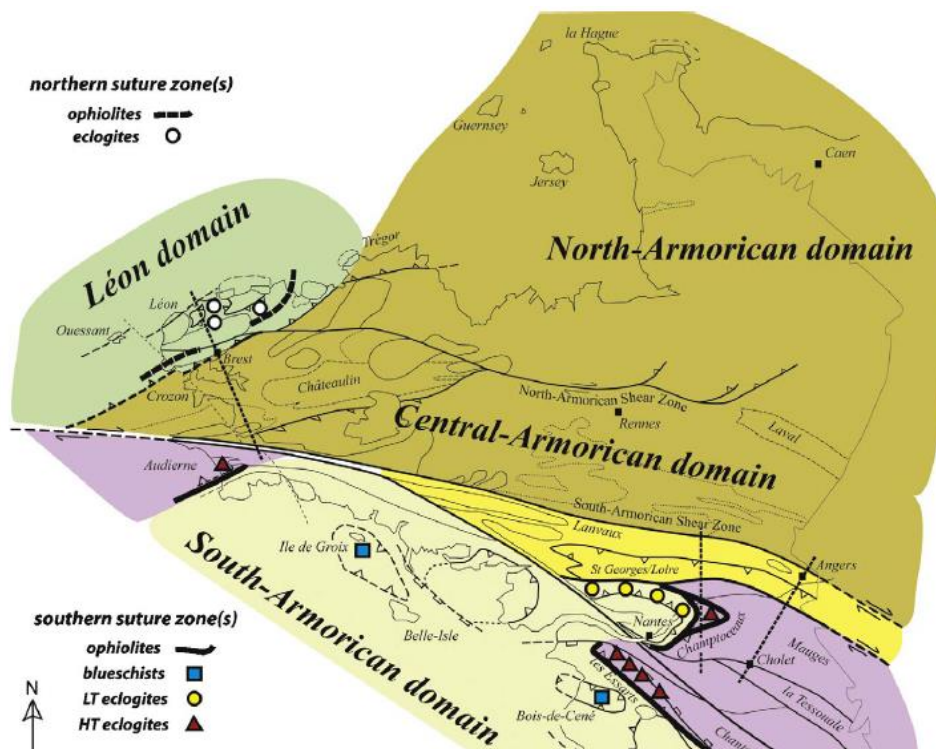


Figure 2. 2. Simplified map of the different domains in the Armorican Massif. After (Ballèvre et al., 2009).

Armorican Shear Zone (NASZ) (Gore & Le Corre, 1987; Gumiaux, Brun, et al., 2004; Gumiaux, Gapais, et al., 2004; Jegouzo, 1980) :

- a) The South Armorican Domain (SAD, Fig 2.2): Corresponds to the internal thickened part of the Variscan belt. It comprises intermediate to high grade metamorphic rocks. Three metamorphic zones, separated by low-angle ductile faults and detachments, have been observed in this area (Bosse et al., 2002; Gapais et al, 2015 . From North to South, the first zone is represented by granitoids, migmatites and gneiss (Jones & Brown, 1990). The second one is mainly composed by mica-schists in greenschist to amphibolite facies (Triboulet & Audren, 1988). The third one consists of high grade metamorphic rocks including the blueschist from Ile de Groix (Bosse et al., 2002).
- b) The Central Armorican Domain (CAD, Fig 2.2): Corresponds to the external un-thickened part of the Variscan belt, its mostly represented by terrigenous sedimentary rocks (“Brioverian”) of Neoproterozoic to Cambrian age (635-530Ma) in central Brittany (Chantraine et al., 1994; Ballèvre et al, 2009; Néraudeau and Dabard, 2023) (Ballèvre et al., 2009; Barrois, 1899; Chantraine et al., 1994). All of them overlain by successions of sandstones, shales and rare limestones from Ordovician (e.g. Grès Armorican) to Devonian age. The Variscan metamorphism is mainly in the greenschist facies conditions or above (Ballèvre et al., 2009; Barrois, 1899; Chantraine et al., 1994). The first main magmatic event recorded in this domain is the intrusion of Ordovician granites (Ballèvre et al., 2009; Barrois, 1899; Chantraine et al., 1994). The second main magmatic event is marked by several swarm of sills and dykes of dolerites that has been documented in this area (Le Gall, 1999), their emplacement age was determined at 360Ma (Pochon et al., 2016). The third main magmatic event is marked by the

emplacement of syntectonic granitoids intruded around 320-310 Ma (Ballouard et al., 2017; Tartèse et al., 2011).

- c) The North Armorican Domain (NAD, Fig 2.2) is mainly formed by the sedimentary “Brioverian” sequence and a Neoproterozoic basement affected by Cadomian deformation and intruded by pre-Cambrian granites (Brun et al., 2001; Gumiaux, Gapais, et al., 2004). Both, the sedimentary sequence and the granite are overlain by a lower Cambrian to Devonian sedimentary sequence, mainly composed of sandstones and shales. This Domain is slightly affected by the variscan deformation (thrusts and faults) and intruded by scarce Carboniferous mafic intrusion (e.g. Saint-Jean-du-Doigt complex emplaced between $347. \pm 0.4$ and 345.5 ± 0.5 Ma, Barboni et al, 2013) and numerous felsic plutons (e.g. Flamanville intrusion dated at 318 ± 1.5 , U/Pb on zircon, Martin et al, 2018; Huelgoat intrusion dated at 314.8 ± 2 Ma, U/Pb on zircon, Ballouard, 2016).

2.2.3. The southern Variscan Domain (SVD).

2.2.3.1. The Iberian Massif

The Iberian Massif (Fig. 2.3 and 2.4) is divided into 6 tectonic zones (Farias et al., 1987; Julivert et al., 1974; Lotze, 1945) corresponding to: the Cantabrian Zone (CZ), the Western Asturian-Leonese zone (WALZ), the Galicia-Tras-Os-Montes Zone (GTMZ), the Ossa Morena Zone (OMZ), the South Portuguese Zone (SPZ) and the Central Iberian Zone (CIZ, main study domain in this work, explained in detail in section 2.4).

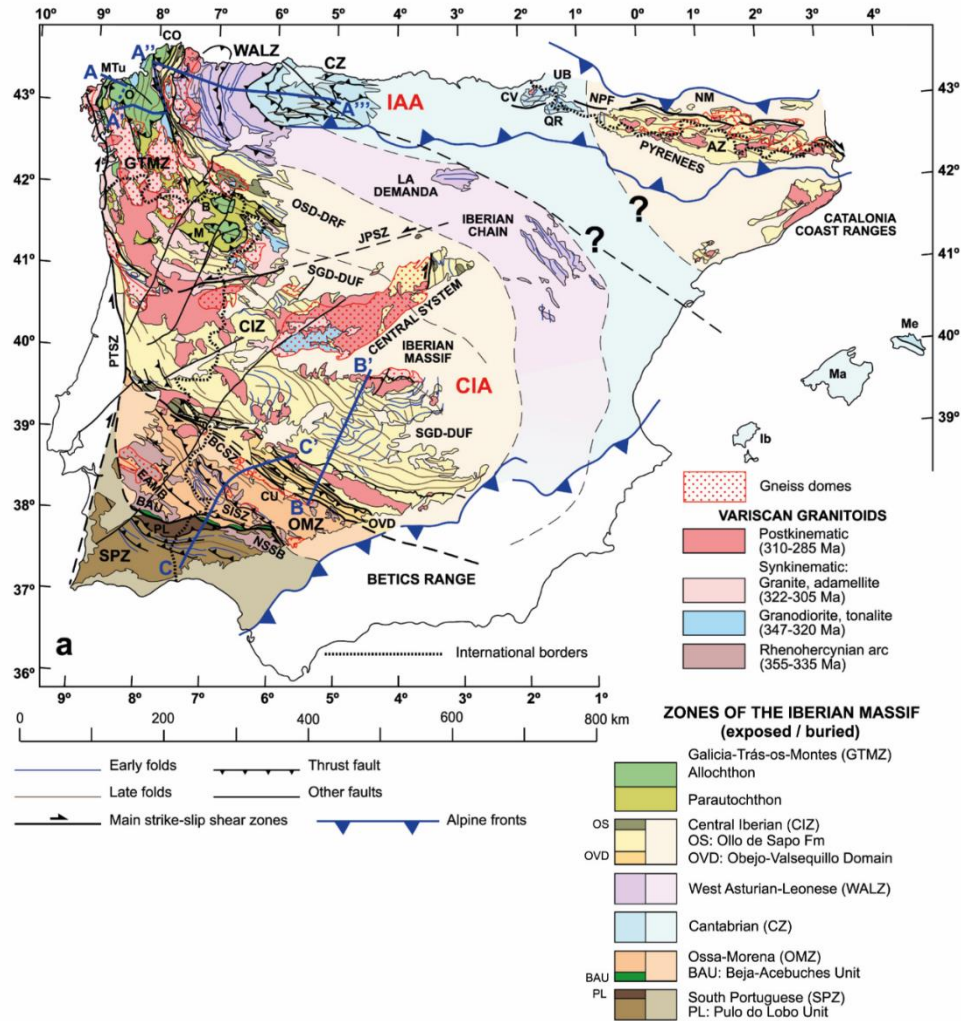


Figure 2. 3. (a) Geological map of the Iberian Peninsula showing the Variscan massifs and the zones of the Iberian Massif, continued into the Pyrenees, Iberian Chain and Catalonia Coast Ranges. Based on the Geological map of Spain and Portugal to scale 1:1000 000 (IGME-LNEG, 2015) and in Martínez Catalán (2012). The most important structures are shown, including early and late folds, thrust faults, and the main ductile strike-slip shear zones. **(b)** Detail of the geology of the Galicia allochthonous complexes showing the distribution of the three Allochthons and the Parautochthon. **(c)** Detail of the geology of the Portuguese allochthonous complexes. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Trás-os-Montes; OMZ, Ossa-Morena; SPZ, South Portuguese; WALZ, West Asturian- Leonese. **Domains of the CIZ (D):** DRF, of Recumbent Folds; DUF, of Upright Folds; OSD, Ollo de Sapo; OVD, Obejo-Valsequillo; SGD, Schist-Greywacke. **Allochthonous complexes:** B, Bragança; CO, Cabo Ortegal; M, Morais; MT, Malpica-Tui; O, Órdenes. **Other units:** BAU, Beja-Acebuches; CU, Central Unit; EAMB, Évora-Aracena Metamorphic Belt; NSSB, Northern Sierra de Sevilla Batholith; PL, Pulo do Lobo Unit. **Shear zones (SZ) and faults (F):** BCSZ, Badajoz- Córdoba; JPSZ, Juzbado-Penalva; NPF, North Pyrenean; PTSZ, Porto-Tomar; SISZ, Southern Iberian. **Arches (A):** CIA, Central Iberian; IAA, Ibero-Armorican. **Pyrenees:** AZ, Axial Zone; NM, Northern Massifs; Basque Massifs: CV, Cinco Villas; QR, Quinto Real; UB, Ursuya-Baygura. **Balearic Islands:** Ma, Majorca; Me, Menorca; Ib, Ibiza.

Allochthonous groups: LA, Lower Allochthon; MA, Middle Allochthon; PA, Parautochthon; UA, Upper Allochthon (IP, Intermediate-P; HP-HT, High-P/ High-T). After Martínez Catalán et al, (2021).

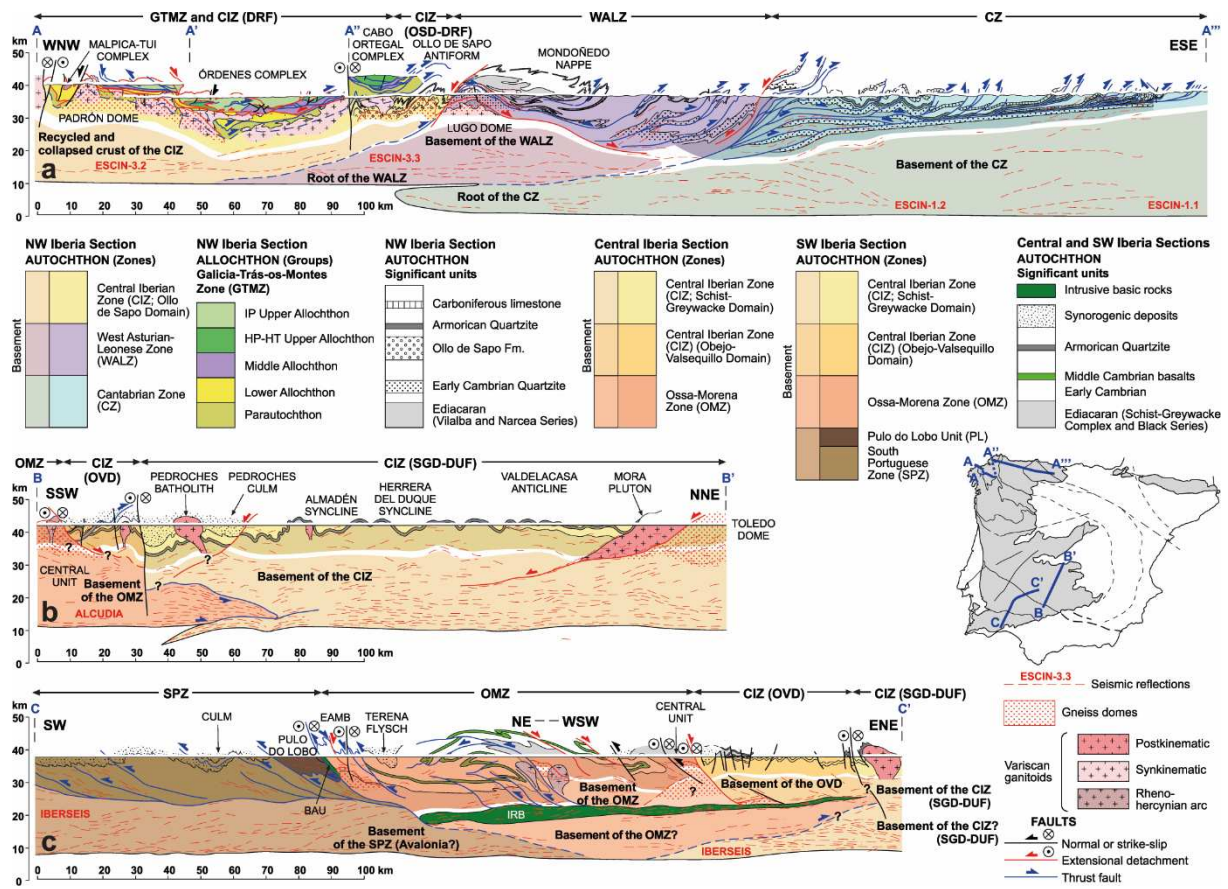


Figure 2. 4. Cross sections representative of the structure of the Iberian Massif including the Variscan sutures. (a) Northwest Iberian section A-A'', modified from Martínez Catalán et al. (2014). (b) Central Iberian section B-B', based on Martínez Poyatos et al. (2012). (c) Southwest Iberian section C-C', based on Simancas et al. (2003) and partly on Rubio Pascual et al. (2013b). The sections are built from field geology and partly using deep seismic reflection profiles. For section A-A'', these are ESCIN-1 (Pérez-Estaún et al., 1994, 1995), ESCIN-3.2 (Alvarez-Marrón, 1995, 1996) and ESCIN-3.3 (Martínez Catalán et al., 1995; Ayarza et al., 1998). The two latter were acquired offshore, while section A-A'' derives from onshore geology. In the parts of section A-A'' roughly corresponding to these two profiles, (GTMZ, CIZ and WALZ), the seismic reflections have been placed approximately. Section B-B' roughly follows the seismic line ALCUDIA (Martínez Poyatos et al., 2012). Section C-C' follows the seismic line IBERSEIS (Simancas et al., 2003). Whrench faults are continued at depth avoiding to cross low-dipping reflections. Colors corresponding to zones or groups are superposed to frames or grey shades indicating lithologies or units. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Trás-os-Montes; OMZ, Ossa-Morena; SPZ, South Portuguese; WALZ, West Asturian-Leonese. **Domains of the CIZ (D):** DRF, of Recumbent Folds; DUF, of Upright Folds; OSD, Ollo de Sapo; OVD, Obojo-Valsequillo; SGD, Schist-Greywacke. **Other units:** BAU, Beja-Acebuches; EAMB, Évora-Aracena Metamorphic Belt; IRB,

Iberian Reflective Body. **Other:** Upper Allochthon: IP, Intermediate-P; HP-HT, High-P/High-T. See Fig. 2 for location of the sections. After Martínez Catalán et al. (2021) and references therein.

The Cantabrian Zone (CZ)

Located at the innermost part of the Ibero-Armorican arc (Fig. 2.3 and 2.4), this zone comprises an Ediacaran sequence overlain unconformably by a Paleozoic succession as well as alkaline and tholeiitic intrusions associated to Cambrian-Ordovician rifting (Corretgé & Suárez, 1990). It represents a foreland thrust belt that belonged to the passive margin located at the northern part of Gondwana (Martínez Catalán et al., 2021; Schulmann et al., 2022). The deformation that helped to the development of this zone is related to an eastward thrusting taking place at 325-300Ma during the Variscan orogeny (Alonso et al., 2009; Pérez-Estaún et al., 1988).

The West Asturian Leonese Zone (WALZ)

This unit represents a slate belt (Fig. 2.3 and 2.4) presenting early Cambrian (terrigenous) to Lower Devonian (shallow marine) sequences (Pérez-Estaún et al., 1990). The unit was affected by MP Barrovian metamorphism, which is related to the presence of thrusts and recumbent folds (Arenas & Martínez Catalán, 2003; Capdevila, 1969; Martínez Catalán et al., 2014). The folding in the eastern part of this zone was dated at 335Ma, this process has been considered as diachronic and its propagation was directed to the external parts of the belt (Dallmeyer et al., 1997). This diachronism is consistent with the dating of the folding in the internal parts of the CIZ (360Ma), the basal thrust in the GTMZ (343Ma) and the dating of the limit WALZ-CZ at 321Ma (Dallmeyer et al., 1997; Martínez Catalán et al., 2021). After the compressive deformation, several detachments as well as gneiss domes were produced during the extensional collapse of the chain (Arenas & Martínez Catalán, 2003; Capdevila, 1969; Martínez Catalán et al., 2014). These detachments were dated at 315-300Ma (Dallmeyer et al., 1997).

The Galicia Trás-Os-Montes Zone (GTMZ)

This zone comprises a parautochthon overlain by three allochthonous units (with five complexes, Fig. 2.3 and 2.4), stacked during early Carboniferous times (Arenas et al., 2016; Ballèvre et al., 2014; Martínez Catalán et al., 2009). Two of these complexes outcrop in Portugal and correspond to the Braganca and Morais complexes. The other three are exposed in Galicia and include the Malpica Tui, the Órdenes and Cabo Ortegal Complexes (Arenas et al., 2016; Ballèvre et al., 2014; Martínez Catalán et al., 2009)..

- a) The Upper Allochthon comprises Cambrian metasedimentary sequences which are intruded by mafic rocks of tholeiitic affinity and granitoids of calc-alkaline affinity (Arenas et al., 2016; Martínez Catalán et al., 2009). Ultramafic serpentinite rocks can be also observed. The upper allochthon is divided in two groups, lower and upper, separated by a detachment (Martínez Catalán et al., 2009). The lower group consist mainly of highly metamorphic paragneisses affected by eclogite facies metamorphism at 400Ma whose maximum depositional age was dated at 510Ma (Albert et al., 2015; Arenas & Martínez Catalán, 2002; Hubregtse, 1973; Ordóñez Casado et al., 2001; Vogel, 1967). On the other hand, the upper group registered granulite facies metamorphism, dated at 495-482Ma (Albert et al., 2015; Arenas & Martínez Catalán, 2002; Hubregtse, 1973; Ordóñez Casado et al., 2001; Vogel, 1967). These rocks are believed to be a peri-Gondwanan terrane that was rifted at around 500Ma in an extensional event related to the opening of the Rheic Ocean (Matte, 2001).
- b) The Middle Allochthon consist mainly of oceanic units of Cambrian-Ordovician and Lower Devonian age (Albert et al., 2015; Martínez Catalán et al., 2009). The oldest rocks have been divided into to three different groups (Martínez Catalán et al., 2021 and references therein). The first group includes amphibolites, gabbros, pyroxenites,

tonalites and ultramafic rocks showing geochemical signatures of N-MORB, tholeiites and within plate basalts (Martínez Catalán et al., 2021 and references therein). Their gabbroic protolith was dated at 495-475Ma. This group underwent high deformation (dated at 363-367Ma) marked by mylonitic foliation together with greenschist facies (Martínez Catalán et al., 2021 and references therein).. The second group is composed by rocks with transitional affinity: Is represented by mafic rocks with N-MORB affinity, as well as schist and phyllites. These rocks underwent blueschist and amphibolite facies metamorphism dated at 363 ± 2 Ma and 337 ± 3 Ma (extensional collapse of the chain, Martínez Catalán et al., 2021 and references therein). They are believed to be formed in a transitional crust between Gondwana and an oceanic domain; iii) The third one represents a mélange between metasedimentary rocks and ophiolites. The latest show protolithe ages between 527 and 485Ma presenting a cal-alkaline and tholeiitic affinities (Martínez Catalán et al., 2009, 2021). They are well exposed in the Cabo Ortegal complex

The Lower Devonian rocks consist of ophiolites including metagabbros, diabase dykes and metaperidotites (Martínez Catalán et al., 2021; Schulmann et al., 2022). Their protolith has been dated at 405-395Ma. These rocks show a N-MORB and island arc tholeiitic geochemical signature (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein).

- c) The Lower Allochthon is composed of paragneisses and several metasedimentary rocks including schists, quartzites, phyllites (Dias da Silva et al., 2016; Martínez Catalán et al., 2014). All of them were intruded by granodiorites at 490Ma, granites at 475Ma and alkaline to peralkaline intrusions at 475-470Ma signature (Martínez Catalán et al., 2021;

Schulmann et al., 2022 and references therein). This unit was affected by LT-HP metamorphism represented by the presence of eclogites, blueschists in addition to orthogneisses signature (Dias da Silva et al., 2016; Martínez Catalán et al., 2014).

- d) Parautochthon: This unit comprises synorogenic deposits (turbidites with Carboniferous depositional age) and a preorogenic sequence (similar to the CIZ) of limestones, slates and sandstones (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein). These rocks underwent pervasive metamorphism in greenschist facies up to amphibolite facies (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein).

The Ossa Morena Zone (OMZ)

It represents a slate belt including a Paleozoic sequence as well as a Neoproterozoic basement, Fig. 2.3 and 2.4). This unit shows a relevant Cadomian imprint that was dated in the amphibolite facies of the Black series at 600Ma (collision arc-continent , Bandrés et al., 2004). Upper Neoproterozoic ages (560-550Ma), related to the collapse of the arc, were also obtained in the overlying volcanic rocks (Bandrés et al., 2004; Robardet & Gutiérrez-Marco, 1990). Alkaline magmatism related to the Ordovician rifting episode that followed the collapse of the Cadomian arc has been also reported in this zone, and dated at 470-460Ma (Bandrés et al., 2004; Robardet & Gutiérrez-Marco, 1990).

At the northern limit of the OMZ (boundary between CIZ-OMZ) outcrops the Central Unit (Fig. 2.3 and 2.4), which comprises relics of eclogites, gneisses, amphibolites, schists and Ordovician orthogneisses (García Casquero et al., 1985). The HP metamorphism here has been dated at 377 ± 19 Ma and its conditions were estimated at 1.45-1.9GPa and 550°C (García Casquero et al., 1985). The presence of these eclogites together with the oceanic signature of the basic rocks in this unit and the differences in faunas between CIZ and OMZ has helped to

suggest the hypothesis of a suture that could be Cadomian, Cambro-Ordovician or Variscan (Martínez-Catalán et al 2021 and references therein). Nevertheless, lack of ophiolitic sequences questions the existence of this suture, which could be covered by the Badajoz-Córdoba Shear Zone (BCSZ), located between the OMZ and the CIZ (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein).

At the southern part of the OMZ outcrops the Évora-Aracena Metamorphic Belt (EAMB). This unit is represented by the Évora Massif in Portugal and by the narrow Aracena belt in Spain (Fig. 2.3 and 2.4c). It is composed by schists, gneisses, phyllonitic rocks (with blueschists and eclogite lenses) as well as ophiolitic fragments (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein). The latest present a MORB affinity, were dated at 480Ma, and are thought to be the relicts of the Rheic ocean (Rubio Pascual et al., 2013). The HP metamorphic event was dated at 370-360Ma whereas the LP-HT granulite event was dated at 343-330Ma (Dallmeyer et al., 1997; Dallmeyer & Quesada, 1992; Rubio Pascual et al., 2013).

Underlying the EAMB lies the Beja-Abejuches Unit (BAU), which represents the boundary between the OSM and the SPZ (Fig. 2.3 and 2.4c). It consists of mafic and ultramafic metabasites (345-330Ma) in addition to granodiorites and diorites dated at 352Ma (Azor et al., 2008; Pin et al., 2008). The BAU has been considered to be a subducted ocean ridge; an ophiolite; the relicts of a slab break-off; related to an arc; the relicts of the opening of a small ocean associated to a mantle plume (Andrade, 1985; Martínez Catalán et al., 2021). The emplacement of this unit has been related to an extensional event taking place from late Devonian to Carboniferous times leading to an elevation of the thermal gradient in the crust in addition to the production of important amounts of magmatism (Rubio Pascual et al., 2013; Simancas et al., 2003).

The South Portuguese Zone (SPZ)

This zone represents an equivalent of the Rhenohercynian Zone and a Variscan foredeep. It is separated from the OMZ by the BAU and the accretionary prism of the Pulo do Lobo unit (Fig. 2.3 and 2.4c, Onézime et al., 2002; Simancas et al., 2003). The latest together with the ophiolite relicts of the Cubito-Moura Unit (dated at 480Ma) have been interpreted as the Rheic suture (Franke et al., 2017). The basement under the SPZ has been related to the one of Avalonia, this is supported by the ages of both inherited zircons in granitoids and detrital zircons (Braid et al., 2011; De La Rosa et al., 2002; Rodriguez et al., 2015). The lithology of the SPZ is composed by slates, quartzites and volcanosedimentary sequence. This unit is believed to have been accreted during Devonian times (as well as the OMZ), based on the extensional deformation and the magmatism that affected this zone (Martínez Catalán et al., 2021; Schulmann et al., 2022 and references therein).

The Central Iberian Zone (CIZ)

The CIZ consist of a Paleozoic sequence composed of slates, schists, quartzites and calcareous rocks; which are unconformably overlying the Neoproterozoic to Cambrian sequence known as the Schist-Greywacke Complex (Martínez Catalán et al., 2021; Schulmann et al., 2022; Teixeira, 1955). All of these successions have been intruded by several magmatic events ranging from Neoproterozoic to Cenozoic times (Villasca et al., 2022 and references therein).

2.3. Correlations among the Iberian and French units-The Ibero-Armorican Arc

Several equivalences can be observed among the different tectonic domains and massifs present in the Variscan belt. One of the most relevant ones comprises the so called “Ibero-Armorican Arc” (Ballèvre et al., 1992; Dias & Ribeiro, 1995), which includes tectonic domains

from both, the Iberian and the Armorican Massif. It represents the most important Variscan macrostructure in western Europe (8000km long, 1000km width) that goes from Brittany (France), passes by the Cantabrian sea into Western Iberia and ends up in southern Spain at the Betic Alpine front (Weil et al., 2010).

Not all the tectonic zones described in the Iberian Massif, such as the CZ and the WALZ, present an equivalent in the Armorican Massif. Other domains like the OMZ are not well represented, a possible equivalent to this zone could be represented by the eclogites of the León domain (Balé & Brun, 1986). On the other hand, the Órdenes and Malpica complexes belonging to the lower allochthon of the GTMZ show important similarities with several parts of the SAD, such as the Champtoceaux and Vendée units (Ballèvre et al., 2014). The high P metamorphism is only 10 Ma older in the GTMZ units and the lithologies and photoliths in both domains are the same (Ballèvre et al., 2014). The Parautochthon in the GTMZ can be compared with the one in the SAD, these units are underlying the lower Allochthon and are represented by porphyroids of Ordovician age together with black cherts and ampelites of Silurian age and several syn-orogenic sediments (Ballèvre et al., 2014; Martínez Catalán et al., 2021). The Parautochthon in NW Iberia shows also some similarities with the CAD represented by the Saint Georges sur Loire unit and the “blocky” subunit (Cartier & Faure, 2004; Dias da Silva et al., 2014; González Clavijo et al., 2016; Lardeux & Cavet, 1994; Ribeiro, 1974).

The oceanic units of the Órdenes and Malpica-Tui, representing the Middle Allochthon in NW Iberia, can be compared to the Bois-de-Cené, Ile de Groix and the Audierne Bay units in the SAD (Martínez Catalán et al., 2021). In NW Iberia the oceanic affinity units were affected by a high grade metamorphic event dated at 363-367 Ma (Dallmeyer et al., 1997) which matches with the high-P metamorphism dated at 360 Ma in the SAD (Bosse et al., 2000; Paquette et al., 2017).

The intermediate-P Upper Allochthon in NW Iberia can be correlated to the Cambro-Ordovician high-T Essart Unit in the SAD (Martínez Catalán et al., 2021). In the intermediate-P units of NW Iberia traces of a high-T Cambro-Ordovician event have been found and dated at 500-485 Ma in monazite (Fernández-Suárez et al., 2002)

The CIZ (explained in detail in part 2.4 of this chapter) present important similarities with the AM. The Schist-Greywacke Complex in the CIZ can be directly related to the upper part of the so called Upper “Brioverien” of the CAD (Martínez Catalán et al., 2021). Important correlations between the Ordovician to Devonian sequence in the CIZ and the CAD were proposed based on paleontological and sedimentological studies as well as detrital zircon ages (Dabard et al., 2021; Henry et al., 1974; Paris & Robardet, 1977; Robardet & Gutiérrez-Marco, 1990). The Carboniferous syn-orogenic succession in the CIZ and in the CAD is related to an extensive event taking place at early Carboniferous and its unconformably overlying the pre-orogenic succession (Martínez Catalán et al., 2021). The SAD and the northern part of the CIZ can be both correlated based on the presence of Cambrian-Ordovician rocks together with the possible occurrence of Armorican quartzite as well as the existence of Ordovician slates and Silurian cherts (Ballèvre et al., 1992).

2.4. The Central Iberian Zone (CIZ)-Main study domain

The CIZ corresponds to the internal domain of the Iberian Massif (Fig. 2.3 and 2.4b-c). It is limited to the South by a transpressive structure called the Tomar-Badajoz-Córdoba-Shear-Zone, which defines the border between the Ossa-Morena-Zone and the CIZ (Sanderson et al., 1991). This unit was overlapped at the north by thrust sheets of both oceanic and continental crust, belonging to the GTMZ (Arenas et al., 2016; Díez Fernández & Arenas, 2015).

2.4.1 Sedimentation: From Cadomian to Variscan times.

At the Iberian margin of Gondwana, the last stages of the Cadomian orogeny were followed by an important extensive event that marked the transition between a Cadomian arc into a Cambrian rift (Linnemann et al., 2008; Sánchez-García et al., 2019). This extension progressively affected the OMZ, the CIZ, the WALZ and CZ (Sánchez-García et al., 2019). It allowed the formation of graben structures that were simultaneously filled with sediments and later intruded by important amounts of felsic magmatism at ≈ 500 -465 Ma (e.g. Ollo de Sapo Domain, Bea et al., 2006; Martínez-Catalán et al., 2004; Rubio-Ordóñez et al., 2012; Valverde-Vaquero & Dunning, 2000; Zeck et al., 2007). The sedimentary succession reflecting the arc-rift transition is known as the Schist Greywacke Complex (SGC), and represents one of the most important stratigraphic units in the Iberian Massif (Teixeira, 1955). The SGC is composed of sandstones and shales with minor limestones and conglomerates showing Neoproterozoic to lower Cambrian ages and a variable thickness (>5 km) (Bea et al., 2003; M. F. Pereira et al., 2012). Glacio-marine deposits related to an Ediacaran glaciation have been also reported in southern CIZ (Linnemann et al., 2018; Martínez Catalán et al., 2021).

The extensional event related to the arc-rift transition eventually led to the continental break-up and the opening of the Rheic ocean at late Cambrian to Ordovician times (Linnemann et al., 2008; Nance et al., 2012; M. F. Pereira et al., 2012; Sánchez-García et al., 2019). This oceanic event marked the beginning of a passive margin stage that lasted until middle Devonian times and that involved the sedimentation of marine platform deposits (Gutiérrez-Marco et al., 2019; Sánchez-García et al., 2019) as well as important amounts of alkaline magmatism (e.g. Almadén syncline, Higuera, 1995, 2000; Higuera et al., 2013 and references therein). In the CIZ the Neoproterozoic to lower Cambrian sequence is separated from the lower Ordovician succession by the Toledanian unconformity, whose limit is located below the Cambrian-Ordovician boundary (Lotze, 1956). The lower Ordovician strata is represented by transgressive

deposits composed of conglomerates, sandstones, pelites and silts; all of them overlain by the Armorican Quartzite (Gutiérrez-Marco et al., 2019; Martínez Poyatos et al., 2004). The middle Ordovician is marked by a transgression taking place from Dapingian to late Darriwilian times, which is the result of the almost total erosion of the rift shoulders bordering the opening of the Rheic Ocean (Gutiérrez-Marco et al., 2019). During this transgression important amounts of fossiliferous mudstones were deposited above the Armorican quartzite, these deposits were accompanied by siltstones, minor sandstones and a well-known ironstone ooidal bed (Gutiérrez-Marco et al., 2019; Martínez Catalán et al., 2021). The late Darriwilian times in the CIZ are marked by a regression that is represented by several sandstone units (SE part or the CIZ) whose distribution and thickness decrease northwards possibly indicating that the shoreline was located in the place where the Obejo Vasequillo Domain is found nowadays (Gutiérrez-Marco et al., 2019). The late Ordovician sequence starts with shallow shelf environments deposits, including alternations of shales, siltstones and sandstones (Gutiérrez-Marco et al., 2019). During Katian times an important global warming event took place leading to the formation of important amounts of limestones (e.g. Caliza Urbana, CIZ, Martínez Catalán et al., 2021 and references therein). Finally, the Upper late Ordovician sequence consist mainly of glaciomarine diamictites, representing the vestiges of the Hirnatian Glaciation that mostly occurred in the African part of Gondwana (Ghienne et al., 2007; Gutiérrez-Marco et al., 2019). The presence of glaciomarine deposits represents a key to understand the paleogeographic location at high latitudes of Iberia at late Ordovician times (Ghienne et al., 2007; Gutiérrez-Marco et al., 2019). Other important lithologies reported at the Uppermost part of the late Ordovician succession comprise the Criadero quartzite (Gutiérrez-Marco et al., 2010).

During Silurian times the passive margin stage sedimentation, related to the extension of the Rheic ocean, continues. In the case of the CIZ, several lithologies have been reported in the lowermost part of the Silurian sequence, including the Criadero quartzite (Upper

Ordovician-Lower Silurian age, Almela et al., 1962) and black shales, whose sedimentation continued until Wenlock and even Ludlow times (Gutiérrez-Marco et al., 2019). The late Silurian sequence is represented mainly by sandstones as well as some alternation of siltstones and shales from Ludlow to Pridoli times (Gutiérrez-Marco et al., 2019). It is important to note that the Silurian period is also marked by several intraplate magmatic events (see part 2.7.3 and 2.9 of this chapter), that took place mainly in the southern part of the CIZ at early Silurian to late Devonian times (e.g. Almadén and Valongo-Tamames synclines; (Gutiérrez-Alonso et al., 2008; Higuera et al., 2013; and references therein).

The Silurian-Devonian transition is placed in sequences consisting mainly of shales and sandstones (Gutiérrez-Marco et al., 2019). The most complete Devonian succession in the CIZ has been described in the southern part of this domain, more specifically in the Almadén and Guadalmez synclines (main study object in this thesis, see part 2.9 of this chapter), as well as in the Herrera del Duque syncline (García Alcalde et al., 2002; Gutiérrez-Marco et al., 2019). The lithologies are mostly represented by alternations of shales and sandstones together with limestones, massive packages of quartzites and volcano-sedimentary rocks (García Alcalde et al., 2002).

The closure of the Rheic ocean and the collision between Gondwana and Laurussia marked the onset of the Variscan orogeny during upper Devonian to lower Carboniferous times (Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012; Paquette et al., 2017). In the OMZ and the southern part of the CIZ, sinistral displacement along the Badajoz-Córdoba shear zone allowed to accommodate the Variscan deformation and led to the generation of transtensional basins as well as transpressional uplift (Gutiérrez-Marco et al., 2019 and references therein). No limit marking the Devonian-Carboniferous transition has been documented in the CIZ. The early Carboniferous (Mississippian) sequence is absent in the northern part of the CIZ, whereas in the southern part of this domain is distributed in several

locations, such as: **i)** the Codosera syncline (main study object in this thesis, see part 2.5 of this chapter), where the Mississippian strata is represented by the Gévora Formation composed mainly of slates with alternations of sandstones and some limestones levels such as the Calizas de la Calera and Calizas de San Antonio (Gumiel et al., 2002; Rodríguez González et al., 2007; Santos Garcia & Casas Ruiz, 1979); **ii)** In the Sierra de San Pedro syncline the lower Carboniferous sequence presents a thickness of $\approx 600\text{m}$ and is represented by volcano-sedimentary rocks, limestones and shales belonging to the Perna, Valedelascasas and the Huertas formations, respectively (Soldevila Bartolí, 1992).

The Carboniferous strata has been also documented at the north of the Obejo-Valsequillo Domain, where two main sequences have been described (Armendáriz et al., 2008; Mira López, Ortega Gironés, Rodríguez Pevida, et al., 1983): The first shows a thickness of $\approx 100\text{m}$, it comprises shales and limestones and has been interpreted as olistoliths of late Viséan age (Gutiérrez-Marco et al., 2019); the second one belongs to the ‘culm’ facies in the synorogenic Variscan Pedroches basin (early Carboniferous age) and consists mainly of shales and greywackes presenting $\approx 4000\text{m}$ (Mira López, Ortega Gironés, Rodríguez Pevida, et al., 1983).

2.4.2. Deformation and metamorphism: From Pre-Variscan to Variscan times

Pre-Variscan deformation

The northern and southern parts of the CIZ show a record of Pre-Variscan deformation that has been attributed to both, the Cadomian (Pre-Cambrian, Ediacaran) and the Toledanic (Middle to upper Cambrian) events (Azor et al., 2019). These two episodes are responsible for most of the Pre-Variscan structures and unconformities in the CIZ.

The Cadomian event affected the sequence known as the Schist Greywacke Complex (SGC or Alcudian Succession; Lotze, 1945) and generated folds with no evidence of

metamorphism (Azor et al., 2019). Among the SGC, an important unconformity, which separates the upper and lower part of the sequence, has been related to the Cadomian episode (Ortega & Gonzalez-Lodeiro, 1986; Palero, 1993; Talavera et al., 2015). The time gap between both parts of the succession was tentatively dated using zircons from both parts of the sequence (Talavera et al., 2015). Based on these analyses, this event is believed to have lasted at least ≈ 20 Ma, starting at 575 until 555 Ma (Talavera et al., 2015). The Cadomian event has been identified in both, the northern and the southern part of the CIZ, based on the presence of the Intra-Alcudian unconformity (Azor et al., 2019). Furthermore, the southern part of the CIZ shows an important tectonic imprint (dated at 560-540Ma) marked by the foliation of the Ediacaran sequence at the Peraleda anticline (Blatrix & Burg, 1981; Dallmeyer & Quesada, 1992; Henriques et al., 2016).

The Toledanic event is marked by the well-known Toledanian unconformity, which is located at the limit between pre-Ordovician and lower Ordovician sequences (Lotze, 1945). Considering the variability of the thickness into the Ordovician sequence, the origin of this contact has been attributed to a folding or faulting as well as to the possible existence of a paleorelief during middle to upper Cambrian times (McDougall et al., 1987).

Variscan deformation

The most representative deformation structures in the CIZ were inherited from the Variscan orogeny (Azor et al., 2019; Martínez Catalán et al., 2014). This collisional event, between Gondwana and Laurussia, took place after the closure of the Rheic ocean during late Devonian to Carboniferous times and eventually led to the formation of Pangea. (Ballèvre et al., 2009, 2014; Franke et al., 2017; Kroner & Romer, 2013; Schulmann et al., 2022). The Variscan orogeny involved crustal thinning and thickening related to three compressional (C1, C2 and C3) and two extensional deformation phases (E1, E2) (Alcock et al., 2009; Azor et al., 2019; Dias da Silva et al., 2010; Martínez Catalán et al., 2009, 2014). The phases C1, C2 and

E1 show an important diachronism (Fig. 2.5) whereas C3 took place at the last stages of the Variscan orogeny and was associated with the ongoing formation of the orocline (Gutiérrez-Alonso et al., 2015). The deformation shows a progression of the orogenic front towards the east (Fig. 2.6) and the ages of the different deformations phases (ranging from ≈ 360 Ma to ≈ 290 Ma) get younger from the allocthonous units towards the autochthonous units and from the CIZ to towards the CZ (Azor et al., 2019; Dallmeyer et al., 1997; Martínez Catalán et al., 2014; Rubio Pascual et al., 2013).

The first compressional deformation stage (C1, Fig. 2.5) is represented by recumbent folds with NW-SE subvertical axial planes, accompanied by slaty cleavage (S1) and down dip lineation implying that the strike slip elements were not relevant and that the main deformation was perpendicular to the orogen (Martínez Catalán et al., 2009, 2014). All of these structures were generated by a NE-SW shortening related to the collision between Gondwana and Laurussia. In the CIZ, the C1 deformation phase started at 359 Ma (^{40}Ar - ^{39}Ar on the axial planar foliation) and moved inwards until the limit with the CIZ at ≈ 336 Ma (Dallmeyer et al., 1997). In the southern part of the CIZ, the Badajoz-Cordoba shear zone accommodated the C1 deformation by sinistral displacement allowing the formation of transtensional basins (e.g. Los Pedroches basin) as well as transpressional uplift (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016). Considering the geometry and features of the different folds related to C1 the CIZ was divided into two different domains (Dias et al., 2013; Díez Balda et al., 1990; Martínez-Catalán et al., 2004): **i)** the northern one, represented by overturned folds with a NE and E vergence; **ii)** and the southern one, represented by vertical folds with SW to NE vergence. In the southern part of the CIZ C1, is also characterized by medium P conditions and a very low grade metamorphism that can go up to greenschist facies (Alcock et al., 2009; Martínez Catalán et al., 2009, 2014).

The second deformation phase (C2, Fig. 2.5) is characterized by recumbent folds associated with crenulation cleavage (S2, cutting S1), sub-horizontal shear zones and involved the overlapping of the GTMZ thrust sheet along three fault systems: the Lalín-Forcarei thrust (LFT) in which the lower allochthon overlapped the parautochthon; the Out of Sequence Thrust System (OSTS) where the basal autochthon was overlapped by the upper and middle allochthons; and finally the Parautochthon Basal Thrust (PBT) where the allochthon units carried by the parautochthon were positioned (Martínez Catalán et al., 2014). All of these systems carried out both units of oceanic and continental crust (Alcock et al., 2009; Martínez Catalán et al., 2009, 2014). Several mylonitic zones were developed next to the thrust faults in the CIZ, in the GTMZ and the WALZ (Martínez Catalán et al., 2014). In the CIZ, the second compressional deformation phase was active during ≈ 345 -325 Ma (Azor et al., 2019; Martínez-Catalán et al., 2016; Martínez Catalán et al., 2014).

Both deformation phases C1 and C2 are related to the collisional stage and crustal thickening of ~ 50 km at ≈ 360 Ma, C2 was related to the nappe stacking of GTMZ units starting at ≈ 350 Ma (Bea et al., 2003; Dias da Silva et al., 2010; Expósito et al., 2002)

At the last stages of C2, the continental crust was enough thickened and heated (Alcock et al., 2015; Azor et al., 2019; Martínez Catalán et al., 2014). This change in temperature led to an important thermal relaxation that marked the beginning of the E1 (Fig. 2.5) deformation phase (Alcock et al., 2015; Azor et al., 2019; Martínez Catalán et al., 2014). This extensional event is characterized by the development of basins, synforms, exhumation of high-grade rocks (gneiss domes, e.g. Guadamarra, Somosierra) and partial melting that consequently led to the intrusion of several granitoid units (Alcock et al., 2009; Díez Fernández & Pereira, 2016; Martínez Catalán et al., 2014). Important detachments associated to the gneiss domes as well as a crenulation cleavage (S_{E1}) were developed during this deformation phase, that was interpreted as non-coaxial (Alcock et al., 2015; Martínez Catalán et al., 2014). The beginning

and end of E1 were determined based on the formation age of the anathetic domes between $\approx 330\text{Ma}$ - 320 Ma (Azor et al., 2019 and references therein).

Following the extensional collapse related to E1, a new compressional phase C3 occurred (Fig. 2.5). C3 is marked by the formation of new folds and its divided into both, ductile and brittle deformation. The first one is represented by vertical (sometimes overturned) folds with NW-SE subvertical axes, crenulation cleavage (S3) and stretching lineation parallel to the fold axes (Dias et al., 1998; Martínez Catalán et al., 2014). These folds are related to dextral or sinistral shear zones that also controlled the intrusion of syn C3-granites. (Diez Montes & Gallastegui, 1992; Gutiérrez-Alonso et al., 2015). The brittle deformation is represented by NW-SE, NE-SW and NNE-SSW fracture systems and shear zones, responsible for the controlling of post C3 granitoids intrusions (Alcock et al., 2009; Dias da Silva et al., 2010; Dias et al., 1998; Martínez Catalán et al., 2014; Pereira et al., 1993).

The last extensional phase, E2 (Fig. 2.5), is related to the formation of extensional detachments that helped to the exhumation of high-grade metamorphic rocks, the formation domes and partial melting (Arenas & Martínez Catalán, 2003; Martínez Catalán et al., 2003). The fault systems related to this stage overprinted previous structures (Alcock et al., 2009; Martínez Catalán et al., 2009, 2014).

Variscan metamorphism

The metamorphic evolution registered in the Iberian Massif has been divided into three main paths (M1, M2 and M3; Fig. 2.5) that are temporally associated to the main deformation phases (C1, C2, E1, C3 and E2; Azor et al., 2019; Martínez Catalán et al., 2014). The gneiss domes appearing during E1-E2 in the OMZ, the WALZ and the CIZ; represent an important key to understand the metamorphism in the Iberian Massif (Azor et al., 2019). In order to understand the metamorphic evolution, relevant petrogenetical and thermobarometrical studies

have been performed in several dome units of the CIZ such as Gredos, Tormes, Somosierra, Sanabria, Toledo, among others (Barbero & Villaseca, 2000; Díez Montes, 2007; Escuder Viruete et al., 1997; Pereira Gómez & Shaw, 1997; Rubio Pascual et al., 2013).

M1 is related to the thickening of the continental crust during C1 and C2, this process was accompanied by a medium to high pressure prograde Barrovian metamorphism and was followed by a thermal relaxation, marking the beginning of E1 (Azor et al., 2019; Martínez-Catalán et al., 2016; Martínez Catalán et al., 2014). The P-T conditions at the first stages of M1 are not well constrained, nevertheless, peak pressures have been estimated at 1.4GPa at the Guadarrama dome and between 0.8-1.0GPa at the Tormes, Sanabria and Somosierra domes (Azor et al., 2019; Barbero & Villaseca, 2000; Martínez Catalán et al., 2014). The high pressures for the retrograde eclogites of the Guadarrama dome, would indicate a total burial between 40-50 km as well as an intracontinental crustal subduction and thickening of around 70-80 km in this area (Barbero & Villaseca, 2000). In spite of the Guadarrama data, the rest of the domes showed similar conditions during M1 that are related to a Barrovian metamorphism (Díez Montes, 2007; Escuder Viruete et al., 1997; Pereira Gómez & Shaw, 1997; Rubio Pascual et al., 2013).

The decompression associated to the extensional collapse in E1 originated the second metamorphic pathway (M2, Fig. 2.5), characterized by a HT-LP metamorphism as well as by a classical path marking crustal thickening followed by a decompression-exhumation path (Azor et al., 2019; Martínez-Catalán et al., 2016; Martínez Catalán et al., 2014). During M2, the highest P-T conditions were estimated in the range of 05-08 GPa and between 750°C-850°C, at the Tormes, the Toledo and the Gredos domes (Barbero, 1995; Escuder Viruete et al., 1997; Pereira Gómez & Shaw, 1997). In the case of the Tormes dome the P-T conditions decreased from 770°C to 750°C and from 08 to 05 GPa (Escuder Viruete et al., 1997). An M2 overprinting, marked by the destabilization of almandine garnet kyanite, together with an E1-

M2 exhumation range between 12-15 km was determined at the Somosierra dome (Rubio Pascual et al., 2013).

During the last stages of the Variscan orogeny, the gradual exhumation accompanied by decreasing of pressure and temperature, led to a final P-T trajectory (M3, Fig. 2.5) marked by a retrograde metamorphism (Azor et al., 2019; Martínez-Catalán et al., 2016; Martínez Catalán et al., 2014). During M3 the P-T conditions in the Tormes dome decreased to 645-680°C and 0.33-0.39 GPa, leading these rocks to a retrograde metamorphism that reached low amphibolite to greenschist facies. (Escuder Viruete et al., 1997).

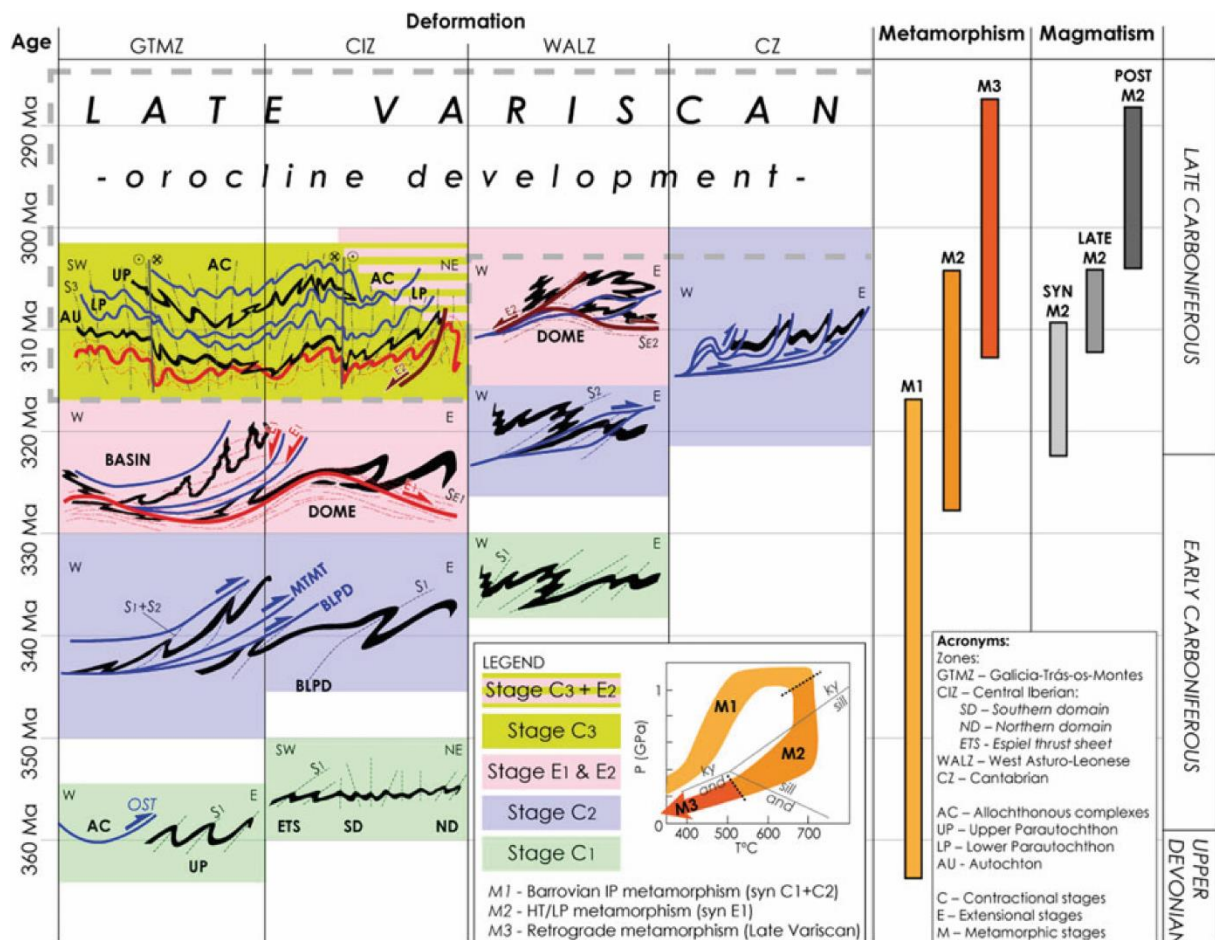


Figure 2. 5. Evolution of the Variscan deformation, metamorphism and magmatism in the GTMZ, CIZ, WALZ and CZ. Modified after Azor et al. (2019) based on the work performed by Dallmeyer et al. (1997); Martínez-Catalán et al. (2016); Martínez Catalán et al. (2014).

The highest metamorphic grades reported in the CIZ, reaching up to granulite and eclogite facies, are associated to the anathetic domes (Fig. 2.6). All of these units are located at the N-NW part of the CIZ and were bounded by a black thick line in Fig. 2.6 (Martínez Catalán et al., 2014). Outside the thick line, where the studied areas of this thesis are located, only low grade metamorphism (anchizonal up to greenschist facies) as well as very low P-T conditions (100-200°C and pressure <0.1GPa) have been reported (Martínez Catalán et al., 2014 and references therein).

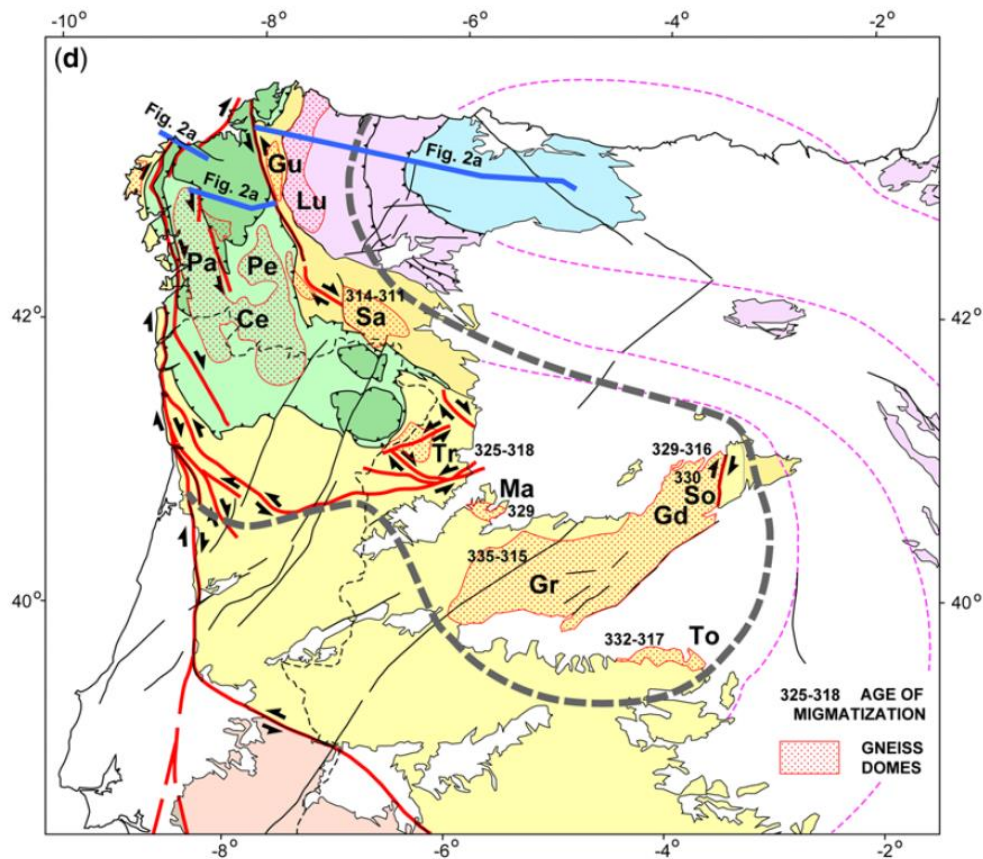


Figure 2. 6. Distribution of the Variscan Gneiss domes with published ages of migmatization. Ce: Celanova; Gd: Guadarrama; Gr: Gredos; Gu: Guitiriz; Lu: Lugo; Ma: Martinamor; Pa: Padrón; Pe: Peares; Sa: Sanabria; So: Somosierra; To: Toledo; Tr: Tormes. Modified after Martínez Catalán et al. (2014) and references therein.

2.4.3. Mafic magmatic stages in the CIZ: Pre-Variscan and Variscan times.

The CIZ comprises several magmatic intrusions of different ages: from Pre-Cambrian, Cambrian-Ordovician (Pre-Variscan), Variscan, Permian, Triassic-Jurassic (related to the opening of the Atlantic ocean) and Mesozoic to Cenozoic (Villaseca et al., 2022). The Pre-Cambrian to Carboniferous period is characterized, at least, by six mafic magmatic events (Villaseca et al., 2022):

Cadomian (Panafrican).

A mafic event has been related to the extension at the last stages of the Cadomian orogeny. Magmatic rocks belonging to this stage have been reported at the border between the CIZ and the OMZ at the Mérida-Montoro complex (MMC, Fig. 2.7), and include tonalites, gabbros, diorites, and ultramafic rocks, intruding both metavolcanic and metasedimentary sequences. The diorites of this complex have been dated using SHRIMP and ID-TIMS by U-Pb method in zircon at 580-570Ma, representing their crystallization age (Bandrés et al., 2004). These rocks belong to the calc-alkaline series and are related to an immature arc setting (Bandrés et al., 2004). Sm-Nd ages allowed to propose the hypothesis of arc construction episodes at 593Ma, followed by crystallization and high-grade metamorphism (amphibolite to granulite facies) at 555Ma. According to this study the arc building episode occurred between 600-575 Ma followed by collision-related metamorphism at 555Ma (Bandrés et al., 2004).

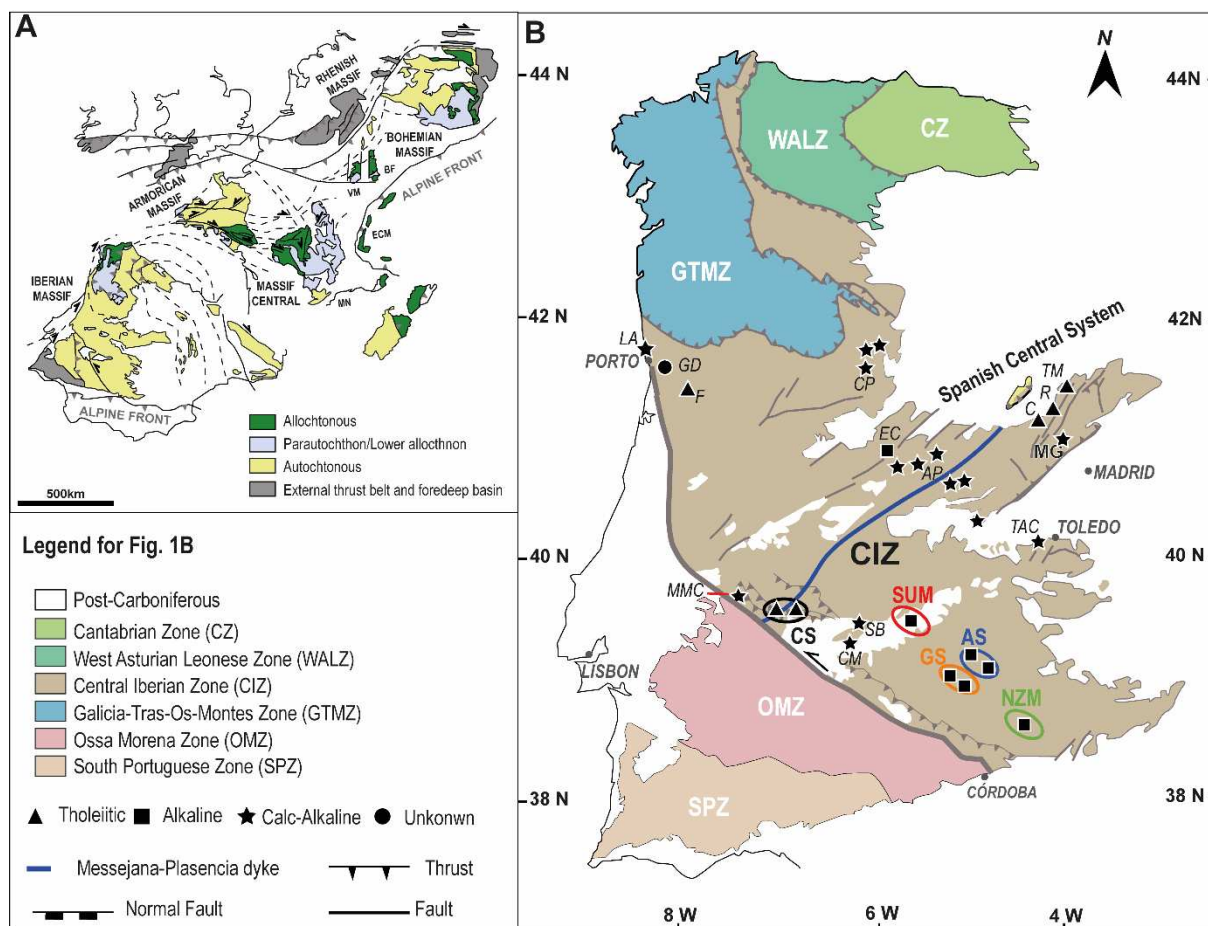


Figure 2. 7. A) Geological sketch of the Variscan Belt showing the main terranes and domains, modified after Martínez Catalán et al. (2014); B) Simplified geological map of the Iberian Massif showing mafic rocks in the studied areas and the mafic suites reported in the Central Iberian Zone (CIZ) from Ordovician times to the late stages of the Variscan orogeny. The map was designed based on the studies made by Julivert et al. (1974) and Simancas (2019). Abbreviations: OMZ: Ossa Morena Zone; GTMZ: Galicia-Tras-Os Montes-Zone; WALZ: West Asturian Leonese Zone (WALZ); CZ: Cantabrian Zone; MN: Montagne Noire; ECM: External Crystalline Massifs of the Alps; VM: Vosges Massif; BF: Black Forest; CP: Calzadilla Plutón (López-Moro et al., 2017); LA: Praia de Labruga (de Almeida Coelho, 2021); GD: Godomar (Medeiros et al., 1981); F: Farinhao (Cotrim et al., 2021); AP: Appinites (Montero, Bea, et al., 2004; Montero, Zinger, et al., 2004; Scarrow et al., 2009); TAC: Toledo Anatetic Complex (Bea et al., 2006); C: Caloco Sector (Orejana et al., 2017; Villaseca et al., 2015); R: Revenga Sector (Orejana et al., 2017; Villaseca et al., 2015); TM: Tenzuela Massif; MMC: Mérida Montoro Complex (Bandrés et al., 2004); SB: Sierra Bermeja (Errandonea-Martin et al., 2019); CM: Carrascal Massif (Solá et al., 2010); MG : Microgabbros (Orejana et al., 2020) ; CS: Codosera Syncline (López-Moro et al., 2007); AS: Almadén Syncline (Higueras, 1995; Higueras et al., 2013); GS: Guadalmez Syncline (Gumiel & Arribas, 1987; Lorenzo Álvarez et al., 1995); SUM: Susana Mine (Gumiel, 1982); NZM: Nazarena Mine (Gumiel, 1982).

Ordovician.

The Ordovician times are marked by a rifting episode that lead to the opening of the Rheic ocean (Arenas et al., 2007; Martínez Catalan et al., 2007; Matte, 2001; Nance et al., 2012), the mafic magmatism emplaced during this time comprises: **i)** alkaline gabbros from the Carrascal Massif (CM, Fig. 2.7) emplaced at 479 ± 3 Ma (Solá et al., 2010). **ii)** mafic rocks of tholeiitic affinity from the Spanish Central System (Revenge and Caloco sectors, R and C Fig. 2.7; and Fig. 2.8), and the Tenzuela Massif, emplaced between $473. \pm 3.8$ and 453.3 ± 4.6 Ma (Orejana et al., 2017; Villaseca et al., 2015); **iii)** as well as the metagabbros, amphibolites and ultramafic rock of calc-alkaline affinity located at Farminhao (F, Fig. 2.7) in northern Portugal, which are believed to be emplaced at ≈ 480 Ma, due to the strong geochemical similarities with the rocks of the Tenzuela Massif (Cotrim et al., 2021).

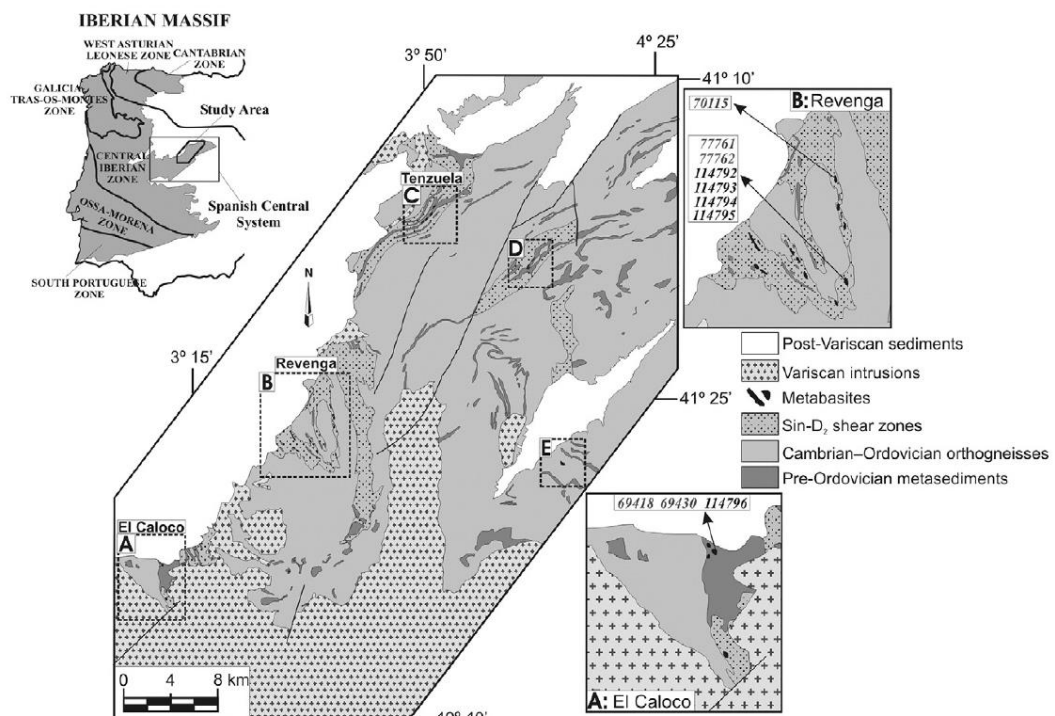


Figure 2. 8. Location of the Tenzuela Massif, the Revenge and El Caloco sectors in the Spanish Central System. (Orejana et al., 2017).

Silurian.

During Silurian times alkaline intraplate mafic magmatism occurs in the Almadén syncline (Fig. 2.9), which host the world class mineralization of Almadén (Hall et al., 1997; Higuera, 1995; Higuera et al., 2000, 2013). The rocks emplaced during this event show an intraplate geodynamic signature and display distinct structures such as subvolcanic mafic intrusions (microgabbro) with doleritic texture as well as porphyritic lavas and diatremes of basaltic composition with ultramafic xenoliths, also known as the Frailesca unit (Hall et al., 1997; Higuera, 1995; Higuera et al., 2000, 2013). The latter yielded emplacement ages ranging between Silurian (427 Ma) and Upper Devonian (365Ma, $^{40}\text{Ar}/^{39}\text{Ar}$ on fuschite, Hall et al., 1997), although this geochronological data is questioned considering the alteration features of these rocks (Palero-Fernández et al., 2015).

The mafic volcanism in the Almadén syncline is suggested to have led to an important hydrothermal activity that highly contributed to the formation of Hg mineralization (Fig. 2.9), mainly hosted in the Criadero Quartzite of Silurian age (Higuera, 1995; Higuera et al., 2013). The Almadén syncline corresponds to one of the main studied areas in this thesis, more detailed description about this structure will be found in part 2.6 of this chapter.

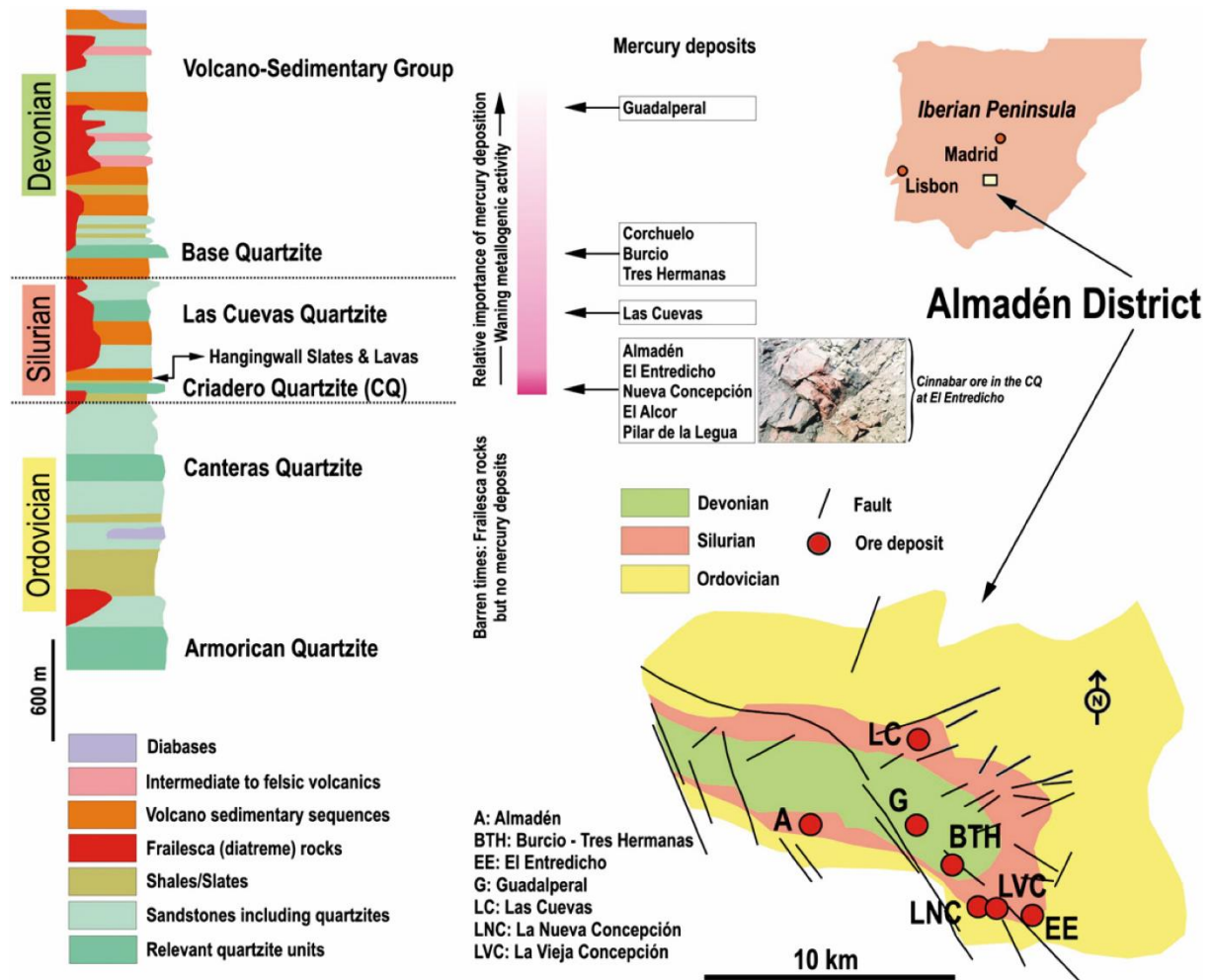


Figure 2. 9. Geology and metallogenic activity of the Almadén district taken from Higuera et al. (2013) and modified from Higuera (1995); Higuera et al. (2013); Palero & Lorenzo (2009).

Middle to late Devonian.

From middle to late Devonian times other alkaline mafic suites intrude the AS (Hall et al., 1997; Higuera et al., 2013; Palero-Fernández et al., 2015) and the Valongo-Tamames syncline. The latest comprise the basalts of El Castillo (EC, Fig. 2.7 and Fig. 2.10) whose emplacement age was dated by U-Pb zircon yielding 394.7 ± 1.4 Ma (Gutiérrez-Alonso et al., 2008).

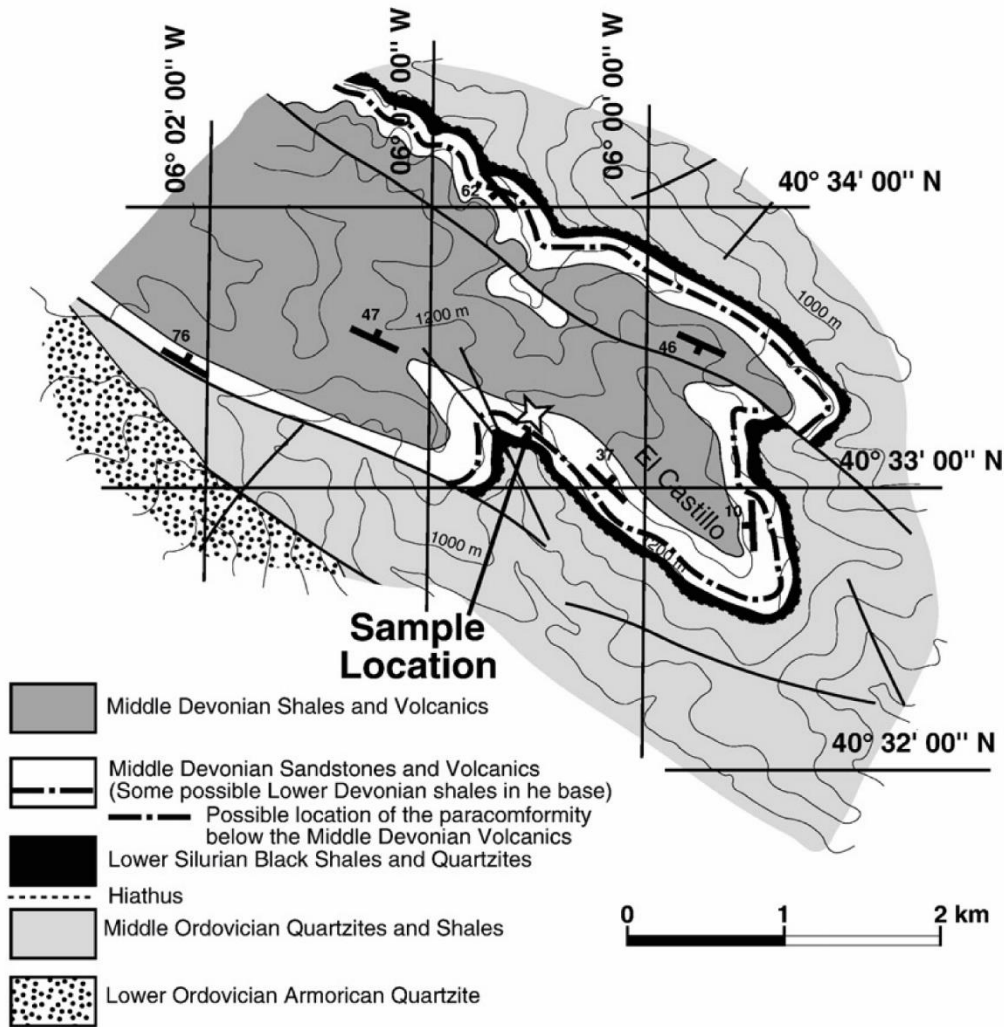


Figure 2. 10. Simplified geological map of the Valongo-Tamames syncline showing the location of El Castillo basalts. Modified from Gutiérrez-Alonso et al. (2008) and references therein.

Late Devonian to early Carboniferous-Onset of the Variscan orogeny

The late Devonian to early Carboniferous times mark the closure of the Rheic Ocean and the onset of the Variscan orogeny (Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012; Paquette et al., 2017). The magmatism emplaced in this period comprises:

- i) Mafic rocks of tholeiitic affinity from la Codosera syncline (CS, Fig 2.7; Fig. 2.11), emplaced within the Carboniferous slates quartzites and sandstones of the Gévora Formation (Carnicero & Castro, 1983; López-Moro et al., 2007, 2020b; Rodríguez

González et al., 2007). These rocks are believed to predate the Variscan orogeny based on tectono-metamorphic studies (López-Moro et al., 2005, 2007, 2020b). According to Sm/Nd signature, geochemical features and LILE enrichment, it has been proposed that the possible source of these intrusions concerns a metasomatized mantle source with a significant crustal contamination (López-Moro et al., 2007). The Codosera syncline corresponds to one of the main studied areas in this thesis, more detailed description about this structure will be found in part 2.5 and 2.8 of this chapter.

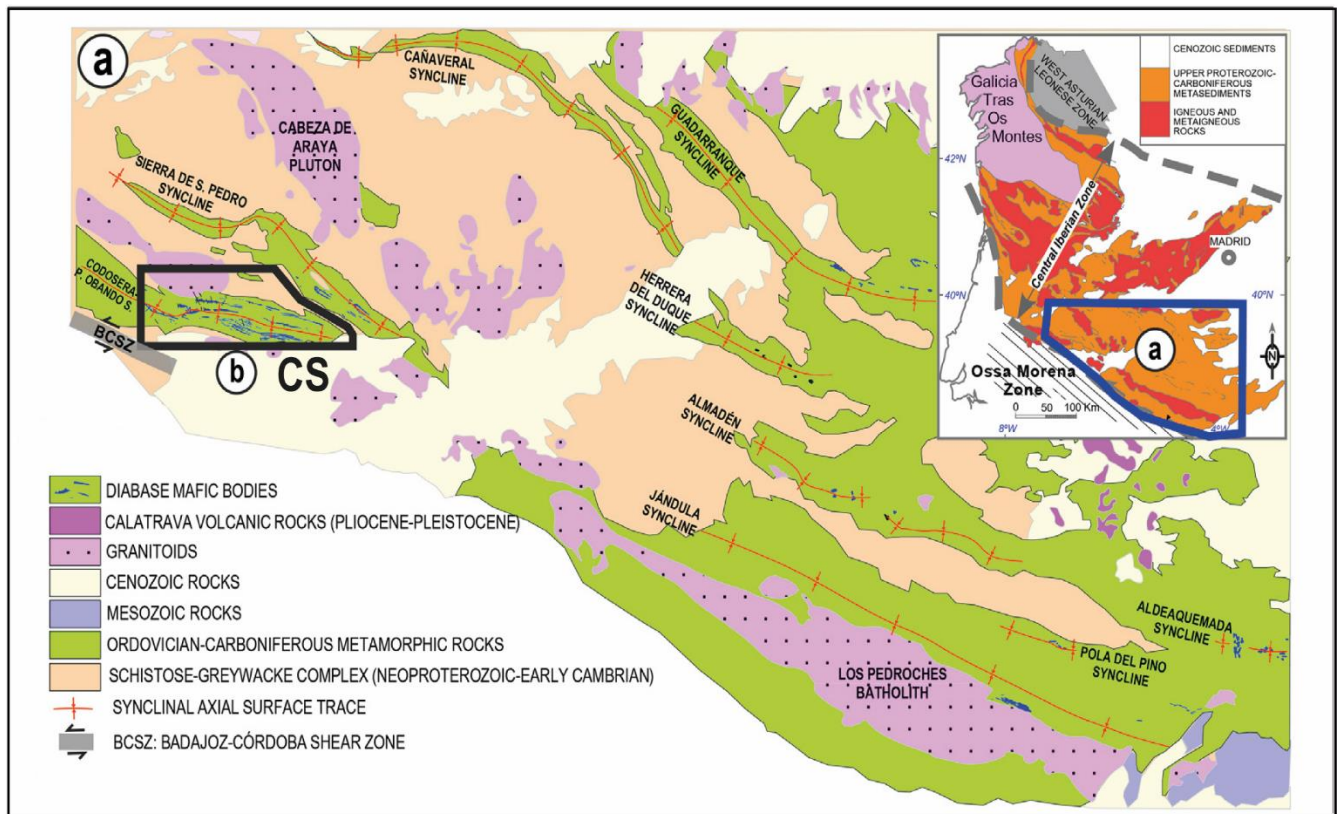


Figure 2. 11. Simplified geological map of the Iberian Massif showing the southern part of the CIZ. Modified after López-Moro et al. (2020) and references therein ; B) Location of La Codosera syncline (CS) in the Southern part of the CIZ. Modified after López-Moro et al. (2020)

- ii) The dolerites from the Gondomar (GD, Fig. 2.7) area in Portugal are intruding a Neoproterozoic to Devonian sequence and present an intensive alteration state that

makes difficult to obtain geochemical data (Medeiros et al., 1981). The rocks show altered plagioclase, ilmenites, amphiboles (hornblende-epidote) and chlorite (Medeiros et al., 1981)

Last stages of the Variscan orogeny

During the late stages of the Variscan orogeny several calc-alkaline mafic suites were emplaced all over the CIZ (Fig. 1B). During this time, a period of extensional collapse of the Variscan belt in response to adiabatic melting of the lithospheric mantle is proposed to occur during the Pennsylvanian, yielding both mafic and ultramafic rocks (Bea et al., 2006; Errandonea-Martin et al., 2019; López-Moro et al., 2017; Montero et al., 2004b). These mafic rocks are represented by:

- i) The mafic precursors, also called ‘appinites’, found in the Gredos sector of the Avila Batholith (Fig. 2.12) and divided into the San Martín del Pimpollar (a), El Arenal (b), Prado de las Pozas (c), the San Esteban del Valle (d), the Becedillas (e), and the Sta María del Berrocal (f). $^{207}\text{Pb}/^{206}\text{Pb}$ zircon dating was performed in these rocks yielding ages of $319\pm 3\text{Ma}$ (a), $312\pm 2\text{Ma}$ (b), to $312\pm 5\text{Ma}$ (c), $310\pm 3\text{Ma}$ (d), $313\pm 3\text{Ma}$ (e), $312\pm 2\text{Ma}$ (f) (Bea et al., 1999, 2006; Montero et al., 2004; Scarrow et al., 2009). These ultramafic rocks were related to a mixing between mafic, ultramafic magmas and crustal material (Bea et al., 1999, 2006; Scarrow et al., 2009). The mafic precursors are coeval with the main extensional collapse phase of the Central Iberian Orogen that was dated between 325Ma and 305Ma, based on $^{207}\text{Pb}/^{206}\text{Pb}$ on zircon in granitoids; they present a primary alkaline composition related to extension and mark an adiabatic melting of the lithospheric mantle (Bea et al., 1999, 2006; Montero et al., 2004; Scarrow et al., 2009).

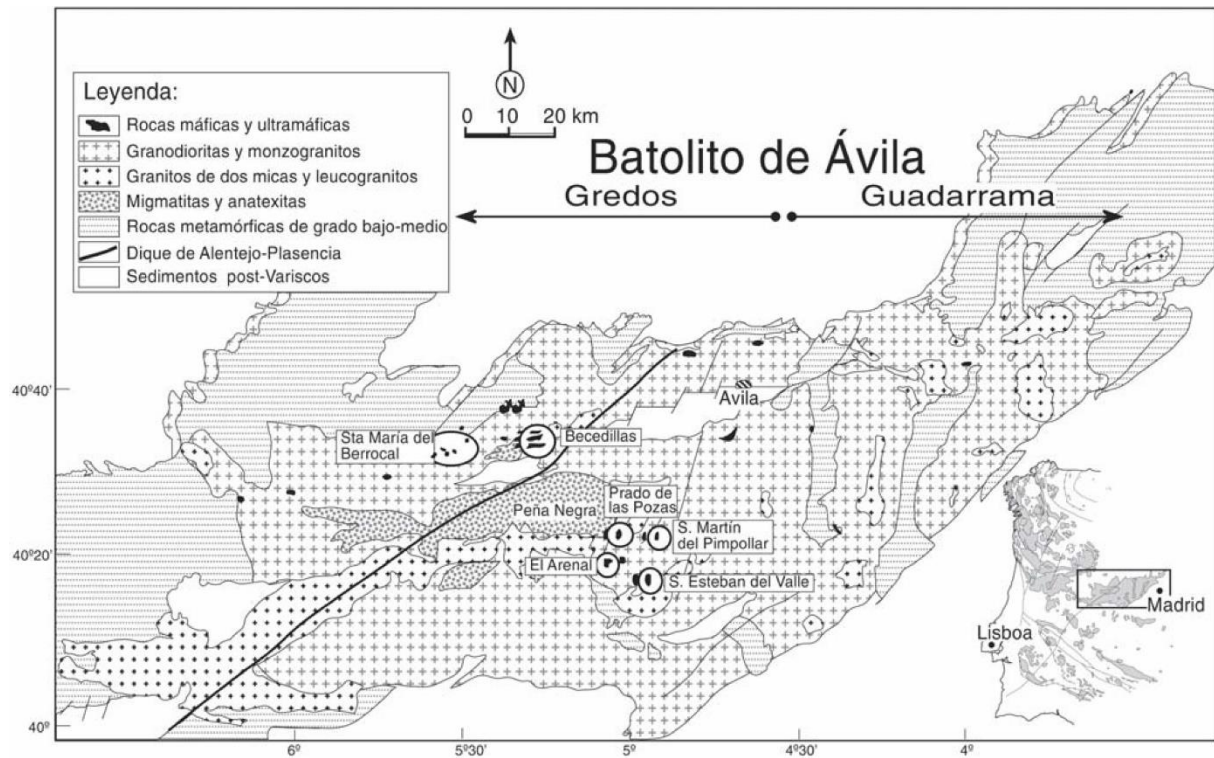


Figure 2. 12. Geological simplified map showing the location of the Avila batholith and the mafic rocks in it.

After (Montero et al., 2004)

- ii) The gabbroic intrusions of Talavera, Mercadillo, Gallegos and Solanilla and Navahermosa (Fig. 2.13), located in the Spanish Central System (Orejana et al., 2009; Zeck et al., 2007). The last was dated using Ion microprobe (SIMS) U-Pb on zircon giving an average crystallization age of 305.6 ± 1.4 Ma (Zeck et al., 2007). In general, all of these rocks are enriched in LREE, LILE, Pb and are depleted in Ta, Nb and Ti. Since there is no evidence of oceanic plate subduction at the last stages of the Variscan

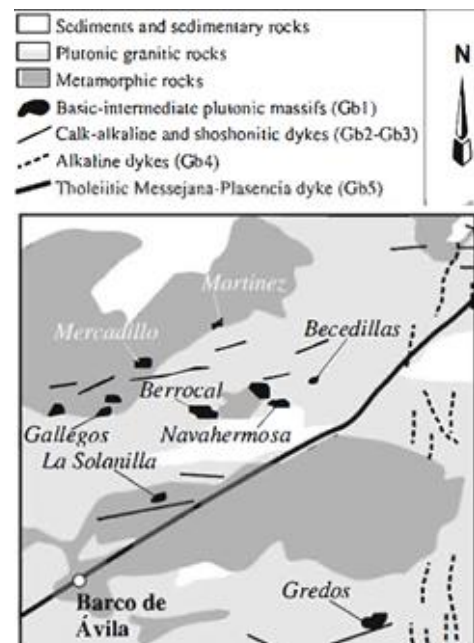


Figure 2. 13. Geological map showing other outcrops of mafic/intermediate rocks located in the Spanish Central System. Modified after (Orejana et al., 2009)

Orogeny in Iberia, these geochemical signatures have been interpreted as a metasomatism of the lithospheric mantle with involvement of crustal recycling (Orejana et al., 2009).

- iii) The gabbros of the Toledo Anatetic Complex (TAC, Fig. 2.7) dated by ion microprobe U-Pb on zircon at 307 ± 2 Ma (Bea et al., 2006). These rocks were emplaced in a cooling anathetic zone and had almost no impact on the anatexis of the Variscan middle crust (Bea et al., 2006).
- iv) The microgabbros of calc-alkaline affinity (MG, Fig. 2.7) located at the Spanish Central System. These rocks outcrop as dyke swarms (GB2, Fig. 2.13) at the eastern part of the Avila batholith (Orejana et al., 2020). They show emplacement ages between 292-299 Ma and display enrichments in LILE, LREE as well as in Pb. The microgabbros are depleted in Nb and Ta and show an important influence of crustal contamination (Orejana et al., 2020).
- v) Finally, the dolerites from the Praia de Labruga in Portugal (West of Porto, LA Fig. 2.7) dated using $^{40}\text{Ar}/^{39}\text{Ar}$ in mica at 299.8 ± 4.5 Ma (de Almeida Coelho, 2021), showing an important effect of crustal contamination (de Almeida Coelho, 2021).

2.5. Main study area #1: La Codosera syncline

The Codosera syncline outcrops between the Badajoz and Cáceres provinces, at the center of the Extremadura region in Spain (Fig. 2.14). This NW-SE trending structure extends over 100km of length and 10km width. It is composed by a Paleozoic sequence of slates, sandstones, quartzites, greywackes and calcareous rocks, which are unconformably overlying the so-called Schists and Graywackes complex of Late Precambrian age (San José et al., 1990). The whole sequence has been mainly affected by the C1 Variscan deformation phase generating a steep slaty cleavage (López-Moro et al., 2007). In the location area of the structure in both

countries, Portugal and Spain, several studies have been carried out regarding paleontology (Gonçalves, 1971, 1973; Gonçalves & Perdigão, 1978; Rodríguez González et al., 2007) and lithology (Gumiel, 1982; Gumiel et al., 1976; Rodríguez González et al., 2007; Santos Garcia & Casas Ruiz, 1979, 1982; Soldevila Bartolí, 1992). The first description focalized on the Paleozoic sequence of the structure was made by Santos Garcia & Casas Ruiz (1979, 1982). The oldest rocks in the sequence of the structure are represented by Lower Ordovician sandstones, quartzites, greywackes and slates, overlain by the Lower Ordovician Armorican Quartzite and by middle to Upper Ordovician slates, quartzites and sandstones (Gumiel et al., 2002; Santos Garcia & Casas Ruiz, 1979). The Silurian-Devonian sequence is composed by quartzites, schist, slates, and sandstones (Gumiel et al., 2002; Santos Garcia & Casas Ruiz, 1979). Overlying the Devonian rocks and located at the core of the CS, lies the Gévora Formation (Fig. 1B), consisting mainly of slates with minor quartzites and sandstones. This unit presents 1200 m of thickness and a Lower Carboniferous (Mississippian) age according to paleontological studies (Rodríguez González et al., 2007). Some levels of limestones can be found within the Gévora Formation, such as the Calizas de San Antonio (Gumiel et al., 2002; Santos Garcia & Casas Ruiz, 1979)

The Gévora formation is intruded by several sill-like mafic bodies (Dolerites, Fig. 2.14) showing a N80E-N120E strike and a steep dip (López-Moro et al., 2005, 2007, 2020b). Their thickness is very variable and range from a few meters up to 400m, with a maximum length of 300m (López-Moro et al., 2005, 2007, 2020b). The intrusions have not been dated but are believed to be emplaced during late Devonian to early Carboniferous times, based on stratigraphic observations (López-Moro et al., 2020b).

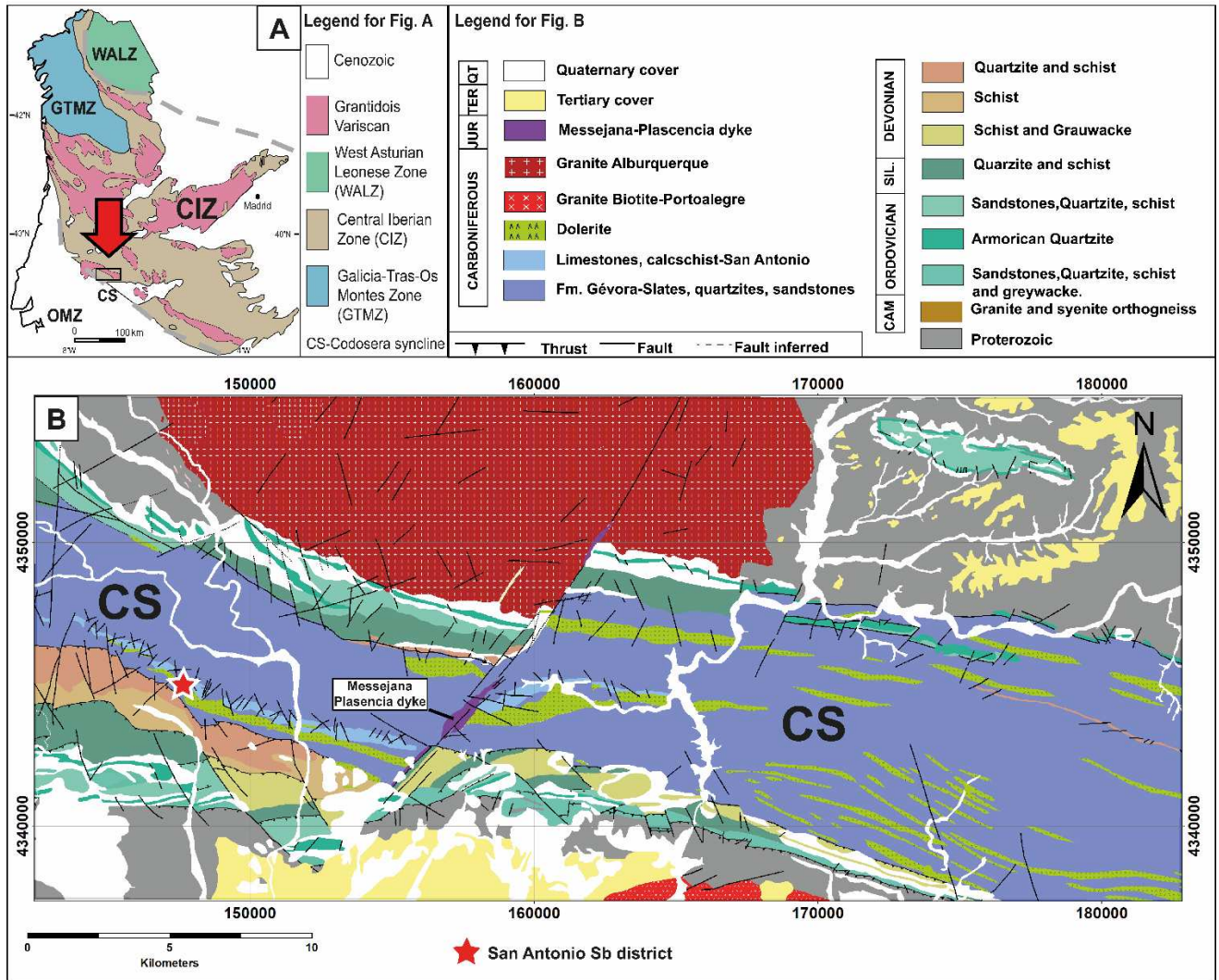


Figure 2. 14. Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline (CS). Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the mafic samples studied in this work. Reference (c): Sampling points from Rodríguez González (2007). The map was redesigned based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).

The whole CS structure and all the mafic swarm of sills are crosscut by the Messejana-Plasencia crustal fault (Fig. 2.14) injected by the Messejana-Plasencia dolerite dyke, late Triassic in age (203 ± 2 Ma, Dunn et al., 1998). This dyke, of continental tholeiitic basalt composition (Cebriá et al., 2003), is related to the beginning of the rifting stage which led to the opening of the central Atlantic Ocean. The lack of lava is probably related to the erosion of the ante-Mesozoic basement during the Late Jurassic and Cretaceous time spans (De Vicente et

al., 2021). Toward the end of Cretaceous (Campanian), the Alpine orogeny starts in the Pyrenees and is followed by the start of the Betic orogeny. This led progressively to an intense intraplate deformation of the Iberian basement (e.g. Cunha et al., 2019; De Vicente et al., 2011). The north-south compression locates a left-lateral strike-slip deformation belt of 5 to 20 km in thickness along the Messejana-Plasencia dyke with the formation of strike-slip (transpressional to transtensional) and thrust basins (De Vicente et al., 2011). The sedimentary infill of these basins ranges from the Eocene up to the end of Pliocene. This infill is highly variable depending of the basin type and numerous breaks of the sedimentation occur. The main sedimentary infill, related to the importance of the subsidence, is between the lower to middle Eocene and during the Oligocene up to the Middle Miocene (De Vicente et al., 2011 and references therein). The Badajoz Cenozoic basin starts on the south border of the La Codosera syncline. This basin is a thrust or open-ramp basin (De Vicente et al., 2011) limited in the west by the Messejana-Plasencia fault and in the north by the East-West North Badajoz thrust fault that crosscut the eastern part of both the La Codosera syncline and its south-eastern border (Fig. 2.14). Thus, the North Badajoz thrust fault is responsible for the uplift of the eastern part of the La Codosera syncline relatively to its western part. Then, deepest structural levels crop East of the Messejana-Plasencia fault and highest structural levels crop West of the fault. The translation of these structural contrast within the La Codosera Syncline is: i) the highest number and thickness of dolerite sills in the East compared to the West and ii) the occurrence of numerous gold (Dee & Roberts, 1993; Murphy & Roberts, 1997; Roberts et al., 1991) and antimony hydrothermal systems, among them the San Antonio district (Arribas & Gumiel, 1984; Gumiel & Arribas, 1987), the largest known antimony resource of Iberia, in the west and their absence in the east.

2.6. Main study areas #2 and #3: The Almadén and Guadalmez synclines

The Almadén and Guadalmez synclines (Fig. 2.15) are located at the Ciudad Real and Cordoba provinces at around 260km to the NE of Sevilla. They both represent WNW-ESE trending structures showing sub-vertical axial planes with 25-30km long and 12-15km width. The AS hosts the world class Almadén deposit, which comprises the largest mercury deposit in the world (Hall et al., 1997; Higuera et al., 1995, 2013; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009), whereas the GS hosts several Sb occurrences and mineralization (Barquero et al., 2022; Lorenzo Álvarez et al., 1995). Like the CS, the AS and GS include a Paleozoic sequence overlying the Precambrian succession known as the Schist-Graywacke Complex (San José et al., 1990). The whole sequence has been mainly folded and affected by the C1 Variscan deformation phase generating a slaty cleavage (Higuera, 1995; Higuera et al., 2013; Higuera & Oyarzun, 2005; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009). A very low grade ranging from zeolite to prehnite-pumpellyite facies has been reported in the AS (García San Segundo et al., 1985; Higuera et al., 1995; Saupe, 1973). In the case of the GS the metamorphism reported can go from very low grade up to greenschist facies, based on mineral associations ranging from quartz+muscovite to quartz+muscovite+chlorite+albite (Lorenzo Álvarez et al., 1995). In both structures the low grade metamorphism has been associated to the Variscan deformation (García San Segundo et al., 1985; Higuera et al., 1995; Lorenzo Álvarez et al., 1995).

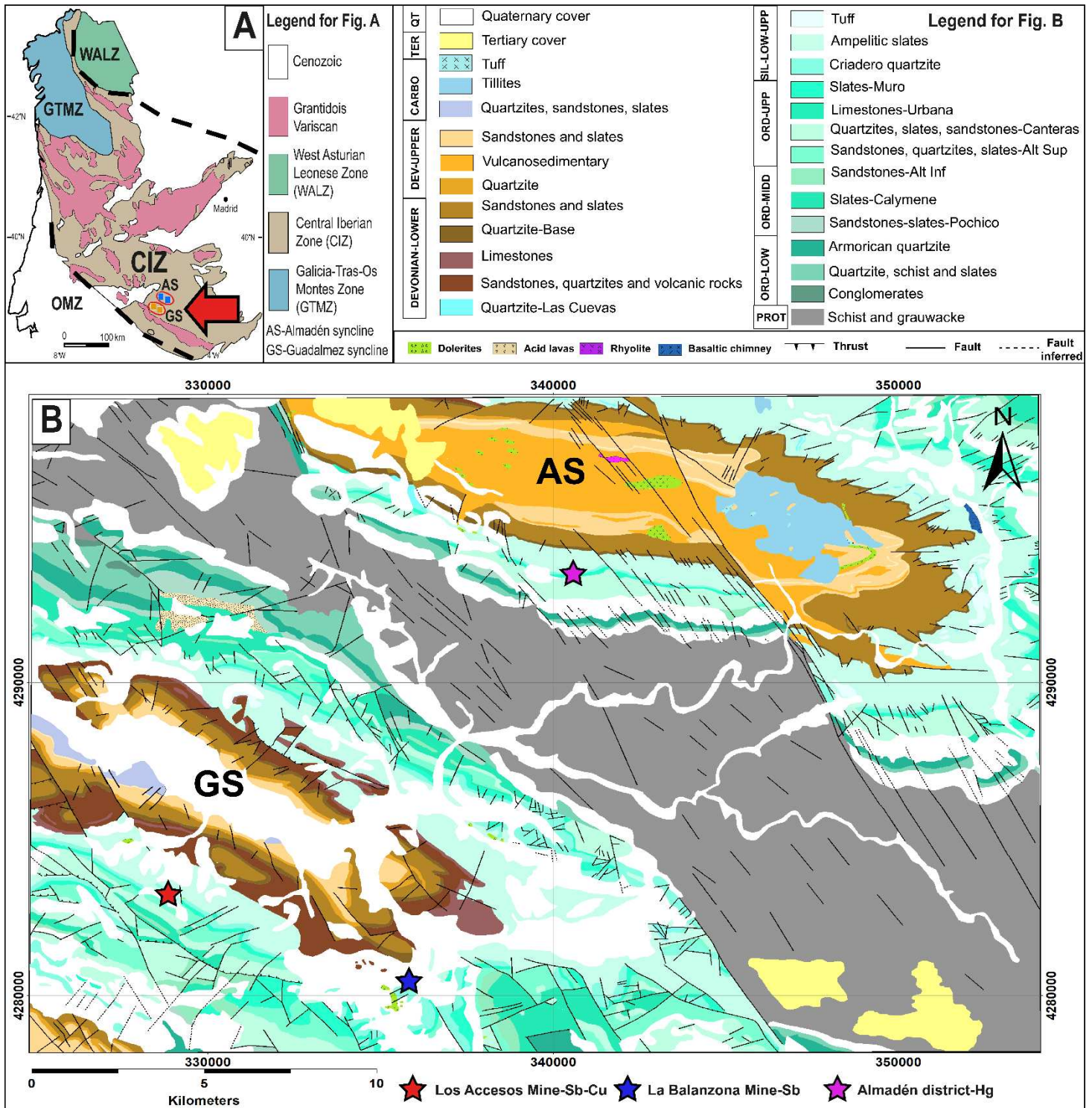
In the AS and GS, the Paleozoic sequence comprise three main lithologies, which include orthoquartzites, siltstones, and slates, with several intercalations of volcanic rocks (Almela et al., 1962; García San Segundo et al., 1985; San José et al., 1990). Among these lithologies, the most relevant one present in both structures is the orthoquartzites, which include four main

units presenting ages from Lower Ordovician to Lower Devonian (Higueras et al., 2013; Palero-Fernández et al., 2015). From bottom to the top these rocks have been described as follows (Almela et al., 1962; García San Segundo et al., 1985; Lorenzo Álvarez et al., 1995; Villas et al., 1999): **i)** the Lower Ordovician Armorican Quartzite, showing a thickness of 300-350m in the AS (García San Segundo et al., 1985) and 150-200 in the GS (Lorenzo Álvarez et al., 1995), overlain by the Pochico unit (sandstones, slates, and quartzites), the Calymene slates, and the sandstones from the Alternancia Inferior (García San Segundo et al., 1985); **ii)** the Upper Ordovician Canteras Quartzite, presenting a thickness of about 40m-70m (AS) and 120m (GS), overlain by the rocks of the Alternancia Superior (sandstones, quartzites and slates) and the Muro slates (Almela et al., 1962; García San Segundo et al., 1985; Lorenzo Álvarez et al., 1995); **iii)** the Upper Ordovician-Lower Silurian Criadero Quartzite (Almela et al., 1962), which in the case of the AS is 6-60m thick and hosts the world class Almadén Hg deposit and, in the GS, is 60-100m thick and hosts small Sb mineralization in the GS (Higueras, 1995; Higueras et al., 2013, 2022; Higueras & Oyarzun, 2005); **iv)** the quartzite-Base, which shows a thickness of 50m-60m in the AS and 30-40m in the GS and is overlain by intercalations of slates, sandstones, quartzites, limestones tuff and lavas (García San Segundo et al., 1985).

The Carboniferous rocks in the Paleozoic sequence of the AS (Fig. 2.15) are represented mainly by tillites as well as tuffs of trachytic and rhyolitic composition and basalts (García San Segundo et al., 1985). In the case of the GS, the Carboniferous sequence is represented by the slates and limestones of the Casa de la Vega Formation showing a thickness of 40-60m overlain by sandstones, greywackes and conglomerates (Lorenzo Álvarez et al., 1995; Pardo & García-Alcarde, 1984).

In the whole metasedimentary succession of the AS, important amounts of mafic syn-sedimentary intraplate suites of Paleozoic age have been reported (Hall et al., 1997; Higueras, 1995; Higueras et al., 1995, 2000, 2013; Palero-Fernández et al., 2015; Palero & Lorenzo,

2009). The mafic units are represented by sills, dykes, volcano sedimentary rocks, porphyritic lavas and diatremes (breccia-tuffs) and are mostly present in the Lower Silurian to Devonian rocks (García San Segundo et al., 1985; Higuera, 1995; Higuera et al., 2013; Higuera & Oyarzun, 2005; Palero-Fernández et al., 2015). In the GS the presences of mafic rocks is limited to some diabases intruded mostly into Silurian Shales (Barquero et al., 2022; Lorenzo Álvarez et al., 1995).



One of the most common and most relevant mafic unit in the AS comprises the breccia tuffs known as the “Frailesca” rocks. This unit is composed mainly by volcanic material of basaltic composition with several fragments of ultramafic rocks, black shales and quartzites. It is important to note that the Frailesca rocks were dated using $^{40}\text{Ar}/^{39}\text{Ar}$ on fuschite and yielded emplacement ages ranging between 427 Ma and 365 Ma (Hall et al., 1997). Nevertheless, this geochronological data was considered as non-precise considering that the mica could have been an alteration product and not formed during the volcanic event (Palero-Fernández et al., 2015). In spite of this, field observations allowed to determine that these rocks are crosscutting the Criadero quartzite and therefore they are older than this unit (Higueras et al., 2000, 2013; Palero-Fernández et al., 2015). Several diabase bodies showing a tholeiitic affinity and sub-parallel to the stratification are crosscutting the Frailesca rocks (Higueras et al., 2000, 2013; Palero-Fernández et al., 2015).

It has been proposed that the mafic volcanism in the AS acted as a strong trigger for the hydrothermal activity resulting in the formation of the Hg world class deposits of the Almadén district (Higueras, 1995; Higueras et al., 2000, 2013; Higueras & Oyarzun, 2005; Palero-Fernández et al., 2015). The extraction of Hg from the volcanic rocks together with the CO_2 degasification is considered to be one of the main feeding source for the hydrothermal system leading to the formation of the Hg ore deposits (Higueras, 1995; Higueras et al., 2000, 2013; Higueras & Oyarzun, 2005; Palero-Fernández et al., 2015).

In the Almadén district (Fig. 2.15) two main types of Hg deposits have been reported, these were classified as stratabound and stockwork (Hernández et al., 1999; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009). The largest and most common ones comprise the stratabound which are located within the lower and upper parts of the Criadero Quartzite (e.g. Almadén, Entredicho and Vieja Concepción mines; Hernández et al., 1999; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009). The stockwork deposits are smaller and essentially hosted in volcanic

and detrital rocks (e.g. Las Cuevas and Nueva Concepción mines; Hernández et al., 1999; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009). Palero-Fernández et al. (2015) dated several mineralization events using Pb isotopic ratios on cinnabar samples at late Silurian-Devonian (420-375 Ma), late Variscan (300 Ma), Permian-Triassic (290-220 Ma), late Jurassic-Cretaceous (200-150 Ma) and Eocene-Oligocene (50-25 Ma). All of these ages allowed to determine a strong correlation between cinnabar crystallization/mobilization and extensional geotectonic settings (Palero-Fernández et al., 2015).

2.7. The Susana and Nazarena mines

Two other locations corresponding to the Susana (Badajoz province) and Nazarena (Ciudad Real province) mines were studied in this work (see part 2.9.2.1. of this chapter). The first one represents a Sb occurrence hosted in the Schist Greywacke Complex. The second one is hosted within a sequence composed of slates and quartzites known as the “Capas o Alternancias Pochico” of Ordovician age (Gumiel, 1982). In both localities mafic intrusions were found next to the mines, these mafic rocks will be treated in this thesis.

2.8. Antimony mineralization in the Ibero-Armorican arc

2.8.1. Sb in the Armorican Massif

The Armorican Massif hosts several Sb deposits located in the SAD, the CAD and the NAD, and observed within Paleozoic sequences (Fig. 2.16). The Sb mineralization is represented by both, mineralized quartz-carbonate veins and stratabound deposits. Among them, the most common paragenesis consist of (i) stibnite-gold, (ii) only stibnite, (iii) Sb-Sulfosalts (with or without Au), (iv) only Sb (Pochon, 2018 and references therein).

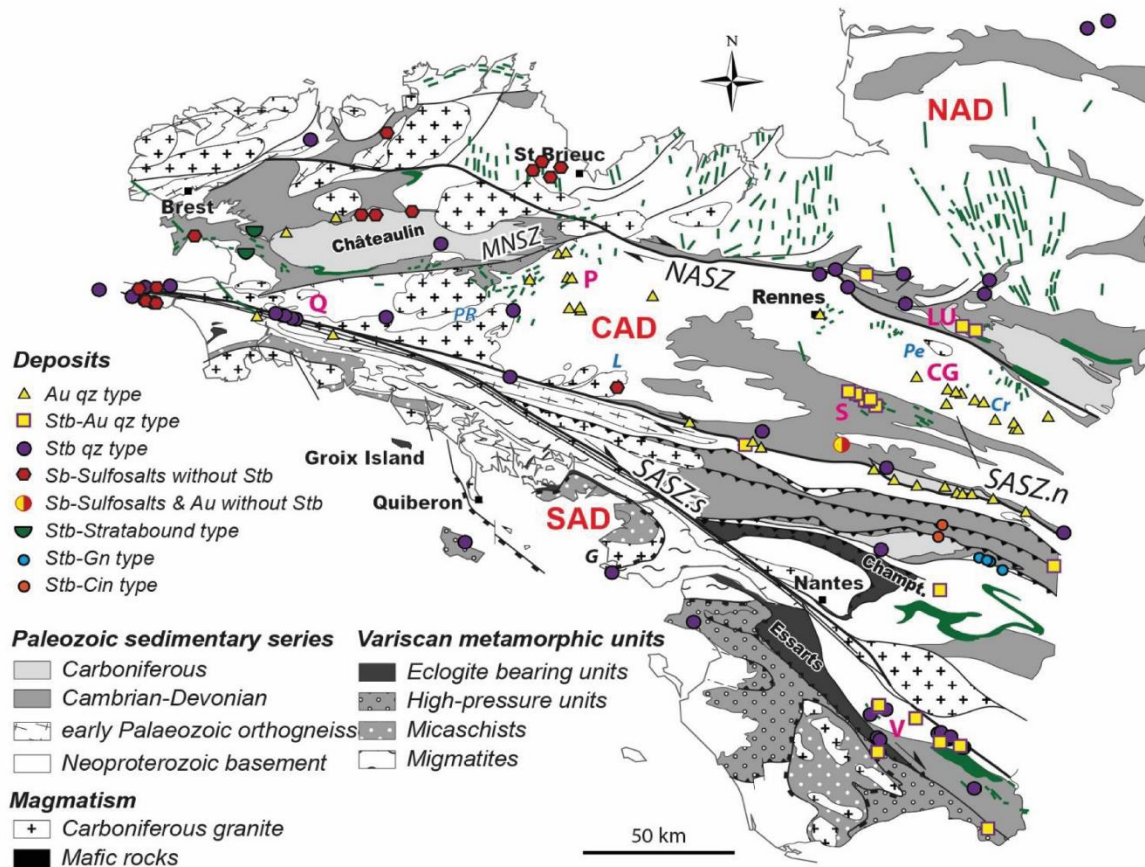


Figure 2. 16. Simplified geological map of the Armorican Massif showing several Sb and Au mineralization located in the Southern Armorican Domain (SAD), the Central Armorican Domain (CAD) and the North Armorican Domain (NAD). Legend: LU: Sb-Au district of La Lucette, S: Sb-Au Semnon-La Coëfferie district, V : Sb-(Au) Vendée district, Q : Sb Quimper-Cap Sizun CG district ; Au district of Château-Gontier, P : Au district of Pontivy-Loudéac, L : Lizio granite, PR : Pontivy-Rostrenen Complex, Pe : granite of Pertre and Cr : granite of Craon. Modified after Pochon (2018) and references therein.

The Armorican Massif represents one of the most important geological domains in terms of Sb production in France during the 20th century (Guilloard, 2009). Four main districts were responsible for the production of at least 1450kt of Sb (Chauris & Marcoux, 1994; Guilloard, 2009; Laznicka, 2010; Serment, 1978), these include La Lucette, The Vendée, The Semnon-La Coëfferie and the Quimper-Cap Sizun districts.

In terms of Sb production:

- La Lucette district produced around 42kt of Sb and 8.2kt from 1900 until 1934 (Guilloard, 2009; Serment, 1978).

Chapter 2

- The Vendée exploited ≈ 18.8 kt from 1907-1934 (Blouin, 1991; BRGM, 1987; Marcoux et al., 1984; Moyroud et al., 1979).
- The Semnon-La Coëfferie district produced from 1913 to 1918 at least ≈ 500 t of Sb (BRGM, 1987; Chauris & Marcoux, 1994; Gloaguen et al., 2016; Moyroud et al., 1979).
- The Quimper-Cap Sizun district 890t of Sb were exploited from 1913 until 1928 (BRGM, 1990; Fouquet, 1980; Gorichon & Kerjean, 1979; Moyroud et al., 1979).

The main data concerning the four districts can be observed in Table 2.1 and Table 2.2.

Chapter 2

Table 2. 1. Main minerals present in the paragenetic sequences of the Sb districts in the Armorican Massif. (Blouin, 1991; BRGM, 1987; Chauris et al., 1985; Chauris & Marcoux, 1994; Fouquet, 1980; Gloaguen et al., 2016; Gorichon & Kerjean, 1979; Marcoux et al., 1984; Moyroud et al., 1979; Serment, 1978). Po: Pyrrhotite; Sch: Scheelite; Gn: Galena; Sl: Sphalerite; Stbn: Stibnite; Btr: Berthierite.

District/Minerals	Quartz	Pyrite	Marcasite	Arsenopyrite	Chalcopyrite	Po	Carbonates	Sch	Gn	Sl	Au	Stbn	Btr	Native Sb
La Lucette														
Vendée														
Semnon-La Coëfferie														
Quimper-Cap Sizun														

Chapter 2

Table 2. 2. Main data for the Sb districts in the Armorican Massif

District	Host rock/Age of the host rock	Fluid inclusions data	Dating of the mineralization
La Lucette	Ordovician to Silurian Metapelites of	Minimum P-T conditions for the trapping and formation of the mineralization at 100MPa and 225°C-380°C (Pochon, 2018). P-T conditions of 3.5-6km and 350°C-250°C) in the mineralizing stages (Cheval-Garabédian et al., 2023)	U-Pb in hydrothermal apatites: 299±11 Ma (Cheval-Garabédian et al., 2023), later questioned by Gloaguen et al. (2024), due to issues with the results.
Vendée	Neoproterozoic to Cambrian Metagreywackes and metapelites (Blouin, 1991; BRGM, 1987; Marcoux et al., 1984 and references therein)	Homogenization temperatures for primary stibnite inclusions of 140°C and 160°C and 215°C for secondary inclusions (Bailly et al., 2000). The primary inclusions show moderate salinity (3.5-4.75wt % NaCl equiv) whereas a low salinity (1.35-2.2wt % NaCl equiv) was obtained for the secondary ones (Bailly et al., 2000).	⁴⁰ Ar/ ³⁹ Ar crystallization ages of illites associated to the main mineralizing stibnite stage dated between 358-359 Ma (Pochon et al., 2018).
Semnon-La Coëfferie	Dolerite sills dated at 358.5±7.1 by U-Pb dating on apatite (Pochon et al., 2016b)	The fluid inclusions demonstrated a cooling from 330°C-240°C related to the Sb mineralizing events, suggesting a single event related to a shallow thermal source at ≈2.5km of depth (Pochon et al., 2018)	⁴⁰ Ar/ ³⁹ Ar crystallization ages of illites associated to the main mineralizing stibnite stage dated between 358-359 Ma (Pochon et al., 2018).
Quimper-Cap Sizun	Granitoids dated at 320±25Ma (U-Pb zircon; Béchenec et al., 2006)		Late Variscan based on the age of the granitoids (Béchenec et al., 2006; Chauris & Marcoux, 1994; Cocherie, 2001)

Possible origin of the Sb in the Armorican Massif

Several hypotheses have been proposed to understand the possible origin and sources of the Sb deposits in the Armorican Massif. One of the first theories suggest an important relation with felsic magmatism emplaced at ≈ 300 Ma at the last stages of the Variscan orogeny (Fouquet, 1980; Marcoux et al., 1984; Serment, 1978). This model is based on the distribution of different types of mineralization and their distance from the granitic bodies. The W-Sn-Au deposits are the closest to the felsic intrusions, the Sb mineralization is found at an intermediate distance whereas the mineralization with the lowest formation temperatures (Pb, Zn, Ba, F) is located far from the intrusions (Fouquet, 1980; Marcoux et al., 1984; Serment, 1978). This model was proposed for the Quimper and the Vendée districts implying the coeval formation of the Sb mineralization and the emplacement of the felsic magmatism, suggesting not only a spatial and temporal relationship but also a genetical association related to magmatic fluids (Chauris & Marcoux, 1994; Fouquet, 1980; Marcoux et al., 1984; Serment, 1978). Nevertheless, for these deposits, there is no evidence of magmatic fluid signatures and no geochronological data support that the mineralization is coeval with the emplacement of the felsic intrusions.

In the case of La Lucette deposit, the occurrence of a hydrothermal system with a strong structural control where the magmatism acted as a heating source (Cheval-Garabédian, 2016). The fluids responsible for the Sb-Au stage are proposed to represent a mixing between an initial metamorphic fluid (related to the first scheelite mineralizing stage) with cold meteoric fluids (Cheval-Garabédian et al., 2023). The Cheval-Garabédian et al. (2023) model was latter questioned by Gloaguen et al. (2024), who asserted that the results presented by Cheval-Garabédian et al. (2023) are insufficient to support the idea of a generalized and unique metallogenic peak in the French Variscan belt at Carboniferous-Permian transition.

In the Quimper-Cap Sizun district where the mineralization presents a structural control related to the main shear zones, it is younger than late Variscan granitoids and the origin of the mineralizing fluids is believed to come from the lower crust (Chauris et al., 1977; Chauris & Marcoux, 1994; Fouquet, 1980). Bouchot et al. (2005) suggested that most of the Sb mineralization in the Massif Central in France may be associated to a same hydrothermal event taking place between 310-300Ma, the “Or 300” event. This hypothesis is consistent with the globally known “Orogenic gold” model (Goldfarb & Groves, 2015; Groves et al., 1998), in which the fluids present an important metamorphic signature of deep crustal origin, related to metamorphic reactions that can be triggered by several processes such as: magmatic heat, crustal thickening, slab-rollback, mantle plume, asthenosphere upwelling (oceanic ridge-subduction).

Considering the relevant amount of mafic bodies in the Armorican Massif, a link between Sb mineralization and mafic magmatism has been proposed in recent years. Pochon et al., (2016a) suggested a spatial link between Sb mineralization in the surface and mafic bodies in depth, based on geophysical data showing high magnetic and high-density zones. The emplacement ages of several mafic sills and dykes within the Laval Basin, the Martigné Ferchaud group, and the Saint Malo group were dated at ca. 360 Ma using U-Pb LA-ICP-MS on apatite (Pochon et al. 2016b). The Sb mineralization and the mafic magmatism in the Semnon district were demonstrated to be coeval at ca. 360 Ma by dating both the Sb mineralization stage ($^{40}\text{Ar}/^{39}\text{Ar}$ on Illite) and the host mafic dolerite dyke (U-Pb apatite; Pochon et al., 2018). The Sb±Au mineralization of Saint-Aubin-des-Châteaux in the Vendée district of the CAD was also dated at ca. 360 Ma using $^{40}\text{Ar}/^{39}\text{Ar}$ on Tobelite (Pochon et al., 2019). All of these studies, allowed to proposed that the 360 Ma mafic magmatism in the Armorican Massif played an important role as trigger of the mineralizing Sb hydrothermal peak taking place at the

same period, during late Devonian to early Carboniferous times (Pochon et al., 2016a, 2016b, 2018, 2019).

2.8.2. Sb in the Iberian Massif.

In the Iberian Peninsula most of the antimony deposits are found in the Iberian Massif (Gumiel, 1982; Gumiel & Arribas, 1987). Other deposits have been reported in the Pyrenees, in the Iberian range as well as in the Variscan basement of the Alpine orogen (Table 1 and Fig. 19). Gumiel & Arribas (1987) described three main Sb deposits-type, based on their morphological features: **i)** strata-bound deposits present an important lithological and structural control and the mineralization is mainly in a stratiform shape (although veins crosscutting the sequence due to the remobilization following the main fractures are also observed), hosted in breccias, siliceous layers, shales, slates and calcareous rocks; **ii)** vein deposits in which the mineralization occurs as irregular lenses or crosscutting vein systems with no lithological control; **iii)** Sb-mineralization related to felsic volcanic dykes strongly associated to post-orogenic volcanism and hosted in dykes of rhyodacitic composition and within their host rocks.

In these deposits 8 different mineral assemblages have been described (Gumiel & Arribas, 1987):

- a) Quartz-stibnite: quartz stibnite veins, in some cases with berthierite found in the deposits 13, 18, 27-29, 32-34, 36, 39, 41, 44 and 51 in Fig. 2.17 and Table 2.3.
- b) Quartz-stibnite gold: lodes of stibnite, arsenopyrite, pyrite and gold (related to quartz, arsenopyrite and pyrite). The highest gold concentrations are presented in the Gondomar district (Porto) in Portugal. In Spain, the most important deposit showing this assemblage is the Mari Rosa Mine located in the NW of the La Codesera syncline. Other deposits presenting this mineral association are 16, and 26 in the Fig. 2.17 and Table 2.3.

- c) Carbonate-quartz-stibnite-sphalerite-gold: In this mineral assemblage the paragenesis starts with the deposition of pyrite, arsenopyrite and gold. The latest together with the sphalerite, chalcopyrite, tetrahedrite and berthierite are related to the stibnite. This assemblage can be found in the deposits 17 and 35 in Fig. 2.17 and Table 2.3.
- d) Carbonate-quartz-stibnite-galena-silver: in this paragenesis pyrite, ullmannite and chalcopyrite are deposited first, followed by galena, lead sulfo-antimonides, and finally Sb-Ag sulfosalts. Only one deposit in the Iberian Massif shows this mineral assemblage, the Diógenes Mine in the Ciudad Real province.
- e) Quartz-stibnite-sphalerite: sphalerite and stibnite with berthierite inclusions. This type of mineralization is commonly found in sequences of slates and quartzites of Lower Ordovician age. The most important deposits showing this assemblage are the San Felipe Mine (Ciudad Real province, 37, Fig. 2.17 and Table 2.3), the Arroyo de Tanujar (Ciudad Real, 42, Fig. 2.17 and Table 2.3), the Nazarena Mine (Ciudad Real, 43, Fig. 2.17 and Table 2.3) and the San Agustín mine (Jaén province, 47, Fig. 2.17 and Table 2.3).
- f) Quartz-stibnite-scheelite: in this paragenesis pyrite, arsenopyrite and scheelite are deposited first, followed by berthierite, stibnite and finally Sb oxides (Arribas & Gumiel, 1984; Gumiel, 1982). The most important deposits showing this mineral assemblage is the San Antonio mine (Badajoz province, 30, Fig. 2.17 and Table 2.3) and the Javier-Jesus mine in the Córdoba province.

- g) Quartz-stibnite-relagar-orpiment-cinnabar: This assemblage consists of orpiment, realgar, cinnabar, pyrite, minor arsenopyrite, cinnabar and stibnite. It has been only reported in the Cantabrian Zone.
- h) Quartz-stibnite-copper: in this mineral assemblage arsenopyrite, chalcopyrite, and famatinite (Cu_3SbS_4) are deposited first, followed by stibnite, commonly replaced by Sb-oxides. The most important deposits presenting this mineral assemblage include the Accesos Mine (Guadalmez syncline, Córdoba, 38, Fig. 2.17 and Table 2.3), Sierra Morena (Córdoba, 48, Fig. 2.17 and Table 2.3) and the Nerón mine (Huelva, 51, Fig. 2.17 and Table 2.3).

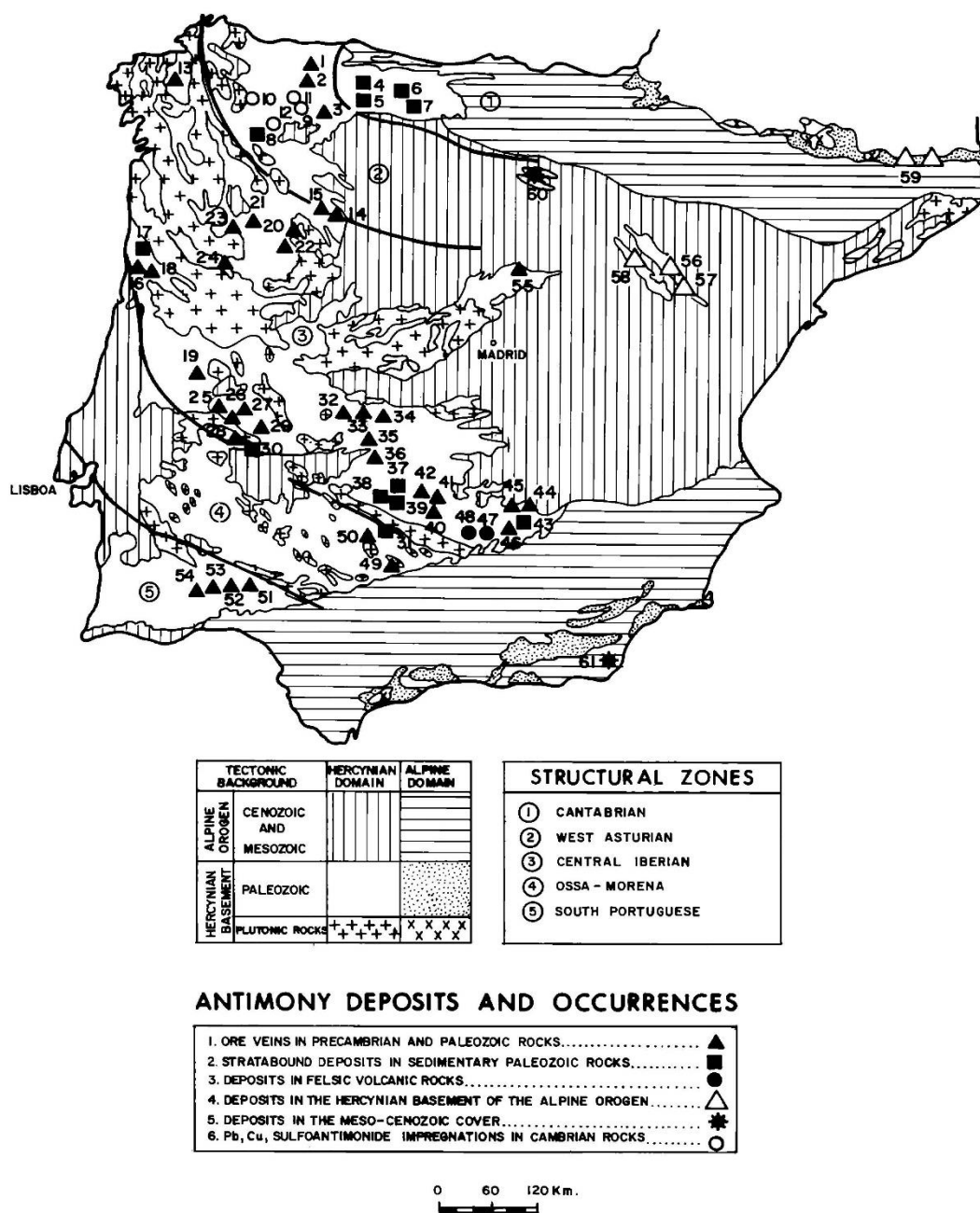


Figure 2. 17. Distribution of the antimony deposits and occurrences in the Iberian Peninsula (Gumiel & Arribas, 1987).

Table 2. 3. Antimony deposits in the Iberian Massif. (Gumiel & Arribas, 1987).

1. Tineo (Oviedo)	33. Las Hambrientas, Navezuelas (Cáceres)
2. Cangas del Narcea (Oviedo)	34. Dolores, Anchuras de los Montes (Ciudad Real)
3. Murias de Paredes (León)	35. Pilar, Herrera del Duque (Badajoz)
4. Soterraña, Mieres (Oviedo)	36. Susana, Puebla de Alcocer (Badajoz)
5. Pola de Lena (Oviedo)	37. San Felipe, Almadenejos (Ciudad Real)
6. Tarna, Puerto de Tarna (León)	38. Los Accesos, Guadalmez (Córdoba)
7. Pedrosa del Rey, Riaño (León)	39. La Balanzona, Santa Eufemia (Córdoba)
8. Villarbacú, Sierra del Caurel (Lugo)	40. Diógenes, Solana del Pino (Ciudad Real)
9. Cuevas del Sil (León)	41. San Gabriel, Mestanza (Ciudad Real)
10. Castroverde (Lugo)	42. Arroyo de Tamujar, Cabezasrribas del Puerto (Ciudad Real)
11. Degaña (Oviedo)	43. La Nazarena, Almuradiel (Ciudad Real)
12. Torral (León)	44. San Cristobal, Torrenueva (Ciudad Real)
13. Pandeiro, Ordenes (La Coruña)	45. Bilbao, Santa Cruz de Mudela (Ciudad Real)
14. Las Cogollas, Losacio (Zamora)	46. Santo Cristo, Viso del Marqués (Ciudad Real)
15. Occurrences: La Cabrera, Marrón, and Valdeconejos, Losacio (Zamora)	47. San Agustín, Baños de la Encina (Jaén)
16. Alto de Sobrido, Oporto (Portugal)	48. Occurrences: María Luisa, El Contadero, and la Casa del Barranquillo, La Carolina, (Jaén)
17. Ribeiro de Igreja, Oporto (Portugal)	49. Sierra Morena 2ª, Santa María de Trasierra (Córdoba)
18. Pinheirinhos and Corgo, Oporto (Portugal)	50. Occurrences: Don Beck and Pepín, Espiel (Córdoba)
19. Castelo Branco (Portugal)	51. Nerón, Montes de San Benito (Huelva)
20. Vimioso, Tras os Montes (Portugal)	52. Occurrences: Angelita and Alquería del Pozo, Montes de San Benito (Huelva)
21. Macedo de Cavaleiros, Tras os Montes (Portugal)	53. Cabezas del Pasto (Huelva)
22. Mogadouro, Tras os Montes (Portugal)	54. Alcoutim (Portugal)
23. Mirandela, Tras os Montes (Portugal)	55. Cerezo de Arriba (Segovia)
24. Vila Nova de Foscoa, Alto Douro (Portugal)	56. Barranco Rollo, Lanzuela (Teruel)
25. Mari Rosa, Valencia de Alcántara (Cáceres)	57. El Carrascal, Maicas (Teruel)
26. Portoviejo, Valencia de Alcántara (Cáceres)	58. Occurrences: La Plana, Leonor, and Pozo del Fraile, Valtorres (Zaragoza)
27. Cuadrillas de Barbellido, Valencia de Alcántara (Cáceres)	59. Valle de Ribes (Gerona)
28. Santa Aurelia, San Vicente de Alcántara (Badajoz)	60. Santa Rufina, Urrez (Burgos)
29. Mari Pepa, San Vicente de Alcántara (Badajoz)	61. Las Minillas, Carboneras (Almería)
30. San Antonio, Alburquerque (Badajoz)	
31. Javier-Jesús, Añora (Córdoba)	
32. Suerte, Aldeacentenera (Cáceres)	

2.9.2.1. Antimony mineralization in the Central Iberian Zone

The majority of the Sb deposits in the Iberian Massif occur in the CIZ (Gumiel, 1982; Gumiel & Arribas, 1987). The most relevant ones are found in the following provinces (Fig. 2.17 and Table 2.3): Badajoz (e.g. Mina San Antonio); Ciudad Real (e.g. San Felipe), Córdoba (e.g. Los Accesos and La Balanzona) and Jaén (e.g. San Agustín).

Main Sb mineralization in the studied areas.

The San Antonio district-Sb-W-La Codosera syncline

The San Antonio district comprises the largest known antimony resource of Iberia and is located in the Badajoz province at La Codosera syncline, close to the limit between the CIZ and the OMZ (Gumiel et al., 1976). This Sb-W stratabound mineralization (number 30, (Fig. 2.17 Gumiel, 1982, Gumiel & Arribas, 1987) is hosted in an intraformational polygenic breccia showing a thickness of 1.8-2.2m and contains fragments of shales, limestones, chert and quartz

in a carbonate matrix (Arribas & Gumiel, 1984; Gumiel, 1982). The breccia represents a horizon belonging to the Gévora Formation, which is composed of shales, slates and black limestones of early Carboniferous age (Rodríguez González et al., 2007). The mineralization presents a continuity of 35m length / 600m deep and shows a channel shape within the breccia (Gumiel et al., 1990). Three main stages have been documented for this ore-deposit **i)** quartz and carbonates with pyrite, arsenopyrite and scheelite; **ii)** a second generation of quartz and carbonates followed by pyrite, berthierite and stibnite; **iii)** alteration of Sb sulfides into Sb oxides. The Sb ore appears in irregular and stretched shape along bedding planes, surrounding quartz, limestone and chert (Gumiel, 1982). The stibnite can be found filling cracks in the scheelite (Arribas & Gumiel, 1984). Differently, W ore occurs as nodules and sometimes euhedral crystals following the bedding of the sequence (Arribas & Gumiel, 1984; Gumiel, 1982). The mineralization was mainly affected by the C1 deformation, described above (Arribas & Gumiel, 1984). Gumiel et al. (1976) first suggested that the Albuquerque granite, dated between 309-306 Ma (Solá et al., 2009), was the source of the San Antonio deposit, based on its proximity to the intrusion. Nevertheless, a hydrothermalism associated with basic volcanism was later proposed as the possible source of the mineralizing fluids (Arribas & Gumiel, 1984). According to Arribas & Gumiel (1984), this processes took place during Devonian times in an outer continental shelf that was affected by relevant extensive tectonics generating a fault system that allowed the formation of the intraformational breccias as well as the hydrothermal exhalative activity related to basic volcanism responsible for the formation of the Sb deposit.

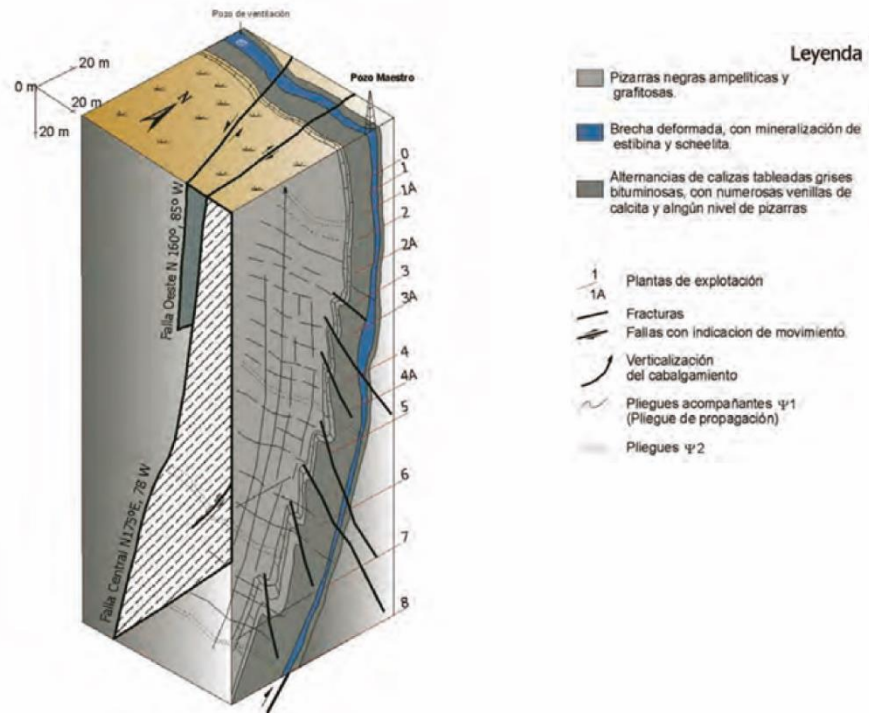


Figure 2. 18. Isometric section of the San Antonio Sb-deposit. After Gumiel (1982).

Los Accesos Mine (Sb-Cu), Guadalmez syncline

The Accesos Mine (number 38, Fig. 2.17 and Table 2.3) comprises a Sb-Cu stratabound deposit, located in the Cordoba province within the contact of the units known as the “Alternancias Superiores” and “Pizarras de Muro” or Ordovician age (Gumiel, 1982). The mineralization is presented as disseminated in a horizon of silicified sandstones (20-50cm thick) at the upper part of the Alternancias Superiores unit (Gumiel, 1982). Other stratigraphic units, such as the Criadero Quartzite, show some Sb occurrences in fractures (Gumiel, 1982). Two main mineralizing stages were reported (Gumiel, 1982): **i**) pyrite and quartz, followed by famatinite, berthierite, stibnite, native antimony (within the stibnite) and marcasite; **ii**) supergene alteration represented by malachite, Fe oxides (goethite) and Sb oxides (bindheimite, senarmontite).

La Balanzona Mine (Sb), Guadalmez syncline

The Balanzona Mine (number 39, Fig. 2.17 and Table 2.3) represents a Sb stratabound deposit located at the Northern flank of the Guadalmez syncline in the Cordoba Province (Gumiel, 1982). The Sb ore is located in the upper Ordovician-lower Silurian formation known as the Criadero Quartzite (strike-N160-N170) and is presented as fractures (up to 5cm thick) showing two main directions N25-N30 and N150-N160 with an almost vertical dip (Gumiel, 1982). Two main stages have been documented for this deposit (Gumiel, 1982): **i)** pyrite and quartz, followed by berthierite, stibnite and native antimony; **ii)** supergene alteration including Sb oxides (stibiconite, senarmontite and kermesite) and Fe oxides.

La Nazarena Mine (Sb, Zn)

This Sb-Zn stratabound deposit is located in the Almuradiel locality in the Ciudad Real Province (43, Fig. 2.17 and Table 2.3). It is hosted within a sequence composed of slates and quartzites known as the “Capas o Alternancias Pochico” of Ordovician age (Gumiel, 1982). The mineralization is presented as lenses (3-10cm thick) and disseminated in the host rock usually filling fractures. Three main stages have been documented for this ore-deposit (Gumiel, 1982; Gumiel & Arribas, 1987): **i)** quartz, pyrite, chalcopyrite and sphalerite **ii)** a second generation of quartz, berthierite, stibnite, native antimony and marcasite; **iii)** Fe-oxides and alteration of Sb ores into Sb oxides (cervantite and valentinite).

La Susana Mine

It represents a small occurrence located at the Puebla de Alcocer in the Badajoz province (36, Fig. 2.17 and Table 2.3). The deposit is hosted within a sequence of slates and greywackes belonging to the so known Schist Greywacke Complex (Gumiel, 1982). The mineralization occurs disseminated in quartz lenses (2-5cm) showing a N150°E-N160°E strike and a subvertical dip (Gumiel, 1982).

*Synthesis of the relevant Sb deposits in the CIZ***Table 2. 4.** Main minerals present in the paragenetic sequences of the Sb districts in the CIZ. (Gumiel, 1982; Gumiel & Arribas, 1987 and references therein).

District/Minerals	Quartz	Pyrite	Marcasite	Arsenopyrite	Chalcopyrite	Carbonates	Sch	Gn	Sl	Au	Stbn	Btr	Native Sb	Main Elements
San Antonio														S, Fe, As, C, W
Los Accesos														S, Fe
La Balanzona														S, Fe
La Nazarena														S, Fe, Cu, Zn
Mari-Rosa														S, Fe, As, Au
Pilar														S, Fe, As, Cu, C, Zn, Au
San Agustín														S, Fe, As, C, Zn
La Susana Mine														S, Fe, As, C, W
Durico-Beirao District														S, Fe

Chapter 2

Table 2. 5. Main data available for the most relevant Sb deposits in the CIZ.

District	Host rock/Age of the host rock	Fluid inclusions data
San Antonio	Polygenic breccia hosted in Carboniferous shales of the Gévora Formation (Rodríguez González et al., 2007).	
Los Accesos	“Alternancias Superiores” and “Pizarras de Muro” of Ordovician age (Gumiel, 1982)	
La Balanzona	Upper Ordovician-lower Silurian formation known as the Criadero Quartzite (Gumiel, 1982)	
La Nazarena	Slates and quartzites known as the “Capas o Alternancias Pochico” of Ordovician age (Gumiel, 1982)	
Mari-Rosa	Phyllites and metagraywackes of the Precambrian-Cambrian Schist Greywacke Complex (Gumiel, 1982)	The precipitation of the stibnite occurred in a range of 300°C-260°C at 1kbar (Ortega & Vindel, 1995).
Pilar	Precambrian-Cambrian Schist Greywacke Complex (Gumiel, 1982)	
San Agustín	Rhyodacitic dyke within a Carboniferous sequence of slates, sandstones, conglomerates and sometimes quartzites (Gumiel, 1982)	
La Susana Mine	Slates and greywackes of the Precambrian-Cambrian Schist Greywacke Complex (Gumiel, 1982).	
Durico-Beirao District	Precambrian-Cambrian Schist Greywacke Complex (Gumiel, 1982)	

CHAPTER 3: Evolution of the mafic magmatism in the Central Iberian Zone, Spain. Insights from: La Susana Mine, La Nazarena Mine, La Codosera, Almadén and Guadalmez synclines.

This chapter is currently in peer review at the Bulletin de la Société Géologique de France (BSGF) as the following article: Campos-Rodríguez, H. R., Gloaguen, E., Tuduri, J., Pochon, A., Iacono-marziano, G., Poujol, M., Higuera, P., Virtanen, V. J., Lorenzo, S., Esbri, J. M., & Mollé, V. (2024). Geochemistry and geochronology of the Paleozoic mafic magmatism in the Codosera, Almadén and Guadalmez synclines, Central Iberian Zone, Spain. Submitted (Peer review).

3.1-Introduction

Petrological, geochemical and geochronological studies of mafic rocks are crucial for identifying mantle sources, crustal contamination, and tectonic settings that prevailed in magmatic provinces (Chauvel et al., 2008; Orejana et al., 2020; Tappe et al., 2013; Villaseca et al., 2022; Zhao et al., 2009). In the Variscan belt (Fig. 3.1A), several studies on Precambrian to Carboniferous mafic suites suggest the existence of different sources and an important interaction between mantellic and crustal magmas as recorded by their geochemical signatures (e.g. Dostal et al., 2019; Martínez Catalán et al., 2021; Schulmann et al., 2022; Villaseca et al., 2022). In the Armorican Massif (Fig. 3.1A), geochronological and geochemical studies on mafic dykes propose the occurrence of a magmatic event that took place during the early stages of the Variscan orogeny (~360 Ma), possibly related to the melting of an enriched lithospheric mantle (Pochon et al., 2016b). In the case of the Central Iberian Zone (CIZ) of the Iberian Massif (IM, Fig. 3.1B), the geochemical signatures of the mafic rocks are related to metasomatized mantle sources, crustal contamination and other processes and they have significantly evolved through time (e.g. Villaseca et al., 2022 and references therein).

Previous studies identified several magmatic events spanning from the Neoproterozoic (573 Ma, late Pan-African (Cadomian) cycle; e.g. Bandrés et al., 2004) to the early Permian (274 Ma, at the end of the Variscan Orogeny; e.g. Orejana et al., 2020), in various domains of the CIZ (Fig. 3.1B), such as: the Mérida Montoro Complex (Bandrés et al., 2004); the Spanish Central System (SCS, Barbero & Villaseca, 2000; Orejana et al., 2017, 2020; Villaseca et al., 2002, 2015); the Carrascal Massif (Solá et al., 2003, 2010); the basalts from El Castillo in the Valongo-Tamames Syncline (Gutiérrez-Alonso et al., 2008); the CS mafic rocks (Carnicero & Castro, 1983; Garcia de Figuerola et al., 1974; López-Moro et al., 2005, 2007, 2020a); the AS

mafic rocks (Hall et al., 1997; Higuera, 1995; Higuera et al., 1995, 2013; Saupé, 1990; Saupé & Arnold, 1992); the Avila Batholith in the SCS (Bea et al., 1999; Montero et al., 2004; Scarrow et al., 2009); the Sierra Bermeja pluton (Errandonea-Martin et al., 2019); the Calzadilla pluton (López-Moro et al., 2017) and the Toledo Anatectic Complex (Bea et al., 2006). These mafic magmatic events in the CIZ are characterized by various geochemical features, such as the occurrence of enriched and metasomatized mantle sources (e.g. López-Moro et al., 2007; Orejana et al., 2009, 2017; Villaseca et al., 2015); as well as crustal recycling or crustal contamination (e.g. de Almeida Coelho, 2021; Montero et al., 2004; Orejana et al., 2009).

Despite the extensive work related to the mafic magmatism in the CIZ, the geochemical characteristics and emplacement ages of some of these mafic suites are still not totally constrained. This is the case for the mafic intrusions emplaced within five localities into folded metasedimentary sequences (Fig. 3.1B): The Codosera syncline (CS), the Almadén syncline (AS), the Guadalmez syncline, la Susana Mine (SUM) and the Nazarena Mine (NZM). Indeed, the CS, hosts the biggest swarm of mafic sills reported in the Iberian Massif (López-Moro et al., 2007, 2020a) and one of the largest Sb-W districts in Spain (Gumiel & Arribas, 1987). Mineralogical, structural and geochemical studies performed in this area propose that the mafic rocks were emplaced during an extensive event preceding the Variscan Orogeny (Carnicero & Castro, 1983; Garcia de Figuerola et al., 1974; López-Moro et al., 2007, 2020a). The mafic magma is suggested to derive from a metasomatized mantle and a significant crustal contamination (López-Moro et al., 2007, 2020a). The AS hosts the world class Almadén Hg deposit. Based on geochronological data and field observations, the mafic magmatism in this structure is believed to have been mainly emplaced at early Silurian times followed by minor magmatic events from middle Silurian to Devonian times (Hall et al., 1997; Higuera, 1995; Higuera et al., 2013; Palero-Fernández et al., 2015). Finally, the mafic rocks from SUM, NZM, and, those from the GS have not been studied yet.

In this study, we present new petrological and geochemical data for some of the mafic intrusives from the CS, AS, GS, SUM and NZM. We constrain the emplacement ages of these mafic magmas by U-Pb dating on apatite. We analyze the geochemical evolution and the possible mantle sources of the Ordovician to Carboniferous mafic magmatism in the CIZ. In addition, we discuss the timing of the magmatism in the CS, AS and GS and then at the scale of the Variscan orogeny.

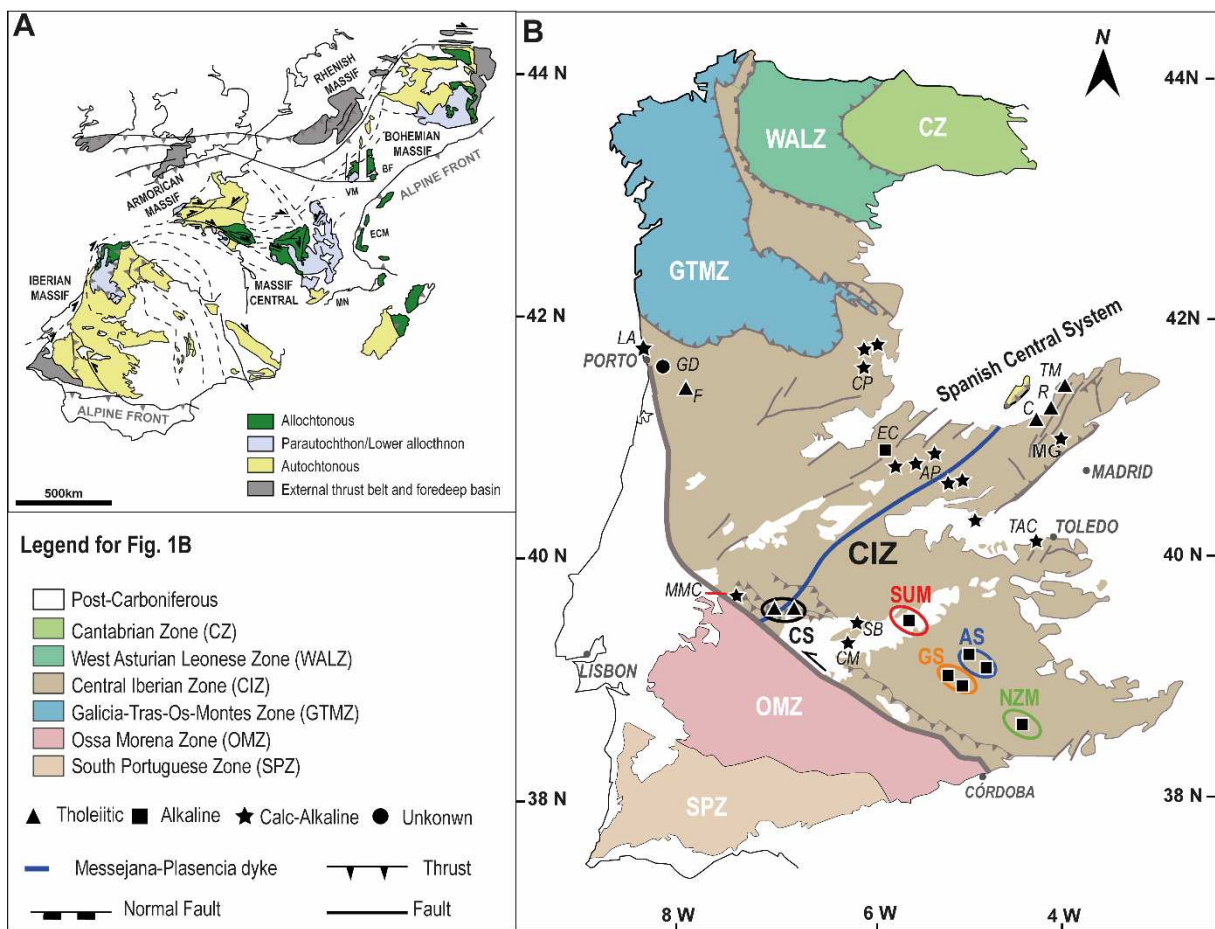


Figure 3. 1. A) Geological sketch of the Variscan Belt showing the main terranes and domains, modified after Martínez Catalán et al. (2014); B) Simplified geological map of the Iberian Massif showing mafic rocks in the studied areas and the mafic suites reported in the Central Iberian Zone (CIZ) from Ordovician times to the late stages of the Variscan orogeny. The map was designed based on the studies made by Julivert et al. (1974) and Simancas (2019). Abbreviations: OMZ: Ossa Morena Zone; GTMZ: Galicia-Tras-Os Montes-Zone; WALZ: West Asturian Leonese Zone (WALZ); CZ: Cantabrian Zone; MN: Montagne Noire; ECM: External Crystalline Massifs of the Alps; VM: Vosges Massif; BF: Black Forest; CP: Calzadilla Plutón (López-Moro et al., 2017); LA: Praia de Labruga (de Almeida Coelho, 2021); GD: Godomar (Medeiros et al., 1981); F: Farminhao (Cotrim

et al., 2021); AP: Appinites (Montero, Bea, et al., 2004; Montero, Zinger, et al., 2004; Scarrow et al., 2009); TAC: Toledo Anatetic Complex (Bea et al., 2006); C: Caloco Sector (Orejana et al., 2017; Villaseca et al., 2015); R: Revenga Sector (Orejana et al., 2017; Villaseca et al., 2015); TM: Tenzuela Massif; MMC: Mérida Montoro Complex (Bandrés et al., 2004); SB: Sierra Bermeja (Errandonea-Martin et al., 2019); CM: Carrascal Massif (Solá et al., 2010); MG : Microgabbros (Orejana et al., 2020) ; CS: Codosera Syncline (López-Moro et al., 2007); AS: Almadén Syncline (Higuera, 1995; Higuera et al., 2013); GS: Guadalmez Syncline (Gumiel & Arribas, 1987; Lorenzo Álvarez et al., 1995); SUM: Susana Mine (Gumiel, 1982); NZM: Nazarena Mine (Gumiel, 1982).

3.2-Analytical methods

3.2.1- Sampling

Nineteen dolerite intrusions were sampled in the CS, AS, GS, SUM, and NZM localities (Figs. 3.2, 3.3, 3.4 and 3.5). Ten samples from the CS were located within a sequence known as the Gévora Formation of Lower Carboniferous age (Rodríguez González et al., 2007), consisting of black slates, quartzites and sandstones (Fig. 3.2; SA2008, SA2013, SA2014A, SA2014B, SA2015, SA2022A, SA2022B, SA2022C, SA2026 and SA2042).

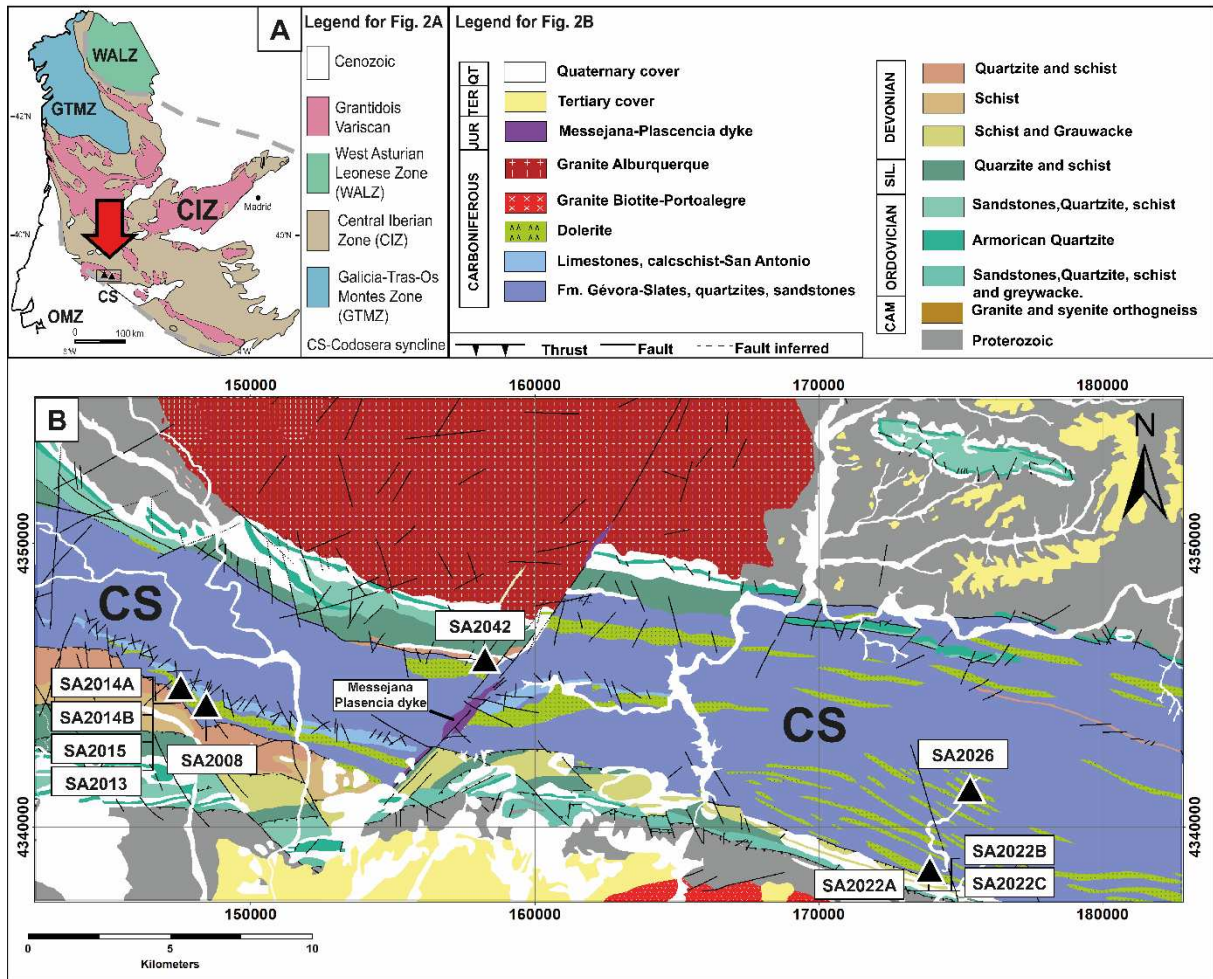


Figure 3. 2. A) Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the mafic samples studied in this work. Reference (c): Sampling points from Rodríguez González (2007). The map was redesigned based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).

Four samples from the AS, were found within volcano sedimentary rocks of Upper Devonian age, composed of tuffs and volcanic breccias (Fig. 3.3; AL2076, AL2077A, AL2077B and AL2088), three samples from the GS, were located within a sequence of Upper Ordovician to Lower Silurian age, represented by the units known as Pizarras de Muro, Criadero Quartzite and ampelitic slates (Fig. 3.3; AL2072, AL2073, AL2075).

One dolerite sample (AL2058) from SUM (Fig. 3.4), located within the Schist Greywacke Complex of Precambrian-Cambrian age (Lotze, 1945; San José et al., 1990).

One dolerite sample (AL2085) from sample from NZM (Fig. 3.5), located within the Slates “Rio” Unit of Ordovician age (Martín-Parra et al., 1996).

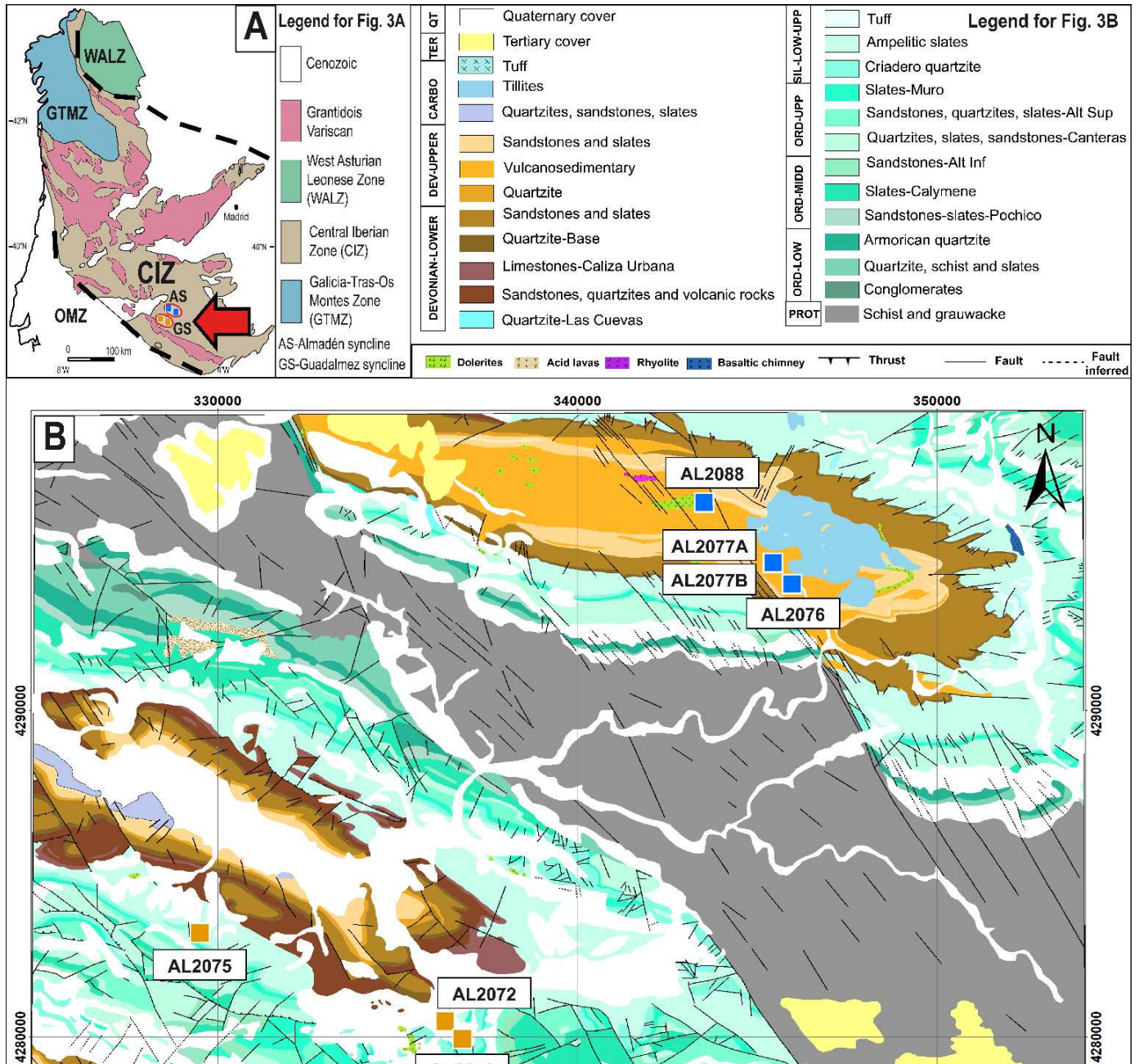


Figure 3.3. A) Simplified geological map of the Iberian Massif showing the studied area of the Almadén (AS) and Guadalmez (GS) synclines. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the of the Almadén (AS) and Guadalmez (GS) synclines showing the mafic samples studied in this work. The map was redesigned based on the Geological Maps (scale 1:50000) of Chillón (Lorenzo Álvarez et al., 1995), Almadén (García San Segundo et al., 1985), Hinojosa del Duque (Mira López et al., 1983) and San Benito (Mira López et al., 1983).

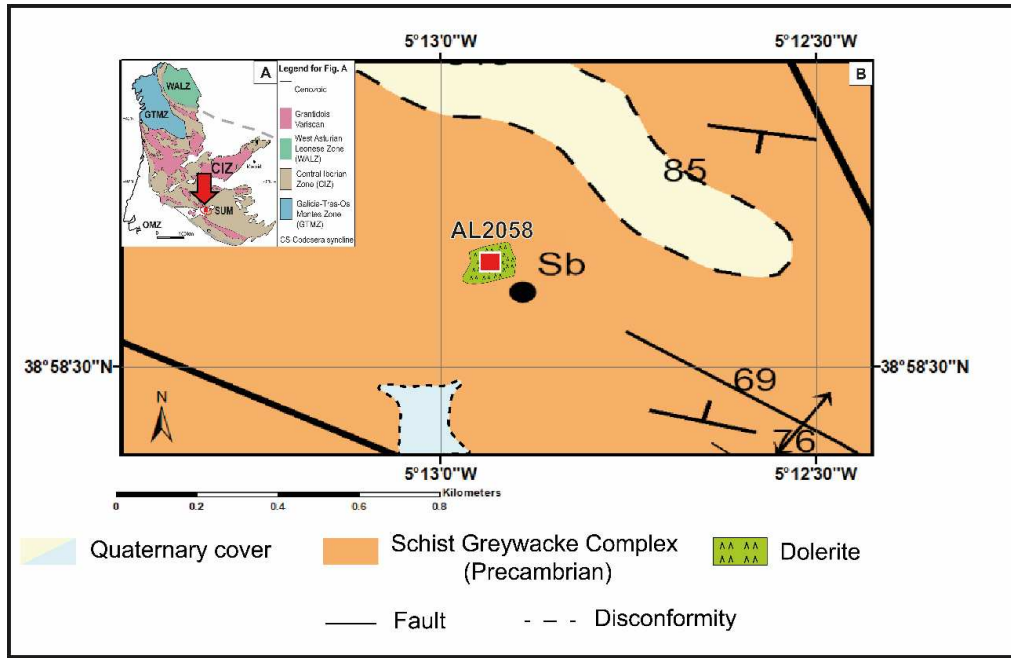


Figure 3. 4. Simplified geological map of the Iberian Massif showing the studied area of the Susana Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Susana Mine (SUM) showing the mafic samples studied in this work. The map was redesigned based on the Geological Map (scale 1:50000) of Puebla de Alcocer (Martín Herrero et al., 1994).

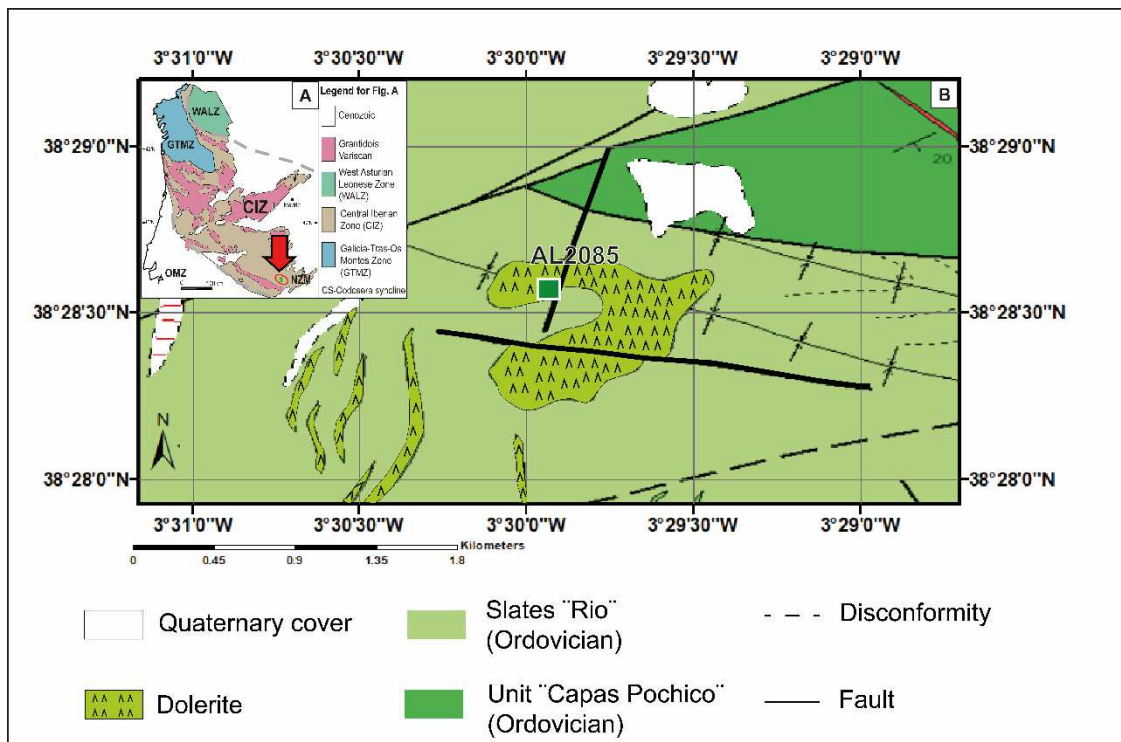


Figure 3. 5. Simplified geological map of the Iberian Massif showing the studied area of the Nazarena Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Nazarena Mine

(NZM) showing the mafic samples studied in this work. The map was redesigned based on the Geological Map (scale 1:50000) of Aldequemada (Martín-Parra et al., 1996).

3.2.2-Whole rock geochemistry analyses

Whole rock geochemistry analyses of the 19 mafic rocks were performed at ALS laboratories in Dublin (Ireland). The samples were crushed using a riffle splitter and the pieces were sieved to < 2mm fraction with 70 % passing rate. The pieces were pulverised to <75 μ m using a low chromium steel ring mill. To measure total C and S, the pulverised samples were inductively heated and analysed with infrared spectroscopy (IR). For other analyses, the samples powders were fused using lithium borate (LiBO₂). For the major element measurements, the fused samples were digested in acid before analysing it with inductively coupled plasma atomic emissions spectrometry (ICP-AES). For most of the trace elements, the same acid solution was used but the measurements were done using inductively coupled plasma-mass spectrometry (ICP-MS). The base metals (Ag, Cd, Co, Cu, Li, Mo, Ni, Pb, Sc, Zn) were digested from the fused samples using a four-acid solution and measured with the ICP-MS. Aqua regia digestion of the fused samples was done to measure As, Bi, Hg, In, Re, Sb, Se, Te and Tl, with the ICP-MS. In-house quality control samples and duplicate measurements of the samples were used to evaluate the precision of the data. The precision for most of the major elements is <2% with the exception of Fe₂O₃ (<3%), MnO (<7%) and P₂O₅ (<8%). For most of the trace elements, the precision is <5% with the exception of Cs, Eu, Ga, Lu, Ta, Tm, Yb (precision <10%) as well as Cd and Pb (precision <22%).

3.2.3-Electro probe micro analyses

Electro Probe Micro Analyses (EPMA) with a Cameca SXFive at the analytical laboratory of the Institut des Sciences de la Terre (ISTO) in Orléans, France. The main elements analyzed for apatite include Ca, P, F, Cl, Fe, Mg, Si, Mn, Sr, Na and S. All of the analyses were made perpendicular to the c axis, in order to improve the quality of the analysis for Cl and F, giving

that the X ray flux can be disturbed depending on the orientation of the crystal (Goldoff et al., 2012; Stormer et al., 1993). X-ray elemental maps were also carried out with a beam current of 100nA. The mineral standards used in this study were topaz (FK α), apatite (PK α , CaK α), hematite (FeK α), vanadinite (ClK α), albite (SiK α , NaK α), barite (SK α), pyrophanite (TiK α , MnK α), celestine (SrK α), MgO (MgK α). The OH was calculated using EPMA contents of F and Cl by charge balance, considering that all of the halogen sites are filled (Piccoli & Candela, 2002).

Ilmenite was analyzed using an accelerating voltage of 15 kV, a beam current of 10 nA, and a focused beam, using the following mineral standards: albite (SiK α), hematite (FeK α), MgO (MgK α), and pyrophanite (TiK α , MnK α).

3.2.4-U-Pb dating on apatite

Apatite is the most common U-bearing mineral in mafic rocks and may represent an important asset for U-Pb dating of small mafic bodies like sills or dykes, which experienced a fast cooling and were not heated above the closure temperature of apatite (375-550°C, Cochrane et al., 2014; Schoene & Bowring, 2007). As apatite can incorporate non-negligible amounts of common Pb in its crystal structure, and because it usually has low U and therefore low radiogenic Pb contents, the resulting radiogenic Pb/common Pb ratios are usually low (Hughes & Rakovan, 2015).

The geochronological analyses were performed in both thick-polished sections of 150 μ m and separated apatite crystals from nine dolerite samples. Selected apatite grains were imaged by cathodoluminescence (CL) at the ISTO-BRGM facilities, in order to observe possible zoning and identify the best locations for LA-ICP-MS analyses. We used a Cathodyne-OPEA cold cathode instrument, in which the samples are placed into an argon pressure of ~50

mTorr, and irradiated by an electron beam with ~15 kV and ~100 mA. The angle between the axis of cannon and the horizontal is 25°.

We performed U-Pb geochronology in the LA-ICP-MS facilities of the GeOHeLiS platform at the University of Rennes. The LA-ICP-MS system is equipped with an Excimer ESI NWR193UC coupled to a Q-ICP-MS Agilent 7700x.

Instrument calibration was carried out before each batch of analyses by monitoring the signal of the ^{238}U , the ratio between the uranium and thorium and by minimizing the ThO^+/Th^+ ratio (<0.5%) using a NIST SRM 612 reference glass. All the material produced by the ablation is carried by He then mixed with Ar and N_2 before being injected into the plasma source. The signals of ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , $^{204}(\text{Pb}+\text{Hg})$ and ^{43}Ca are collected during each analysis. The ^{235}U is calculated based on the $^{238}\text{U}/^{235}\text{U}$ ratio of 137.818 (Hiess et al., 2012).

Each measurement consisted of 20 seconds of background collection, followed by 60 seconds of ablation, and 15 seconds of wash-out delay. The laser pulse rate was 5 Hz. In the first session a rectangular spot was used (30 μm x 40 μm) for samples SA2022C, SA2026, AL2058 and AL2073. In the second session, two types of spots were used, the first one consisted of a rectangular spot of 25 μm x 50 μm for samples AL2072, AL2075 and AL2085; whereas the second one was a round spot of 40 μm diameter used in samples SA2014A and AL2076.

The sequence of measurements was the following: two measurements of the Madagascar apatite standard (ID-TIMS age of $473 \pm 0.7\text{Ma}$, Thomson et al., 2012), one measurement of the Durango apatite standard ($31.44 \pm 0.18\text{Ma}$, McDowell et al., 2005), one measurement of the McClure apatite standard ($523.51 \pm 2.09\text{Ma}$, Schoene & Bowring, 2006), followed by six measurements of apatite crystals from the samples. This sequence was repeated four to six times, and the end of the session consisted on three analyses: one of the Durango and two of

the Madagascar standards. Regarding the quality control and validation of the standards, the McClure apatite standard was dated at 528 ± 5 Ma ($n=31$, MSWD=0.5) in the first session and at 509 ± 12 Ma ($n=26$, MSWD=3) in the second session. The Durango standard was dated at 32 ± 0.5 Ma ($n=33$, MSWD=1.1) in the first session and at 30.6 ± 0.6 Ma ($n=16$, MSWD=1.1) in the second session- Further information on the dating protocol can be found in Pochon et al. (2016) and in Supplementary material 3.

3.2.5- Laser ablation inductively coupled plasma mass spectrometry

Trace element concentrations of ilmenite were determined by laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) at ISTO, using a RESolution-SE (ASI) 193 nm excimer laser with an S155 ablation cell (Laurin Technic), coupled to an Agilent 8900 triple inductively coupled plasma quadrupole mass spectrometer (QQQ-ICP-MS). Ablation was carried out using He as carrier gas, mixed with Ar as a cell and nebulizer gas. For spot analyses, a laser beam size of 20 μm , a repetition rate of 10 Hz and a fluence of 3 J/cm^2 were used. Traverse profiles of ilmenite were acquired with a laser beam of 30 μm , a repetition rate of 7 Hz, a fluence of 3 J/cm^2 and a scanning speed of 20 $\mu\text{m}/\text{s}$. The Ti content of the ilmenite determined from EPMA was used as the internal standard to quantify trace element concentrations. GSE-2g was the primary reference material, and NIST610 and BCR-2g glasses used as quality control materials. Data reduction was carried out using the commercial data reduction software GLITTER (Griffin et al., 2008).

3.4-Results

3.4.1-Relationships between dolerites and C1 Variscan schistosity cleavage

Regarding the structural data, the strike and dip of the contacts between the mafic intrusions and the host rocks were measured (Fig. 3.6). Most of them generally lie roughly parallel to the S_{0-1} cleavage developed in their host metasedimentary sequences (Fig. 3.6),

suggesting that most of the intrusions are sills. The border of sills is affected by the C1 Variscan schistosity cleavage whereas the cores of the dolerite sills are generally preserved. This observation demonstrates by itself that dolerites are emplaced at least at the beginning of the Variscan orogeny.

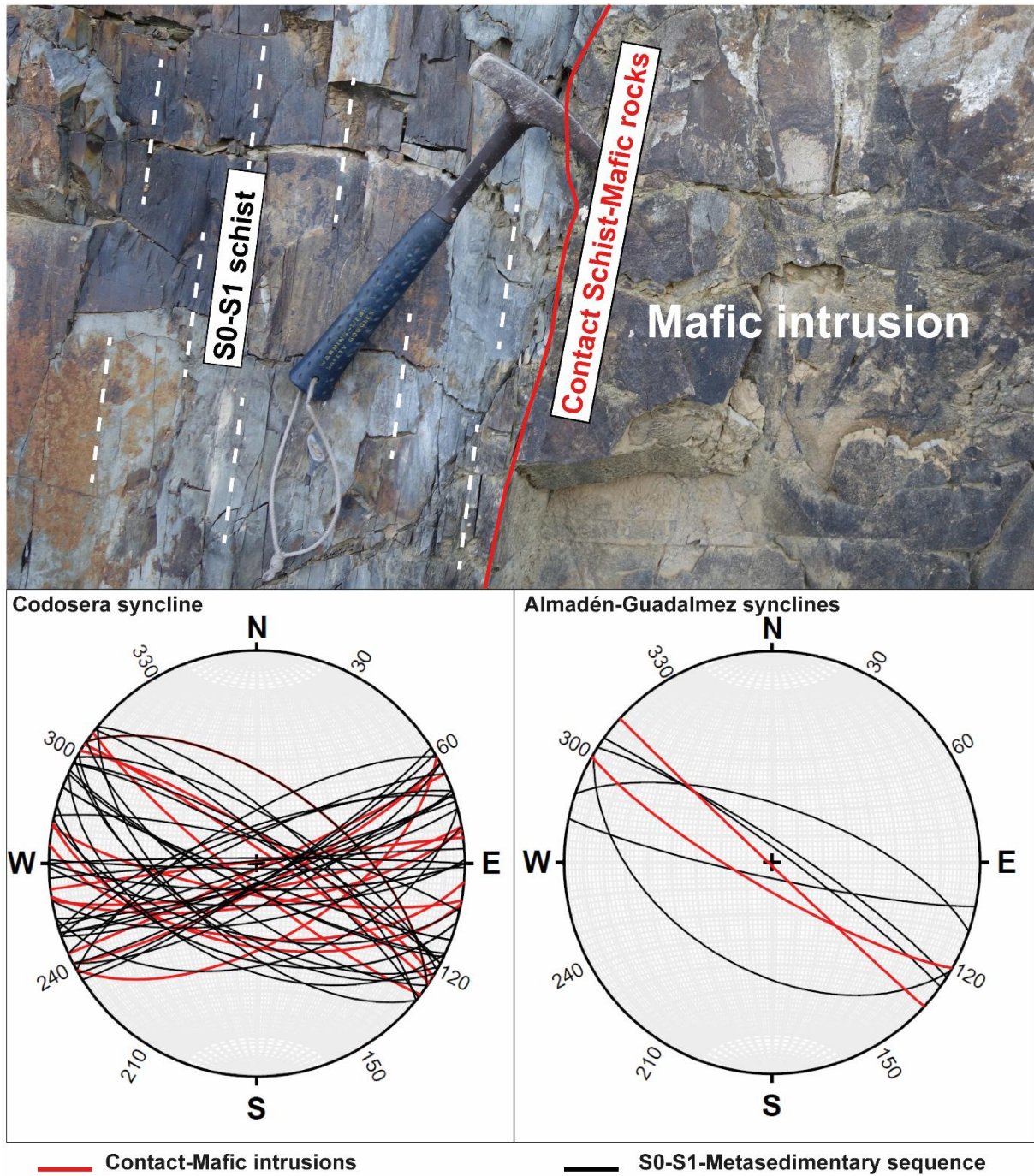


Figure 3. 6. Structural data of the mafic sills and metasedimentary sequence in the studied areas.

3.4.2-Dolerite petrography

Samples from CS present a doleritic texture and are mainly composed of Ca-plagioclase and clinopyroxene (Figs. 3.7A-B and 3.8A-B). Samples from the GS and the AS also present a doleritic texture and are mainly composed of plagioclase (Figs. 3.7C-F and 3.8C-F), with minor clinopyroxene (present only in the rocks from AS, Fig. 3.7D). Other primary minerals include pyrrhotite, pentlandite, apatite and ilmenite. Ilmenite is less abundant than apatite and usually slightly altered to leucoxene. Accessory phases can also be found, either in the groundmass or locally filling some porosity, these include: leucoxene, chalcopyrite, zircon and baddeleyite (too small and too scarce to be dated). Secondary phases are ubiquitous and consist of actinolite, epidote, chlorite, calcite, and, in lesser amount, chalcopyrite and pyrite (Fig. 3.8). The dolerites from GS are generally more altered than those from the CS and AS (Figs. 3.8C-F). The least altered samples with low LOI (see Tables 3.1 and 3.2) show primary features and abundant primary minerals compared to the samples with moderate to high alteration degree (Figs. 5 and 6). Samples with high LOI (see Tables 3.1 and 3.2) show abundant secondary phases such as calcite and chlorite (Figs. 3.7 and 3.8).

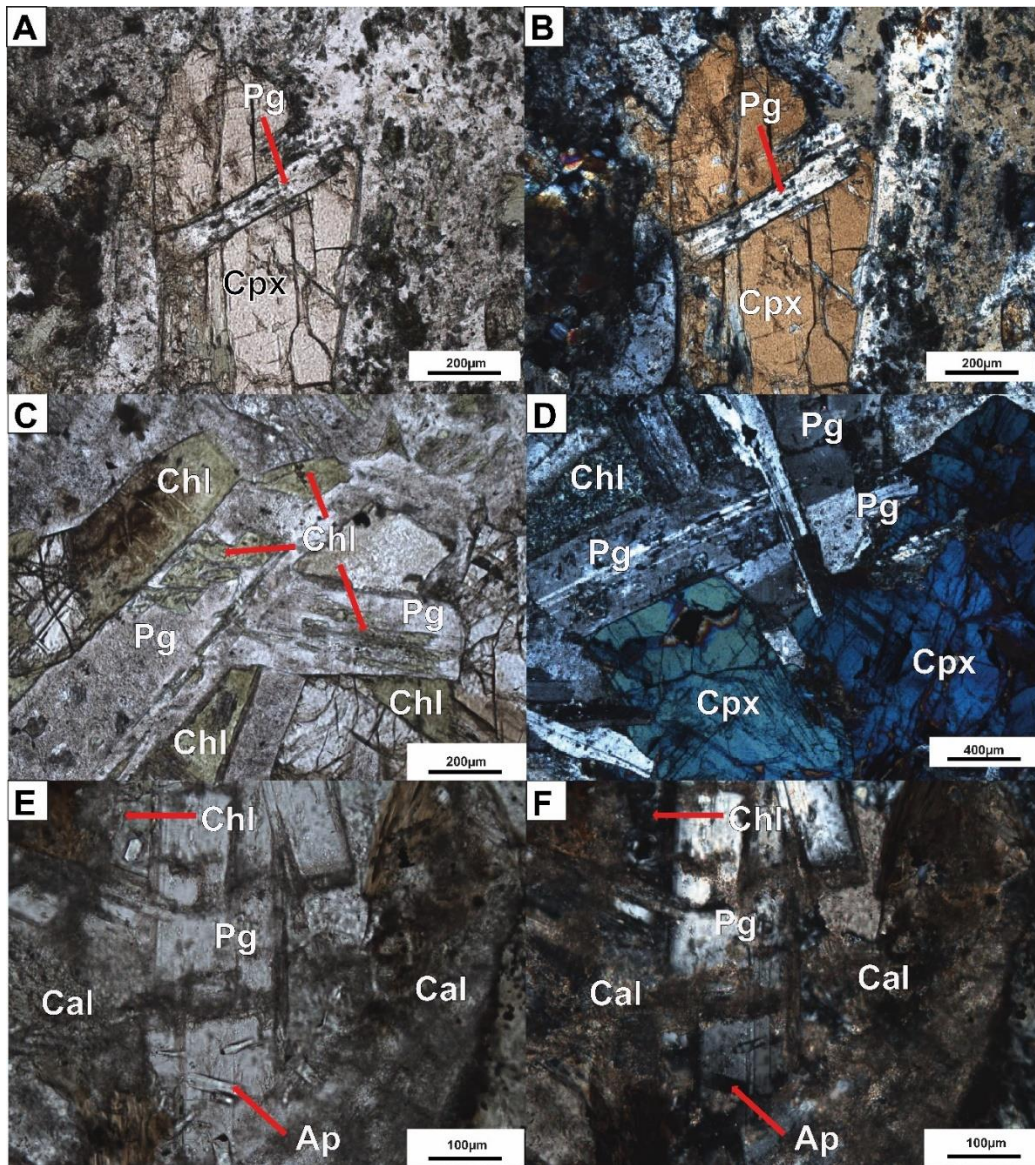


Figure 3. 7. Thin section micro-photographs showing the least altered samples A-B) plagioclase (Pg) and clinopyroxene (Cpx) showing their primary features in sample SA2014 from CS. C-D) typical mineralogical assemblage from AS dolerites with plagioclase, Cpx, and secondary chlorite (Chl); E-F) typical mineralogical assemblage from GS dolerites with plagioclase, apatite (ap), and secondary calcite (Cal) and chlorite.

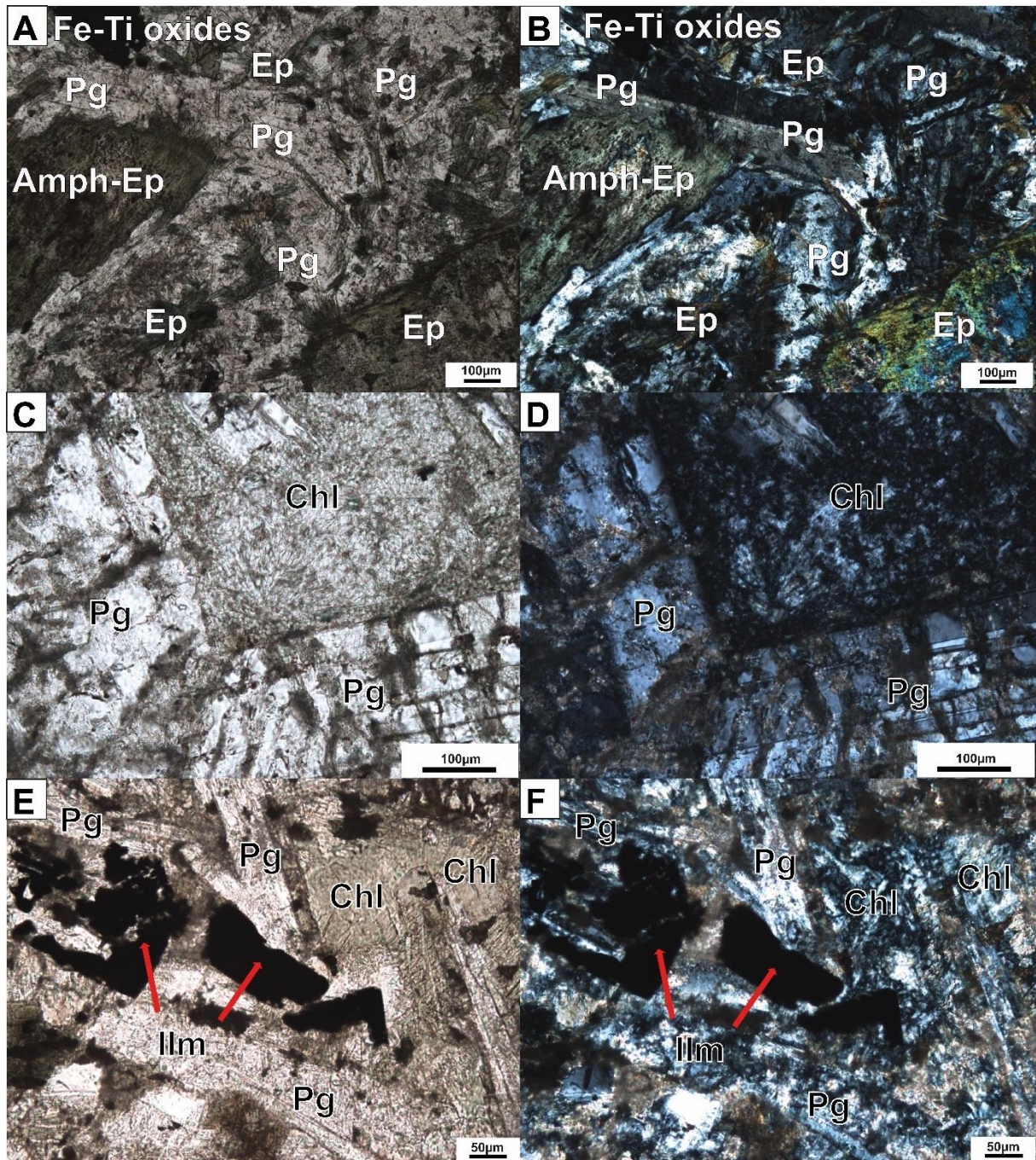


Figure 3. 8. Thin section micro-photographs showing the most altered samples: A-B) amphibole and plagioclase altered to epidote (Amph-Ep), as well as ilmenite (Fe-Ti Oxides), in sample SA2042 from CS; H-I) chlorite (Chl) and Plagioclase (Pg) in sample AL2077B from AS; H-I) plagioclase altered to Chlorite (Chl) and ilmenite in sample AL2073 from GS.

In most of the mafic rocks, apatite is relatively abundant and appears as acicular crystals within several mineral phases (e.g. plagioclase, clinopyroxene, ilmenite) as well as in the groundmass (Figs. 3.7E-F and 3.9).

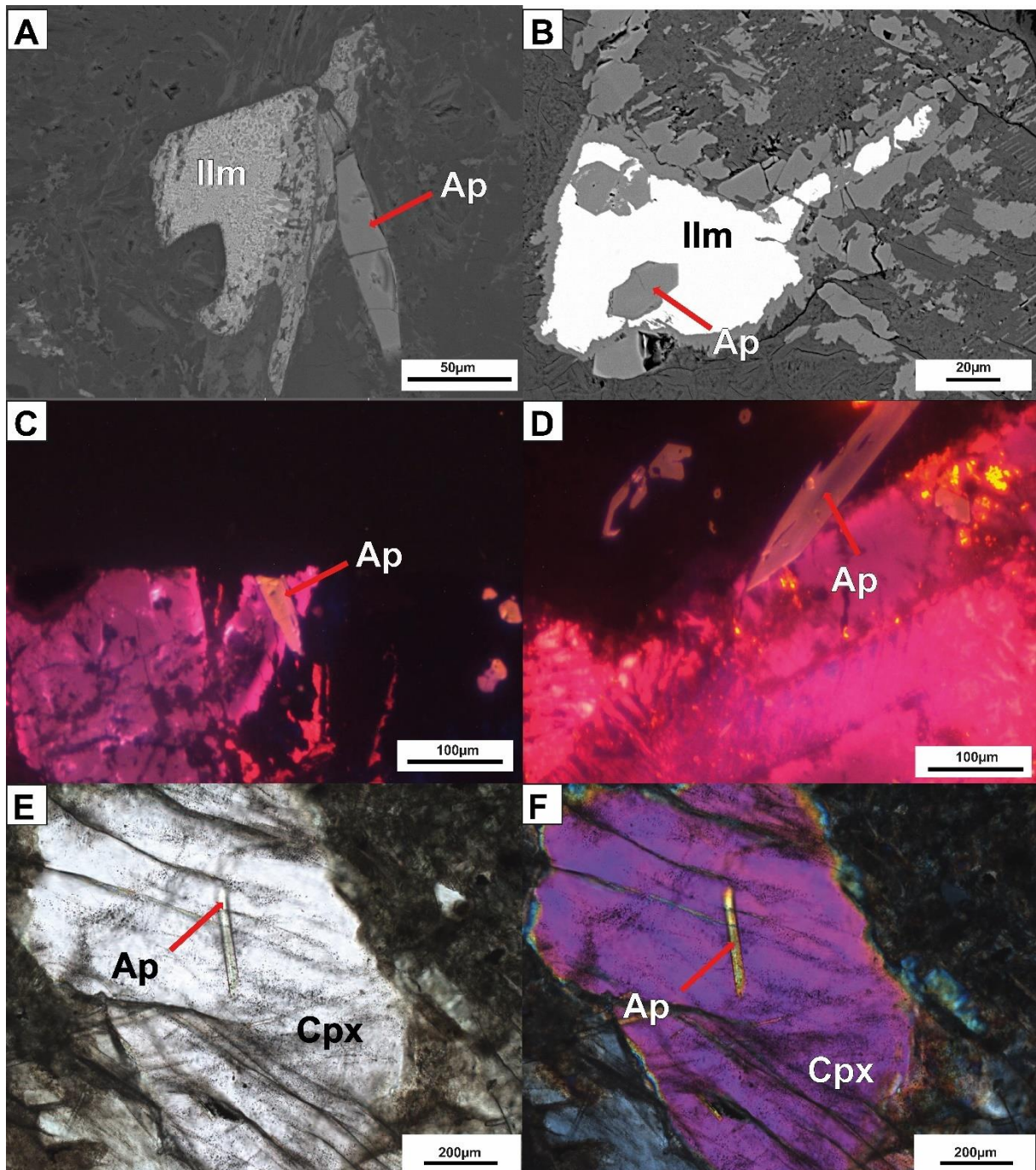


Figure 3. 9. Selected thin section micro-photographs illustrating the studied apatite crystals. A) Optical image showing apatite associated to primary ilmenite; B) BSE image showing apatite associated to primary ilmenite; C-D) cathodoluminescence micro-photographs of the studied apatite crystals, E-F) Thin section micro-photographs showing apatite related to primary clinopyroxene. The apatite appears as acicular crystals (Ap) associated to the primary plagioclases, clinopyroxene (Cpx) and ilmenite (Ilm).

4.3-Dolerites geochemistry

Whole rock compositions of the studied samples are shown in Tables 3.1 and 3.2.

Table 3. 1. Whole-rock geochemistry data for studied mafic samples from la Codosera syncline-Central Iberian Zone.

La Codosera Syncline										
Latitude	39.176783°	39.181694°	39.181595°	39.181595°	39.182142°	39.134611°	39.134611°	39.134611°	39.160815°	39.194392°
Longitude	-7.069648°	-7.080958°	-7.080377°	-7.080377°	-7.080537°	-6.772404°	-6.772404°	-6.772404°	-6.757820°	-6.956690°
Sector	Road BA007	San Antonio Mine	San Antonio Mine	San Antonio Mine	San Antonio Mine	Villar del Rey Quarry	Villar del Rey Quarry	Villar del Rey Quarry	Obando	Albuquerque
Sample	SA2008	SA2013	SA2014A	SA2014B	SA2015	SA2022A	SA2022B	SA2022C	SA2026	SA2042
Lithology	Dolerite	Dolerite	Andesite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite
SiO ₂	44.6	43.6	45.6	46.2	45.1	46.5	40.6	47.6	49.6	48
Al ₂ O ₃	13.9	13.45	13.9	14.15	14.05	9.89	14.8	14.4	14.5	15.4
Fe ₂ O ₃	12.65	12.8	13.55	13	12.9	16.25	16.8	12.9	11.5	12.6
CaO	6.87	8.06	11.35	9.28	9.43	11.6	16.4	10.85	9.15	10.25
MgO	6.15	5.83	6.19	6.25	6.35	6.79	4.26	6.67	6.56	6.61
Na ₂ O	2.54	2.48	2.22	1.86	2.86	2.39	0.19	2.68	4.12	3.38
K ₂ O	0.14	0.04	<0.01	0.02	<0.01	0.14	0.09	0.5	0.25	0.07
Cr ₂ O ₃	0.02	0.021	0.025	0.024	0.024	0.004	0.003	0.031	0.034	0.014
TiO ₂	2.35	2.35	2.3	2.31	2.3	4.45	2.73	2.63	2.1	2
MnO	0.23	0.2	0.24	0.23	0.23	0.28	0.29	0.18	0.17	0.19
P ₂ O ₅	0.23	0.22	0.23	0.22	0.24	0.23	1.29	0.23	0.22	0.2
SrO	0.03	0.01	0.02	0.01	0.01	<0.01	0.11	0.02	<0.01	0.01
BaO	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
LOI	9.19	10.9	3.57	5.8	5.62	1.33	1.95	1.79	2.51	1.69
Total	98.91	99.96	99.2	99.36	99.11	99.86	99.51	100.49	100.72	100.42
C	1.39	2.02	0.18	0.75	0.55	0.17	0.08	0.06	0.04	0.06
S	0.04	0.04	0.09	0.1	0.03	0.01	0.01	0.2	0.08	0.29
Ba	78.7	36.8	22.3	49.3	28.5	49.9	16.7	85.3	55.2	63.7
Ce	30.1	29.9	28.8	28.5	29.2	35.1	70.9	31.1	32.1	23.7
Cr	150	150	170	180	180	10	10	250	270	100
Cs	7.72	2.64	0.7	7.14	4.41	1.29	2.37	0.49	0.28	1.25
Dy	6.23	6.11	6.21	5.87	6.22	8.1	13.4	5.95	6.38	4.89
Er	3.16	3.39	3.03	3.23	3.31	4.24	6.32	3.2	3.13	2.69
Eu	1.97	1.91	1.7	1.8	1.84	2.26	5.44	1.84	1.74	1.47
Ga	24.2	24.2	21.5	23.6	21.9	21	47.8	24.3	20.5	21.4
Gd	6.13	5.84	5.51	6.22	6.17	7.92	14.95	6.03	6.36	4.81
Ge	<5	<5	<5	<5	<5	<5	5	<5	<5	<5
Hf	4.1	4.1	4	4.2	4.1	5.3	4.9	4.5	4.6	3.4
Ho	1.14	1.18	1.1	1.15	1.13	1.51	2.41	1.07	1.14	0.95
La	12.6	12.1	11.5	11.4	11.3	14	27.2	13	13.1	10
Lu	0.4	0.47	0.37	0.44	0.45	0.53	0.69	0.4	0.42	0.37
Nb	13.5	13	12.8	13.4	13.6	19.3	23.3	14.9	13.5	12.3
Nd	19.8	19.4	18.9	18.7	19.4	23.7	48.6	19.7	20	15.8
Pr	4.21	4.17	3.89	3.9	4.06	5.05	10.1	4.21	4.34	3.35
Rb	9.4	2.8	0.7	1.2	0.6	2.9	3.4	15.2	4.7	1.8
Sm	5.12	5.05	4.9	5.17	5.2	6.59	12.75	5.3	5.41	4.35
Sn	2	2	4	2	2	2	2	2	2	2
Sr	332	167	269	251	201	166.5	1115	329	144.5	223
Ta	0.4	0.4	0.4	0.5	0.6	0.8	0.7	0.7	0.7	0.6
Tb	1.03	0.97	0.93	0.96	0.95	1.23	2.17	0.92	1.05	0.78
Th	1.47	1.4	0.93	0.98	1.01	1.43	1.68	1.42	1.88	0.85
Tm	0.42	0.42	0.42	0.46	0.45	0.55	0.79	0.42	0.42	0.35
U	0.37	0.37	0.29	0.27	0.3	0.35	0.51	0.43	0.5	0.26
V	380	377	371	392	388	483	211	427	329	333
W	1	1	<1	2	1	2	2	1	2	2
Y	31.2	30.2	29.5	30.5	30.4	38.1	60.6	29.2	30.3	23.5
Yb	2.68	2.92	2.77	2.85	2.81	3.48	4.82	2.49	2.88	2.05
Zr	168	165	153	168	167	204	211	182	176	127
As	1.7	26.3	0.9	3.6	1.5	0.7	1.7	1	0.4	65.8
Bi	0.01	0.01	0.01	0.02	0.01	<0.01	0.01	0.01	<0.01	0.17
Hg	49	59	75	64	58	136	61	38	60	48
In	67	76	39	41	49	23	19	6	14	23
Re	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sb	2.77	2.16	0.88	0.51	0.41	0.15	0.56	0.5	0.06	2.61
Se	0.4	0.3	0.5	0.7	0.2	0.4	0.4	0.4	0.5	0.3
Te	<0.01	<0.01	0.02	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.03
Tl	0.02	<0.02	0.02	0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	1.1	1.2	1	0.9	1.3	1.6	1.2	1	0.8	1.1
Co	44	46	47	45	46	41	30	45	40	47
Cu	89	101	140	134	147	11	4	109	111	141
Li	70	190	80	80	60	20	20	30	40	50
Mo	<1	<1	1	<1	1	1	1	1	1	1
Ni	51	61	60	57	62	8	2	92	97	64
Pb	49	47	12	18	6	7	11	5	4	8
Sc	37	37	39	32	39	56	24	38	35	38
Zn	132	137	143	123	122	139	129	110	96	109

Chapter 3

Table 3. 2. Whole-rock geochemistry data for studied mafic samples from Susana Mine, Nazarena Mine, Guadalmez, Almadén synclines-Central Iberian Zone.

Latitude	38.977419°	38.656070°	38.654757°	38.680771°	38.780114°	38.785083°	38.785083°	38.476086°	38.802365°
Longitude	-5.215434°	-4.879868°	-4.877470°	-4.960326°	-4.773258°	-4.778172°	-4.778172°	-3.498885°	-4.802235°
Sector	La Susana Mine	La Balanzona Mine	La Balanzona Mine	Los Accesos Mine	Almadén	Almadén	Almadén	La Nazarena Mine	Almadén
Sample	AL2058	AL2072	AL2073	AL2075	AL2076	AL2077A	AL2077B	AL2085	AL2088
Lithology	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite	Dolerite
SiO ₂	45.9	40.6	45.5	42.6	52.8	40.1	42.6	42.2	52.1
Al ₂ O ₃	14.75	10.05	14.3	12.5	16.4	11.95	12.35	13.05	15.8
Fe ₂ O ₃	12.65	10.95	10.4	11.65	7.74	9.94	9.72	13	9.26
CaO	6.78	9.38	9.22	7.84	5.95	9.44	9.36	5.71	8.52
MgO	3.99	10.95	5.55	8.83	5.8	6.1	7.52	10.75	5.52
Na ₂ O	4.59	0.97	3.03	2.05	3.54	1.8	1.58	1.96	4.64
K ₂ O	0.31	0.07	0.55	0.33	0.89	0.81	0.32	0.08	0.58
Cr ₂ O ₃	0.003	0.123	0.03	0.036	0.022	0.044	0.042	0.048	0.024
TiO ₂	3.21	2.33	3.11	2.45	1.1	1.58	1.5	3.1	1.59
MnO	0.19	0.14	0.1	0.14	0.09	0.12	0.12	0.14	0.12
P ₂ O ₅	1.54	0.29	0.66	0.36	0.18	0.18	0.17	0.5	0.16
SrO	0.05	0.02	0.06	0.03	0.03	0.03	0.04	0.08	0.02
BaO	0.05	0.01	0.13	0.02	0.03	0.02	0.02	0.09	0.03
LOI	5.78	12.5	7.06	10.5	6.48	17.6	15.1	8.75	2.74
Total	99.79	98.38	99.7	99.34	101.05	99.71	100.44	99.46	101.1
C	0.88	2.23	1.22	1.88	1.04	4.23	3.43	1.05	0.07
S	0.04	0.07	0.1	0.1	0.07	0.11	0.01	0.06	0.06
Ba	410	71.1	1090	203	302	192.5	215	802	251
Ce	117.5	46	88.3	55	29.4	25.3	23.7	75.6	23.3
Cr	<10	1000	230	280	170	340	320	370	180
Cs	1.93	2.53	2.36	2	0.93	5.29	3.23	1.88	0.58
Dy	9.35	4.45	7.68	5.15	2.47	2.74	2.54	5.49	2.95
Er	4.1	1.86	3.23	2.29	1.09	1.38	1.13	2.36	1.5
Eu	4.84	1.74	3.74	2.2	1.14	1.07	1.05	2.37	1.15
Ga	24.8	17.6	27	19.7	18.3	16.4	16.7	22.1	20.1
Gd	12.35	5.42	10.25	6.61	2.92	3.28	3.02	7.09	3.31
Ge	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hf	6.8	4.6	8.5	4.7	2.1	2.1	2.1	6	2.3
Ho	1.56	0.77	1.26	0.85	0.47	0.46	0.44	0.93	0.51
La	54	20.5	39.6	28.5	15.3	12.3	11.9	37	11.1
Lu	0.44	0.25	0.37	0.28	0.12	0.16	0.12	0.28	0.15
Nb	67.6	25.2	49.2	36.5	21.7	18.4	17	51.2	16.3
Nd	63.7	25.3	48.4	28.1	13.7	13.2	12.3	37.4	12.4
Pr	14.9	5.87	11.35	6.71	3.38	3.1	2.98	9.15	2.87
Rb	7.2	2.7	13.5	11	21.3	25	10.2	1.7	13.5
Sm	12.95	5.64	10.55	6.24	2.68	2.91	2.84	7.22	3.15
Sn	3	2	3	2	1	2	2	2	1
Sr	543	268	675	434	404	341	489	787	302
Ta	3.4	0.8	2.2	1.2	1.1	0.6	0.5	2.2	0.9
Tb	1.73	0.75	1.37	0.94	0.47	0.44	0.45	1.01	0.51
Th	5.29	2.72	4.55	3.1	2.04	1.84	1.72	4.17	1.48
Tm	0.52	0.24	0.4	0.31	0.16	0.15	0.15	0.29	0.17
U	1.67	0.73	1.42	0.77	0.54	0.51	0.53	1.1	0.39
V	208	224	237	214	133	168	161	274	203
W	4	1	2	2	2	1	2	2	1
Y	40.3	20.5	33.3	23.2	11.9	12	11.7	23.4	14
Yb	2.99	1.56	2.46	1.72	0.96	1.06	0.9	1.57	1.07
Zr	298	186	372	189	85	84	79	248	83
As	2	0.6	0.8	1.2	0.9	0.6	<0.1	1	0.7
Bi	0.04	0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01
Hg	57	107	196	322	>25.0	>25.0	3.78	1 260	119
In	77	52	67	67	40	44	39	29	20
Re	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Sb	0.45	<0.05	0.49	0.59	0.06	0.2	0.09	0.07	0.07
Se	0.3	<0.2	0.3	<0.2	<0.2	<0.2	<0.2	0.2	<0.2
Te	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	0.03	0.02	0.04	0.03	<0.02	0.02	<0.02	<0.02	<0.02
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	0.8	0.9	1	1.1	0.6	0.8	0.6	1.1	0.6
Co	23	65	35	51	34	54	48	62	34
Cu	3	67	43	43	41	55	39	65	55
Li	30	90	50	110	50	50	50	100	20
Mo	2	2	3	2	1	1	1	3	1
Ni	1	526	103	207	117	255	237	298	60
Pb	3	<2	4	6	<2	9	<2	11	<2
Sc	12	21	18	19	17	18	17	24	24
Zn	127	110	132	114	68	96	77	121	83

In order to quantify the alteration degree of the dolerites, we employed the AI-CCPI alteration box plot (Large, 2001) , the AI-AAAI diagram (Williams & Davinson, 2004) and the isocon diagram (Grant, 1986, 2005) for metasomatic alteration (Figs. 3.10A, 3.10B). Most of

the studied samples fall into the basalt field of the AI-CCPI alteration box plot (Fig. 3.10A), and into the unaltered box of the AI-AAAI diagram (Fig. 3.10B), showing that, even if they experienced some mineral transformations (Fig. 3.8). Only four samples fall outside of the unaltered basalt field of the AI-CCPI diagram (Fig. 3.10A): SA2022B, SA2014B, AL2072, and AL2085, of which only the first one also falls outside of the AI-AAAI unaltered box (Fig. 3.10B).

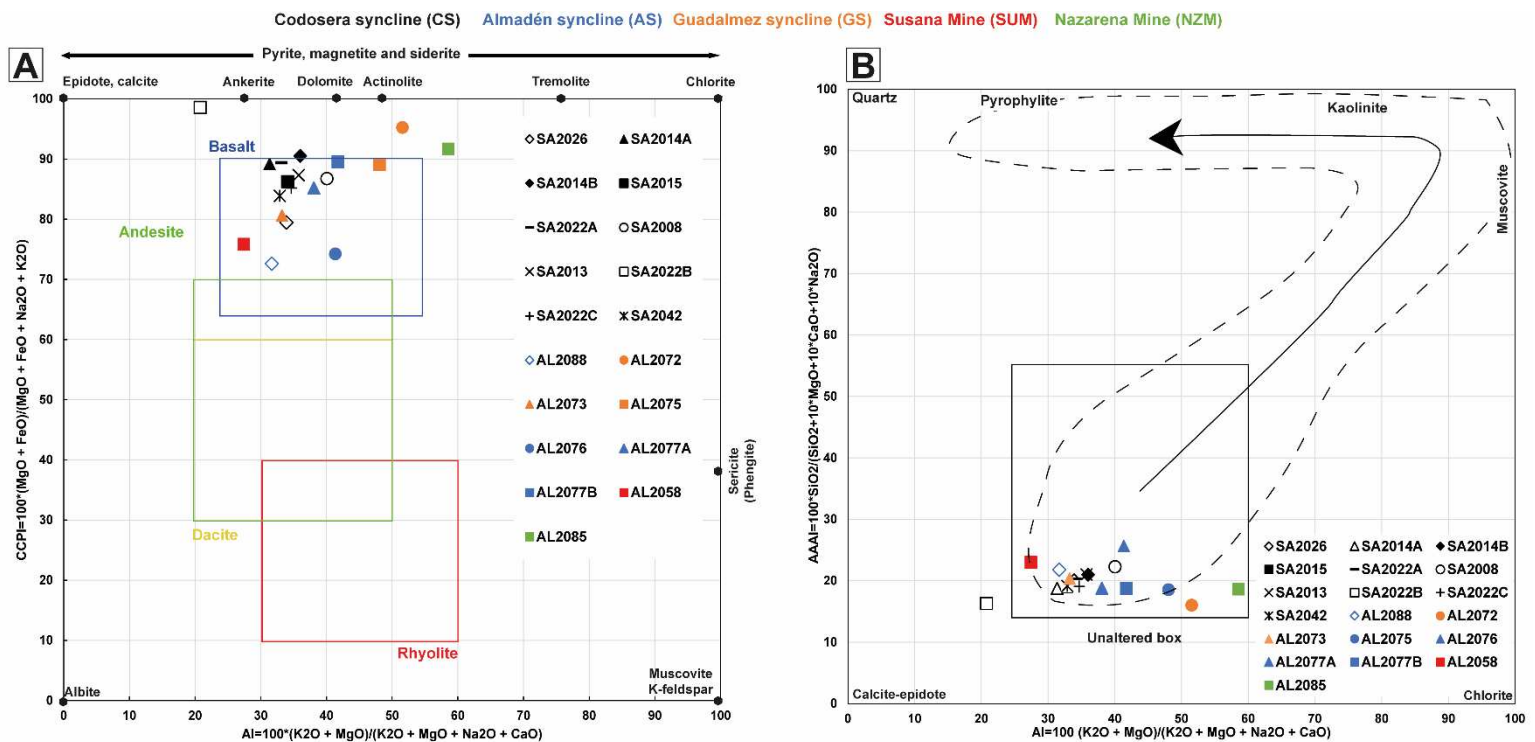


Figure 3. 10. Hydrothermal alteration diagrams for the samples in this study. A) Alteration box plot diagram of Large (2001). AI: Alteration Index, CCPI: Chlorite-Carbonate-Pyrite-Index; B) Alteration diagram of Williams and Davinson (2004), AAAI: Advanced-Argilic-Alteration-Index.

The isocon diagram can be used to undertake a more detailed study of the alteration degree between lightly and heavily altered rocks, as well as the mobilization of major and trace elements (Grant, 1986, 2005). This diagram allows for the plotting of an altered composition against a non-altered (original) composition, thus facilitating the determination of its degree of alteration (Grant, 1986, 2005). Considering the petrographical analyses and whole rock

geochemical data, we selected the least altered sample from CS (SA2026, LOI=2.51) and plotted the rest of the CS samples against it (Fig. 3.11A). In the case of the AS-GS, both synclines present the same stratigraphic succession and are located in the same region which is why we decided to select only one least altered sample for both of them (AS-AL2088, LOI=2.74, Fig. 3.11B). Considering that samples AL2058 (SUM) and AL2085 (NZM) come from isolated places showing different stratigraphic successions, both cannot be plotted against any sample from CS, AS or GS. Both samples are altered and show moderate to high LOI (AL2058=5.78; AL2085=8.75), similar to the samples in the GS-AS. Interpretations on these two sample will be based on the rest of the results and the similarities with the dolerite samples in this study. To ensure the effective organization of trace and major elements ranging from 10-300 on the x-axis of the diagram, it was necessary to multiply each element value in the whole rock geochemical analyses by a coefficient. In Fig. 3.11A, the coefficients are: LOI (3.98); Pb (5); Th (16); U (80); Nb (3.7); Ta (85.8); La (5.35); Ce (2.5); Pr (20.8); Sr (0.69); Nd (5.5); Zr (0.68); Sm (24.03); Eu (80.46); Gd (23.59); Ti (0.01277); Dy (26.65); Y (5.95); Lu (476.2); Rb (44.7); Ba (4); K (0.111); SiO₂ (4.84); Al₂O₃ (17.25); P₂O₅ (1181.9); Fe₂O₃ (23.48); CaO (30.7); MgO (44.21); Na₂O (72.82). In Fig. 3.11B, the coefficients are: LOI (3.65); Pb (10); Th (20.28); U (102.6); Nb (3.07); Ta (66.7); La (6.31); Ce (3.44); Pr (31.4); Sr (0.333); Nd (8.88); Zr (1.45); Sm (41.3); Eu (121.8); Gd (45.32); Ti (0.0168); Dy (57.63); Y (12.86); Lu (1333.34); Rb (15.6); Ba (0.88); K (0.0478); SiO₂ (4.61); Al₂O₃ (15.83); P₂O₅ (1625); Fe₂O₃ (29.16); CaO (32.87); MgO (52.54); Na₂O (64.66).

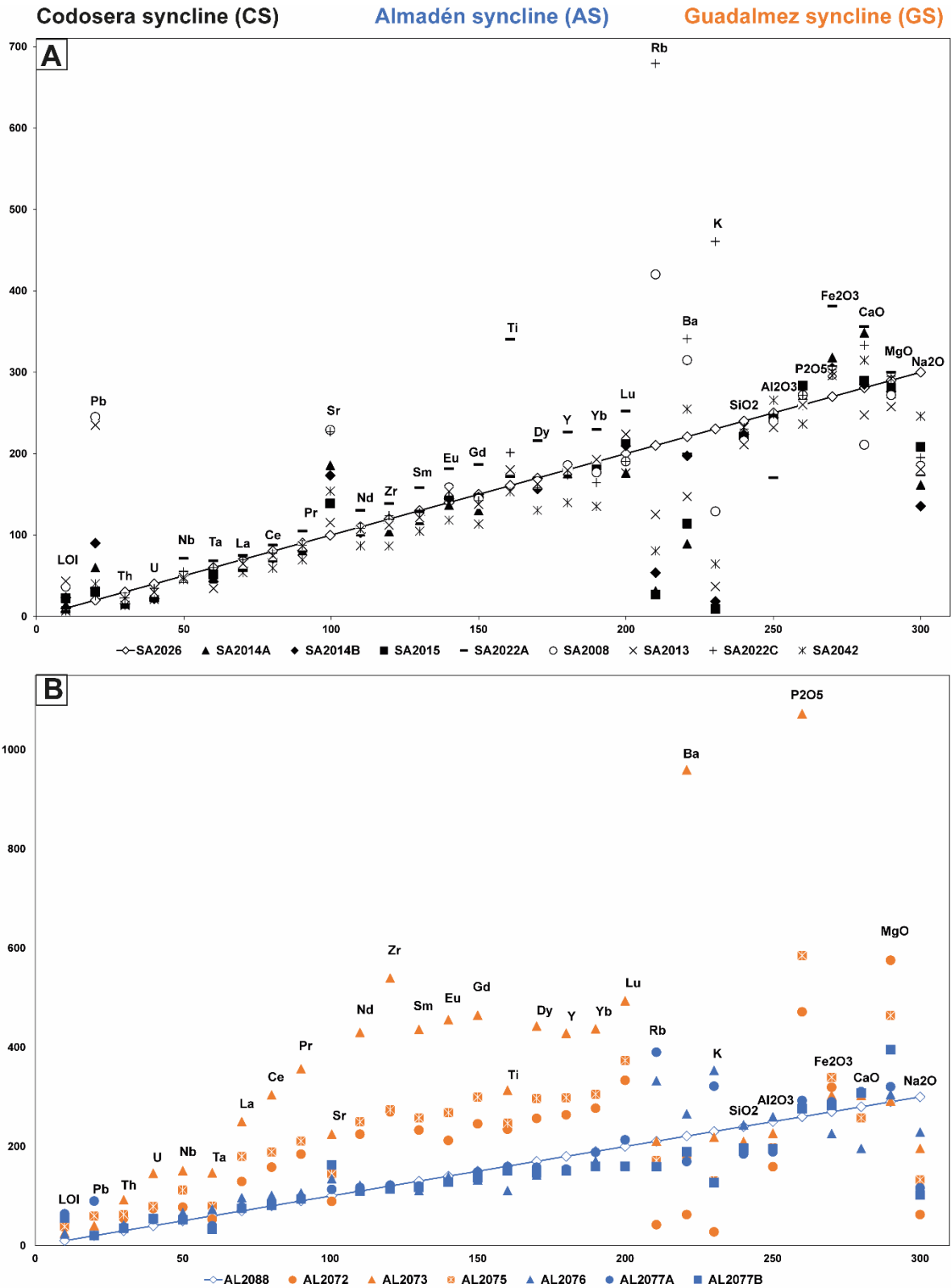


Figure 3. 11. Isocon diagrams for metasomatic alteration of Grant (2005), showing samples from CS (A) and (AS-GS). These diagrams allow to determine the alteration degree of all samples by plotting an altered composition against an original composition. A) Samples from CS plotted against the least altered sample from CS (SA2026); B) Samples from AS-GS plotted against the least altered sample from AS (AL2088), both synclines present the same stratigraphic succession and are found in the same region which is why GS samples where plotted against an AS sample.

In the case of the CS, the isocon diagram (Grant, 1986, 2005) shows that Ca, Fe, Pb and Sr contents are higher and that Na, K are lower when plotting all CS samples against SA2026 (Fig. 3.11A). The variation on Mg, Al, and P is relatively low. Ba and Rb exhibit significant variations either higher or lower. The CS samples show higher LOI values compared to SA2026 (Fig. 3.11A). These LOI contents can be associated to secondary mineral phases such as chlorite and calcite observed in microscope. The samples with the higher LOI show the highest Pb contents (Fig. 3.11A). The REE contents exhibit no or very little variation. These results together with the Al-CCPI alteration box plot (Large, 2001) and the Al-AAAI diagram (Williams & Davinson, 2004) allow us to determine that K, Rb, Ba, Pb and Sr were affected by alteration processes and they cannot be used for further petrogenetical interpretations. Regarding REE and other immobile elements the primary geochemical features are preserved and therefore they can be used for further interpretations.

For AS-GS, all samples present higher LOI contents compared to AL2088. The samples from the GS present high REE, Ba, P, and Mg contents as well as low Rb, Al, Na contents compared to AL2088. Impoverishments in Rb, K and Na can be also observed for GS samples (Fig. 3.11B). AS samples show no or little REE and trace element variation even for the samples with the highest LOI values (AL2077A and AL2077B, see Supplementary material 2). Sr, Rb and K contents are higher whereas the Si, Al and Na are lower. As observed in the CS, the major elements were also affected by alteration processes in the GS-AS, according to this study. The primary geochemical signatures related to immobile elements are generally preserved and we can use it for further interpretations.

The TAS diagram (Le Bas et al., 1986) show that most of the samples in this study have basaltic compositions, except two samples from the AS, which are a basaltic andesite and a basaltic trachyandesite, and the only sample from the NZM, which is a trachybasalt (Fig.3.12)

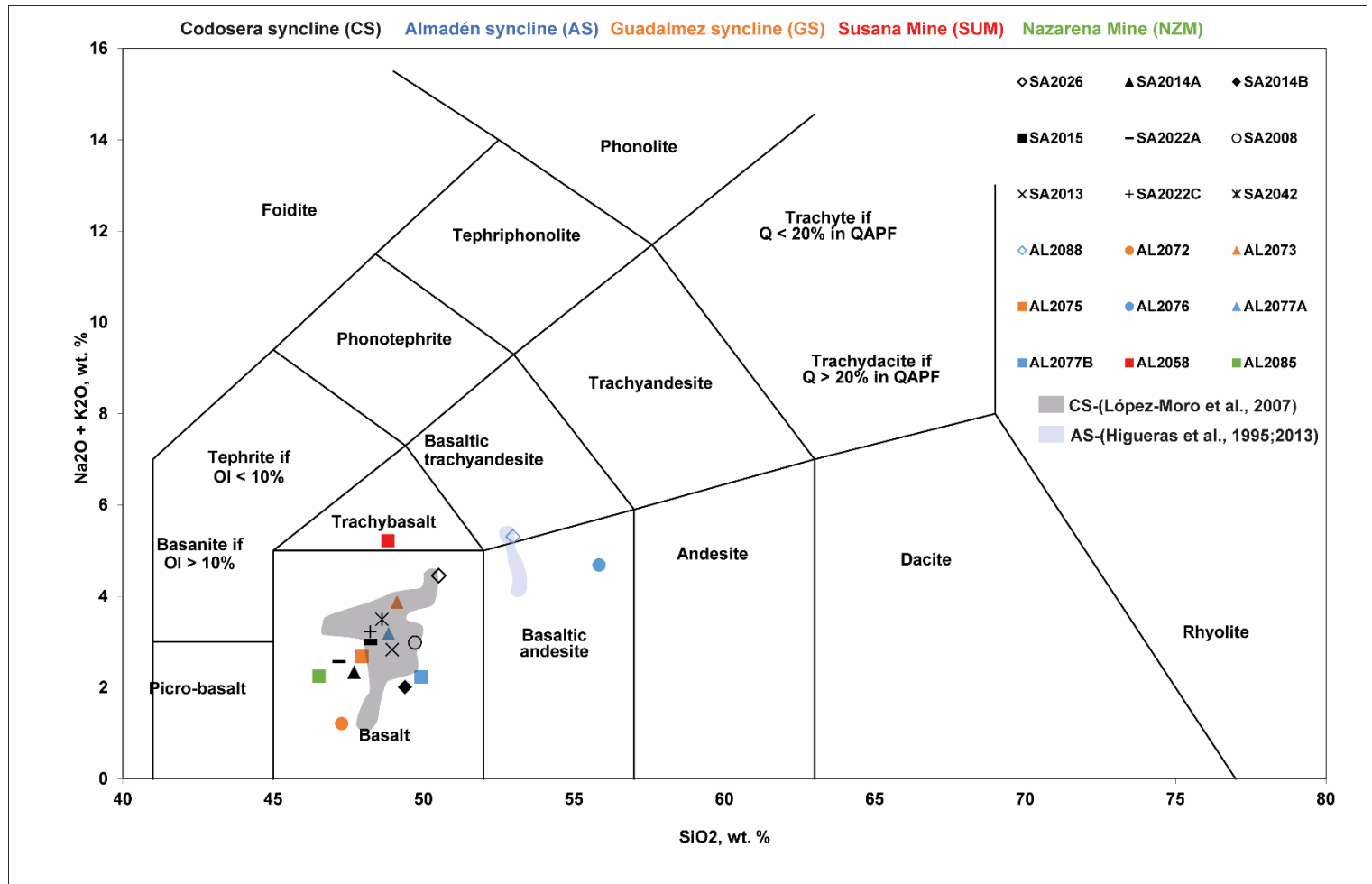


Figure 3. 12. Total Alkali Silica diagram (TAS) from Le Bas et al. (1986) showing the samples studied in this work and in previous studies done by Higuera (1995); Higuera et al. (2013); López-Moro et al. (2007).

According to the Nb/Y vs Zr/Ti diagram (Pearce, 1996), the mafic sills from CS show a basaltic composition, whereas the mafic sills from the AS, GS, SUM and NZM present an alkali basaltic composition (Fig. 3.13A). When using a Zr/Y vs Th/Yb diagram (Ross & Bédard,

2009), most rocks from CS are at the transition between the tholeiitic and the calc-alkaline series (Fig. 3.13B).

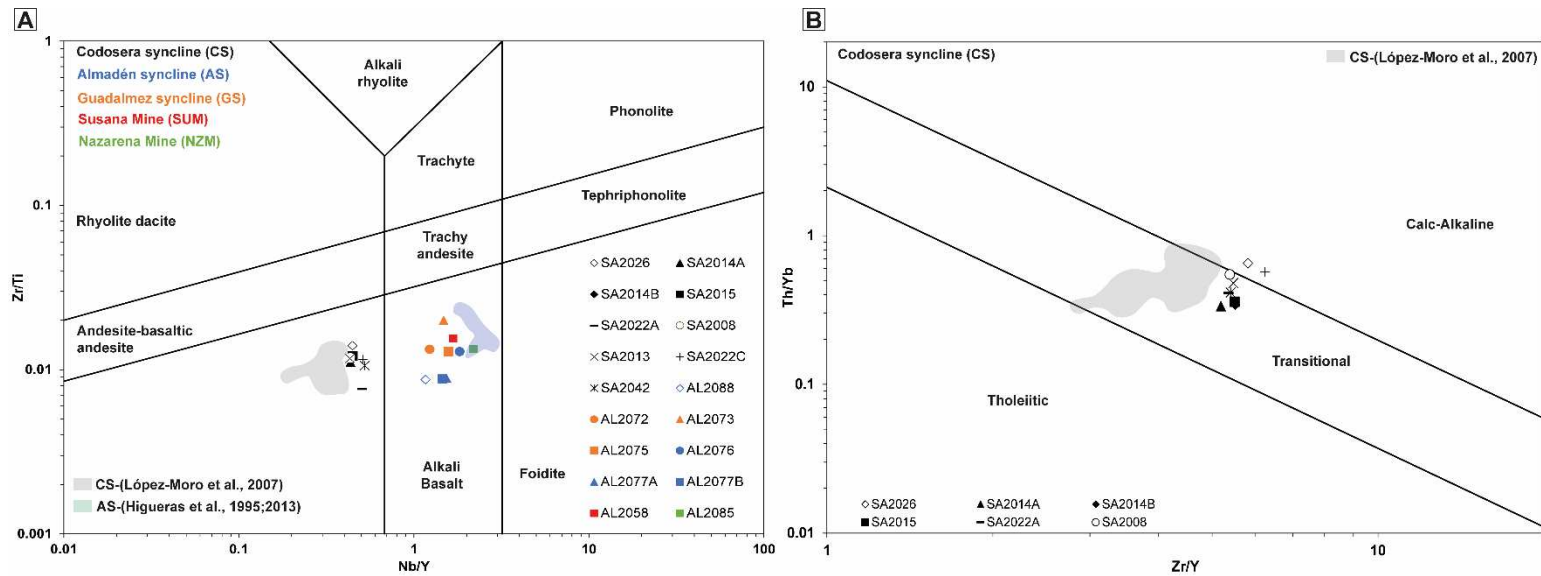


Figure 3. 13. Discrimination diagrams for the mafic samples of the CS, AS, GS, SUM and NZM. A) Nb/Y vs Zr/Ti diagram with field boundaries taken from Pearce (1996); B) Zr/Y vs Th/Yb diagram with field boundaries taken from Ross and Bedard (2009).

Within chondrite normalized diagrams (Sun & McDonough, 1989), intrusions display a slight enrichment in LREE with respect to HREE (Figs. 3.14A and 3.14B). In detail, samples coming from CS show a regular REE pattern free of Eu anomaly but highlighting a discrete Lu enrichment (Fig. 3.14A). Mafic rocks collected at the AS and GS display a slight Eu anomaly and Lu enrichments (Fig. 3.14B). These samples also show higher La/Yb ratios (AS=11.88; GS=11.07) than those from the CS (3.27). Mafic rocks from SUM and NZM display REE patterns similar to the GS samples, with the SUM sample showing the highest REE enrichment (Fig. 3.14B). The GS, AS, SUM and NZM rocks are enriched in LREE with respect to those from the CS. Primitive mantle normalized diagrams (values from Sun & McDonough, 1989) display positive Pb anomalies, and negative Rb anomalies for most samples (Fig. 3.14C,D). Slight positive Ti anomalies are observed for the dolerites from CS, AS, NZM and not for GS and SUM. Conversely, a slight positive Sr anomaly is observed only for the dolerites from AS.

Negative K anomalies are observed in the dolerites from CS, GS, SUM and NZM, whereas this anomaly is almost absent in the dolerites from AS (Figs. 3.14C and D).

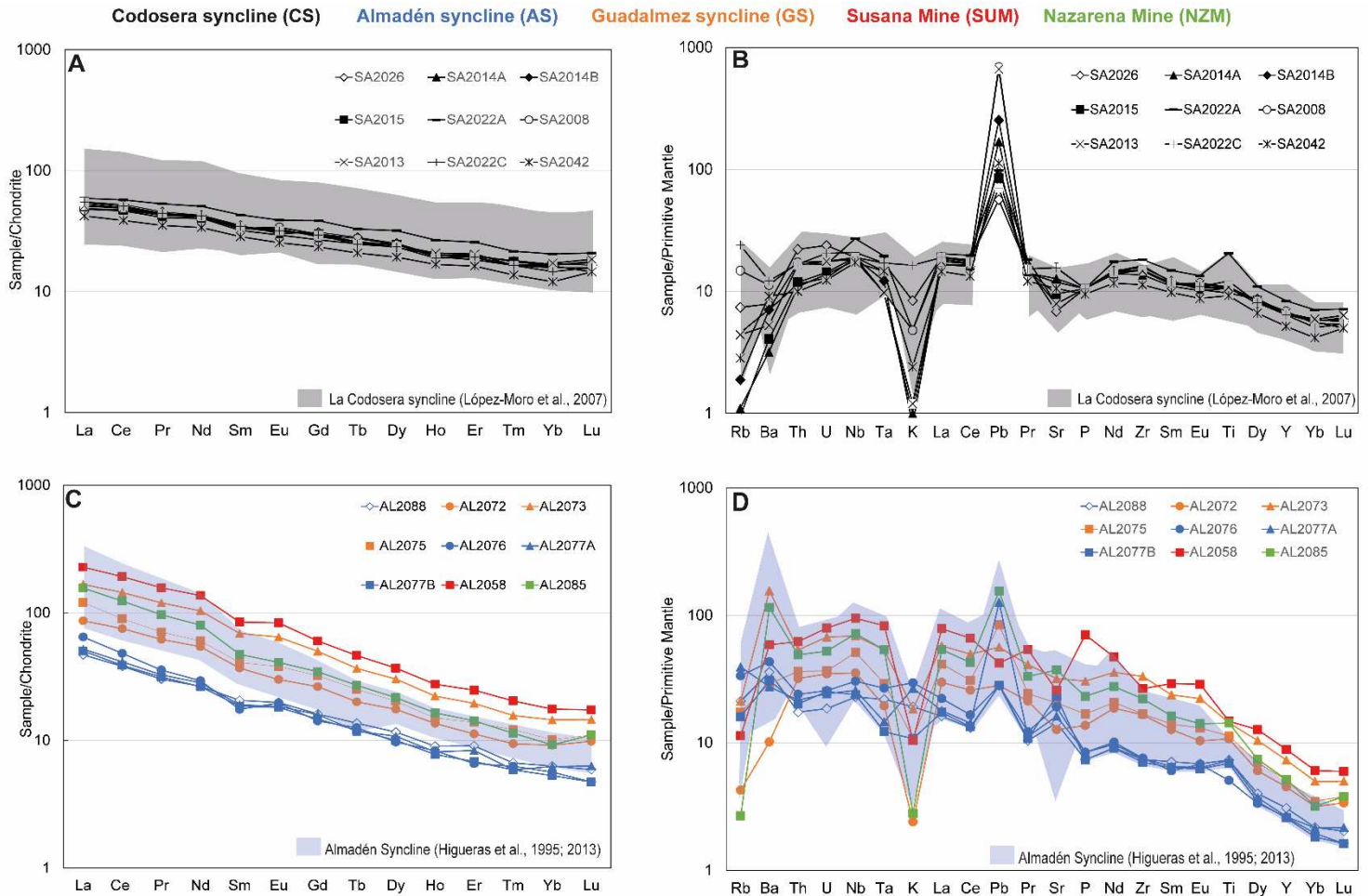


Figure 3. 14. A-B) Chondrite normalized spider diagram for samples from CS (A) and AS-GS-SUM-NZM (B); C-D) primitive mantle normalized spider diagrams for samples from CS (C) and the AS-GS-SUM-NZM (D). Primitive mantle normalizing values are from Sun & McDonough (1989).

4.4-Dolerite geochronology

Apatite features

Whatever the dolerite samples, apatite crystals consistently exhibit an acicular shape, with lengths ranging from 30 μm to 400 μm and widths between 20 μm and 60 μm . In cathodoluminescence images, the apatite crystals do not show any oscillatory zoning (Fig. 3.15). The lack of zoning along fractures suggests the lack of hydrothermal

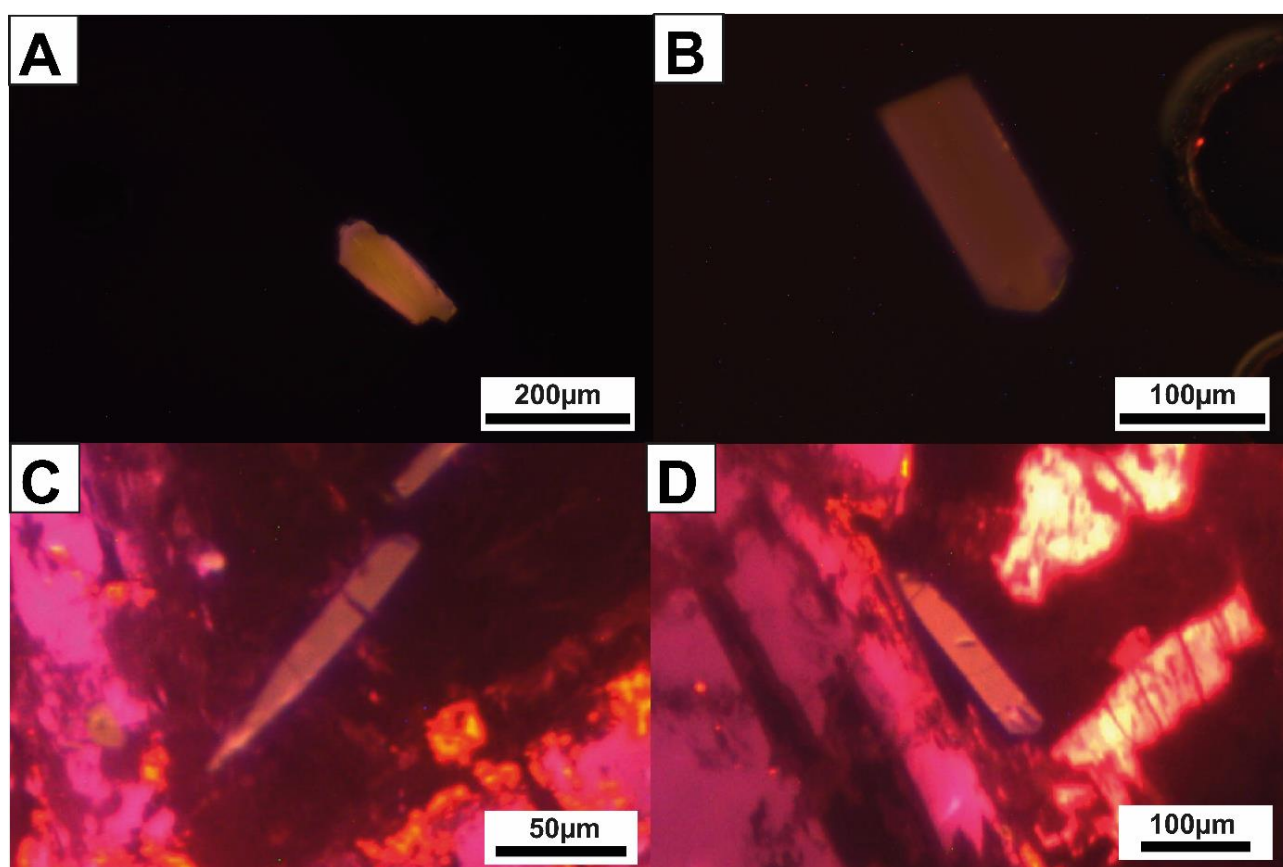


Figure 3. 15. Cathodoluminescence micro-photographs of the studied apatite crystals for samples A) SA2022C; B) SA2026; C) AL2075; D) AL2076. In cathodoluminescence images, the apatite crystals do not show any oscillatory zoning. The lack of any zoning along fractures suggests the lack of hydrothermal dissolution/recrystallization processes and supports their main primary character. The apatites exhibit homogeneous colours ranging from yellow, green, violet and blue

dissolution/recrystallization processes and supports its primary character (i.e. magmatic). The apatite grains exhibit variable colors, ranging from yellow, green, violet and blue, with an homogeneous distribution within the crystal (Fig.3.15).

Chapter 3

Chemical compositions of the apatite grains from the nine dated dolerite samples are shown in Table 3.3 A total of 25-50 apatite crystals were analyzed for each rock sample, depending on the quantity and size of the available apatite

Table 3. 3. Average electron microprobe analyses and corresponding structural formulas of apatite for the mafic samples dated in this study.

Average electron microprobe analyses and corresponding structural formulas of apatite

Average electron microprobe analyses and corresponding structural formulas of apatite																		
APATITE																		
Sample	SA2014 (n=16)		SA2022C (n=18)		SA2026 (n=23)		AL2058 (n=6)		AL2072 (n=13)		AL2073 (n=9)		AL2075 (n=18)		AL2076 (n=32)		AL2085 (n=17)	
		σ		σ		σ		σ		σ		σ		σ		σ		σ
CaO	54.67	0.64	55.33	1.77	55.59	0.76	56.02	1.10	55.56	2.87	54.66	1.41	57.34	0.44	54.83	1.04	55.46	1.39
SrO	0.01	0.04	0.02	0.05	0.01	0.03	0.06	0.10	0.03	0.07	0.10	0.11	0.01	0.04	0.01	0.03	0.16	0.11
MgO	0.25	0.05	0.08	0.13	0.22	0.08	0.31	0.10	0.86	1.49	0.39	0.15	0.22	0.06	0.09	0.19	0.22	0.09
MnO	0.00	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	1.13	0.22	0.32	0.31	0.44	0.17	0.18	0.21	1.13	0.83	0.27	0.30	0.65	0.17	0.54	0.27	0.24	0.23
Na ₂ O	0.01	0.03	0.08	0.09	0.02	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.07	0.06	0.08	0.02	0.06
P ₂ O ₅	41.48	0.62	43.38	0.88	43.88	0.57	43.58	1.08	42.42	2.61	43.12	0.83	43.88	0.76	41.52	0.76	42.28	0.83
SiO ₂	0.53	0.27	0.20	0.24	0.20	0.12	0.28	0.08	1.31	1.88	0.52	0.28	0.30	0.12	0.36	0.34	0.42	0.27
SO ₃	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.00	0.00	0.02	0.05	0.00	0.00	0.00	0.00	0.01	0.03
F	2.32	0.23	2.72	0.27	2.72	0.11	2.51	0.18	2.91	0.44	3.07	0.18	2.57	0.18	3.03	0.24	2.06	0.28
Cl	0.58	0.05	0.38	0.17	0.79	0.11	0.33	0.06	0.31	0.05	0.31	0.05	0.33	0.11	0.52	0.06	0.43	0.14
Total	101.16	0.86	102.76	2.04	102.76	2.04	103.60	2.09	104.70	1.79	102.75	1.91	105.53	1.01	101.15	1.48	101.52	2.08
O=F	0.98	0.10	1.14	0.11	1.14	0.11	1.06	0.08	1.22	0.19	1.29	0.08	1.08	0.08	1.28	0.10	0.87	0.12
O=Cl	0.13	0.01	0.09	0.04	0.09	0.04	0.08	0.01	0.07	0.01	0.07	0.01	0.07	0.03	0.12	0.01	0.10	0.03
Total	100.05	0.88	101.53	2.03	101.53	2.03	102.46	2.10	103.41	1.65	101.38	1.91	104.38	1.00	99.75	1.42	100.55	2.09
Structural formula on the basis of a 12.5 oxygen equivalent																		
Ca	4.92	0.04	4.89	0.07	4.85	0.04	4.89	0.03	4.82	0.20	4.82	0.05	4.93	0.04	4.96	0.06	4.94	0.04
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01
Mg	0.03	0.01	0.01	0.02	0.03	0.01	0.04	0.01	0.11	0.19	0.05	0.02	0.03	0.01	0.01	0.02	0.03	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.08	0.02	0.02	0.02	0.03	0.01	0.01	0.01	0.08	0.06	0.02	0.02	0.04	0.01	0.04	0.02	0.02	0.02
Na	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.01
P	2.95	0.02	3.02	0.03	3.02	0.02	3.00	0.01	2.91	0.15	3.01	0.03	2.98	0.02	2.97	0.03	2.98	0.02
Si	0.04	0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.11	0.16	0.04	0.02	0.02	0.01	0.03	0.03	0.03	0.02
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.62	0.06	0.70	0.07	0.70	0.03	0.65	0.05	0.75	0.11	0.80	0.05	0.65	0.04	0.81	0.06	0.54	0.08
Cl	0.08	0.01	0.05	0.02	0.11	0.02	0.05	0.01	0.04	0.01	0.04	0.01	0.04	0.02	0.07	0.01	0.06	0.02
OH ^a	0.30	0.06	0.24	0.08	0.19	0.03	0.31	0.04	0.21	0.11	0.16	0.05	0.30	0.04	0.12	0.06	0.40	0.07

Notes: Oxide contents in wt.%, cationic contents in apfu and σ : standard deviation

X ray maps (Fig. 3.16) show that the distribution of F is more homogeneous than that of Cl.

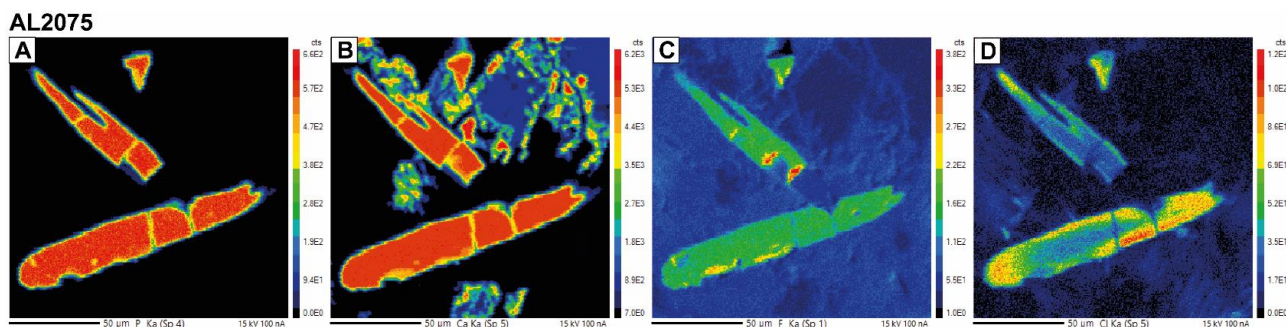


Figure 3. 16. X-ray maps showing P (A), Ca (B), F (C) and Cl (D) distribution within an apatite crystal from sample AL2075 in the GS. The Ca and the P seem to be less enriched in the rim. The F distribution in the crystal is homogeneous whereas the Cl present a heterogeneous distribution.

To examine the chemistry of apatite, EPMA data were plotted in the OH-Cl-F diagram. All data lies near the F apex, highlighting fluorapatite compositions in line with F contents exceeding 0.62 apfu (Fig. 3.17). Apatite grains from the Almaden dolerite (AL2076) are the closest to the fluorapatite pole. These fluorapatite composition match quite well that of apatite crystals extracted from the Armorican dolerites (green field in Fig. 3.17).

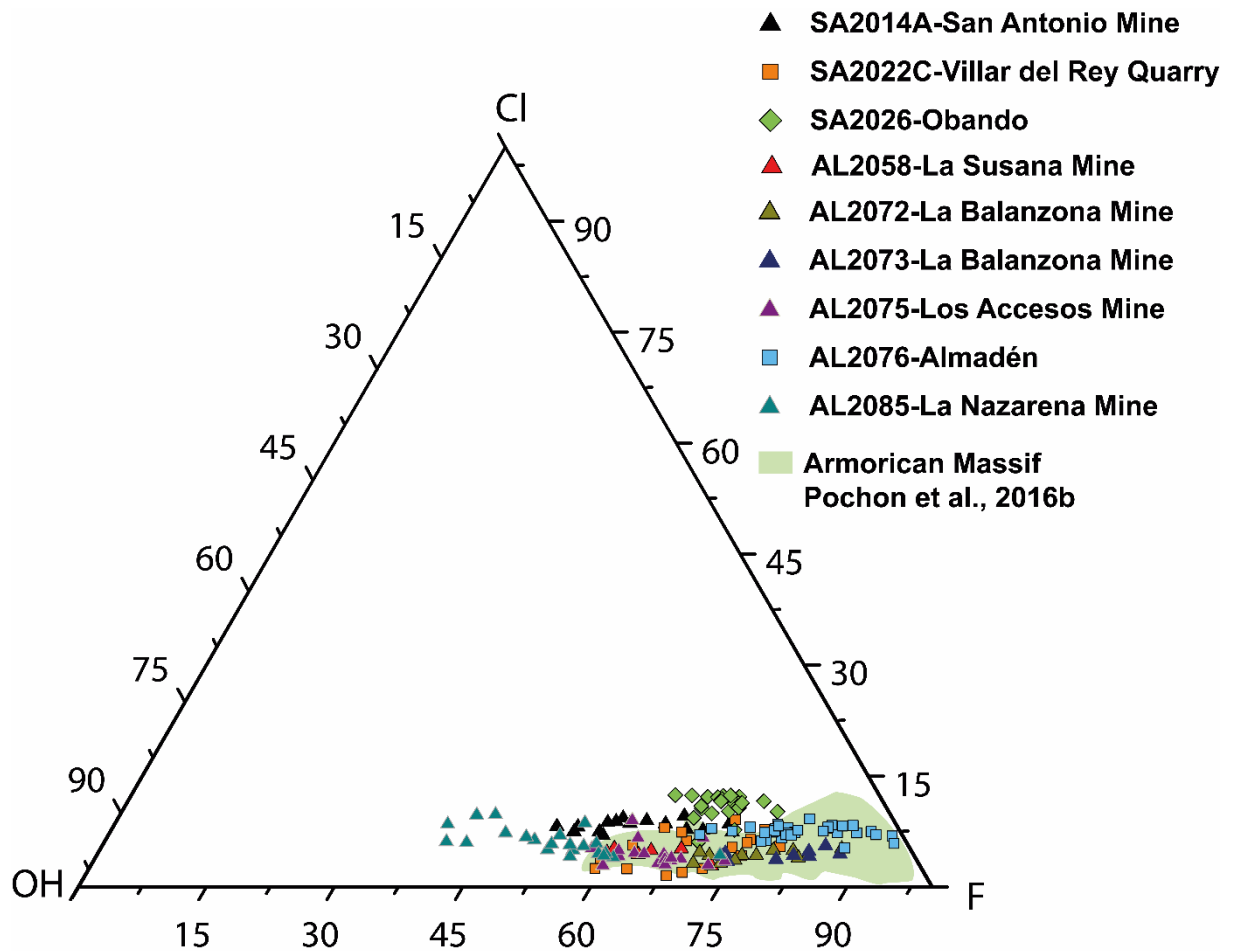


Figure 3. 17. Average electron microprobe analyses of apatite for the dolerite samples dated in this study, compared to the apatites from the Armorican massif dolerites (field in green) by Pochon et al. (2016b). The halogens content plot has been modified from Boudreau (1995).

U-Pb dating on apatite

The U-Pb data of apatite from nine samples, three from CS (SA2014A, SA2022C and SA2026), three from GS (AL2072, AL2073 and AL2075), one from AS (AL2076), one from the SUM (AL2058) and one from the NZM (AL2085) are presented in the Tera-Wasserburg diagrams

(Figs.3.17, 3.18, and 3.19) that were made using IsoplotR (Vermeesch, 2018). All errors are provided at 2se% level, as shown in Figures 3.18, 3.19, 3.20 and in Supplementary material 8.

Sills from CS yielded 3 dates (Fig. 3.17): sample SA2014A (Fig. 18A) yielded a lower intercept date of 359 ± 21 Ma (MSWD=1.5; n=34) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.834 ± 0.077 ; sample SA2022C (Fig. 18B) provided a lower intercept date of 353 ± 19 Ma (MSWD=0.95; n=35) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.857 ± 0.034 ; sample SA2026 (Fig. 18C), provided a lower intercept at 332 ± 17 Ma (MSWD=0.97; n=58) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.819 ± 0.039 .

The rocks of the GS yielded 3 dates: the sample AL2075 (Fig. 19A, GS) provided a lower intercept date of 422 ± 11 Ma (MSWD=1.1; n=33) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.828 ± 0.010 ; for the sample AL2072 (Fig. 19B, GS), the lower intercept is 387 ± 18 Ma (MSWD=0.92; n=21) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.812 ± 0.033 ; sample AL2073

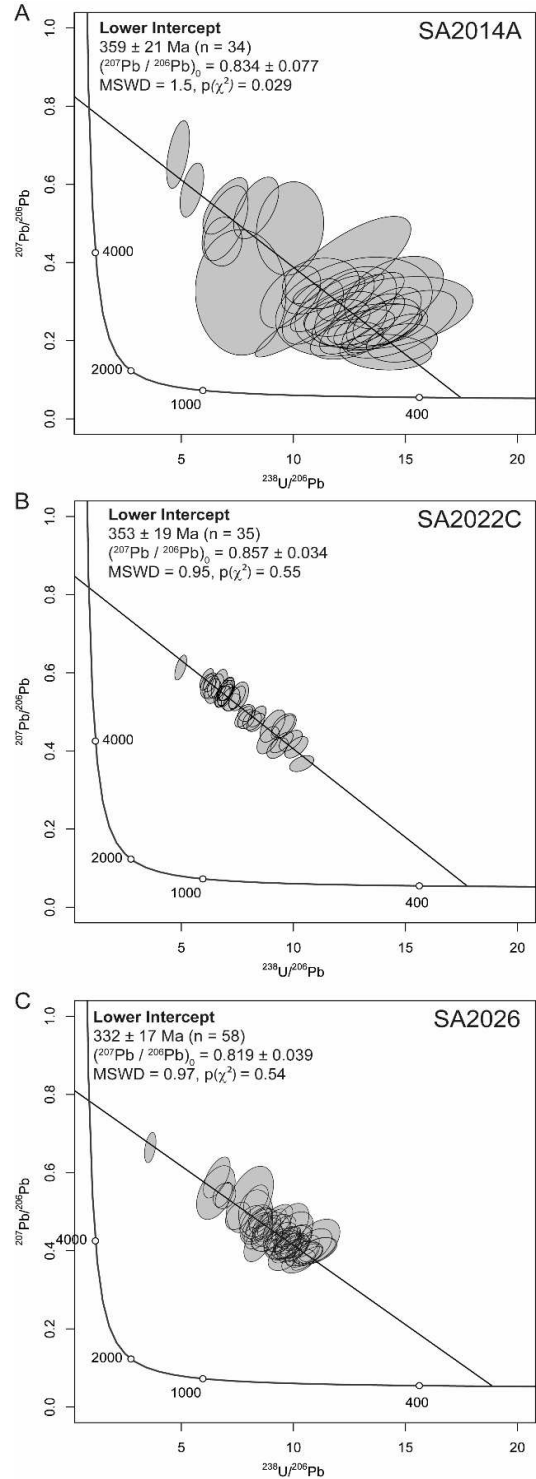


Figure 3. 18. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks of the CS.

(Fig. 19C, GS) yielded a lower intercept date of 361 ± 22 Ma (MSWD=2, n=34) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.796 ± 0.054 .

One date was obtained for the AS: sample AL2076 (Fig. 19D, AS) provided a lower intercept date of 358 ± 12 Ma (MSWD=0.92; n=34) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.818 ± 0.020 .

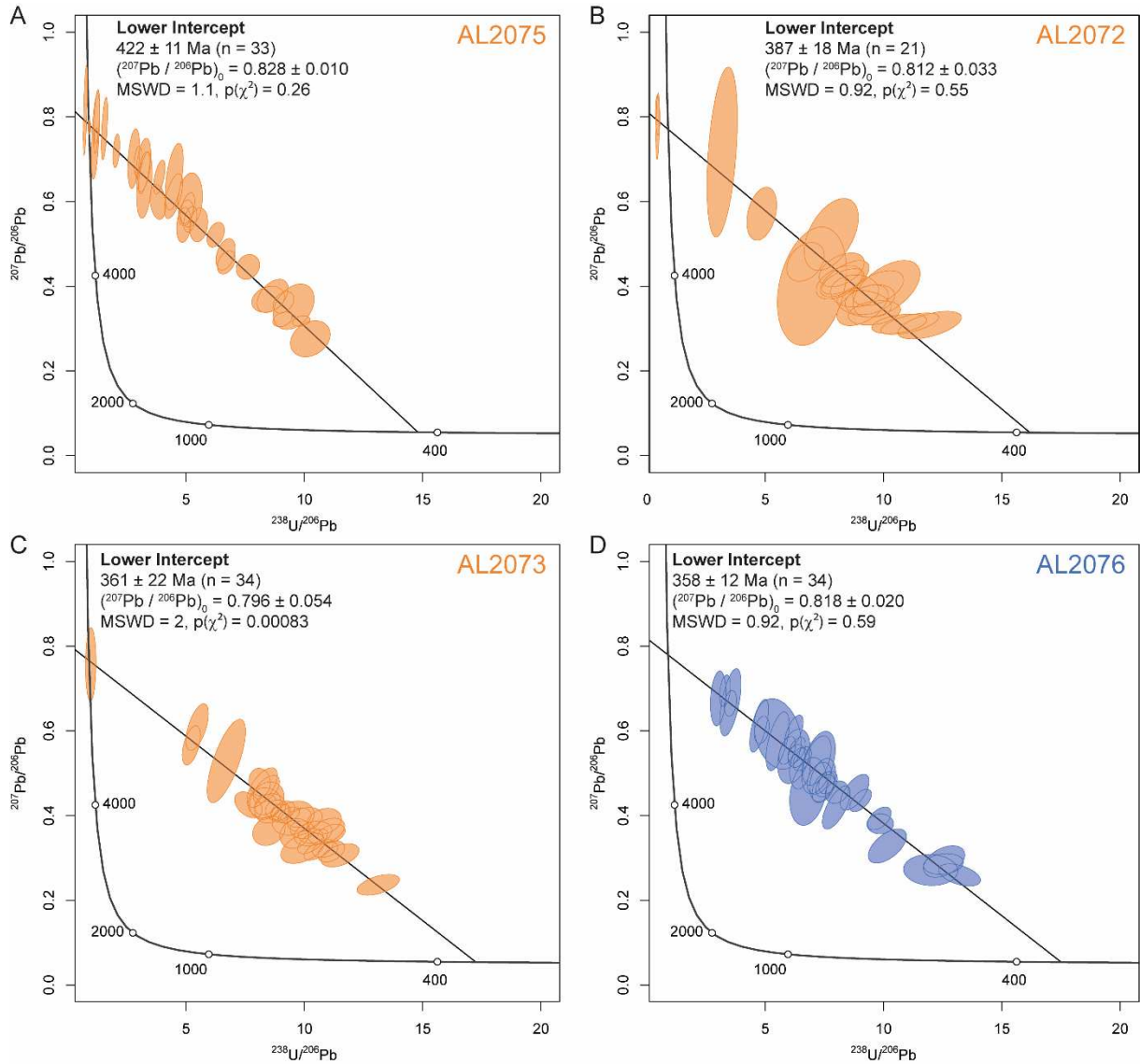


Figure 3. 19. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks coming from GS (A-C) and AS (D).

One date was obtained for the SUM and one for the NZM: sample AL2058 (Fig. 3.20A, SUM) provided a lower intercept date of 381 ± 28 Ma (MSWD=1.9; $n=28$) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.83 ± 0.05 ; sample AL2085 (Fig. 3.20B, NZM) provided a lower intercept date of 483 ± 24 Ma (MSWD=0.47; $n=32$) with an initial $^{207}\text{Pb}/^{206}\text{Pb}$ value of 0.83 ± 0.0089 .

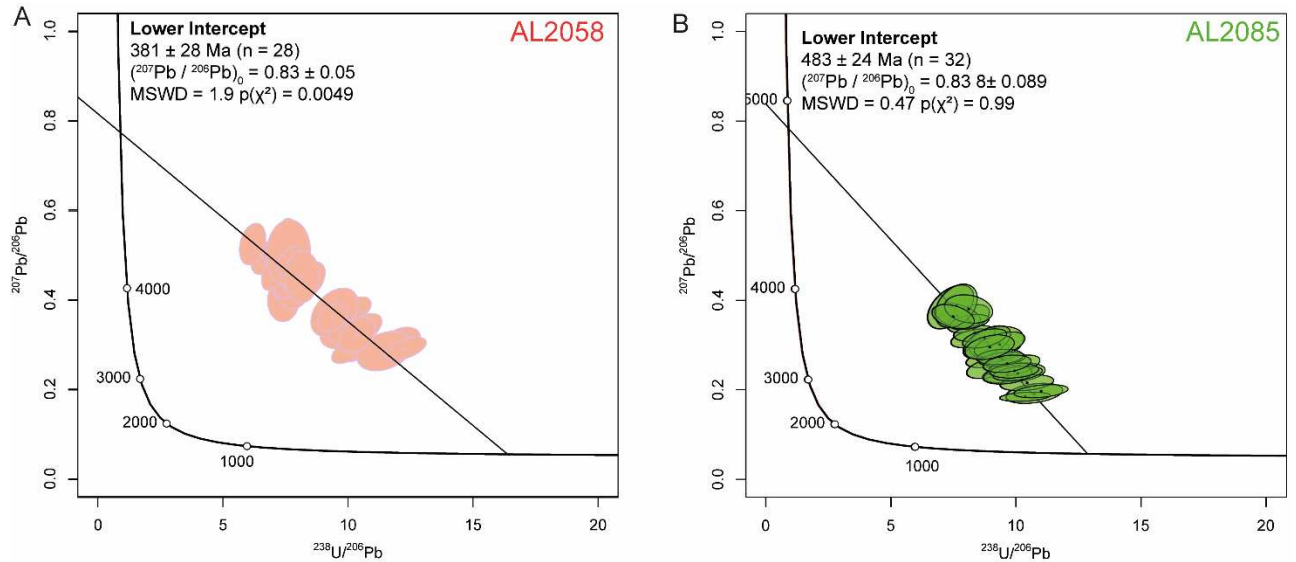


Figure 3. 20. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks coming from SUM (A) and NZM (B).

3.4.5-Fluid inclusion bearing ilmenite

Primary fluid inclusions (FI) were observed in ilmenite crystals within two samples of the CS, suggesting the occurrence of a fluid phase in the magma at the time of ilmenite crystallization (Chatelin, 2022; Pochon et al., 2024). LA-ICP-MS analyses performed on the ilmenites show that the FI are characterized by a solute composition dominated by Na-Ca-Cl-S, with Sb, Cu, Sn, Mo, W and Pb as metals and metalloids (Chatelin, 2022; Pochon et al., 2023, 2024) (Chatelin, 2022; Pochon et al., 2023, 2024). The LA-ICP-MS traverses evidence an increase of incompatible trace elements contents (*e.g.* Sb, As, Cu, Sr) in the FI-bearing areas (Fig. 3.21, Chatelin, 2022; Pochon et al., 2024).

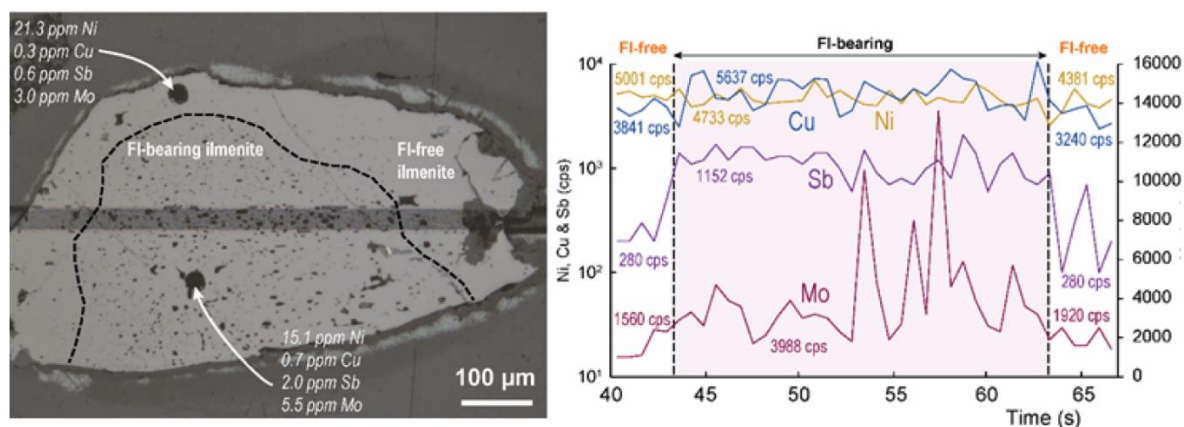


Figure 3. 21. LA-ICP-MS analyses of ilmenite from the Armorican Massif showing the enrichment in incompatible trace elements in FI-bearing areas. Modified after Pochon et al. (in review)

3.5-Discussion

3.5.1-Interpretation of the apatite dating and significance of the ages

As shown in petrographical analyses, the dated apatites in this study are associated to primary magmatic phases (plagioclase, clinopyroxene). Furthermore, the mineral chemistry of the dated crystals in the CS-AS-GS-SUM and NZM (Supplementary material 7) matches with the magmatic apatites dated at *ca.* 360 Ma in the Armorican Massif (*e.g.* Pochon et al. 2016b), allowing us to support their igneous character. The low-grade metamorphism affecting the whole CS area explains the partial replacement of the magmatic minerals in the dolerites by chlorite, green amphibole, albite, calcite and actinolite, which are minerals characteristic of the greenschist facies, as already suggested in previous studies (López-Moro et al., 2007, 2020a). In the case of the Almadén district, Higuera et al. (1995) reported metamorphic conditions that reached a maximum temperature of 240°C and pressure around 200MPa during the Variscan orogeny. Such conditions correspond to the transition between anchizonal and greenschist metamorphic facies reported for the studied areas in the CIZ, including the SUM and NZM (Martínez Catalán et al., 2014). Such a low-grade metamorphism is not likely to have reset the apatite isotopic system (Cherniak et al., 1991; Pochon et al., 2016). The closure temperature of

the isotope system of this mineral commonly range between 375 and 550°C (Dodson, 1973; Webster & Piccoli, 2015). Nevertheless, more recent studies allowed to determine a higher closing temperature range of 770-870°C based on the fast cooling rate and low thickness of several mafic sills in the Armorican Massif (Pochon et al., 2016). Considering that the thickness of each studied sill in this work is relatively small and the fact that these mafic bodies underwent a very fast cooling and solidification, we can use the higher closure apatite temperature range of 770-870°C from Pochon et al. (2016). The paragenetic association of apatite with primary magmatic minerals, their primary mineral chemistry, along with the apatite closing temperature range supports the fact that the measured dates can be interpreted as crystallization ages.

3.5.2-Temporal relationship between dolerites and their host rocks

The relative age of the dolerites and their host sedimentary rocks can also potentially help in constraining the tectonic setting during the magmatic events. The age relationships of the dolerites and their host rocks are discussed below.

3.5.2.1-Guadalmez syncline

The numerous alkaline dolerite sills in the GS intruded mainly black schists that have been ascribed to Silurian, ca. 420-440 Ma, based on their stratigraphic position and graptolite fossils (Almela et al., 1962; García San Segundo et al., 1985; Lorenzo Álvarez et al., 1995; Villas et al., 1999). The three dolerite sills dated in this study provided ages of 422 ± 11 Ma (AL2075), 387 ± 18 Ma (AL2072), and 361 ± 22 Ma (AL2073). The oldest age could be coeval with the host sedimentary rocks (within uncertainty), which means that the dolerites could be formed during or shortly after active sedimentation. In the central part of the GS, sedimentary rocks with Carboniferous ages (ca. 360-300 Ma; see Fig. 3.3) were described (Almela et al., 1962; García San Segundo et al., 1985; Lorenzo Álvarez et al., 1995), which means that the sedimentation in the area continued after the intrusion of the dolerites. The lack of overlap

between the age of the oldest sill and the younger ones suggests at least two different magmatic events in the GS (Fig. 3.22).

3.5.2.2-Almaden syncline

The alkaline dolerite sills in the AS intrude Upper Devonian (ca. 385-370 Ma) volcano-sedimentary rocks (Almela et al., 1962; García San Segundo et al., 1985; Lorenzo Álvarez et al., 1995; Villas et al., 1999; Fig. 3.3). The dated dolerite sample AL2076 yielded an age of 358 ± 12 Ma, which is coeval with the host rock within error, and which indicates that it was intruded during or shortly after the deposition of the volcano-sedimentary unit. This age matches the ages found for the younger dolerites dated in the GS (ca. 15km SW from the AS), which could mean that they were part of the same magmatic event (Fig. 3.22).

3.5.2.3-Codosera syncline

In the CS, the dolerite sills intrude the Gévora Formation, which was deposited during the Carboniferous (Mississippian, ca. 359-323 Ma), an age estimation that is based on the presence of miospores in the black schist and a conodont assemblage in the San Antonio limestone (Rodríguez González et al., 2007; Fig. 3.3). The studied dolerites yielded ages of 359 ± 21 Ma (SA2014A), 352 ± 19 Ma (SA2022C) and 332 ± 17 Ma (SA2026) which are compatible with the Mississippian age of the host schist. This result suggests that the dolerite sills were emplaced during or shortly after the sedimentation. Unfortunately, the uncertainties of the measured ages from the mafic sills of the CS are too large to conclude whether the sills were formed during a long magmatic event or as a sequence of smaller events, as in the GS (Fig. 3.22). The ages of the CS samples are within uncertainty similar with the dolerites of the AS and the younger dolerites of the GS (Fig. 3.22), which are separated ca. 200km SE from the CS. However, the CS dolerites are mostly transitional, whereas the GS and AS dolerites are alkaline.

3.5.2.4-Susana Mine

The alkaline dolerite sill in the SUM intrude the so called ‘Schist Greywacke Complex’ of late Precambrian-Cambrian age (Lotze, 1945; San José et al., 1990). The dated dolerite sample AL2058 yielded an age of 381 ± 28 Ma, which is younger than the host rock.

3.5.2.5-Nazarena Mine

In the NZM, the dolerite sill intrude the unit known as Slates “Rio”, which was deposited during the Ordovician period (García San Segundo et al., 1985). The studied dolerite yielded an age of 483 ± 24 Ma (AL2085), which is compatible within error with the Ordovician age of the host rock. This result suggests that the dolerite sill was emplaced during or shortly after the sedimentation.

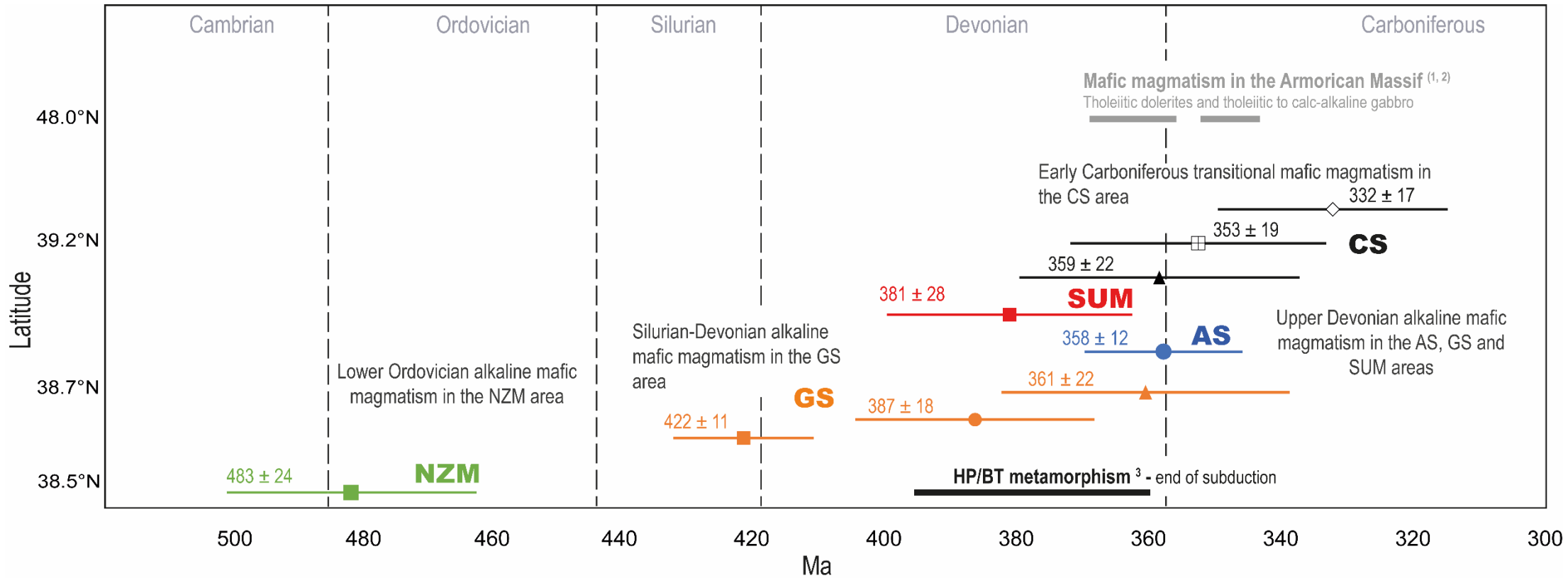


Figure 3. 22. Synthesis of the ages of the mafic samples studied in this work and comparison with previous data on mafic magmatism in the Armorican Massif. References in the figure: ¹(Pochon et al., 2016b); ²(Barboni et al., 2013); ³(Paquette et al., 2017).

3.5.3-Magmatic events in the GS, AS and CS over ≈ 200 Ma

If we synthesize the geochronological data obtained in this work, the emplacement ages of the dolerite sills of the GS, AS, CS, NZM and SUM spread out over 200 Ma (Fig. 3.22), considering the associated uncertainty. Two main types of magmatism are identified, one of alkaline affinity (GS, AS, NZM, SUM) and the second of transitional affinity in the CS (Fig. 3.13). Considering the spatial distribution of the dolerites together with the geochemistry and geochronological data, we propose the existence of at least four mafic magmatic events (Fig.3.22): **i**) the first one of alkaline affinity during the Lower Ordovician (i.e. 483 ± 24 Ma) in the NZM; **ii**) a second one of alkaline affinity belonging to the upper Silurian (i.e. 422 ± 11 Ma) in the GS ; **iii**) a third event of alkaline affinity in the GS, AS and SUM, taking place either as a single long event or as short multiple events between 409 and 339 Ma ; **iv**) a fourth event in the CS, showing a transitional affinity, which took place as a single major event or as a series of shorter events from 381 to 315 Ma. More precise dating of the dolerites could reveal if these magmatic events were characterized by short-lived syncline-scale magma pulses or sequential intrusions of smaller sills at different parts of the synclines.

At the regional scale, our data suggest a migration of the magmatic activity from SE to NW, accompanied by a compositional modification from alkaline to transitional affinity.

3.5.4-Major geological events, evolution and geochemistry of the mafic magmatism in the CIZ

The mafic magmatism in the CIZ has experienced an important geochemical evolution from the Precambrian times until the end of the Variscan orogeny, the signatures of all of these rocks being strongly correlated to their geodynamic setting.

5.4.1-Neoproterozoic to Ordovician

The Cadomian orogeny occurred during the Neoproterozoic Era (Bandrés et al., 2004 and references therein). In the CIZ, the mafic suites temporally associated with the last stage of this event correspond to the gabbros of the Mérida Massif emplaced at 557 ± 4 Ma (Bandrés et al., 2004). These rocks show a calc-alkaline affinity and signatures of an immature arc setting with subduction enrichments, as well as the involvement of crustal components in the mantle source (Bandrés et al., 2004).

The geodynamic setting at Lower Ordovician epoch is strongly related to the opening of the Rheic Ocean (*ca.* 477 Ma; Orejana et al., 2017 and references therein). The age of the oldest dolerite in this study (AL2085, NZM, alkaline affinity; 483 ± 24 Ma) is within uncertainty coeval with the beginning of this extensive event. This dolerite shows an enriched metasomatized mantle source possibly related to the Cadomian slab (Fig. 3.23). During this period, three main lithospheric mantle sources were suggested for other mafic suites intruded in the CIZ (Orejana et al., 2017; Solá et al., 2010). The tholeiitic metabasites of the Tenzuela Massif (SCS, 473 ± 2 Ma; Villaseca et al., 2015), were related to a depleted source with minor involvement of crustal contamination (Orejana et al., 2017; Villaseca et al., 2015). The metabasites in the Revenga-Caloco sectors (SCS, 473-453 Ma; Orejana et al., 2017) are also tholeiitic but show negative Nb-Ta anomalies and high LILE contents that were associated with an enriched mantle source with significant crustal recycling (Orejana et al., 2017). The crustal contamination effect has been also reported in the alkaline gabbros from the Carrascal Massif (471 ± 2 Ma, Solá et al., 2010) whose hydrated mantle source showed an arc signature possibly inherited from a previous Cadomian subduction (Solá et al., 2010)

5.4.2-Silurian to Lower Devonian

The opening of the Rheic ocean stopped during Silurian to Lower Devonian (*ca.* 430-415 Ma; Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012) reaching a

maximum width of ca. 4000km (Nance et al., 2012 and references therein). The age of the oldest dolerite in the GS (AL2075, GS, alkaline affinity; 422 ± 11 Ma) is coeval with the last stage of this extensive period and, within uncertainty, with the depositions of its host sedimentary rocks. This sample shows an enriched metasomatized mantle source possibly related to the Cadomian slab as in the case of the Carrascal Massif (*e.g.* Solá et al., 2010). However, there is no sign of crustal contamination in this mafic sample of the GS.

5.4.3-Lower Devonian to Carboniferous

The subduction of the Rheic ocean started at ca. 415 Ma and lasted until its closure at the Variscan collision during Upper Devonian to early Carboniferous (Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012). In the CIZ, the first collisional stage of the Variscan orogeny has been dated at 359-350 Ma (Dallmeyer et al., 1997). In this geodynamic setting, the Badajoz-Córdoba shear zone accommodated the deformation by left lateral transtensional kinematics, leading to an extensional event documented at the southern part of the CIZ (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016).

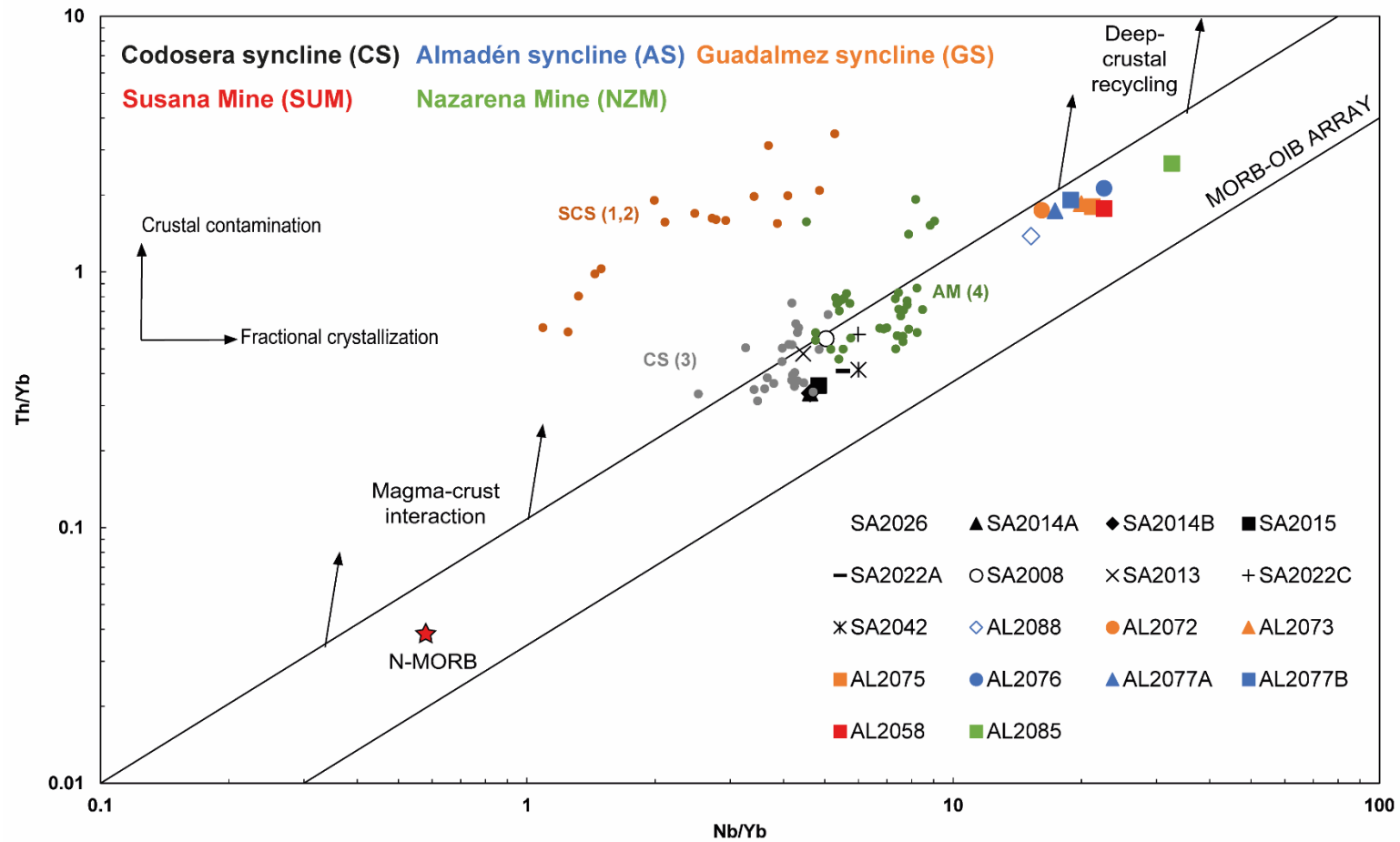


Figure 3. 23. Th/Yb vs Ta/Yb diagram from Pearce (1983, 2008) showing the mafic rocks studied in this work and those reported for the CIZ and the Armorican Massif. The rocks from CS show a less enriched and less metasomatized mantle source compared to the rocks from AS, GS, SUM and NZM. The CS is consistent with the data reported for the Armorican Massif (Pochon et al. 2016). References in the figure: ¹(Orejana et al., 2009); ²(Scarrows et al., 2009); ³(López-Moro et al., 2007); ⁴(Pochon et al., 2016).

The extensional setting facilitated the intrusion of several mafic suites across the CIZ, which correspond to: **i)** the alkaline basalts from El Castillo (394.7 ± 1.4 Ma, Gutiérrez-Alonso et al., 2008); **ii)** the alkaline mafic rocks from the GS, AS and SUM in this study (intruded between 387 ± 18 Ma to 360 ± 22 Ma) as well as those from the AS reported in previous studies (e.g. Hall et al., 1997; Higuera, 1995, 2000; Higuera et al., 2013); **iii)** the transitional to calc-alkaline dolerite sills from the CS reported in this study that were emplaced at 359 ± 21 Ma, 353 ± 19 Ma and 332 ± 17 Ma, and **iv)** the mafic and ultramafic intrusions documented in the IBERSEIS Reflective Body (IRB; Simancas et al., 2003, 2006), which can be observed in the middle crust of the southern CIZ, the Ossa Morena Zone and the South Portuguese Zone (Simancas et al., 2003, 2006). All of them have been related to the transtensional kinematics of the Badajoz-Cordoba shear zone (Azor et al., 2019; Cambeses et al., 2015; Carbonell et al., 2004; Palomeras et al., 2011; Simancas et al., 2003, 2006).

3.5.4.4- Possible sources and geochemical signatures

3.5.4.4.1-GS, AS, SUM and NZM

Regarding the geochemistry of the GS, AS, SUM and NZM rocks in this study, the correlation between Nb/Yb and Th/Yb (Pearce, 2008) suggests a geochemical signature related to an enriched metasomatized mantle source without crustal contamination (Fig. 3.23). In the Nb/Yb and Th/Yb diagram (Pearce, 2008), the most altered samples with high LOI lie into the same field compared to the less altered, supporting that the primary geochemical signatures related to immobile elements were preserved. Furthermore, all of the mafic rocks from the GS and the AS show REE patterns with low LREE/HREE (Fig. 3.14B and D), a feature that has been usually related with the presence of residual garnet in the source (Fig. 3.24), because this mineral is capable of concentrating HREE in its structure (Harrison, 1981; Kamenetsky & Eggins, 2012). Mafic rocks presenting high Gd/Yb (>1.5) and high Ti/Y (>350) ratios, such as the samples from GS (Gd/Yb >3 ; Ti/Y >559), AS (Gd/Yb >2.9 ; Ti/Y >554), SUM (Gd/Yb >4 ;

Ti/Y>477) and NZM (Gd/Yb>4; Ti/Y>790), may indicate the presence of residual garnet in the mantle source (e.g. Kamenetsky & Eggins, 2012; Sarrionandia et al., 2023; Song et al., 2009; Fig. 3.24). The LREE enrichment has also been related to a low degree of partial melting, the lower the degree of partial melting the higher the LREE content (Casetta et al., 2019; Harrison, 1981).

The negative anomalies in K, Rb and Ba observed for the GS, AS, SUM and NZM samples (Fig. 3.14B and D) were also reported in the previously studied mafic rocks in the AS (Higueras, 1995; Higueras et al., 2013). Considering the alteration analyses performed in section 4.3, these anomalies may be attributed to hydrothermal and alteration effects.

Most of the studied samples from GS, AS, SUM and NZM displayed positive Pb anomalies in the primitive mantle normalized diagrams (Fig. 3.14C and D). This may indicate the involvement of sediment addition and/or assimilation of country rocks (e.g. Sun & McDonough, 1989) or a mantle metasomatism associated to the slab devolatilization during subduction (e.g. Hattori and Guillot, 2003). Nevertheless, considering the alteration features, these anomalies could also be related to alteration effects.

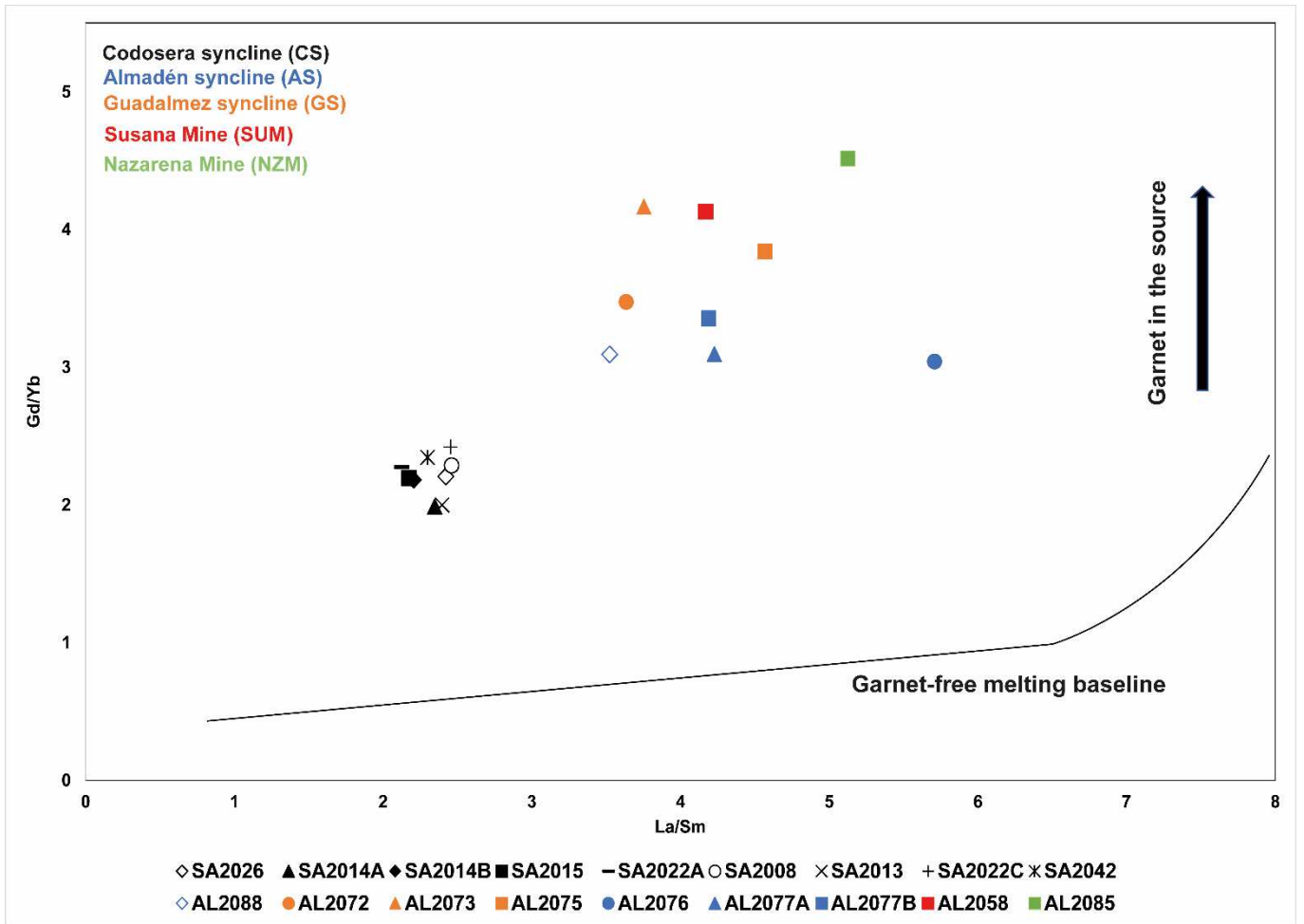


Figure 3. 24. A) La/Sm vs Gd/Yb diagram (Kamenetsky & Eggins, 2012) showing samples coming from CS, GS, AS, SUM and NZM. The data is consistent with the presence of garnet in the source, which also matches with the enrichment in LREE.

The seismic studies and 3D velocity models of Palomeras et al. (2017) show low velocity zones that we could interpret as metasomatized SCLM possibly influenced by a Cadomian/Rheic slab, which has been suggested as the mantle source of several mafic suites in the OMZ and CIZ (Sarrionandia et al., 2023). Based on this, the metasomatized source possibly responsible for the GS, AS, SUM and NZM intrusions could be related to these low velocity zones (Fig. 3.25) marked in the seismic studies of Palomeras et al. (2017).

5.4.4.2-Codosera syncline

In the case of the CS, the magmatic suites reported in this study show a transitional affinity (samples SA2014A- 359 ± 21 Ma, SA2022C- 353 ± 19 Ma and SA2026- 332 ± 17 Ma). Previous studies suggested that the mafic magmas in the CS presented a subalkaline affinity and were derived from a spinel-bearing/garnet-free metasomatized sub lithospheric mantle source (López-Moro et al., 2007). Nevertheless, the trace element systematics of our samples are not compatible with this last hypothesis. The Gd/Yb (1.98-3.10) and Ti/Y (415 to 700) ratios of the dolerites in the CS are geochemically similar to those of the dolerites in the AS, GS, SUM and NZM, as well as of other mafic magmas derived from garnet-bearing mantle sources, in the Iberian Massif and across the globe (e.g. Song et al., 2009; Kamenetsky & Eggins, 2012; Sarrionandia et al., 2023). The presence of residual garnet in the mantle source is also supported by the Gd/Y vs La/Sm diagram from Kamenetsky & Eggins (2012), where all data plot in the garnet-source field but show less amount of garnet in the source compared to AS and GS (Fig. 3.24). The lesser LREE contents of the CS (compared to those from the GS and AS), and the lower La/Yb ratios (3.27 versus 11.88 for AS, 11.07 for GS, 18.06 for SUM and 23.57 for NZM) suggest higher degrees of partial melting to produce the CS rocks. Our data is consistent with previous studies suggesting 10-35% of partial melting for the CS rocks (López-Moro et al., 2007; Villaseca et al., 2022), and $\approx 5\%$ partial melting for the AS mafic suites (Higueras, 1995; Higueras et al., 2013; Villaseca et al., 2022).

Legend for Fig. B and C

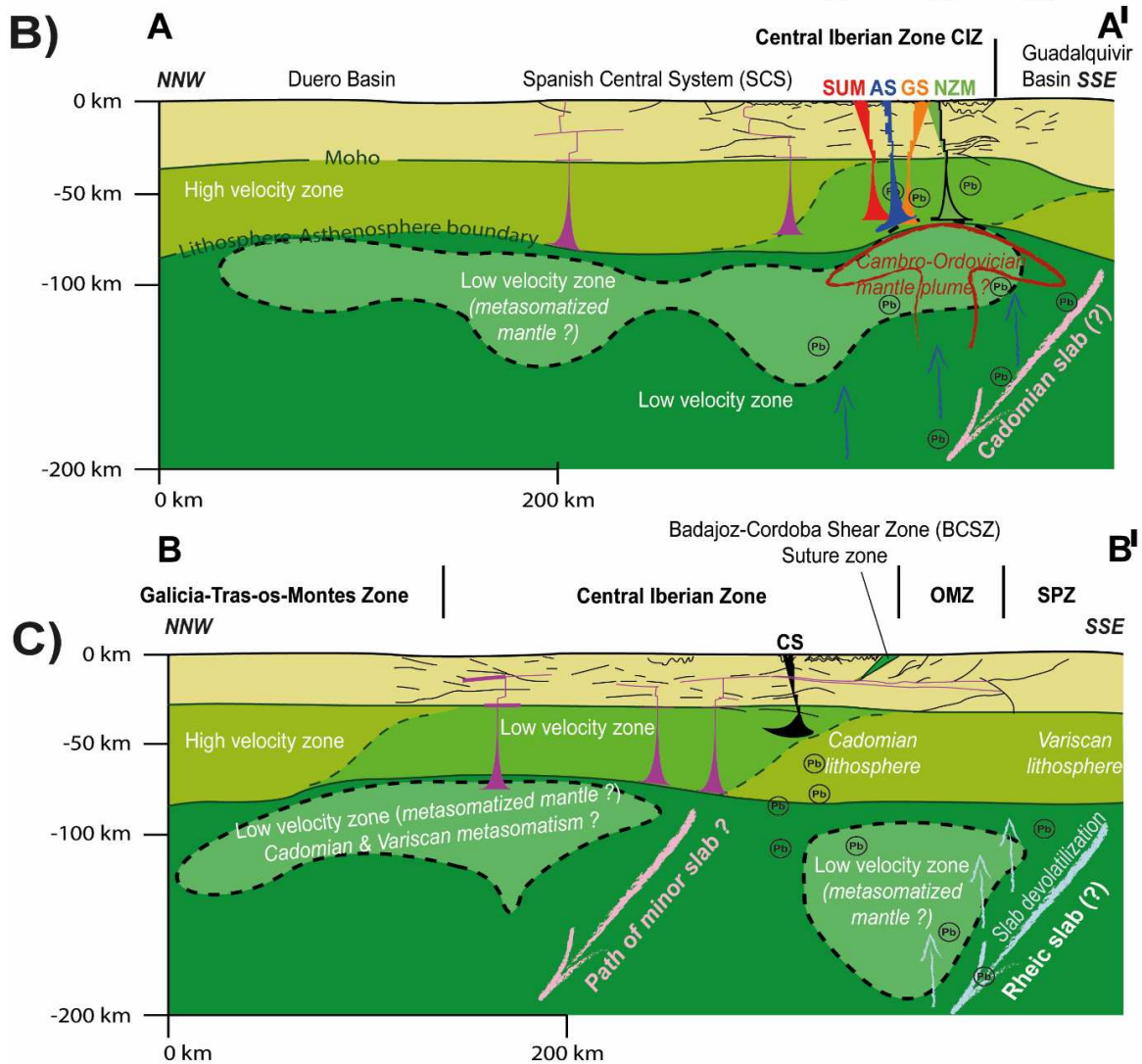
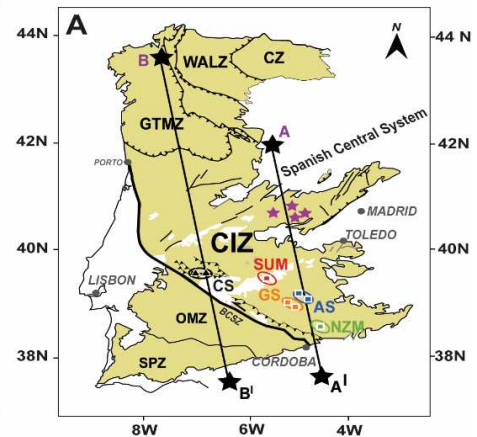
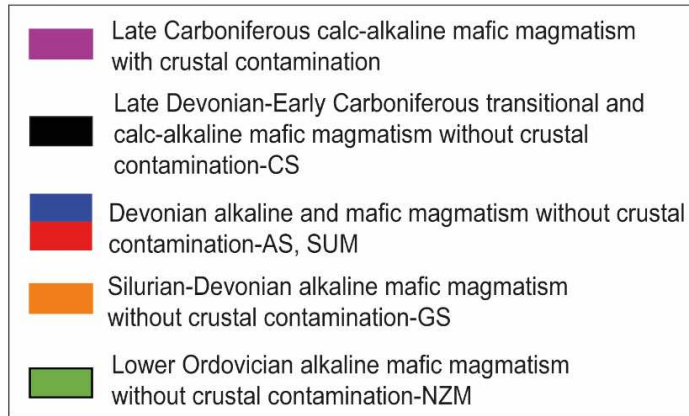


Figure 3. 25. Simplified model for the possible mantle sources of the mafic rocks from the CS, GS, AS, SUM and NZM. A) Simplified geological map of the Iberian Massif (Julivert et al., 1974; Simancas, 2019). Section traces, A-A' and B-B', are those of Palomeras et al. (2017), and only the part of section associated with our studies areas have been retain. B) AS and GS as well as their inferred mantle sources projected on a schematic cross section along the trace A-A'. C) Inferred mantle source of the CS projected on a schematic cross section

along the trace B-B^I. The high and low velocity zones in the mantle are based on the seismic velocity models from Palomeras et al. (2017). The crustal architecture is inspired on the IBERSEIS and ALCUDIA seismic profiles from Simancas et al. (2003; 2006) and Martínez Poyatos et al. (2012), respectively. Mantle plumes, and slabs inspired from the studies done by Azor et al. (2019); Cambeses et al. (2015); Martínez Catalán et al. (2009); Pereira et al. (2022); Rodríguez et al. (2022); Sarrionandia et al. (2023). The intrusions on the Spanish Central System were reported by Orejana et al. (2009) and Scarrow et al. (2009).

In the Nb/Yb and Th/Yb diagram (Pearce, 2008), the most altered samples with high LOI from CS lie into the same field compared to the less altered, supporting that the primary geochemical signatures related to immobile elements were preserved (Fig. 3.23). The mafic rocks from the CS reported by López-Moro et al. (2007) and most of the samples in this work, lie in the MORB-OIB array (Fig. 3.23), indicating an enriched mantle source with lower Nb/Yb and Th/Yb ratios, compared to those from the AS, GS, SUM and NZM (Fig. 3.23). This clear difference in the mantle source justifies treating the magmatism in the CS, AS, GS (second group of dolerites) and SUM as separate events, although their ages are overlapping within uncertainty. A subtle crustal contamination could also be supposed for the CS mafic rocks (Fig. 3.23). Nevertheless, crustal interaction seems to be of minor importance in the all studied areas compared to the rest of the mafic suites in the SCS (Fig. 3.23) emplaced during the last stages of the Variscan orogeny (Orejana et al., 2017; Scarrow et al., 2009).

Similarly to GS, AS, SUM and NZM samples, CS rocks show pronounced negative anomalies in K and Rb, and to a lesser extent in Ba, which were already observed in the CS rocks and attributed to hydrothermal and alteration effects (López-Moro et al., 2007). As for GS, AS, SUM and NZM samples, we relate the pronounced positive Pb anomaly shown by CS samples to a possible alteration effect rather than assimilation of country rocks. The metasomatized mantle source for the CS mafic rocks, could be interpreted as low velocity zones (Fig. 3.25C) in the seismic studies of Palomeras et al. (2017).

5.5-Concordance with local geological events in the Variscan belt: The Armorican Massif and the AS

Some of the ages of the dolerites in this study are coeval with both, the emplacement of mafic intrusions and Sb peak mineralization at about 360 Ma in the Armorican Massif, roughly 1000km to the NE from the CS, GS and AS (Fig. 3.1 and Fig. 3.22; Pochon et al., 2016, 2019). Based on this temporal correlation, we propose the existence of a widespread mafic magmatism that took place from the Upper Devonian to the Lower Mississippian in the CIZ and in the Armorican Massif. The rocks from the Armorican Massif present an enriched metasomatized mantle source with Nb/Yb-Th/Yb ratios similar to CS, and lower compared to the rocks from the AS, GS, SUM and NZM (Fig. 3.23). The mineral chemistry of the dated dolerites in the Armorican Massif (*e.g.* magmatic apatites; Pochon et al. 2016b) matches with the one documented for the CIZ mafic rocks in this study.

Regarding the geodynamic setting at large scale, the emplacement of the dolerites in the Armorican Massif was associated with a slab roll back, followed by a large scale astenospheric upwelling, which led to the partial melting of the Sub Continental Lithospheric Mantle, causing a crustal thinning and an extensional event in the external zone of the Variscan Belt (Central and North Armorican Domain) during a convergent geodynamic setting (Pochon, 2018). In this particular context, the Variscan front was situated in the future South Armorican Domain, a considerable distance (≈ 100 km) from the domains in which dolerites were emplaced (Pochon, 2018). In the case of the Iberian Massif, a slab break-off following oblique subduction for the Rheic ocean and the Variscan collision (late Devonian-early Carboniferous), is proposed for explaining the emplacement of large volumes of mafic magmas in the Ossa-Morena-Zone (*e.g.* Beja Igneous Complex; Pin et al., 2008) and the CIZ (*e.g.* IBERSEIS Reflective Body; Simancas *et al.*, 2003, 2006). This slab break-off hypothesis, may also have contributed to the

emplacement of some of the mafic intrusions reported in this study in the CS and AS, which are located ≈ 100 km from the Variscan front.

As mentioned above, Hg deposits have been identified in the AS. The mineralization of some of these deposits have been dated between 427 and 375 Ma, suggesting that they were emplaced in response to several mineralizing events over a period of 50 M.y (Hall et al., 1997; Higuera et al., 2013; Palero-Fernández et al., 2015; Palero & Lorenzo, 2009). Based on field studies, it was suggested that mafic volcanism was coeval with the Hg mineralization, possibly acting as the trigger for the hydrothermal activity leading to the formation of these deposits (Hernández et al., 1999; Higuera, 1995; Higuera et al., 2013). Our geochronological data confirms that the mafic magmatism was indeed active in the AS, GS and SUM during this period.

6-Link between mafic magmatism and Sb mineralization-Armorican Massif and CIZ.

In recent years, a possible relationship between mafic magmatism and Sb mineralization has been studied in the Armorican Massif and the CIZ (Campos Rodríguez et al., 2023; Chatelin, 2022; Pochon et al., 2016; Pochon, 2018; Pochon et al., 2018, 2019, 2023, 2024). In the Armorican Massif, a spatial and temporal correlation between Sb deposits and mafic rocks was proposed at *ca.* 360 Ma (Pochon, 2018; Pochon et al., 2016 a, b; 2018, 2019). It has been suggested that this temporal concordance might also imply a possible genetical link between mafic magmatism and ore forming processes in the Armorican Massif (Pochon, 2018; Pochon et al., 2018, 2019).

In the case of the CIZ, the mafic samples from the CS, GS, SUM and, NZM are spatially associated to Sb deposits. Furthermore, as shown in this chapter, some of our mafic rocks are temporally related to mafic intrusions and Sb deposits in the Armorican Massif. In the CS, a

hydrothermal event associated with mafic volcanism was proposed as a possible source for the mineralizing fluids that lead to the formation of Sb deposits in the area (Arribas & Gumiel, 1984). However, the lack of geochronological data for the Sb deposits in the CS makes the temporal and genetical link difficult to prove in this area.

The primary fluid inclusions (FI) in ilmenite in the mafic rocks of the Armorican Massif might represent a good example of magma degassing and volatile saturation at the magmatic-hydrothermal transition in highly crystallized mafic magmas (Chatelin, 2022; Pochon et al., 2023, 2024). The study of these FI could help to understand metal enrichment processes related to magmatic fluids (Chatelin, 2022; Pochon et al., 2023, 2024). Further studies are needed in order to better understand this phenomenon.

Conclusions

The LA-ICP-MS dating of apatite together with whole-rock geochemistry analyses helps in the understanding of the geochronological and geochemical characteristics of several intrusive mafic rocks across five different localities of the CIZ (GS, AS, SUM, NZM and CS). The alkaline basalts from the NZM, SUM, GS and AS were emplaced during at least three distinct events, the first one occurring approximately 480 Ma, the second at around 420 Ma ago and the third one between 387 ± 18 Ma and 360 ± 22 Ma. The basalts from the CS were emplaced between 359 ± 21 Ma and 332 ± 17 Ma and are related to a magmatism of transitional affinity. The Lower Ordovician age in the NZM is coeval within uncertainty with the beginning of the opening of the Rheic ocean. The Silurian to Lower Devonian age in the GS is consistent with the final stage of the same extensive event. The Lower Devonian to Carboniferous ages in the GS, AS, SUM and CS span from the subduction/closure of the Rheic ocean to the onset of the Variscan orogeny. This magmatism is related to local extensional settings, which has been documented at the southern part of the CIZ during the initial stage of the C1 collisional setting

of the Variscan orogeny. The AS, GS and SUM rocks are also coeval with Hg mineralization events documented in the AS during Silurian and Devonian periods (Higueras, 1995; Higueras et al., 2013; Higueras & Oyarzun, 2005; Palero-Fernández et al., 2015).

The Upper Devonian to early Carboniferous mafic suites in the GS, AS and CS coincide with the emplacement ages of several mafic rocks in the Armorican Massif (Pochon et al., 2016b), allowing us to propose that a widespread mafic magmatism took place in both domains (CIZ, Armorican Massif) at ca. 360-350 Ma.

According to this study, the alkaline mafic magmatism in the AS, GS, SUM and NZM may be related to a garnet-bearing enriched mantle source with no evidence of crustal recycling or contamination and a low degree of partial melting. The Upper Devonian to Carboniferous mafic magmatism in the CS seems to be associated with a more hydrous metasomatized source with garnet similar to the mafic suites of the Armorican Massif (Pochon et al., 2016). Furthermore, the lower LREE/HREE of the CS compared to GS, AS, SUM and NZM, might imply the highest degree of partial melting among all of the studied samples in this study. Additional geochemical analyses (e.g. isotope geochemistry) are crucial in order to better constrain the sources and the evolution of the Upper Devonian-lower Carboniferous mafic magmatism in the CIZ.

**CHAPTER 4: GEOCHEMICAL AND PALEOTHERMAL
CHARACTERIZATION OF SEDIMENTS AND
METASEDIMENTS AT THE CODOSERA SYNCLINE,
CENTRAL IBERIAN ZONE, SPAIN**

4.1-INTRODUCTION

Black shales and low grade metasedimentary rocks (such as slates or black schists, containing organic material) are known for being the source of several metalloids and metals including Sb, Au, As, Cu, among others (*e.g.* Bloomstein & Clark, 1989; Pitcairn et al., 2006; Pohl, 2011; Ridley, 2013).

One of the most common tools for understanding the thermal conditions of sediments and metasediments is the Raman Spectroscopy of Carbonaceous Material (RSCM). This method is based on the study of the carbonaceous material (CM), which is a common component in sedimentary (black shales) and metasedimentary rocks (slates, schists), and is the product of the diagenetic and metamorphic transformation of organic material initially present in the sediments (Beyssac et al., 2002; Lahfid et al., 2010). The RSCM directly studies the crystallinity of the CM, which is strongly controlled by temperature and pressure. Increasing temperatures and pressures increases the crystallinity of the CM until a final state where the CM is completely transformed into graphite in a process called graphitization (Beyssac et al., 2008; Lahfid et al., 2010). The RSCM method allows to correlate the Raman spectra of CM to temperature, by several empirical calibrations in a range of 200-650°C (Beyssac et al., 2002; Lahfid et al., 2010).

The RSCM method together with whole rock geochemistry have been applied for understanding geochemical and thermal evolution of metasedimentary sequences in different geological domains such as the Kodiak Complex in Alaska (Rajič et al., 2023), the Virginia Formation in the USA (Virtanen et al., 2024), (Virtanen et al., 2024), and the Massif Central in France (Montmartin et al., 2021).

In the Central Iberian Zone (CIZ), the geochemical and thermal characterization of metasedimentary rocks has been mostly performed in the high grade metamorphic areas of the N-NW, nearby the Galicia-Tras-Os-Montes-Zone and the Spanish Central System (Barbero, 1995; Barbero & Villaseca, 2000; Martínez Catalán et al., 2014; Villaseca et al., 2002). The thermal analyses have been mainly made using several thermometers such as garnet pyroxene, garnet-cordierite, or cordierite spinel thermometers (*e.g.* Toledo Anatetic Complex, Barbero, 1995; the Tormes Dome, Escuder Viruete et al., 1997; Guadarrama dome, Barbero & Villaseca, 2000; among others). Other methods, such as the study of paragenetic sequences and metamorphic reactions, have been used for determining pressure-temperature metamorphic conditions in low grade metamorphic areas in the CIZ (*e.g.* Almadén Syncline, Higuera et al., 1995).

The RSCM method has never been used in none of the metasedimentary sequences of the CIZ. The Palaeozoic sequence of La Codosera syncline (CS, Fig. 4.1) is essentially composed by slates, schists, sandstones, quartzites, greywackes and calcareous rocks, unconformably overlying the so-called Schist and Greywacke Complex of Late Precambrian age (Insua Marquez et al., 1990; Rodríguez González et al., 2007; San José et al., 1990; Santos García et al., 1990). Based on petrographical and mineralogical observations, the highest metamorphic degree reported in this area reaches the greenschist facies (López-Moro et al., 2005, 2007, 2020b; Santos Garcia & Casas Ruiz, 1979). The CS also hosts the biggest swarm of mafic sills (main study subject in this thesis, Chapter 3) reported in the Iberian Massif (López-Moro et al., 2007, 2020b) and one of the largest Sb-W mineralization in Spain (Arribas & Gumiel, 1984; Gumiel & Arribas, 1987). In the CS no geochemical data of the metasedimentary sequence has been published.

This work presents a geochemical and thermal characterization of the sedimentary/metasedimentary sequences of the CS, and their implications on both, the

formation of Sb deposits in the area as well as the U-Pb apatite dating of mafic sills in the CS (Chapter 3).

4.2-STUDY AREA AND SAMPLING

4.2.1-La Codosera Syncline

The study area is located within the CS between the Badajoz and Cáceres provinces, at the center the Extremadura region in the CIZ in Spain (Fig 4.1). It corresponds to a NE-SW trending structure extending over 100 km length and 10km width. The detailed geological setting of the studied area can be seen in the Chapter 2 of this thesis.

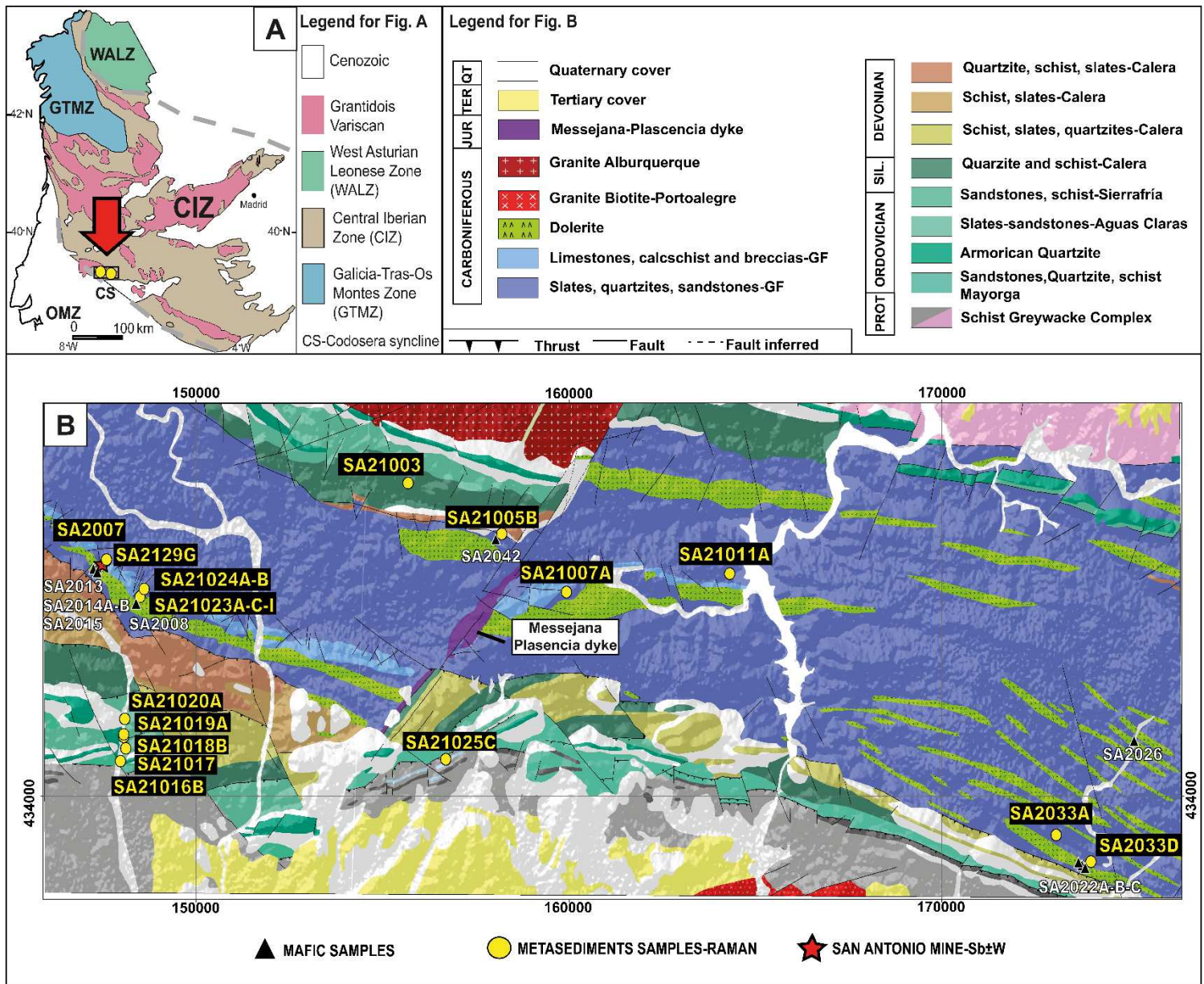


Figure 4. 1. Simplified geological map of the Iberian Massif showing the studied area of La Codocera syncline. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codocera syncline showing the Raman and mafic samples studied in this work. This map was designed based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).

In the CS several Palaeozoic units, unconformably overlying the Precambrian-Cambrian Schist Greywacke Complex (SGC; San José et al., 1990), have been described mainly based on the work done by Santos Garcia & Casas Ruiz (1979); Soldevila Bartolí (1992) and Rodríguez González et al. (2007). From the oldest to the youngest rocks, the Palaeozoic succession (Fig. 4.1 and Fig. 4.2) includes (Gumiel, 1982; Rodríguez González et al., 2007; Santos Garcia &

Casas Ruiz, 1979; Soldevila Bartolí, 1992): **i)** the Mayorga Unit, composed by sandstones, quartzites and schists of lower Ordovician age; **ii)** the Armorican Quartzite, essentially formed of orthoquartzites of lower Ordovician age; **iii)** the Aguas Claras Unit, 200m thick, consisting mainly of slates with some intercalations of sandstones levels; **iv)** the Sierra Fría Unit (SFU), upper Ordovician to lower Silurian, ~350m thick, composed by intercalations of sandstones, quartzites and schists/slates; **v)** the Calera Unit, essentially represented by slates/schists and quartzites and presenting an average thickness estimated at ~260m; **vi)** the Gévora Formation (GF), Lower Carboniferous (Mississippian), ~1200 m thick, consisting of slates, schists, calcareous breccias, limestones, sandstones and quartzites. Several mafic sills (studied in this thesis, Chapter 3) intrude this unit.

4.2.2-Sampling

Nineteen sedimentary and metasedimentary rocks (including black shales, slates and schists) were sampled in La Codosera syncline (Fig. 4.1 and Fig. 4.2), in order to understand the maximum paleotemperatures, their distribution and possible relationships with the mafic sills studied in this thesis (Chapter 3). We collected and analysed (Fig. 4.1 and Fig. 4.2): **i)** one sample (SA21025C) from the SGC of Precambrian-Cambrian age (Lotze, 1945); **ii)** six schists and slates samples (SA21003, SA21016B, SA21017, SA21018B, SA21019A, SA21020A) from the Sierra Fría Unit (SFU) of late Ordovician to Silurian age (Santos Garcia & Casas Ruiz, 1979; Soldevila Bartolí, 1992); **iii)** twelve slates, black shales and schists samples (SA2007, SA2033A, SA2033C, SA21005B, SA21007A, SA21011A, SA21023A, SA21023A, SA21023C, SA21023I, SA21024A, SA21024B and SA21023G) from the Gévora Formation (GF) of Lower Carboniferous age (Rodríguez González et al., 2007), hosting most of the mafic sills analysed in this thesis (Chapter 3).

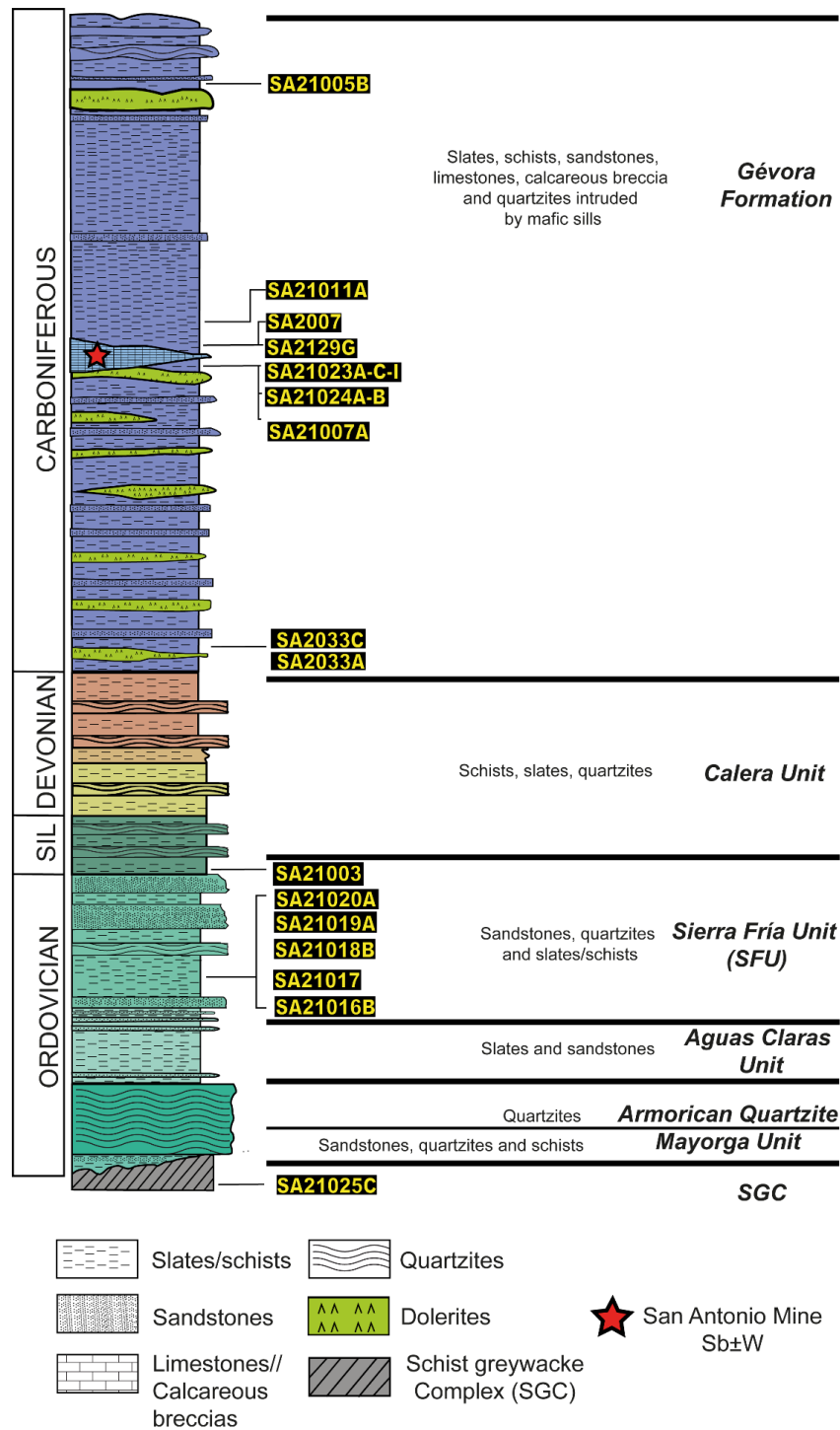


Figure 4. 2. Simplified stratigraphic column showing the Palaeozoic sequence of la Codosera Syncline and the samples studied by RAMAN spectroscopy in this chapter. This column was designed based on the sedimentary and stratigraphic studies done by Gumiel (1982); Rodríguez González et al. (2007); Santos Garcia & Casas Ruiz (1979); Soldevila Bartolí (1992).

4.3-ANALYTHICAL METHODS AND DATA PROCESSING

4.3.1-Petrography

In order to characterize the distribution of CM, we analysed 19 polished thick sections from the sedimentary/metasedimentary sequences of the CS using a Leica DMRX Microscope (coupled to the Archimed software from Microvision Instruments for image acquisition). Other mineral phases were also characterized for better understanding the metamorphic conditions in the CS. These analyses were performed at the Institut des Sciences de la Terre (ISTO) facilities in Orléans, France.

4.3.2-Scanning Electronic Microscope (SEM)

Qualitative phase identification was carried out using a Scanning Electron Microscope (SEM) *Merlin Compact ZEISS* at the Institut des Sciences de la Terre (ISTO) in Orléans France. The SEM was operated at 15KV, it was provided with an energy-dispersive X-ray spectrum analyser (EDS) Bruker QUANTAX-XFlash6-30mm²-resolution 129eV, and a Micro XRF Bruker (XTRACE-Tube Rh-Filters Al, Ti, Ni). The results were analyzed using ESPRIT Software.

4.3.3-Raman spectroscopy of carbonaceous material (RSCM)

In order to determine the paleotemperatures in the CS and to better understand their distribution, thick polished sections (200µm) from 19 metasedimentary rocks were analysed using RSCM. This method uses empirical correlations in order to match the maximum heating temperature with the Raman spectra in a specific range of 200-650°C (Beyssac et al., 2002; Lahfid et al., 2010). The temperature experienced by the organic material is related to its crystallinity, which in turn is strongly related to the transformation of CM into graphite (Beyssac et al., 2002; Lahfid et al., 2010). This will be reflected in the wavenumber and the quantity of peaks in the Raman spectra. The characteristic Raman bands for CM are between 1100-1800cm⁻¹ and 2500-

3100cm⁻¹ (Beyssac et al., 2002; Lahfid et al., 2010). All data presented in this work are for the 1100-1800cm⁻¹ region as these peaks are relevant for the RSCM thermometers in this study.

The Raman measurements were performed using a Renishaw inVia reflex system at the CEMHTI laboratory at the CNRS campus in Orléans, France. The calibration of the machine was carried out using an internal silica standard (wavenumber 520.4cm⁻¹). The power of the argon-ion laser source of 514.5nm was set to <1mW at the sample surface. A Leica DM2500 optical microscope with an 100x objective was coupled with the laser. A CCD NIR/UV detector was used for analyzing the signal. Ten to twelve Raman measurements were taken for each thick polished section with an exposure time of 15 seconds and 15 accumulations. In order to avoid the mechanical damage produced during the preparation and polishing of the thick sections, all of the measurements were carried out on CM located on the subsurface of quartz grains. The processing of all the Raman spectra was carried out using the PeakFit 4.12 software.

Raman spectra in this work is processed with two methods: the calibration of Lahfid et al. (2010), is generally used for low temperatures, whereas the calibration of Beyssac et al. (2002), is used for organic material with higher crystallinity.

The Lahfid et al. (2010) method is decomposed into 5 bands, all of them present a defined position within the wavenumber of the Raman shift: D1 (1350cm⁻¹), D2 (1620cm⁻¹), D3 (1515cm⁻¹), D4 (1250cm⁻¹) and G (1590cm⁻¹) (Lahfid et al., 2010; Sadezky et al., 2005). The shapes, sizes, and positions of the peaks were defined using the Lorentz function. The temperature is obtained using the following formula $T\text{ }^{\circ}\text{C} = RA1 - 0.3758 / 0.0008$ where $RA1 = D1 + D4 / D1 + D2 + D3 + D4 + G$. This formula can be applied in a temperature range between 200°C and 320°C with an uncertainty of ±50°C (Lahfid et al., 2010).

The samples with higher crystallinity present less Raman peaks and are treated with the method proposed by Beyssac et al. (2002). In this method, the measured spectrum is

deconvoluted into 3 bands, which are calculated using the Voigt function. The temperature is calculated using the following linear parametrization: $T\text{ }^{\circ}\text{C} = -445 \cdot R2 + 641$ where $R2 = D1 / (D1 + D2 + G)$. This estimation is effective within a temperature range between 330-650 °C with an uncertainty of $\pm 50\text{ }^{\circ}\text{C}$ (Beyssac et al., 2002).

In order to perform a proper calibration, both authors compared their methods to several geothermometers. The Lahfid et al. (2010) method used quartz-chlorite thermometry, fluid inclusions and calcite-dolomite thermometry. The Beyssac et al. (2002) method was calibrated based on mineral assemblages.

4.3.4-Whole rock geochemistry analyses

Whole rock geochemistry analyses of the 19 CS metasedimentary rocks were performed at ALS laboratories in Dublin (Ireland). The samples were crushed using a riffle splitter and the pieces were sieved to < 2mm fraction with 70 % passing rate. The pieces were pulverized to <75µm using a low chromium steel ring mill. To measure total S, the pulverized samples were inductively heated and analyzed with infrared spectroscopy (IR). For determining non-carbonate carbon, 0.1g of sample was boiled at high temperature in a beaker with 25% HCl for one hour in order to expel carbonates in the form of CO₂. Using a filtering crucible, the solution was filtered and the remainder was analyzed by induction furnace and infrared spectroscopy for determining non-carbonate carbon. For other analyses, the samples powders were fused using lithium borate (LiBO₂). For the major element measurements, the fused samples were digested in acid before analyzing it with inductively coupled plasma atomic emissions spectrometry (ICP-AES). For most of the trace elements, the same acid solution was used but the measurements were done using inductively coupled plasma-mass spectrometry (ICP-MS). The base metals (Ag, Cd, Co, Cu, Li, Mo, Ni, Pb, Sc, Zn) were digested from the fused samples using a four-acid solution and measured with the ICP-MS. Aqua regia digestion of the fused

samples was done to measure As, Bi, Hg, In, Re, Sb, Se, Te and Tl, with the ICP-MS. In-house quality control samples and duplicate measurements of the samples were used to evaluate the precision of the data. The precision for most of the major elements is <2% with the exceptions of Fe₂O₃ (<3%), MnO (<7%) and P₂O₅ (<8%). For most of the trace elements, the precision is <5% with the exception of Cs, Eu, Ga, Lu, Ta, Tm, Yb (precision <10%) as well as Cd and Pb (precision <22%). The whole rock geochemistry analyses with the detection limits for the samples in this study can be found in Supplementary material 1 and 2.

4.3.5- Electro probe micro analyses

Electro Probe Micro Analyses (EPMA) of sulfide minerals were performed with a Cameca SXFive at the analytical laboratory of the Institut des Sciences de la Terre (ISTO) in Orléans, France. The elements analyzed were S, Fe, As, Ni, Cu, Zn, Co, Pb, Si and Sb. Operating conditions were 20 kV accelerating voltage and 30 nA beam current.

4.4-RESULTS

4.4.1-Petrography and phase identification

The slates and schist from the SGC, the SFU and the GF present massive and laminated sections with variable contents of CM and other mineral phases such as pyrite, chalcopyrite, Fe-oxides as well as silicates and carbonates (Figs. 4.3, 4.4 and 4.5).

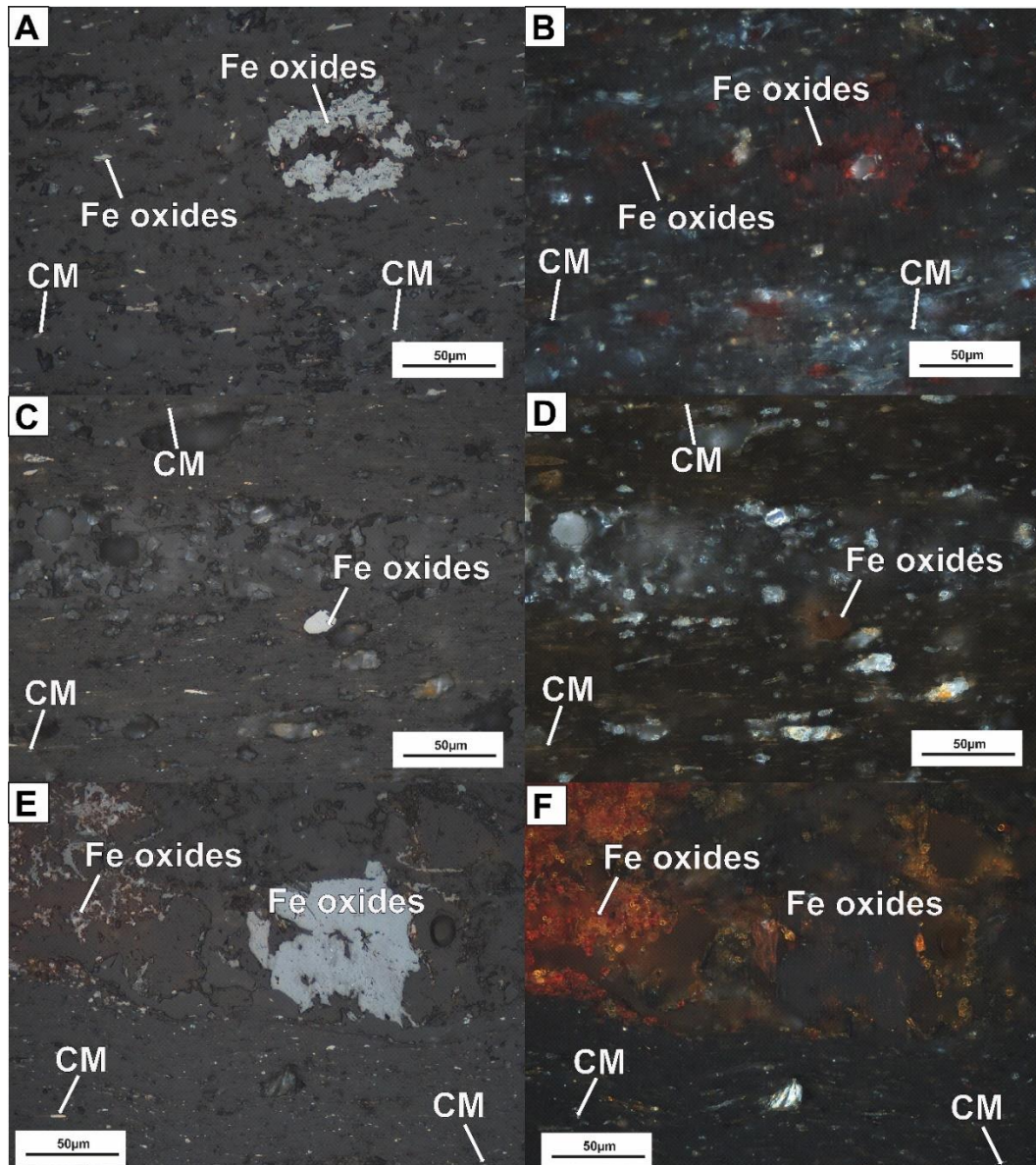


Figure 4. 3. Thin section micro-photographs in reflected light showing the distribution of the carbonaceous material (CM) and the main characteristics of the samples from the Sierra Fría Unit (SFU). All of the samples present OM and Fe-Oxides evenly distributed in the groundmass. A-B) Sample SA21016B (PPL-XPL); C-D) Sample SA21018B (PPL-XPL); E-F) Sample SA21020A (PPL-XPL).

In the case of the SGC and the SFU, the CM is presented as micron-scale interstitial flakes evenly dispersed in the groundmass (Fig. 4.3).

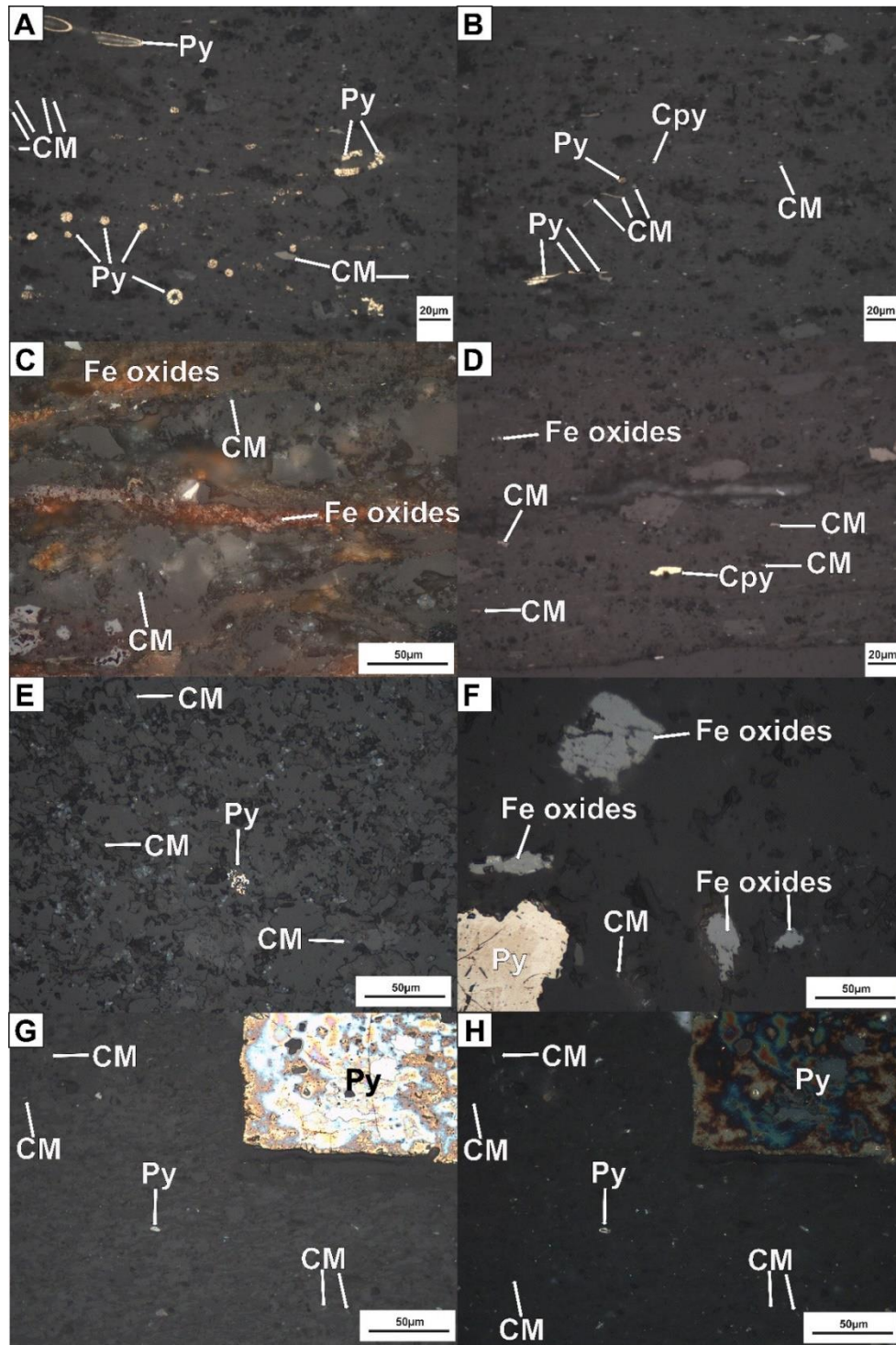


Figure 4. 4. Thin section micro-photographs in reflected light showing the distribution of the organic material (OM) and the main characteristics of the samples from the Gévora Formation (GF). All of the samples present OM, Fe-Oxides and sulfides evenly distributed in the groundmass. A-B) Sample SA2007 (PPL); C) Sample SA21023A (PPL); D) Sample SA21024A (PPL); E) Sample SA21029G (PPL); F) Sample SA2033A (PPL); G-H) Sample SA2033C (PPL-XPL).

The main mineral phases observed in reflected light of the SGC and the SFU are represented by Fe-oxides (Fig. 4.3), mainly hematite (Figs. 4.3E-F), present either as small individual grains dispersed in the groundmass or massive grains and aggregates. No sulfides were observed. Quartz, chlorite, muscovite, rutile and monazite were also identified (Figs. 4.5A, B and C).

Regarding the Carboniferous sequence, the slates of the GF exhibit CM dispersed in the groundmass in the form of interstitial micro-scale flakes (Fig. 4.4). These samples also present hematite as main Fe-oxides. Compared to the SGC and the SFU, the GF shows abundant sulfides, mainly represented by pyrite (Figs. 4.4A, E, F, G, and H) and lesser amounts of chalcopyrite (Fig. 4.4D). The pyrites are observed as framboidal (Fig. 4.4A and E) or large euhedral grains ($>100\mu\text{m}$; Fig. 4.4F, G and H), which are ubiquitously disseminated in the groundmass. The massive euhedral pyrites were only observed at the eastern part of La Codosera syncline (SA2033A and SA2033C). The framboidal ones were observed in the samples from the western part of the structure, close to the San Antonio Mine. Chalcopyrite is sparse and is present as small grains within the groundmass (Fig. 4.4D).

The GF samples are composed by quartz, chlorite, muscovite, calcite, apatite, galena (only found in the samples from the San Antonio Mine) and monazite (Figs. 4.5D, E and F).

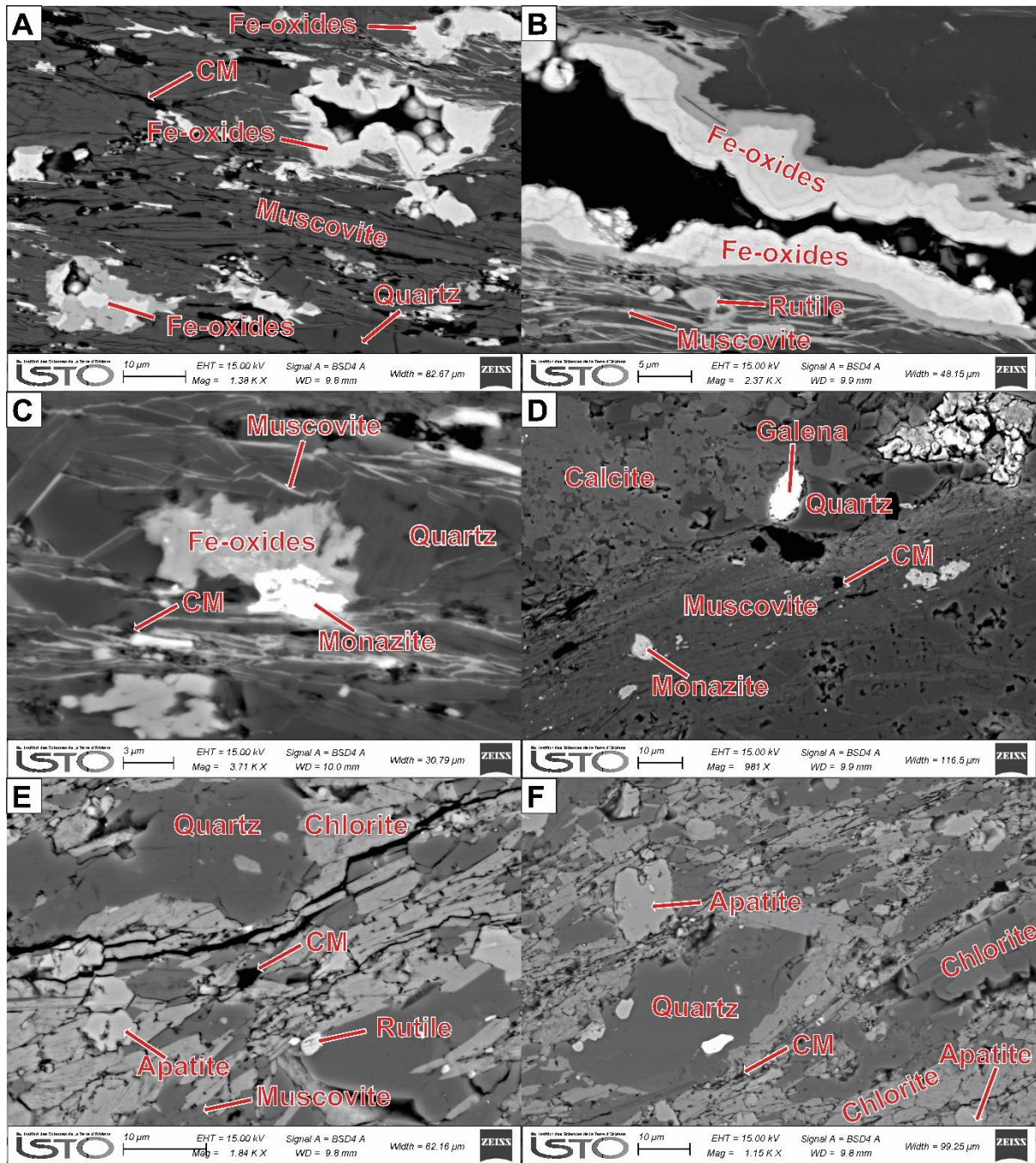


Figure 4. 5. SEM imaging showing the main phases found for the rocks of: A) SFU: Fe oxides, muscovite and quartz; B) SFU: Fe oxides, Rutile and muscovite; C) SFU: Fe oxides, muscovite, quartz and monazite; D) GF: Calcite, galena, quartz, muscovite and monazite; E) GF: Quartz, chlorite, apatite, muscovite and rutile; F) GF: Quartz, chlorite and apatite. CM=Carbonaceous Material

4.4.2-Whole rock geochemistry analyses-Sb distribution in the CS

Whole rock geochemistry analyses were carried out in order to better characterize the CS sedimentary/metasedimentary sequences as well as to understand the distribution of the Sb in the structure. The results can be seen in Tables 4.1 and 4.2.

Table 4. 1. Whole-rock geochemistry for the studied sedimentary/metasedimentary rocks from the Codosera syncline. SGC: Schist Greywacke Complex; SFU: Sierra Fría Unit; GF: Gévora Formation.

WHOLE ROCK GEOCHEMISTRY ANALYSES-CS SEDIMENTARY/METASEDIMENTARY SAMPLES											
Latitude	39.149096°	39.203910°	39.145236°	39.147623°	39.150283°	39.150634°	39.153659°	39.184647°	39.184566°	39.134519°	
Longitude	-6.972226°	-6.987034°	-7.073104°	-7.071964°	-7.072358°	-7.072452°	-7.072153°	-7.080013°	-7.079462°	-6.771801°	
Sample	SA21025C	SA21003	SA21016B	SA21017	SA21018B	SA21019A	SA21020A	SA2007	SA21029G	SA2033A	
Description	Schist	Schist	Slate	Schist	Schist	Schist	Schist	Schist	Slate	Slate	
Age Unit	Precambrian	Ordovician	Ordovician	Ordovician	Ordovician	Ordovician	Ordovician	Carboniferous	Carboniferous	Carboniferous	
	SGC	SFU	SFU	SFU	SFU	SFU	SFU	GF	GF	GF	
SiO ₂	54.3	52.5	57.2	55.8	62.6	59.9	55.6	76.5	65.2	40.6	
Al ₂ O ₃	22.3	22.5	20.9	20.6	23.1	21.3	27	1.94	2.72	15.05	
Fe ₂ O ₃	8.06	9.24	8.13	11.65	1.56	7.13	3.35	2.46	1.36	26.5	
CaO	1	0.15	0.55	0.03	0.05	0.02	0.06	4.06	16.25	3.17	
MgO	1.28	1.14	1	0.22	0.65	0.52	0.71	2.29	0.83	4.12	
Na ₂ O	1.12	0.43	0.8	0.69	0.45	0.33	1.5	0.06	0.02	0.07	
K ₂ O	3.05	4.78	3.84	3.83	3.7	5.69	4.25	0.37	0.74	0.17	
Cr ₂ O ₃	0.016	0.016	0.015	0.014	0.018	0.014	0.019	0.003	<0.002	0.011	
TiO ₂	1.11	0.97	1.06	1	1.18	1.11	1.17	0.05	0.1	0.76	
MnO	0.05	0.03	0.02	<0.01	<0.01	<0.01	0.01	0.1	0.09	0.4	
P ₂ O ₅	0.82	0.18	0.17	0.16	0.02	0.22	0.06	0.12	0.03	2.31	
SrO	0.01	<0.01	0.02	0.02	0.02	0.01	0.02	<0.01	0.03	0.01	
BaO	0.08	0.09	0.08	0.08	0.15	0.13	0.1	<0.01	0.01	<0.01	
LOI	6.03	8.69	5.62	6.32	5.97	4.98	6.33	5.96	14.2	8.76	
Total	99.23	100.72	99.41	100.41	99.47	101.35	100.18	93.91	101.58	101.93	
C %	0.09	0.93	0.4	0.41	0.2	0.28	0.23	1.52	3.83	0.93	
S %	<0.01	<0.01	0.01	0.01	0.01	<0.01	<0.01	2.34	0.02	4.07	
H ₂ O %	1.26	2.19	1.1	1.03	1	0.99	1.26	0.56	0.5	0.83	
C organic%	0.09	0.75	0.34	0.32	0.11	0.15	0.17	0.07	0.05	0.79	
Ba (ppm)	679	812	712	702	1365	1210	894	37.3	103	23	
Ce (ppm)	191.5	120	118.5	45	122.5	133.5	137	11.1	18.3	50.5	
Cr	117	121	110	96	130	104	150	15	17	77	
Cs	4.72	11.4	7.46	5.5	12.6	6.37	9.31	1.8	1.27	0.55	
Dy	15.9	6.32	9.42	5.24	8.42	8.76	8.98	1.23	1.73	6.94	
Er	9.11	3.44	4.44	3.03	4.37	4.14	4.3	0.61	1.24	2.99	
Eu	3.91	1.83	2.22	1.08	2.33	2.32	3.03	0.35	0.34	1.7	
Ga	27.9	31	29.2	28	37	30.6	37.6	2.9	4.1	23.9	
Gd	19.75	7.8	10.35	4.29	9.07	9.13	12.55	1.74	1.85	7.45	
Ge	2.3	1.8	1.3	1.1	1.7	1.2	1.6	4.6	1.1	1.5	
Hf	6.01	3.89	4.92	4.72	5.1	7.07	3.91	0.63	0.46	3.41	
Ho	2.96	1.18	1.84	1.1	1.62	1.51	1.69	0.22	0.32	1.34	
La	91.8	60.4	55.8	24.6	60.1	63.4	72.8	9.4	13	24.2	
Lu	0.96	0.51	0.6	0.5	0.71	0.66	0.65	0.1	0.14	0.39	
Nb	21	18.8	20.2	19.35	25.7	21.9	22.6	1	1.98	15.8	
Nd	90.1	51.6	53.9	21.3	55.9	56	73.7	7	11.3	26.7	
Pr	20.6	13.95	13.85	5.69	15	15.1	18.7	1.66	2.73	6.35	
Rb	137.5	185	177.5	158	186.5	233	198	21.1	30.7	9.2	
Sm	17.85	9.49	12	4.34	10.9	11.25	15.45	1.86	1.88	6.81	
Sn	4.6	3.7	4.3	3.7	5.1	4.3	4.7	1.6	0.8	1.4	
Sr	123	63.4	137.5	104.5	192.5	70.4	191.5	46.3	311	71.8	
Ta	9.5	1.2	1.4	1.2	2.3	1.7	1.7	<0.1	0.1	1	
Tb	3	1.1	1.69	0.85	1.52	1.44	1.7	0.23	0.28	1.22	
Th	18	20.5	17.85	18.25	15.7	21.1	22.1	1.54	2.25	13.05	
Tm	1.16	0.51	0.72	0.5	0.69	0.71	0.68	0.07	0.17	0.44	
U	3.54	4.3	8.6	4.5	6.56	18.55	2.33	0.66	1.03	4.55	
V	152	172	129	117	264	125	159	18	28	132	
W	2.9	2	1.8	1.8	3	4.4	2.5	0.9	1	1.8	
Y	93.8	31.4	49.4	28.7	44.2	43.3	45.8	7.9	12	32.4	
Yb	6.74	3.38	4.23	3.08	4.49	4.12	4.04	0.57	0.96	2.38	
Zr	224	145	183	171	178	269	134	29	21	123	
As	0.7	8.4	2.5	12.4	17.4	29.6	1.3	12.4	20.5	35.7	
Bi	0.03	0.46	0.31	0.28	0.3	0.13	0.37	0.03	0.12	0.95	
Hg	0.01	0.018	0.017	0.037	0.078	0.039	0.025	0.063	0.575	0.117	
In	0.041	0.01	0.016	0.013	0.014	0.013	0.013	0.012	0.016	0.058	
Re	<0.001	<0.001	0.001	0.001	0.001	0.002	<0.001	0.001	0.002	0.001	
Sb	1.04	2.02	7.19	0.68	4.65	6.6	0.46	>250	30.9	52.3	
Se	<0.2	0.3	1.1	0.4	5.9	3.9	<0.2	0.3	0.4	5.8	
Te	0.01	0.04	0.03	0.03	0.07	0.01	0.03	0.01	0.03	0.22	
Tl	0.07	0.43	0.06	0.04	0.6	0.08	0.05	0.04	0.04	0.02	
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.3	
Co	18	13	9	6	5	1	5	<1	6	47	
Cu	17	46	34	64	31	23	20	7	16	123	
Li	100	30	50	20	20	10	170	30	<10	330	
Mo	<1	1	1	<1	17	1	1	1	1	1	
Ni	42	44	28	32	33	32	33	5	18	65	
Pb	8	30	18	40	9	14	27	2	8	24	
Sc	20	21	17	17	22	17	24	3	3	8	
Zn	98	120	69	82	47	80	90	53	43	283	

Chapter 4

Table 4. 2. Whole-rock geochemistry for the studied sedimentary/metasedimentary rocks from the Codosera syncline. GF: Gévora Formation.

WHOLE ROCK GEOCHEMISTRY ANALYSES-CS SEDIMENTARY/METASEDIMENTARY SAMPLES									
Latitude	39.140077°	39.194831°	39.183763°	39.189118°	39.177502°	39.177502°	39.177502°	39.179747°	39.179747°
Longitude	-6.782568°	-6.957381°	-6.936769°	-6.886495°	-7.069058°	-7.069058°	-7.069058°	-7.067522°	-7.067522°
Sample	SA2033C	SA21005B	SA21007A	SA21011A	SA21023A	SA21023C	SA21023I	SA21024A	SA21024B
Description	Slate	Schist	Slate	Schist	Schist	Schist	Schist	Schist	Schist
Age Unit	Carboniferous	Carboniferous	Carboniferous	Carboniferous	Carboniferous	Carboniferous	Carboniferous	Carboniferous	Carboniferous
	GF	GF	GF	GF	GF	GF	GF	GF	GF
SiO ₂	34.8	55.2	62.6	62.5	73.6	68.7	63	61.9	61.3
Al ₂ O ₃	11.6	21.1	20.4	18.65	13.55	13.5	17.7	20	20.4
Fe ₂ O ₃	27.5	8.05	4.92	8.36	6.33	7.46	8.4	6.39	6.4
CaO	3.4	0.35	0.44	0.12	0.05	0.46	0.27	0.12	0.19
MgO	3.13	1.01	1.7	1.75	0.73	0.26	0.86	1.42	1.4
Na ₂ O	0.1	0.21	1.08	1.02	0.68	1.04	0.29	1.06	1.08
K ₂ O	0.4	3.65	3.24	2.99	1.4	1.96	3.69	2.64	2.68
Cr ₂ O ₃	0.008	0.017	0.014	0.014	0.008	0.01	0.017	0.014	0.014
TiO ₂	0.55	0.85	0.81	0.83	0.64	0.63	0.9	0.78	0.8
MnO	0.29	0.03	0.05	0.03	0.02	1.53	0.02	0.12	0.07
P ₂ O ₅	2.48	0.17	0.06	0.13	0.08	0.26	0.2	0.05	0.05
SrO	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.02	0.03
BaO	0.01	0.05	0.04	0.05	0.03	0.05	0.09	0.04	0.04
LOI	13.75	9.56	5.85	5.36	4.79	4.79	5.83	6.07	6.59
Total	98.03	100.26	101.23	101.81	101.92	100.66	101.28	100.62	101.04
C %	0.84	0.15	0.89	0.11	0.08	0.06	0.17	1.01	1.06
S %	13.35	0.04	0.06	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
H ₂ O %	0.93	3.83	0.8	0.96	1.33	1.09	1.76	1.49	1.03
C organic%	0.68	0.17	0.61	0.06	0.08	0.05	0.11	0.78	0.86
Ba (ppm)	45.6	460	354	474	222	392	752	333	356
Ce (ppm)	71.1	111	98.3	88.7	59.1	80.1	47	88.6	89.8
Cr	54	116	99	103	42	66	119	91	95
Cs	1	8.16	6.2	5.27	2.34	6.37	6.44	9.58	10.25
Dy	7.86	6.43	4.98	4.96	4.03	6.94	4.05	5.63	5.29
Er	3.1	3.48	2.68	2.65	2.2	3.43	2.52	2.85	2.87
Eu	2.03	1.56	1.26	1.34	0.89	1.92	0.86	1.19	1.2
Ga	17.3	28.7	27.6	25.7	16	20.6	23.1	27.2	29.3
Gd	8.86	7.46	5.07	5.54	4.01	8.97	3.66	5.7	5.73
Ge	0.8	1.4	1.3	1.4	1.3	0.7	0.6	1.4	1.2
Hf	2.5	3.68	3.95	4.26	6.48	3.58	5.59	3.35	3.21
Ho	1.41	1.3	0.98	0.97	0.81	1.4	0.92	1.07	1.1
La	33.8	53.9	49.5	43.5	27.4	37.9	27.3	45.3	47.2
Lu	0.34	0.55	0.39	0.4	0.34	0.46	0.46	0.48	0.47
Nb	11.25	17.4	18.7	15.85	13.15	11.55	18	16.15	16.9
Nd	37.2	43.5	41.4	36.4	24.5	36.4	20	37	37.7
Pr	8.69	12.3	11.4	10	6.77	9.2	5.71	10.25	10.5
Rb	19.8	143.5	136	135.5	63.2	82.5	138	124	130
Sm	9.15	8.43	6.42	7.14	4.58	8.3	3.75	6.62	7.42
Sn	1.2	2	3.8	3.7	2.4	2.8	3.9	3.8	4.1
Sr	68.3	85.9	277	87.2	65.4	110.5	51.5	190.5	194.5
Ta	1	1.1	1.5	9.5	0.9	0.8	1.2	1.2	1.1
Tb	1.4	1.16	0.86	0.87	0.68	1.26	0.69	1.01	0.95
Th	11.15	18.15	14.85	15.2	10.75	10.15	14.9	14.4	15
Tm	0.43	0.56	0.41	0.45	0.35	0.54	0.46	0.45	0.45
U	5.34	3.08	2.46	3.02	1.78	1.72	2.44	2.39	2.4
V	101	218	187	163	89	142	185	179	186
W	1.4	2	2.2	2.2	1.6	1.6	1.6	2.3	2.3
Y	36.1	35.3	26.7	26.9	20.7	38.8	24.7	27.3	27.3
Yb	2.26	3.49	2.56	2.7	2.17	3.13	2.82	2.6	2.77
Zr	91	135	144	151	246	135	207	118	119
As	148	79.9	6.4	22.2	5.6	78	18.4	35.8	25.1
Bi	2.53	0.06	0.22	0.21	0.11	0.27	0.35	0.18	0.1
Hg	0.216	0.011	0.066	0.037	0.057	0.051	0.072	0.058	0.038
In	0.071	0.008	0.033	0.023	0.029	0.049	0.054	0.054	0.04
Re	0.006	<0.001	0.002	<0.001	<0.001	<0.001	0.001	0.001	0.001
Sb	>250	3.57	2.84	1.53	0.72	2.75	2.83	1.77	1.29
Se	16.2	0.2	<0.2	<0.2	0.2	0.2	1.9	0.2	0.2
Te	0.7	0.07	0.08	0.04	0.03	0.07	0.14	0.1	0.04
Tl	0.05	0.51	0.05	0.07	0.03	0.12	0.06	0.06	0.05
Ag	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	2.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Co	97	14	12	10	10	27	7	21	8
Cu	350	62	77	21	17	27	42	86	64
Li	230	50	90	100	360	30	30	80	80
Mo	2	1	<1	<1	<1	1	1	1	1
Ni	90	53	73	49	64	50	34	85	74
Pb	57	3	14	18	13	36	26	17	9
Sc	7	19	15	14	9	13	15	16	15
Zn	328	61	155	118	138	110	132	180	137

The whole rock geochemistry analyses of the CS sedimentary/metasedimentary sequences show several differences among the SGC, the SFU and the GF (Fig 4.6). GF samples are extremely heterogeneous for most major elements, except Fe_2O_3 (Fig 4.6). In particular, the GF is highly heterogeneous in terms of SiO_2 , showing values between 34.8-76.5 wt%, whereas the SGC-SFU are relatively homogeneous ranging between 52.5-62.6 wt% (Fig. 4.6A). Regarding Al_2O_3 (Fig. 4.6B), the GF shows a more heterogeneous distribution and lower contents (1.94-20.4 wt%) compared to the SGC-SFU (20.6-27 wt%). The Fe_2O_3 values (Fig 4.6C) exhibit a slightly higher median for the SGC-SFU (8.06 wt%) rocks compared to the GF rocks (6.93 wt%). The CaO values (Fig 4.6D) are more heterogeneous for the GF (0.05-16.25 wt%) in comparison to the SGC-SFU (0.02-1 wt%). The GF rocks presents an important heterogeneity in terms of sulfur (0.01-13.35 wt%, Fig. 4.6E), whereas all of the SGC-SFU rocks show 0.01 wt% of Sulfur. Nevertheless, the median values for both sequences are almost similar (Median: GF=0.015 wt%S; SGC-SFU=0.01wt%S). Regarding the distribution of the organic carbon (Fig. 4.6F), the GF presents a higher heterogeneity and relatively higher values, although the median is slightly lower compared to the SGC-SFU (Median: GF=0.14 wt%; SGC-SFU=0.17 wt%).

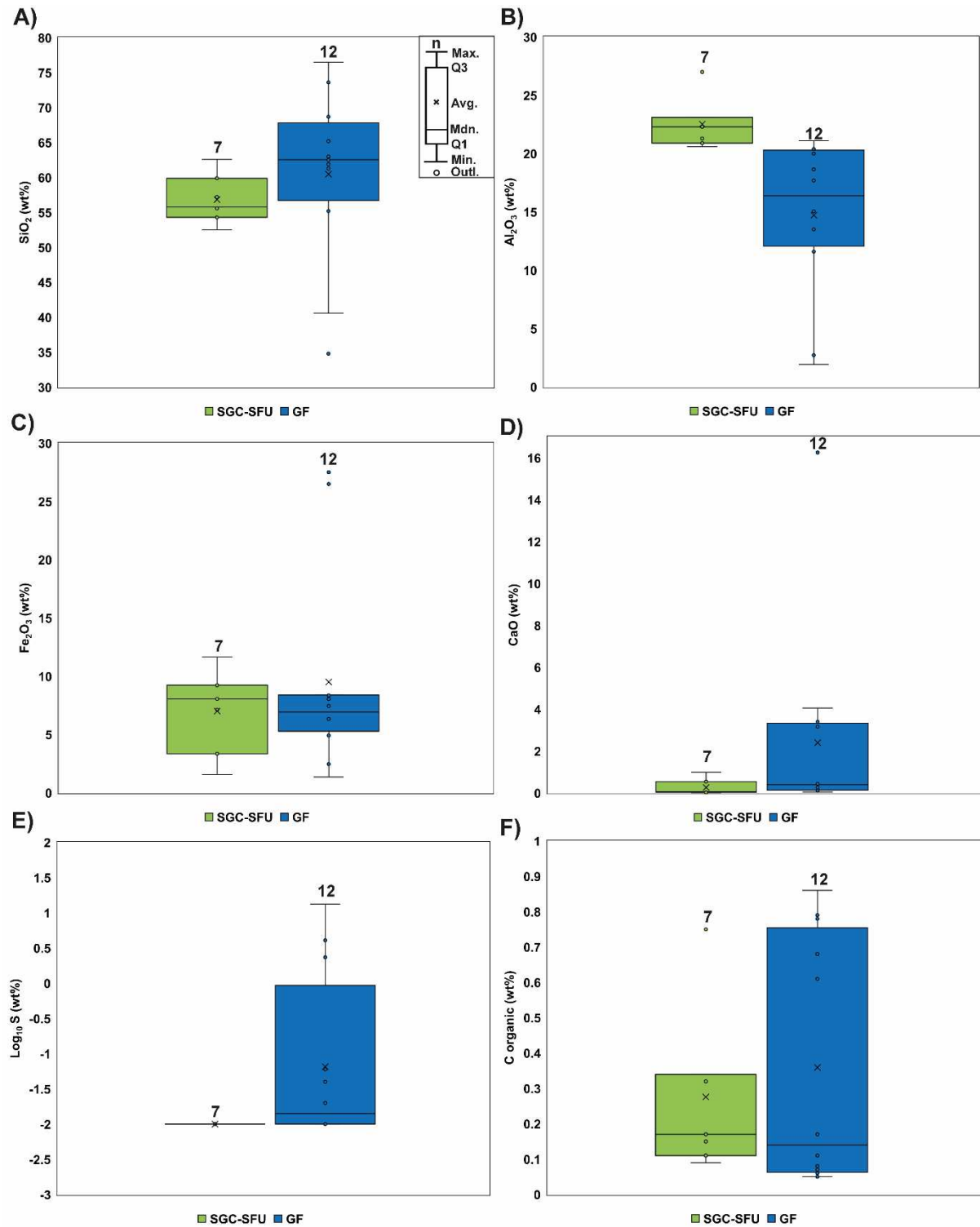


Figure 4. 6. Whisker plots showing the data distribution of SiO₂ (A), Al₂O₃ (B), Fe₂O₃ (C), CaO (D), Log₁₀S (E) and C organic (F) for the SGC-SFU and the GF samples in this study. Legend: SGC = Schist Greywacke

Complex; SFU = Sierra Fría Unit; GF = Gévora Formation; n = number of measurements; AVG = average; Mdn = Median; Q1 = first quartile; Q3 = third quartile; Max = maximum value; Min = Minimum value; Out = outlier.

4.4.2.1- Antimony in the SGC, SFU and the GF

The Sb amounts in the CS are highly variable showing values ranging from 0.72ppm up to >250ppm (Fig. 4.7). The higher values (>250ppm) are observed in the GF at the western (San Antonio Mine, Sb-W) and eastern part (Villar del Rey Quarry) of the CS.

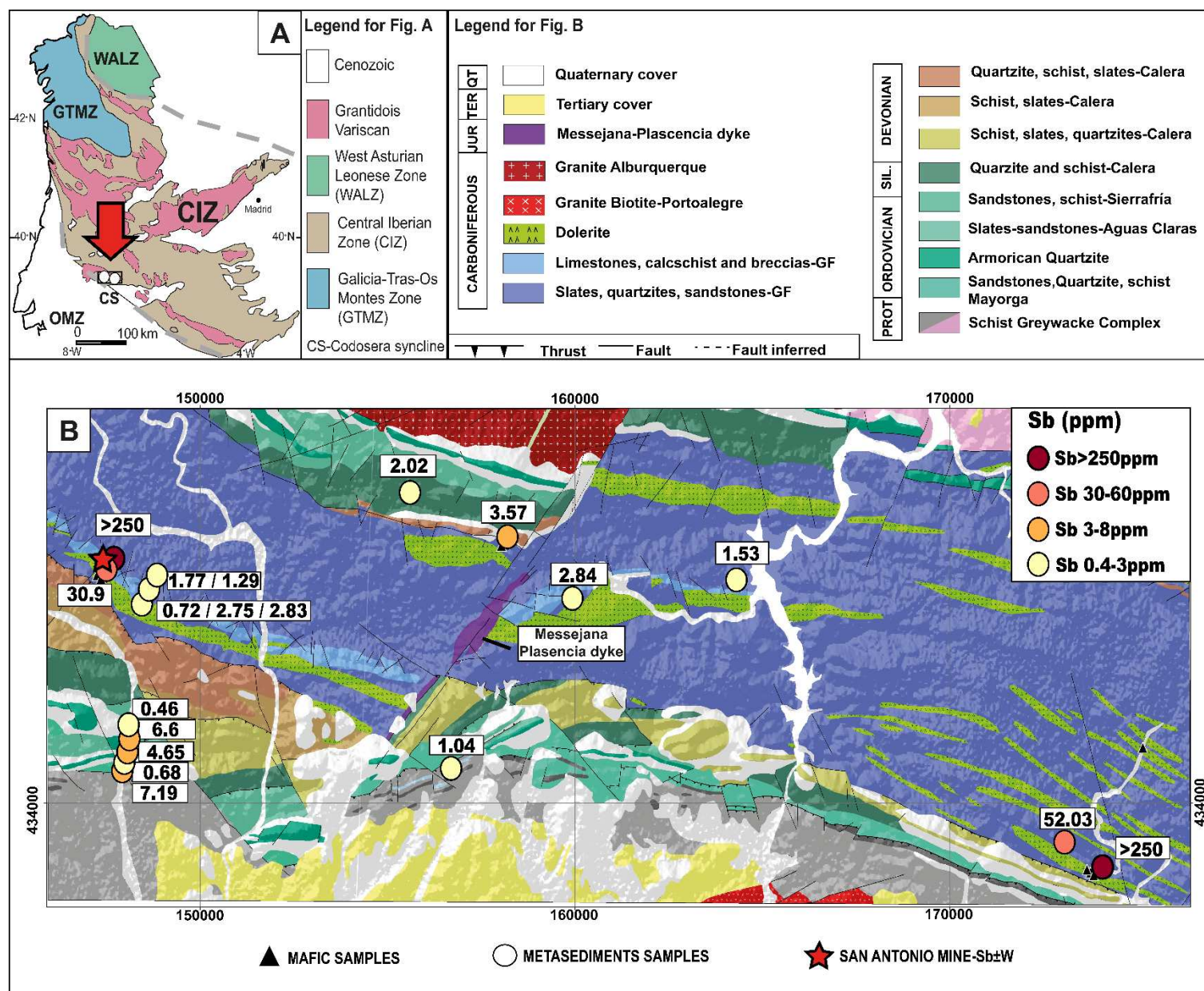


Figure 4. 7. Sb distribution in the CS. The higher values of Sb are found at the western (San Antonio Mine, Sb-W) and eastern part (Villar del Rey Quarry) of the CS.

Several correlations diagrams were made in order to understand if the Sb is related to any element in the CS area (Fig. 4.8), but they do not show any clear correlation either with major elements (Fig 4.8) or with trace elements (Fig 4.9). Only sulfur seems to show a correlation with Sb for both SFU and GF samples (Fig 4.8E), although the S content of GF is highly heterogeneous (Fig 4.6E).

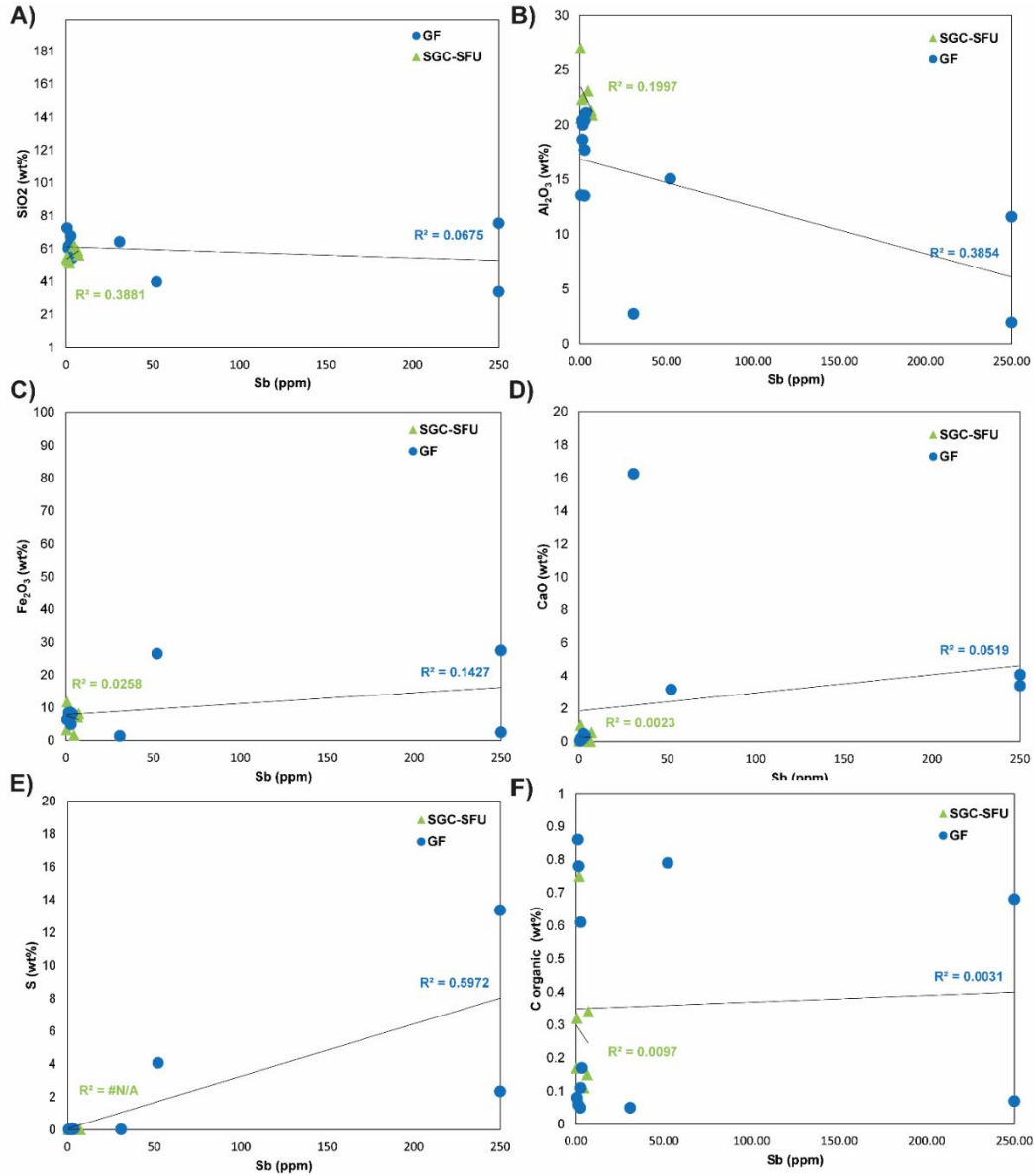


Figure 4. 8. Sb correlation diagrams with SiO₂ (A), Al₂O₃ (B), Fe₂O₃ (C), CaO (D), S (E) and C organic (F), for the SGC-SFU and GF samples in this study.

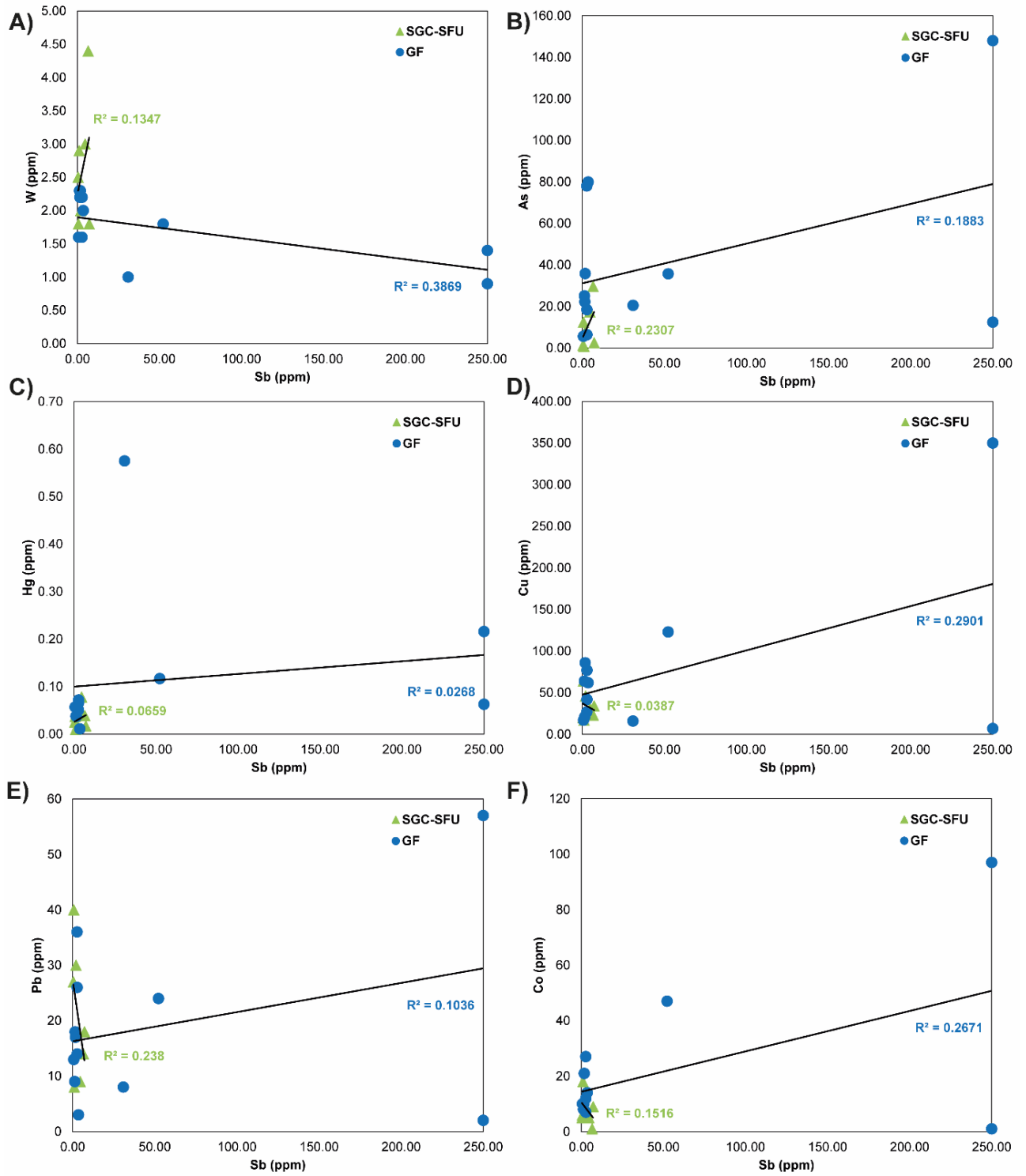


Figure 4. 9. Sb correlation diagrams with W, As, Hg, Cu, Pb and Co for the SGC-SFU and GF samples in this study.

4.4.3-Sb contents of sulfide minerals

Major element composition of pyrite and sphalerite within samples SA2033C and SA2033A were analyzed by EMPA and are reported in Table 4.3. Both samples contain millimetric pyrite crystals, which are larger and contain numerous sphalerite and galena inclusions in sample SA2033C (Fig. 4.4 G, H). Ni, Cu, Zn and Sb contents in pyrite were below detection limits (shown in Table 4.3), as well as As, Ni, Cu and Sb contents in sphalerite. Galena inclusions were too small to be analyzed. The Sb contents of these sulfide phases are always lower than 300 ppm.

Table 4. 3. EMPA of pyrite and sphalerite in samples SA2033A and SA2033C

Sample	N° analyses	S wt%	Fe wt%	As wt%	Ni	Cu	Zn	Sb	Total wt%
SA2033A pyrite	5	54.23 ± 0.17	46.96 ± 0.15	0.06 ± 0.01	<350 ppm	<450 ppm	<500 ppm	<300 ppm	101.30 ± 0.23
SA2033C pyrite	11	54.13 ± 0.20	46.89 ± 0.13	0.06 ± 0.03	<350 ppm	<450 ppm	<500 ppm	<300 ppm	101.12 ± 0.22
SA2033C sphalerite	2	33.80 ± 0.06	8.05 ± 0.50	<400 ppm	<350 ppm	<450 ppm	58.85 ± 2.24	<300 ppm	100.79 ± 1.60

4.4.4-RSCM-TEMPERATURES

The RSCM analyses showed three bands for ten samples and five bands for the rest of the studied metasedimentary rocks. Considering this, both RSCM methods, high and low temperature, were used in order to estimate the temperatures in the studied area. The samples showing three bands were treated using the high temperature method of Beyssac et al. (2002), whereas the ones exhibiting five bands were treated with the low temperature method of Lahfid et al. (2010). All of the results obtained with both RSCM methods are reported in Table 4.3.

Table 4. 4. RSCM temperatures results obtained with Beyssac et al. (2002) and Lahfid et al. (2010). HT: High temperature; LT: Low temperature; SD: Standard Deviation; SGC: Schist Greywacke Complex; SFU: Sierra Fría Unit; GF: Gévora Formation.

Sample	Coordinates		Description	Age	Unit	Method	RA1 or R2	T°C	SD	N
	Latitude	Longitude								
SA21025C	39.149096°	-6.972226°	Schist	Precambrian	SGC	HT	0.59	380	20.05	7
SA21003	39.203910°	-6.987034°	Schist	Ordovician	SFU	HT	0.15	575	27.66	12
SA21016B	39.145236°	-7.073104°	Slate	Ordovician	SFU	HT	0.61	367	8.71	13
SA21017	39.147623°	-7.071964°	Schist	Ordovician	SFU	HT	0.60	373	5.79	14
SA21018B	39.150283°	-7.072358°	Schist	Ordovician	SFU	HT	0.57	388	9.97	12
SA21019A	39.150634°	-7.072452°	Schist	Ordovician	SFU	HT	0.62	366	5.96	14

Chapter 4

SA21020A	39.153659°	-7.072153°	Schist	Ordovician	SFU	HT	0.58	382	15.55	12
SA2007	39.184647°	-7.080013°	Schist-San Antonio Mine	Carboniferous	GF	LT	0.58	274	23.53	10
SA21029G	39.184566°	-7.079462°	Slate- San Antonio Mine	Carboniferous	GF	LT	0.64	327	15.69	10
SA2033A	39.134519°	-6.771801°	Slate Quarry	Carboniferous	GF	HT	0.61	370	13.27	13
SA2033C	39.140077°	-6.782568°	Slate sulphides Quarry	Carboniferous	GF	HT	0.60	372	14.37	12
SA21005B	39.194831°	-6.957381°	Schist-Albuquerque	Carboniferous	GF	HT	0.20	557	31.63	12
SA21007A	39.183763°	-6.936769°	Slate	Carboniferous	GF	LT	0.62	303	6.92	13
SA21011A	39.189118°	-6.886495°	Schist	Carboniferous	GF	LT	0.58	251	19.17	9
SA21023A	39.177502°	-7.069058°	Schist	Carboniferous	GF	LT	0.54	212	66.96	10
SA21023C	39.177502°	-7.069058°	Schist	Carboniferous	GF	LT	0.61	327	4.39	9
SA21023I	39.177502°	-7.069058°	Schist	Carboniferous	GF	LT	0.65	336	57.36	9
SA21024A	39.179747°	-7.067522°	Schist	Carboniferous	GF	LT	0.62	306	7.03	14
SA21024B	39.179747°	-7.067522°	Schist	Carboniferous	GF	LT	0.60	280	22.17	13

4.4.4.1-Schist Greywacke

Complex (Precambrian-Cambrian) and Unidad de Sierra Fría (Ordovician)

Average temperatures were calculated for one sample from the SGC (SA21003) and six from the SFU (SA21003, SA21016B, SA21017, SA21018B, SA21019A, SA21020A). Eighty four spectra from both, the Precambrian and Ordovician sequences, were treated with the high

temperature method from

Beyssac et al. (2002). The

calculated temperatures range between 366°C and 575°C (Fig. 4.10). Overall, the CM is structurally homogeneous as shown by the standard deviation of the calculated temperatures (Table 4.3).

4.4.4.2-Gévora Formation

Average temperatures were calculated for the samples from the Gévora Formation (SA2007, SA2033A, SA2033D, SA21005B, SA21007A, SA21011A, SA21023A, SA21023A, SA21023C, SA21023I, SA21024A, SA21024B and SA21023G). Ninety seven spectra were

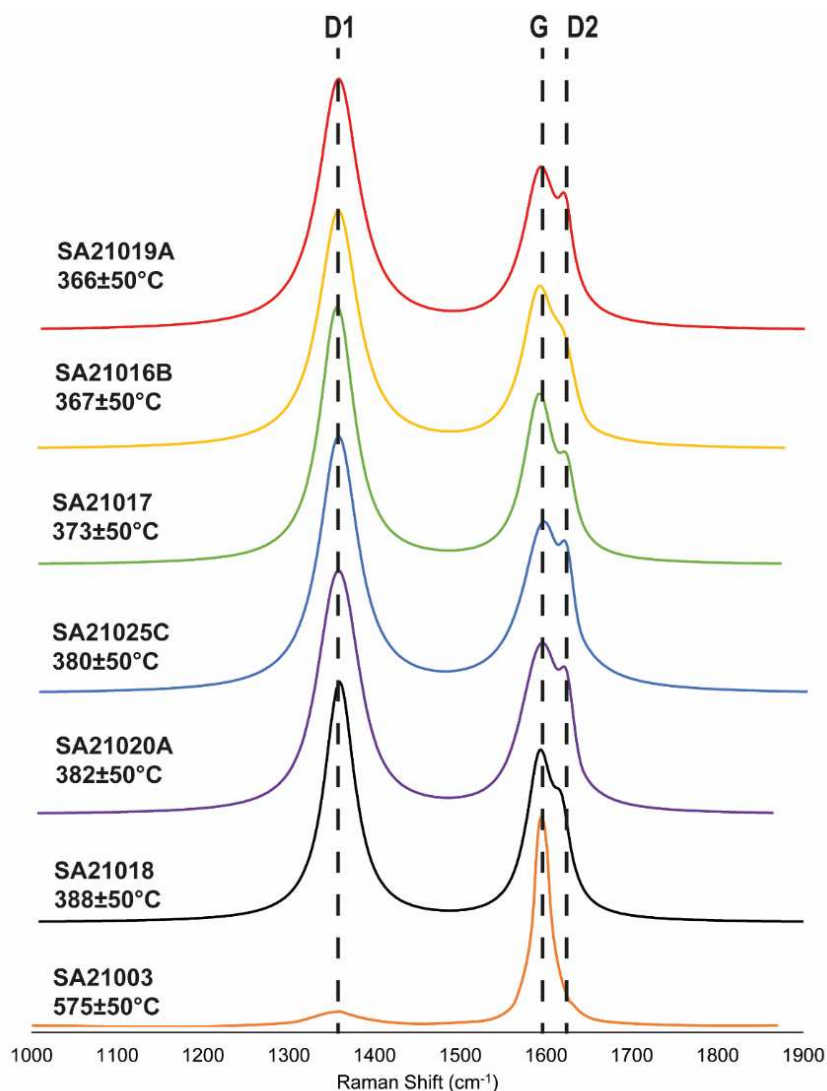


Figure 4. 10. Representative Raman spectra of the SGC and the Sierra Fría Unit samples shown together with the approximate positions of the G, D1 and D2 peaks. The temperatures were calculated using the high temperature method from Beyssac et al. (2002)

processed with the low temperature method of Lahfid et al. (2010) and thirty seven spectra with the higher temperature method of Beyssac et al. (2002).

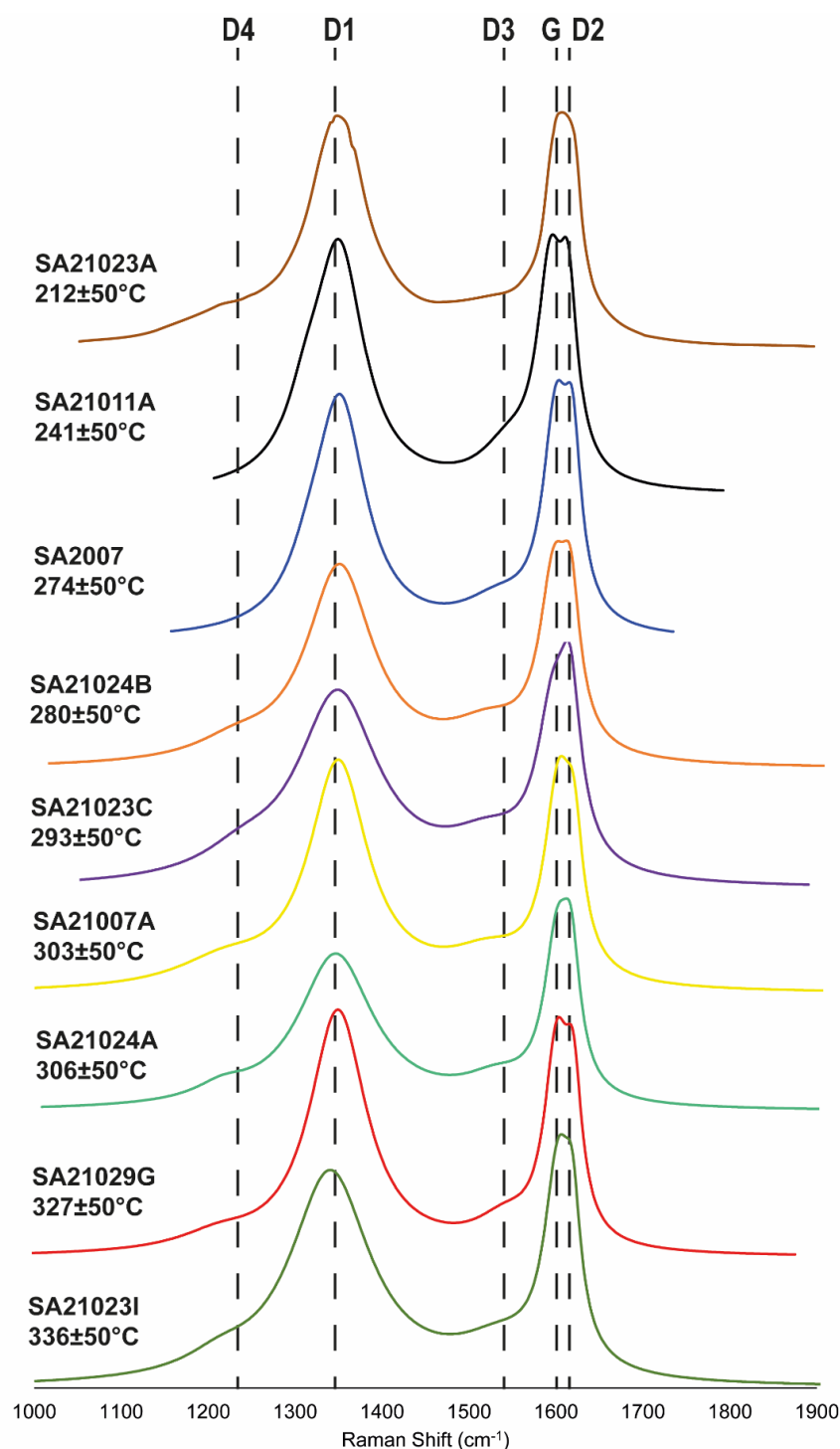


Figure 4. 11. Representative Raman spectra of the GF samples shown together with the approximate positions of the G, D1, D2, D3 and D4 peaks. The temperatures were calculated using the low temperature method from Lahfid et al. (2010).

The temperatures calculated with the method of Lahfid et al. (2010) range between 212°C and 336°C (Fig. 4.11), whereas the ones obtained with the method of Beyssac et al. (2002) range between 370°C and 557°C (Fig. 4.12). The highest temperature obtained (557°C) for the black shales and schists of the Gévora Formation is for the SA21005B sample, which is located between a mafic intrusion and the Alburquerque granite (Fig. 4.1B).

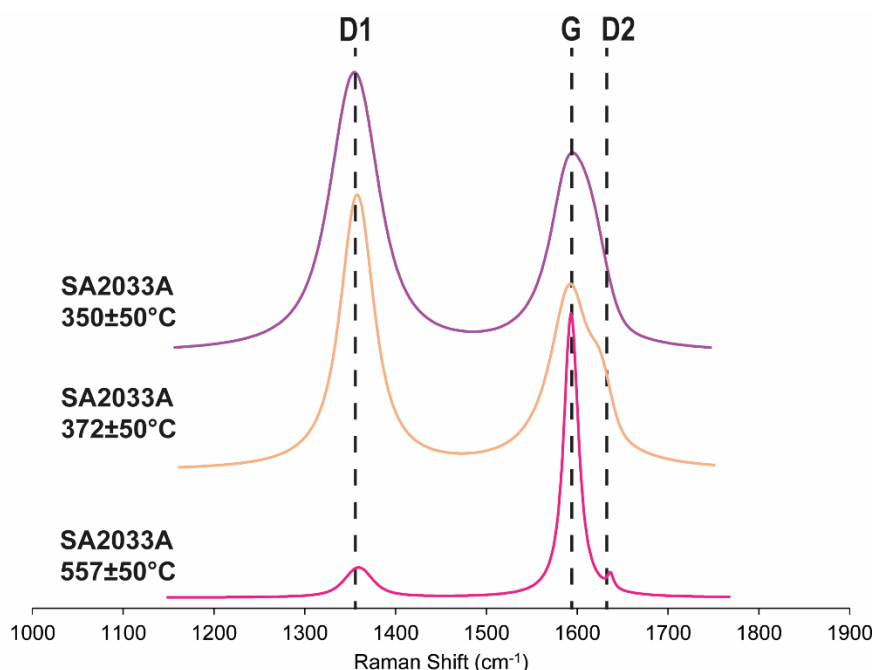


Figure 4. 12. Representative Raman spectra of the GF samples shown together with the approximate positions of the G, D1, D2, D3 and D4 peaks. The temperatures were calculated using the high temperature method from Beyssac et al. (2002)

4.5-DISCUSSION

4.5.1-Geochemistry of the CS sequences

The heterogeneity of the SiO₂, Al₂O₃, CaO and Sulfur in the GF could be related to the higher presence of silicates, carbonates and sulfides in some samples. The SiO₂, Al₂O₃ may be associated to higher amounts of quartz and micas, both observed in petrographic analyses. The highest CaO value consistent with the petrographic observations showing important amounts

of calcite in one sample coming from the San Antonio Mine (SA21029G). The higher sulfur contents are present in the samples coming from the eastern part of the CS (SA2033A and SA2033C), where the highest amounts of pyrite among the GF samples were observed. These two samples present also the highest concentration of organic carbon. None of these variations seems to univocally control the Sb content of the metasedimentary rocks (Fig. 4.8).

4.5.1.1- Sb distribution in the CS

In the CS, the highest Sb values are found in the GF at the western and eastern part of the structure. The samples with high Sb values taken at the western part (SA2007 and SA21029G) come from the San Antonio Mine (Sb $\pm$ W), therefore the Sb contents might be related to Sb the presence of Sb sulfides or oxides. At the eastern part, the samples with high Sb (SA2033A and SA2033C) come from the Villar del Rey Quarry, here no Sb mineralization has been reported and no Sb sulphides or oxides were observed. These samples present the highest amounts of sulfur, which could be related with the Sb-S correlation observed for the GF rocks. No Sb-bearing phase was identified with SEM observations and analyses. Electron probe microanalyses indicate that the Sb contents of pyrite and its sphalerite inclusions are lower than 300ppm in these samples, suggesting that pyrite cannot be the main Sb-bearing mineral. The organic carbon in this part of the structure is also high, nevertheless no hypothesis can be proposed in this case since there is no clear correlation between Sb and organic carbon.

4.5.1.2-Comparison between Sb values in the CS and Sb global contents in black shales

Overall, the CS rocks, especially the ones coming from the GF, seem to be slightly more enriched compared to global data of Pre and post-Cambrian shales (Fig. 4.13). These data include shales from Canada, China, USA and India, and derives from 8 publications (Fan et al., 2004; Goodfellow et al., 2009; Manikyamba et al., 2008; Manikyamba & Kerrich, 2006; Orberger et al., 2007; Pašava et al., 2008; Turner & Kamber, 2012; Xu et al., 2013). The median value for the GF rocks (Med=2.85) is higher compared to the SGC-SFU (Med=2.02) and the

global black shales (Med=2.01). The higher Sb contents measured in GF samples are comparable to the highest values observed worldwide (Fig. 4.13). These extremely high values were measured in the Lower Cambrian black shales of the Niutitang Formation in south and southwest China, in which Sb is hosted within complex intergrowths of sulfides and carbonaceous matter (Orberger et al., 2007; Pašava et al., 2008; Xu et al., 2013). In these black shales, Sb enrichment is syn-sedimentary and originates from anoxic seawater, possibly mixed with hydrothermal fluids (Orberger et al., 2007 and references therein).

As no Sb-bearing minerals were identified in La Codosera samples, it is impossible to assess if the Sb-enrichment of these rocks is pristine and therefore predates magma emplacement or is due to metamorphic processes that occurred after magma intrusion.

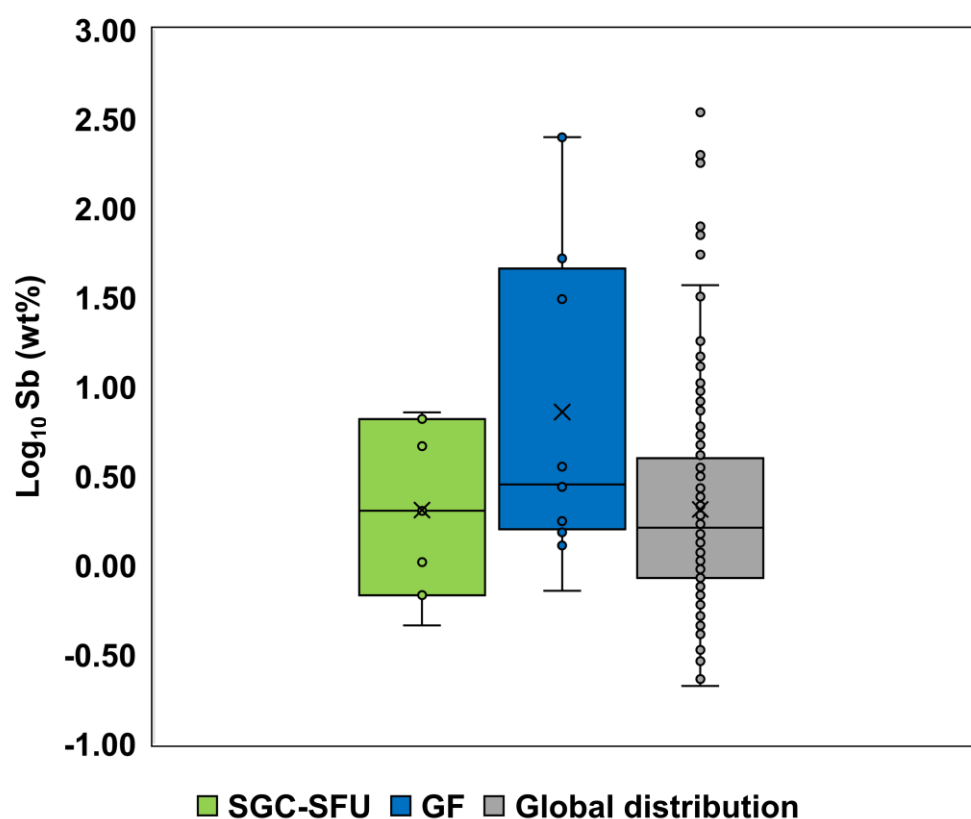


Figure 4. 13. Whisker plots showing the Sb data distribution for the SGC-SFU, the GF compared to global data of Pre and post-Cambrian shales (Fig. 4.13). These data include shales from Canada, China, USA and India, and

derives from 8 publications (Fan et al., 2004; Goodfellow et al., 2009; Manikyamba et al., 2008; Manikyamba & Kerrich, 2006; Orberger et al., 2007; Pašava et al., 2008; Turner & Kamber, 2012; Xu et al., 2013).

4.5.2-RSCM temperatures in the CS

According to this study, the distribution of the temperatures within the CS varies depending on the age of the metasediments and their sampling location within the syncline structure. The Precambrian SGC sample and all samples from the Ordovician-Silurian SFU sequence have peak metamorphic temperatures in the range of 365-390°C, which are indistinguishable within the uncertainty of the RSCM geothermometer of $\pm 50^\circ\text{C}$. The temperatures of the Carboniferous succession seem to be lower at the western part of the CS (210-340°C, increasing from S to N, Fig. 4.14) and higher at south-eastern part of the structure (370°C, Fig 4.14). This thermal feature could be explained by the higher presence of mafic sills in this part of the CS. Overall, the GF shows lower temperatures compared to the Sierra Fría Unit (Fig. 4.14).

During the Cenozoic the North Badajoz thrust fault was responsible for the uplifting of the eastern part of the CS (De Vicente et al., 2011). This event could have led to the outcropping of deeper structural levels of the CS, which could also justify the greater presence of mafic sills and several thrust faults top N in the area (Fig. 4.14).

The two highest temperatures in this study were found at the northern part of the CS in the SFU (575°C -SA21003 and 557°C-SA21005B, Fig. 4.14). These values exceed the limit of greenschist facies, and can be explained by a possible contact metamorphism effect related to their close spatial relationship with both the late Variscan Albuquerque granite (309-306 Ma; Solá et al., 2009) and a mafic body of ~1km wide (Fig. 4.14).

4.5.3-Implications of the RSCM metamorphic temperatures in the apatite dating of mafic rocks in the CIZ

It is well known that the classic closure temperature range of the apatite is found between 375-550°C (Dodson, 1973; Webster & Piccoli, 2015). Nevertheless, more recent studies allowed to determine a higher closing temperature range of 770-870°C based on the fast cooling rate and thickness of several mafic sills in the Armorican Massif (Pochon et al., 2016b). Considering that the thickness of each studied sill in this thesis is relatively small and the fact that these mafic bodies underwent a very fast cooling and solidification (Chapter 3), we can use the higher closure apatite temperature range of 770-870°C from Pochon et al. (2016). Based on this, the RSCM temperatures found for most the metasedimentary rocks of the CS (ranging between 212-370°C) together with the low-grade metamorphism reported in the studied area (see Chapter 2), support the hypothesis that the isotopic system of the dated apatites was not reset after the intrusion of the mafic sills

Chapter 4

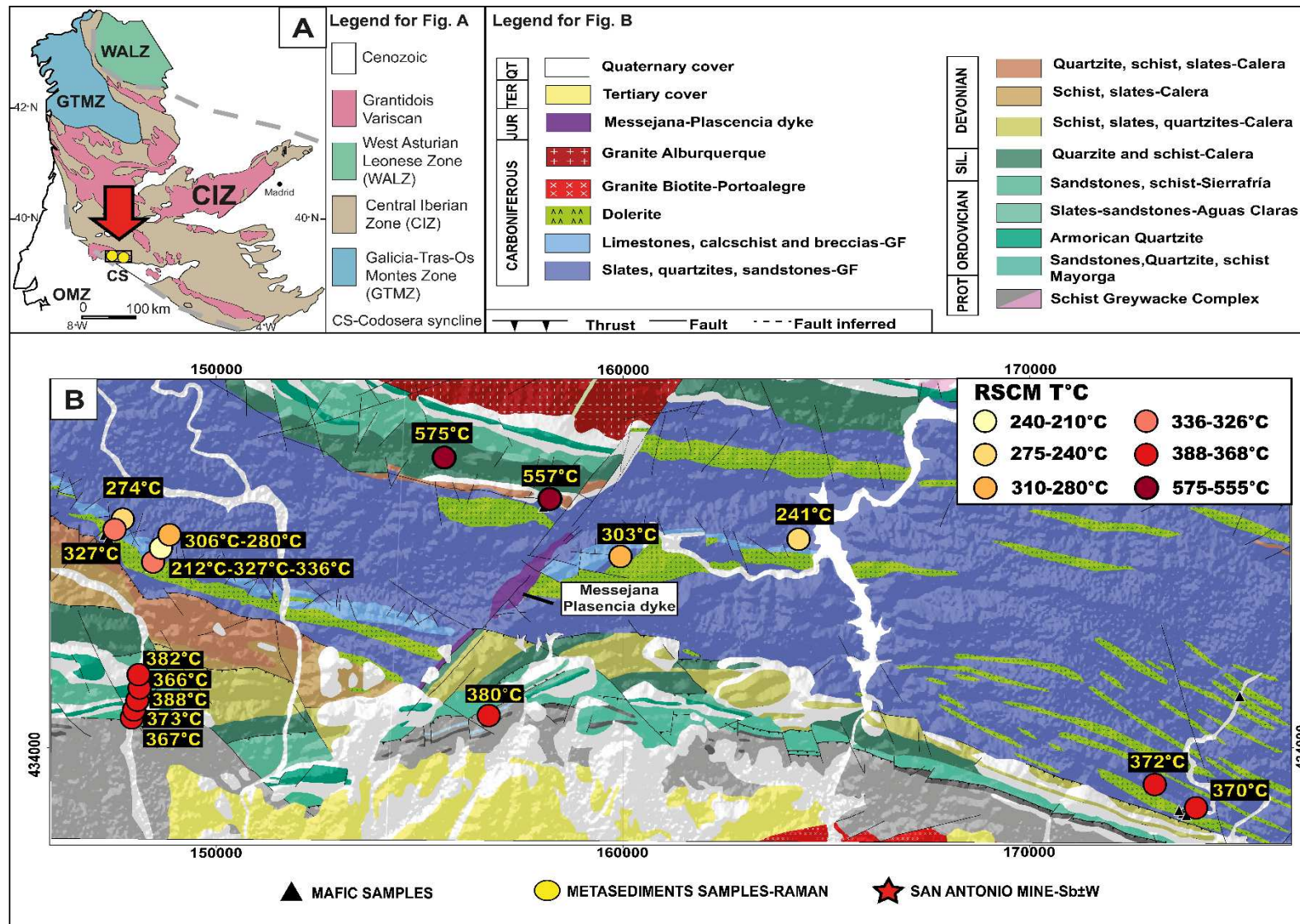


Figure 4. 14. Simplified geological map of the Iberian Massif showing the Codosera syncline, the distribution of the temperatures obtained for the metasediments (yellow circles) and the mafic samples studied in this tesis (back triangles). Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the Raman and mafic samples studied in this work. This map was designed based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).

4.5.4- Metamorphism in the CIZ and in the CS

The Central Iberian Zone presents different metamorphic grades ranging from prehnite-pumpellyite facies (*e.g.* Almadén syncline; Higuera et al., 1995) up to granulite and eclogite facies (*e.g.* Sanabria dome; Azor et al., 2019; Barbero & Villaseca, 2000; Martínez Catalán et al., 2014). The highest metamorphic grades in the CIZ are usually associated to late Variscan gneiss domes located at the N-NW part of the CIZ (Fig. 4.15:

Guadarrama, Gd; Gredos, Gr; Tormes, Tr; Toledo, To; Somosierra, So; Martinamor, Ma; Azor et al., 2019; Barbero & Villaseca, 2000; Martínez Catalán et al., 2014), more specifically in the Spanish Central System and close to the Galicia

Tras Os Montes Zone (Fig. 4.15). These high metamorphic areas were delimited with the grey thick line in Figure 4.15 by Martínez Catalán et al. (2014). The CS is located outside this delimitation in an area where the highest metamorphic degree reported goes from prehnite pumpellyite up to greenschist facies (Purple zone, Fig. 4.15; Azor et al., 2019; Higuera et al., 1995; Martínez Catalán et al., 2014). These observations are supported by the mineralogical associations of epidote±albite±potassic feldspar±micas and chlorite±green

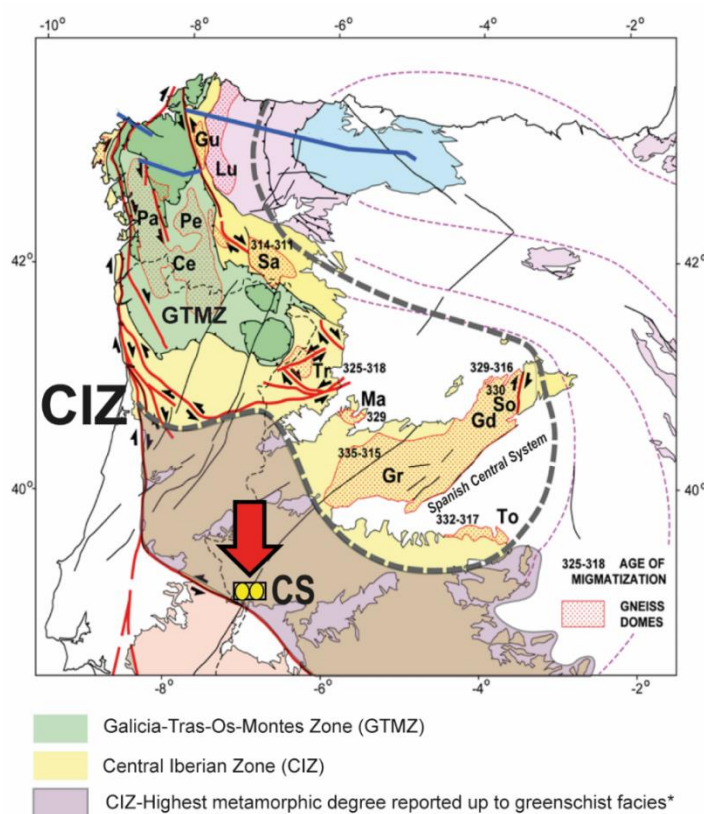


Figure 4. 15. Distribution of the late Variscan Gneiss domes and the location of the Codosera syncline within an area (green zone) where the highest metamorphic degree reported goes up to greenschist facies. Legend: Ce: Celanova; Gd: Guadarrama; Gr: Gredos; Gu: Guitiriz; Lu: Lugo; Ma: Martinamor; Pa: Padrón; Pe: Peares; Sa: Sanabria; So: Somosierra; To: Toledo; Tr: Tormes. Modified after *Martínez Catalán et al. (2014); Azor et al. (2019); Barbero & Villaseca (2000).

amphibole±saussurite±albite reported for the metasediments of the Schist Greywacke Complex and the mafic rocks intruding the CS (López-Moro et al., 2005, 2007, 2020b; Santos Garcia & Casas Ruiz, 1979, 1982) as well as the mineralogical analyses carried out in this study.

The temperature range of $\approx 210\text{--}380^\circ\text{C}$ found for most of the metasediments in this work is consistent with the low metamorphic degree previously reported for the CS syncline and in this part of the CIZ (Fig. 4.14). Considering that the CS has been mainly affected by the C1 deformation phase (López-Moro et al., 2007; Martínez Catalán et al., 2014; Santos Garcia & Casas Ruiz, 1979), these temperatures could be interpreted as the effect of the first stage of the Variscan orogeny metamorphism.

4.5.5- Temperatures and Sb mineralization in the CS

High Sb contents were analyzed in the metasedimentary rocks of CS (Fig.4.7), suggesting a contribution from these rocks to the formation of Sb mineralizations. The most elevated Sb contents are observed at the Villar del Rey Quarry, located at the base of the Gevora Formation (samples SA2033A and C, Fig.4.2) and are comparable to the highest values measured worldwide, which are from the metal-enriched black shales of the Niutitang formation in China (Fig. 4.13). In the rocks from CS, Sb is not enriched in pyrite (Table 4.3), and no other Sb-bearing phases were observed. Possible Sb-bearing phases that are extremely difficult to characterize are (i) small-size disseminated stibnite (stibnite contents lower than 0.02 wt% would be sufficient to account for measured Sb contents in the whole rocks), or (ii) metal-enriched organic matter as in Niutitang black shales (Orberger et al., 2007; Pašava et al., 2008; Xu et al., 2013). Proton induced X-ray emissions (PIXE) analyses would be necessary to measure metals in organic matter (Orberger et al., 2007). At this stage it is therefore impossible to say whether Sb enrichment in the metasedimentary rocks of CS is primary (attained during shale sedimentation), or reached during regional metamorphism.

Raman temperatures indicate that the temperatures attained by regional metamorphism were lower than 400°C. According to the results of Pitcairn et al. (2006), these temperatures may have redistributed Sb within the rock but not efficiently mobilized it. These authors characterized the metal contents of quartzofeldspathic rocks with metamorphic grades up to amphibolite facies, together with their protolites, and observed that the highest Sb depletion is attained for temperatures between 450 and 600°C (Fig. 1.6). For temperatures lower than 450°C, Sb is redistributed among the sulfide phases, without significant bulk loss (Pitcairn et al., 2006). However, temperatures higher than 450°C are likely to have been attained in the contact aureoles of the sills, during magma emplacement. These high temperatures were only observed for samples SA21003 and SA21005B, and are generally difficult to be revealed by RSCM, because the amount of CM generally decreases toward the contact with the sill (Svensen et al., 2023). Nevertheless, Sb is likely to have been efficiently mobilized by the thermal devolatilization of the shales within the sill contact aureoles. To evaluate the effect of such a process, a specific sampling of the sedimentary rocks is necessary: the shales should be sampled perpendicular to the contact with the sill, but also within the same sedimentary horizon to avoid stratigraphic variations (Svensen et al., 2023). In this thesis the sampling was designed to study temperatures attained during regional metamorphism, and a new field campaign would therefore be needed to investigate Sb, C and S behaviour during thermal devolatilization of the shales. Only such a study, coupled to mass balance calculations, could clarify the contribution of thermal devolatilization to the formation of La Codosera Sb mineralization.

4.6-CONCLUSIONS

- The Gévora Formation of Carboniferous age shows lower temperatures compared to the values obtained for the Sierra Fría Unit rocks. Overall, the thermal values decrease towards the center of the CS.

- The highest temperatures found in this study (575°C -SA21003 and 557°C-SA21005B) could be interpreted as the effect of contact metamorphism effect related to the close spatial relationship of these samples with both, the Albuquerque granite and a mafic body (of 1km width).
- The use of the RSCM in the CS helped to support the hypothesis, proposed in Chapter 3 of this thesis, that the isotopic system of the dated apatites was not reset after the intrusion of the mafic sills. Therefore, the geochronological data presented in this thesis (Chapter3) represent the intrusion age of the mafic sills in La Codosera Syncline.
- The temperature range of $\approx 210\text{-}380\pm 50^\circ\text{C}$ found for most of the metasediments in this work is consistent with the low metamorphic degree previously reported for the CS. These values could be interpreted as a heritage from the first stage of the Variscan metamorphism.
- The metasedimentary sequences of the CS show a temperature range between 210-370°C, this would imply that the Sb was redistributed within the sulfide phases in the rock, without mobilizing it efficiently. Higher temperatures, like those attained in the contact aureoles of the mafic sills, would improve Sb mobilization. An adequate sampling of the metasediments perpendicular to the contact with the sill would be essential to evaluate this devolatilization effect.

CHAPTER 5: SYNTHESIS

5.1-Mafic magmatism, metasediments and Sb mineralization in the mineral systems framework: the CIZ and the Armorican Massif

The mineral systems concept has been developed over the past twenty years for understanding the formation of mineral deposits as a combination of several geological processes occurring at different time and space (Goldfarb et al., 2010; Groves et al., 2005; Kerrich et al., 2005; Knox-Robinson & Wyborn, 1997; McCuaig et al., 2010; McCuaig & Hronsky, 2014; Wyborn et al., 1994). It comprises four key elements which are needed for the formation and evolution of mineral deposits including lithosphere architecture, favorable geodynamics, fertility and preservation. This holistic and multiscale approach presents more predictivity power compared to the classic ore deposit models, which are designed for studying mineralization at the deposit scale (McCuaig et al., 2010; McCuaig & Hronsky, 2014). Hereafter a synthesis of the main findings of this study is presented in order to conclude on the application of the mineral system concept to the Ibero-Armorican arc.

5.2.-Evolution of the mafic magmatism in the CIZ

The mafic magmatism in the CIZ was studied to (i) better constrain the possible sources, geochemical features and emplacement ages of numerous mafic suites present in the CIZ, spanning the Ordovician to Carboniferous periods, and (ii) explore its implications for the formation of Sb mineralization in the CIZ. This part was focused on five localities including the Nazarena (NZM) and Susana Mines (SUM), as well as the synclines of la Codosera (CS), Almadén (AS) and Guadalmez (GS).

5.2.1.-Geochronology of the mafic intrusions at the GS, AS, CS, NZM and SUM

The emplacement ages of the dolerite sills of the GS, AS, CS, NZM and SUM range over 200 Ma. The geochronological data in this study identify at least four distinct magmatic

events (Fig. 3.21): **i)** the first occurred at about 480 Ma in the NZM, and coincides within uncertainty with the beginning of the opening of the Rheic ocean reported at the Lower Ordovician epoch (ca. 477 Ma; Orejana et al., 2017 and references therein); **ii)** the second took place at about 420 Ma in the GS, and coincides with the final stage of the opening of the Rheic ocean during Silurian to Lower Devonian (ca. 430-415 Ma; Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012); **iii)** the third, occurred between 387 ± 18 Ma and 360 ± 22 Ma at the SUM, GS and AS; **iv)** and the last one at the CS occurring between 359 ± 21 Ma and 332 ± 17 Ma. The third and fourth events (Lower Devonian to Carboniferous ages) are synchronous within uncertainty with the subduction/closure of the Rheic ocean and the onset of Variscan orogeny, both events reported between ca. 415 Ma- 360 Ma (Arenas et al., 2007; Martínez Catalan et al., 2007; Nance et al., 2012). During the Upper Devonian to early Carboniferous an extensional geodynamic setting occurred in the CIZ at the beginning of the Variscan orogeny. During this period the Badajoz-Córdoba shear zone accommodated the Variscan deformation by left lateral transtensional kinematics leading to an extensional event documented at the southern part of the CIZ (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016).

Mafic magmatism in the GS, AS, SUM and CS is therefore synchronous with mafic magmatism in the Armorican Massif (Pochon et al., 2016b), allowing us to propose the occurrence of widespread mafic magmatism emplaced in both the CIZ and the Armorican Massif at ca. 360-350 Ma.

5.2.2.-Geochemistry and possible sources of the mafic intrusions at the GS, AS, CS, NZM and SUM

Two main types of magmatism were identified in this study, one of alkaline affinity (GS, AS, NZM, SUM) and the second of transitional affinity in the CS (Fig.3.12B).

Regarding the AS, GS, SUM and NZM rocks, the LREE enrichment and the Nb/Yb - Th/Yb - Gd/Yb ratios suggest (i) the involvement of a garnet bearing metasomatized mantle source, potentially associated with the devolatilization of a Cadomian/Rheic slab (Fig.3.24), and (ii) low degrees of partial melting. These rocks show no evidence of crustal recycling or contamination (Fig.3.22).

In the case of the Upper Devonian to Carboniferous mafic magmatism in the CS, the LREE slight enrichments could imply a more hydrous metasomatized garnet-bearing source similar to the one of the mafic suites from the Armorican Massif (Pochon et al., 2016). Therefore, the mafic magmatism reported in the Armorican Massif is similar to the one in the CIZ in terms of emplacement ages and geochemistry. The data presented in this thesis is compatible with a high degree of partial melting and no crustal contamination. The metasomatized mantle source for the CS could be related to the devolatilization of the Rheic slab at the first stages of the Variscan orogeny (Fig.3.24).

5.3-Geochemical and paleothermal characterization of sediments and metasediments at the CS

The sediments and metasediments of the CS were studied in order to (i) understand the maximum metamorphic temperatures that could have affected the U-Pb apatite dating of the mafic sills, and (ii) their possible implications on the formation of Sb deposits.

5.3.1- Maximum metamorphic temperatures in the CS

According to the Raman study, the thermal changes across the CS are dependent on the age of the metasediments and their sampling location within the structure (Fig. 4.14).

The maximum temperatures attained by the Precambrian Schist Greywacke Complex and the Ordovician-Silurian Sierra Fría Unit are 365-390°C. The temperatures of the

Carboniferous Gévora Formation (GF) seem to be higher at south-eastern part of the structure (370°C) and lower at the western part of the CS (210-340°C, increasing from S to N, Fig. 4.14).

Although the Sierra Fría Unit of Ordovician to Silurian age show relatively higher temperatures compared to the Gévora Formation of Carboniferous age (Fig. 4.14), the overall temperature range is consistent with the low metamorphic degree previously reported for the CS syncline and in this part of the CIZ

Only two anomalous values (575°C and 557°C) were observed in the SFU rocks and attributed to the contact metamorphic effect, due to the close spatial proximity to the Albuquerque granite and a mafic body (with a width of approximately 1 km, Fig. 4.14).

5.3.1.1-Thermal implications in the U-Pb apatite dating of mafic sills

The temperature range of $\approx 210\text{--}370^\circ\text{C}$ found for most of the metasediments (Fig. 4.14) and the low-grade metamorphism reported in the studied area (see Chapter 2), support the hypothesis that the isotopic system of the dated apatites was not reset after the intrusion of the mafic sills. The closure temperature values for apatite are indeed classically considered to be between 375 and 550°C (Dodson, 1973; Webster & Piccoli, 2015) and 770-870°C, when the cooling rate of the mafic sills is faster Pochon et al., 2016).

5.3.2.-Geochemistry of the CS metasedimentary rocks

Whole-rock geochemical analyses of sedimentary/metasedimentary sequences from the CS indicate a number of differences among SGC, SFU and GF (section 4.4.2). For most major elements, with the exception of Fe₂O₃, GF samples are extremely heterogeneous. In GF samples SiO₂ varies between 34.8 and 76.5 wt%, whereas in SGC-SFU samples only between 52.5-62.6 wt%. Rocks from GF show a significant heterogeneity in terms of sulfur (0.01-13.35 wt.%), while all rocks from SGC-SFU contain 0.01 wt.% sulfur (Fig.4.6). The SiO₂, Al₂O₃, CaO and S heterogeneity in the GF are associated with variable proportions of silicates,

carbonates and sulfides. Organic carbon distribution also exhibits greater heterogeneity in GF samples, and relatively higher values, although the median is slightly lower than that of SGC-SFU samples (GF=0.14 wt.%; SGC-SFU= 0.17 wt.%).

Antimony contents of the GF are also more variable than those of SGC-SFU samples (Fig 4.7), reaching more than 250 ppm Sb. The highest values (> 250 ppm) are observed in the western (San Antonio mine, Sb-W) and eastern (Villar del Rey quarry) parts of the CS (Fig.4.7). No clear correlation is observed between Sb and major or trace elements (Fig.4.7); only sulfur seems to positively correlate with Sb in GF and SFU samples (Fig.4.7).

5.2.2.4 – Sb-bearing phases in CS metasedimentary rocks

Considering that (i) pyrite is believed to be the main Sb-Au-As bearing mineral in organic material-bearing metasedimentary rocks (Gregory et al., 2015; R. Large et al., 2012; Pitcairn et al., 2006), and (ii) Sb contents seems to correlate with S contents, several analyses were conducted to identify the Sb-bearing phases in the rocks with the highest Sb content, including SEM investigations, LA-ICP-MS and EPMA on sulfides (section 4.4.3). The LA-ICP-MS analyses on pyrite (made from rim to core) revealed that the Sb content in CS rocks is not enriched in pyrite. The data indicate no discernible variation in Sb concentration from the core to rim. The Sb

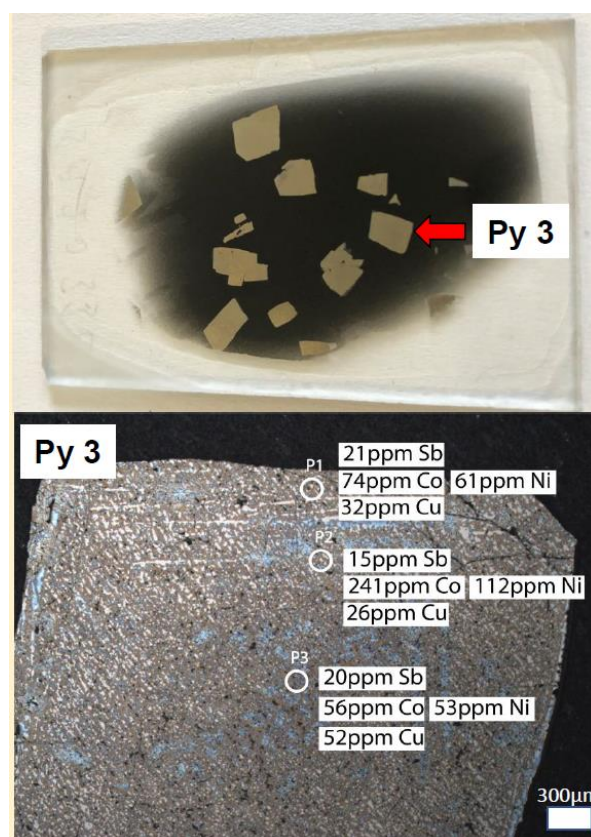


Figure 5. 1. A) Sample SA2033C at the eastern part of the CS, with more than 250ppm of Sb. B) LA-ICP-MS analyses show that pyrite is not the main Sb-bearing phase in the CS.

values range from 5ppm up to 25ppm (Fig 5.1). The EPMA analyses of pyrite demonstrated that the Sb contents were consistently below 300ppm (Chapter 4).

In summary, no Sb-bearing phases were identified, which suggest that the Sb may be contained in either (i) small-size disseminated stibnite difficult to observe (only 0.02wt% stibnite would be sufficient for explaining Sb contents of 250 ppm in the whole rock), or otherwise (ii) metal-rich organic matter like in the Niutitang black shales (Orberger et al., 2007; Pašava et al., 2008; Xu et al., 2013). If Sb is related to organic matter a technique called Proton Induced X-Ray Emission, would be necessary for analyzing metal contents in this material (Orberger et al., 2007).

5.4- Implications for Sb mineralization: mafic magmatism and metasediments as possible Sb sources in the CIZ.

A possible correlation between Sb mineralization and mafic magmatism is suggested at the Armorican Massif and the CIZ (Campos Rodríguez et al., 2023; Chatelin, 2022; Pochon et al., 2016; Pochon, 2018; Pochon et al., 2018, 2019, 2023, 2024). In the Armorican Massif, Sb deposits and mafic rocks are spatially and temporally correlated at *ca.* 360 Ma, strongly suggesting a genetic link between mafic magmatism and ore-forming processes (Pochon, 2018; Pochon et al., 2016 a, b; 2018, 2019). In the CIZ, mafic magmatism within the CS, GS, SUM and NZM is spatially associated to Sb mineralization (Fig. 2.?). According to the results presented hereabove both mafic magmatism and its host metasedimentary sequences may have contributed fluids and metals to the Sb deposits in the CIZ. Mafic magmatism may contribute Sb-bearing fluids by magmatic degassing during crystallization (Pochon et al., 2023, 2024). In the CS, mafic volcanism was already suggested as a possible source of the mineralizing fluids responsible for the formation of the San Antonio Sb±W deposit (Arribas & Gumiel, 1984). According to Arribas & Gumiel (1984), this process took place during Devonian times in an

outer continental shelf that was affected by relevant extensive tectonics generating a fault system that allowed the formation of the intraformational breccias as well as the hydrothermal exhalative activity related to basic volcanism.

An alternative or additional contribution in terms of fluids may come from the devolatilization of the C and S-rich sedimentary rocks, due to magma emplacement within them (*e.g.* Svensen et al., 2015). The amount of fluids produced by this mechanism can be significantly higher than that produced by magmatic degassing and fluid composition is dominated by CH₄, CO₂ and S species (Ganino & Arndt, 2009; Svensen et al., 2015). In addition, thermal devolatilization has been documented to efficiently mobilize Hg from C-enriched shales (Svensen et al., 2023). This process is probably relevant to other metals and metalloids, although no specific studies investigated Sb behavior.

5.4.1-Exsolution of magmatic volatile phases

Sb-bearing mineralizing fluids could have been originated from exsolved magmatic volatile phases (Pochon, 2018; Pochon et al., 2024). These could be represented by primary fluid inclusions in ilmenite that have been documented in mafic rocks of both the Armorican Massif and the CIZ (Fig. 3.20 and Fig 5.1: Chatelin, 2022; Pochon et al., 2023, 2024).

The chemistry of these inclusions is characterized by a solute composition dominated by Na-Ca-Cl-S, and containing metals and metalloids, such as Sb, Cu, Sn, Mo, W and Pb (Chatelin, 2022; Pochon et al., 2024). These fluids are interpreted to be produced by saturation of a magma volatile phase during ilmenite crystallization, resulting in magma degassing at the magmatic-hydrothermal transition (Pochon et al., 2024). The conceptual model is illustrated in Figure 5.2.

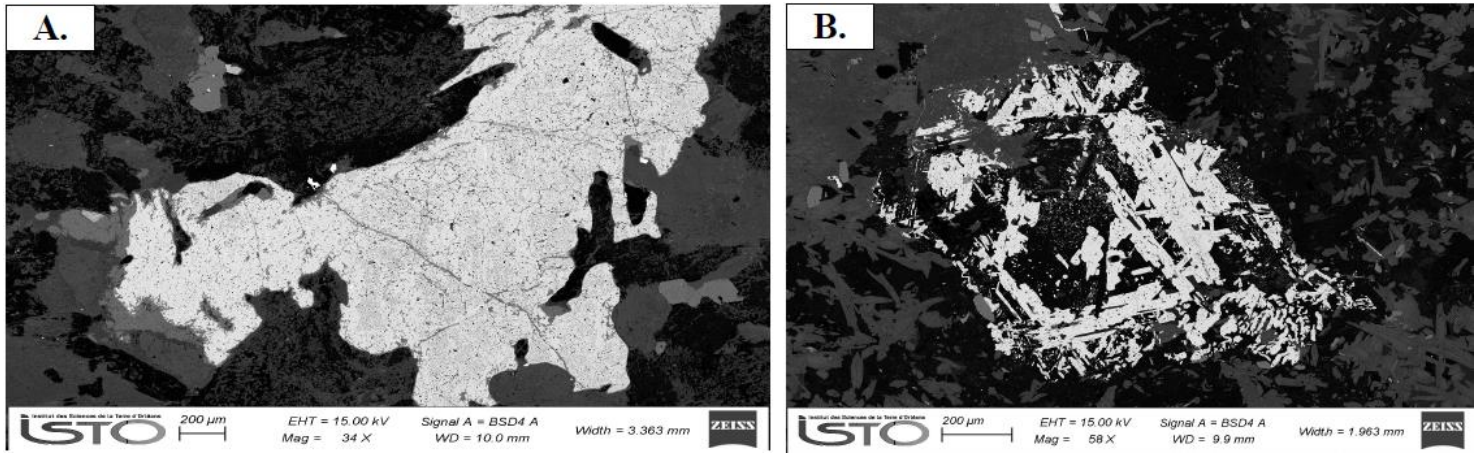


Figure 5. 2. Presence of primary fluid inclusions on ilmenite in the mafic rocks from the CS. A) Sample SA2022; B) Sample SA2042.

Modified after Chatelin (2022).

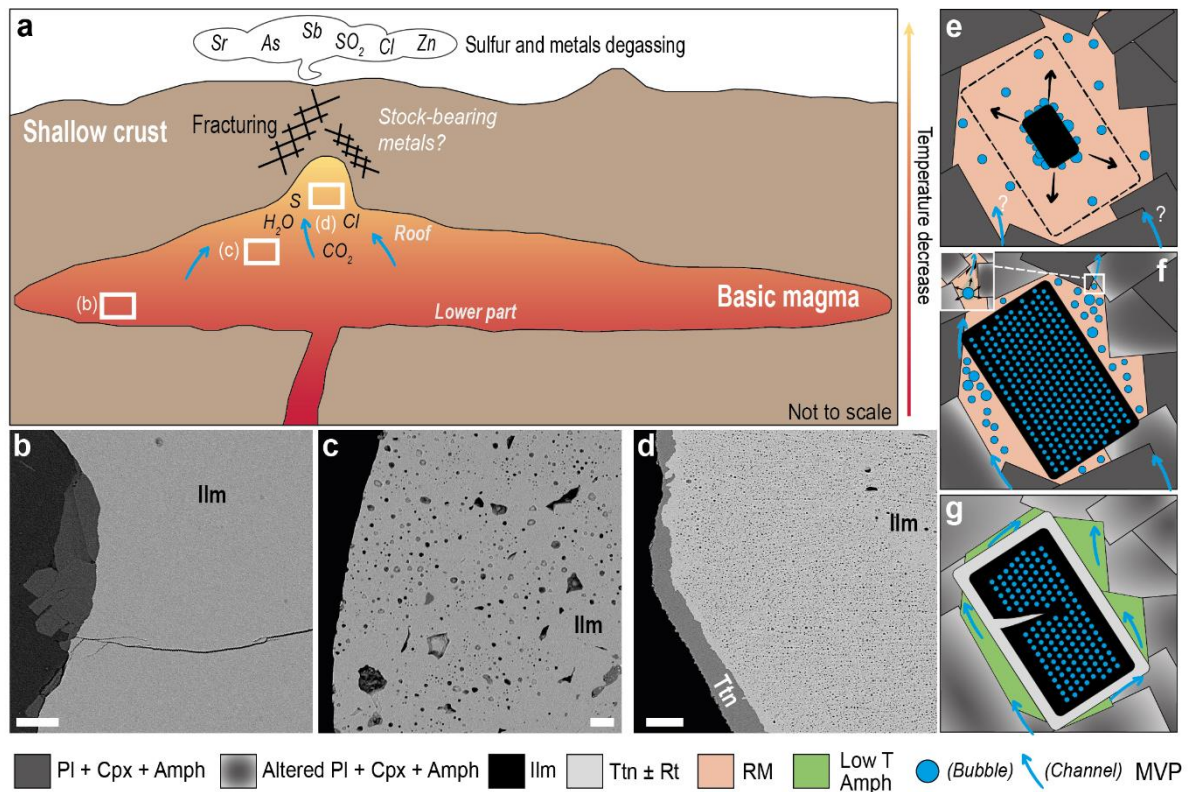


Figure 5. 3. Schematic diagram illustrating the conceptual model of entrapment of magmatic volatile phases within ilmenite from Pochon et al. (2024). (a) General geometry (not to scale) of a gabbroic intrusion with the location of insets (b), (c) and (d). (b-d) Back-scattered electron (BSE) images of ilmenite (Ilm) texture from the lower (b), central (c) and upper (d) parts of the basic intrusion that records magma degassing from the base to the

top. White scale bar represents 20 μm . (e) Onset of volatile exsolution in the residual melt (RM) of the mush and release of a magmatic volatile phase (MVP) via 2nd boiling. Ilmenite may act as a preferential site for nucleation of bubbles during its growth or ilmenite crystallization may act as the trigger of exsolution of bubbles at the growing crystal-melt interface. (f) Ilmenite grain crystallizes more or less quickly and may easily traps abundant MVP as fluid inclusions (FI) during its progressive crystallization and magma cooling. (g) Following ilmenite formation, trapped FI likely undergo re-equilibration via necking, whereas the untrapped MVP likely escapes via capillary fracturing or others processes and probably coalesce towards the surface. The latter MVP interacts with and modifies earlier crystallized silicate phases. Interaction of ilmenite with fluids saturated in Si and Ca (due to alteration of calcic plagioclase (Pl) and mafic minerals) causes ilmenite breakdown. This fracture-controlled subsolidus alteration is responsible for the formation of FI-free ilmenite and the development of secondary titanite (Ttn) $\pm$ rutile (Rt). Abbreviation: Cpx – clinopyroxene, Amph – amphibole, Low T – low temperature.

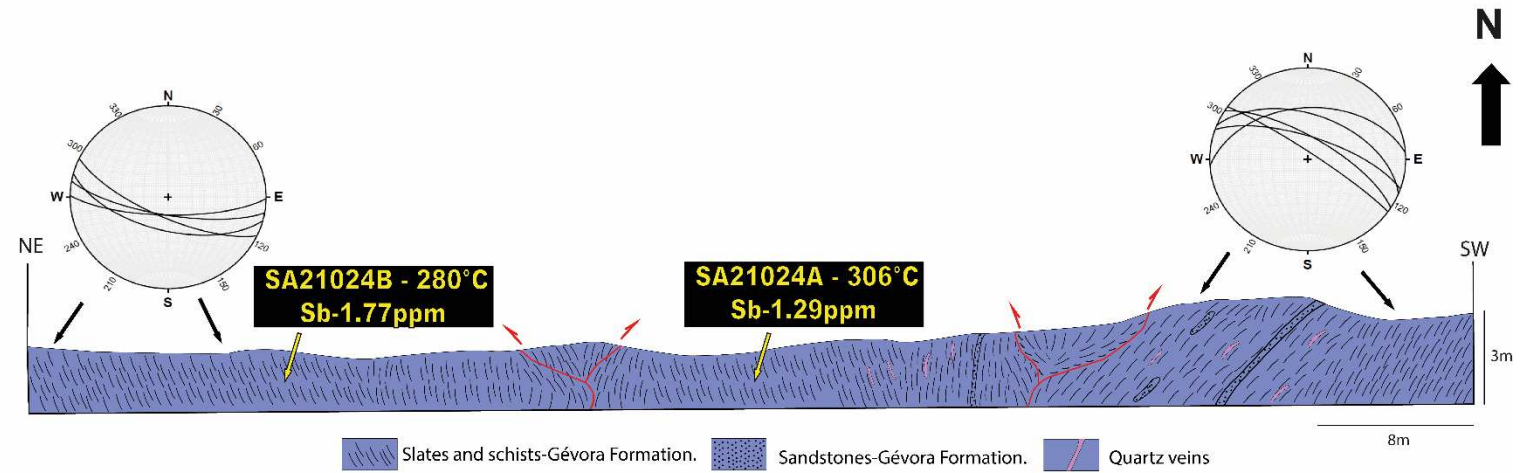
5.4.2-Thermal devolatilization of sedimentary rocks during magma emplacement

Sedimentary/metasedimentary rocks (bearing organic material) such as black shales, slates and greywackes are recognized as potential sources of antimony and other associated elements (Au, As, Cu; *e.g.* Bloomstein & Clark, 1989; Pitcairn et al., 2006; Pohl, 2011; Ridley, 2013). Considering this, several analyses were performed in the CS metasedimentary sequence in order to assess if these lithologies could represent a potential source for the Sb deposits in the CS area.

As mentioned in Chapter 4, one of the most critical parameters influencing the mobilization of Sb and other elements during metamorphic processes is temperature. Pitcairn et al. (2006), determined that the highest Sb depletion occurs at 450°C and 600°C in quartz-feldspathic metamorphic rocks (up to amphibolite facies) and their protolithes (Fig.1.6). Below 450°C, the Sb is redistributed among the sulfide phases (Pitcairn et al., 2006). The metasedimentary sequences of the CS show a temperature range between 210-370°C, this would imply that the Sb was redistributed within the sulfide phases in the rock, without mobilizing it efficiently. Higher temperatures, like those attained in the contact aureoles of the mafic sills, would improve Sb mobilization. An adequate sampling of the metasediments perpendicular to

the contact with the sill would be essential to evaluate this devolatilization effect. Moreover, such a sampling should be performed within the same stratigraphic horizon, to avoid differences due to original stratigraphic variations (Svensen et al., 2023). The sampling used in this thesis had the objective of studying the maximum temperatures reached during regional metamorphism and only occasionally regarded contact aureoles (Fig.5.5).

A)



B)

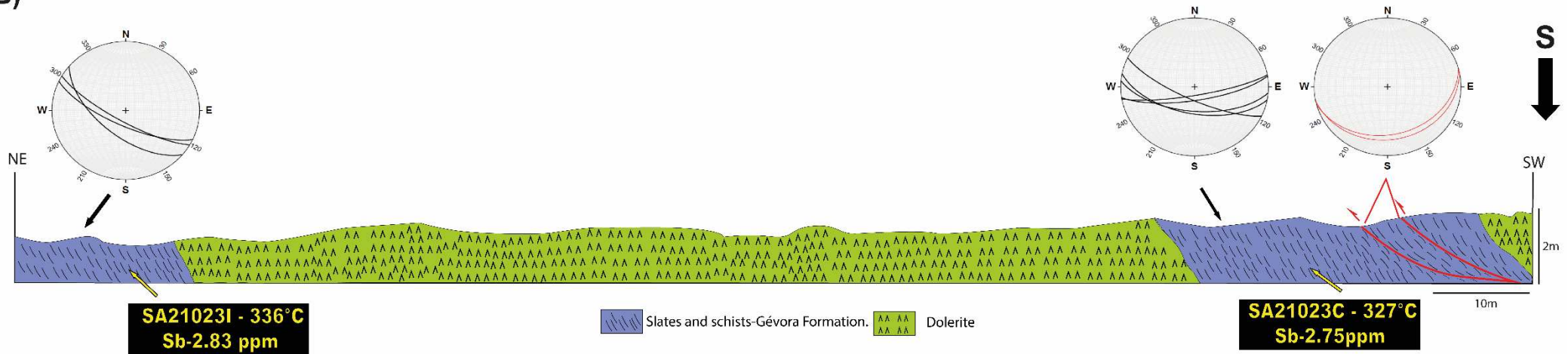


Figure 5. 4. NE-SW Cross-section of the Carboniferous sequence showing the main sampling location of: (A) Samples SA21024A and SA21024B; (B) SA21023C and SA21023I.

5.5- Simplified model considering the possible sources of Sb deposits in the CS.

Considering the geochemical, geochronological and thermal data collected in the CS, a simplified metallogenic model at the camp scale can be proposed for the formation of Sb deposits in the CS during the Variscan geodynamic setting (Fig. 5.5). As mentioned above, at the first stages of the Variscan orogeny the Badajoz Cordoba Shear Zone (BCSZ) accommodated the Variscan deformation by left transtensional kinematics, which created an extensional event in the CIZ that allowed the formation of Carboniferous basins such as the one of the CS (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016). These local extensions would have also facilitated the emplacement of the mafic bodies in the CS. According to the data showed in chapter 3, these mafic magmas originated from an enriched metasomatized mantle source and did not assimilate any crustal rocks. These mafic sills would have acted either as a metal source for Sb deposits (by magma degassing) or as a heating source allowing the devolatilization of Sb-rich sediments and therefore the mobilization of Sb and other elements within the Gévora Formation (GF) in the CS (Fig. 5.5). Local faults and fractures would have facilitated the ascension of these magmatic and/or metamorphic fluids which then precipitated (due to pressure and/or pH changes) when getting in contact with a calcareous unit called the Calizas de San Antonio within the GF. This process allowed the formation of Sb stratabound deposits such as those observed in the San Antonio district (SA, Fig 5.5).

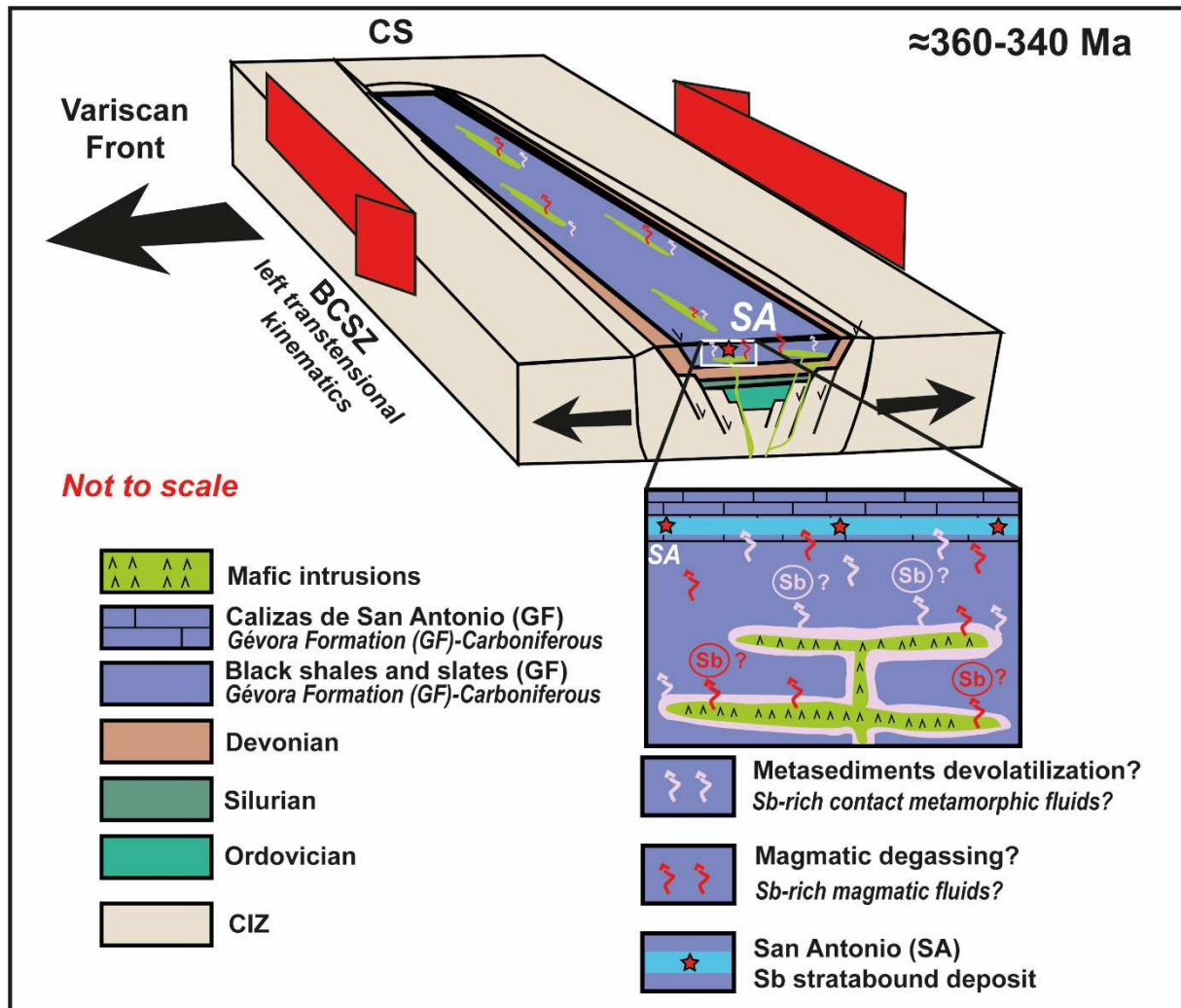


Figure 5. 5. Simplified model for explaining the formation of Sb deposits such as the San Antonio district (SA) at the Codocera Syncline (CS) of the Central Iberian Zone (CIZ). This model considers the accommodation of the Variscan deformation by left transtensional kinematics at the Badajoz Cordoba Shear Zone (BCSZ, (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016) and the emplacement ages of the mafic sills in this thesis between ca. 360-340 Ma. The mafic intrusions would have acted either as a metal source for the Sb deposits (by magmatic degassing) or as a heating source allowing the devolatilization of Sb-rich metasediments and therefore the mobilization of Sb and other elements within the CS.

5.6-The mineral systems approach applied to the study of Sb deposits in the Ibero-Armorican Arc and the CIZ

The Ibero-Armorican Arc represents an ideal case study for the application of the mineral system concept to Sb mineralization. This macrostructure, comprises equivalent domains

within the Armorican and Iberian Massifs, which formed during the Variscan orogeny (Ballèvre et al., 1992; Dias & Ribeiro, 1995). Several critical elements for the formation of Sb deposits can be identified at the continental, province, camp and deposits scales (Table 5.1). The favorable geodynamics and architecture are represented by the opening of the Rheic ocean at the continental (Ibero-Armorican arc) scale, which induced extensional processes, mantle melting, sedimentation in basins and emplacement of mafic magmas within them, at the province scale (CIZ or Armorican Massif). At the camp scale (La Cordosera, Almadén or Guadalmez synclines), the favorable geodynamics consisted in extensional and compressional tectonics leading to magma ascent and storage at upper crustal levels, which led to the emplacement of mafic sills within Sb-rich sediments and their devolatilization, accompanied by volatile degassing induced by the crystallization of the mafic intrusions. At the deposit scale, lithological and structural controls on hydrothermal fluxes caused Sb-enriched fluids to be trapped within favorable layers that facilitated the deposition of Sb mineralization. Later on the closing of the Rheic ocean and the collision between Gondwana and Larussia led to the Variscan orogeny, which preserved Sb mineralization within the Variscan Belt (Table 5.1).

With respect to the fertility, the occurrence of a Sb-enriched mantle source was not attested in this study, but is a possible element that should be investigated at the continental or province scale. At the camp scale, two critical elements were identified: (i) Sb enrichment of the metasedimentary rocks of the CS suggesting possible primary enrichment of the sedimentary rocks in which the mafic magma emplaced, and (ii) Sb enrichment of the magmatic volatile phases exsolved during the last crystallization stages of these mafic magmas (observed at the CS, but also at the Armorican Massif).

More detailed studies are needed to quantify the respective contributions of these processes to the formation of Sb mineralization in the Ibero-Armorican Arc.

Table 5. 1. Critical elements for the mineral systems concept applied to the study of Sb mineralization in the CIZ. This table was created based on the critical elements table in the formation of gold deposits from McCuaig & Hronsky (2014).

	Fertility	Favorable geodynamics	Favorable architecture
Deposit scale (SUM/NZM/San Antonio, Almaden, Accesos-Balanzona)	Not at this scale	Lithological and structural controls on hydrothermal fluxes.	Formation of Sb mineralization within fractures and breccia in slates or quartzitic rocks.
Camp scale (CS/ AS/ GS)	Sb-enriched metasedimentary rocks suggesting possible primary enrichment of the sedimentary rocks in which the magma emplaced. Sb enrichment in magmatic volatile phases exsolved during the last crystallization stages.	Extensional and compressional tectonics leading to magma ascent and storage within the upper crust.	Emplacement of magmatic sills within the Sb-C-S-rich sediments, leading to sediment devolatilization. Volatile degassing induced by the crystallization of magmatic intrusions.
Province scale (CIZ/Armorican Massif)	Possible Sb-enriched mantle sources.	Extensional processes, erosion and sedimentation in basins. Mantle melting.	Formation of large sedimentary basins and emplacement of mafic magmas within them.
Continental scale (Ibero-Armorican arc)	Possible Sb-enriched mantle sources.	Opening and closing of the Rheic ocean, collision between Gondwana and Laurussia and formation of the Variscan orogen.	Preservation of Sb mineralization within the Variscan orogen

5.7-Perspectives

5.7.1-Short term-CIZ

Both magma degassing and thermal devolatilization of the contact aureoles are likely to have occurred in the CIZ. Current data do not allow to determine the relative importance of the

two mechanisms in ore-forming processes. Ulterior studies, described hereafter, are needed to elucidate the contribution of both mechanisms.

In order to improve the understanding of the magmatic degassing phenomena in the CIZ, a more detailed sampling of the mafic intrusions would be essential to determine the distribution of the mafic rocks presenting the primary fluid inclusions on ilmenite. These features need to be studied in detail in the mafic intrusions spatially associated to Sb mineralization in the CIZ.

Sb-bearing phases in the metasedimentary sequences have to be constrained in all Sb-rich metasedimentary rocks to investigate whether Sb enrichment is attained during sedimentary or metamorphic processes.

A new field campaign would be necessary to study the devolatilization phenomena by sampling the metasedimentary sequences of the perpendicular to the contact within the same sedimentary horizon to avoid stratigraphic variations, following the method applied by Svensen et al. (2023) which studied the release and behavior of Hg during contact metamorphism of shales. This campaign should be done in the CS, GS, AS and other structures of the CIZ where Sb mineralization has been reported.

5.7.2-Long term-Moroccan Sb deposits

Considering the mineral systems concept for the study and exploration of Sb deposits at the continental scale in the Ibero-Armorican Arc, further research could be conducted on other domains of the Variscan Chain that have undergone a comparable geological history. These include the Moroccan Central Massif (MCM), the Atlas domain and the Meseta domain in western Maghreb (Fig. 5.6 and 5.7). In this area numerous Au-Sb mineralization have been reported (Azza, 2019; Azza et al., 2019; Fouad & Mustapha, 2024).

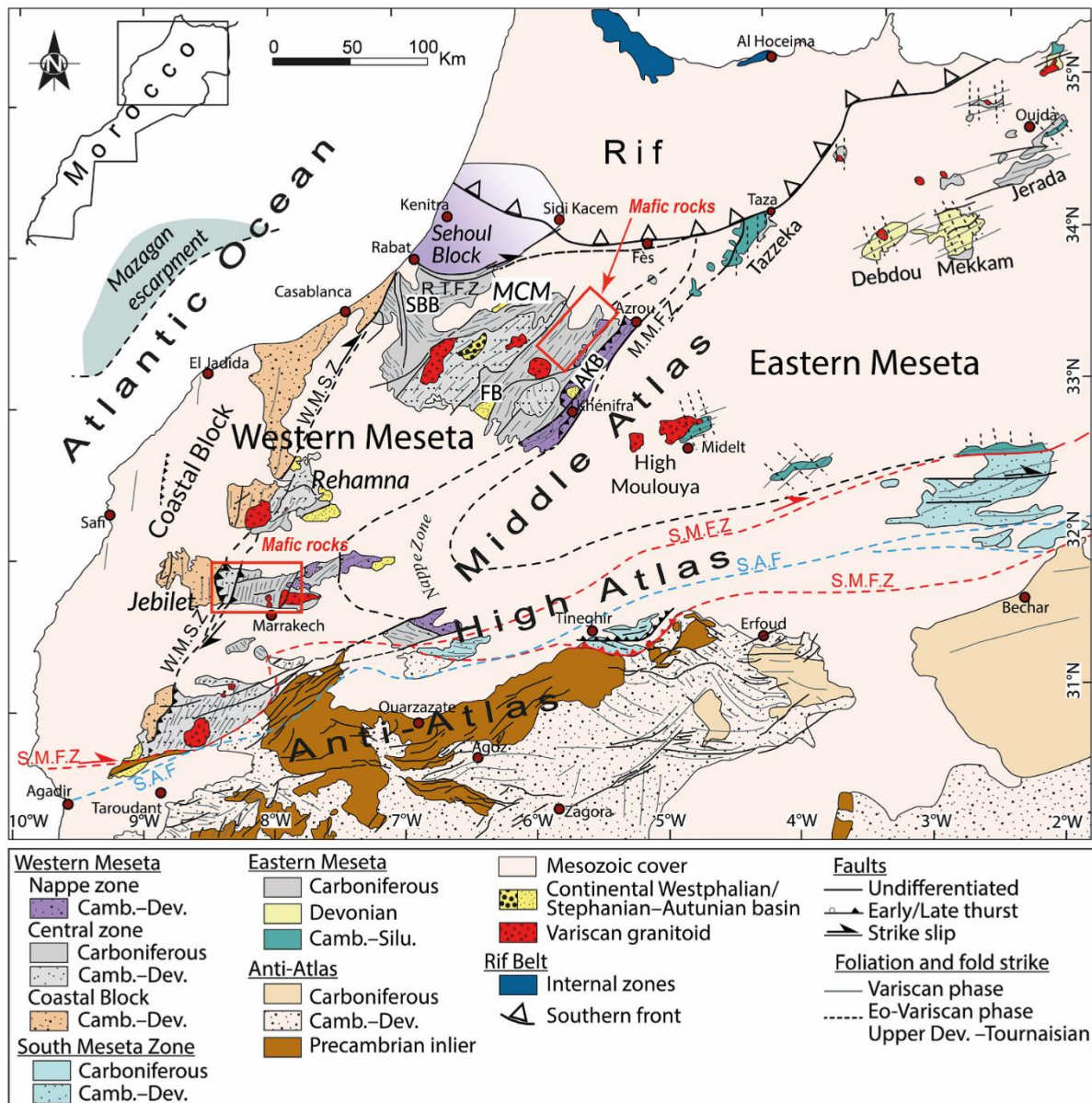


Figure 5. 6. Simplified geological map of the Moroccan Variscides showing the location of the main units and the mafic intrusions. Modified after Moutbir et al. (2024) and references therein. Abbreviations: MMFZ, Middle Meseta Fault Zone; RTFZ, Rabat-Tiflet Fault Zone; SAF, South Atlas Fault; SMFZ, Southern Meseta Fault Zone; WMSZ, Western Meseta Shear Zone; MCM, Moroccan Central Massif; SBB, Sidi Bettache Basin; FB, Fourhal Basin; AKB, Azrou-Khenifra Basin; Camb: Cambrian; Silu: Silurian; Dev: Devonian.

Regarding the MCM, the Sb deposits are located within Paleozoic terrains, some of them can be found close to Variscan granites outside the contact metamorphic aureole. The main ore

is represented by stibnite which can be observed in either as veins-type or stratiform deposits, displaying disseminated stibnite in the host rock (Moutbir et al., 2024). Similarly, to the CIZ, the MCM also exhibits a number of mafic intrusions located within Carboniferous sequences in the Fourhal Basin (Moutbir et al., 2024). The emplacement age of these mafic rocks was estimated between 347-330 Ma (SHRIMP U-Pb zircon, Moutbir et al., 2024), which coincides within error with the ages of the mafic rocks of the CS in the CIZ.

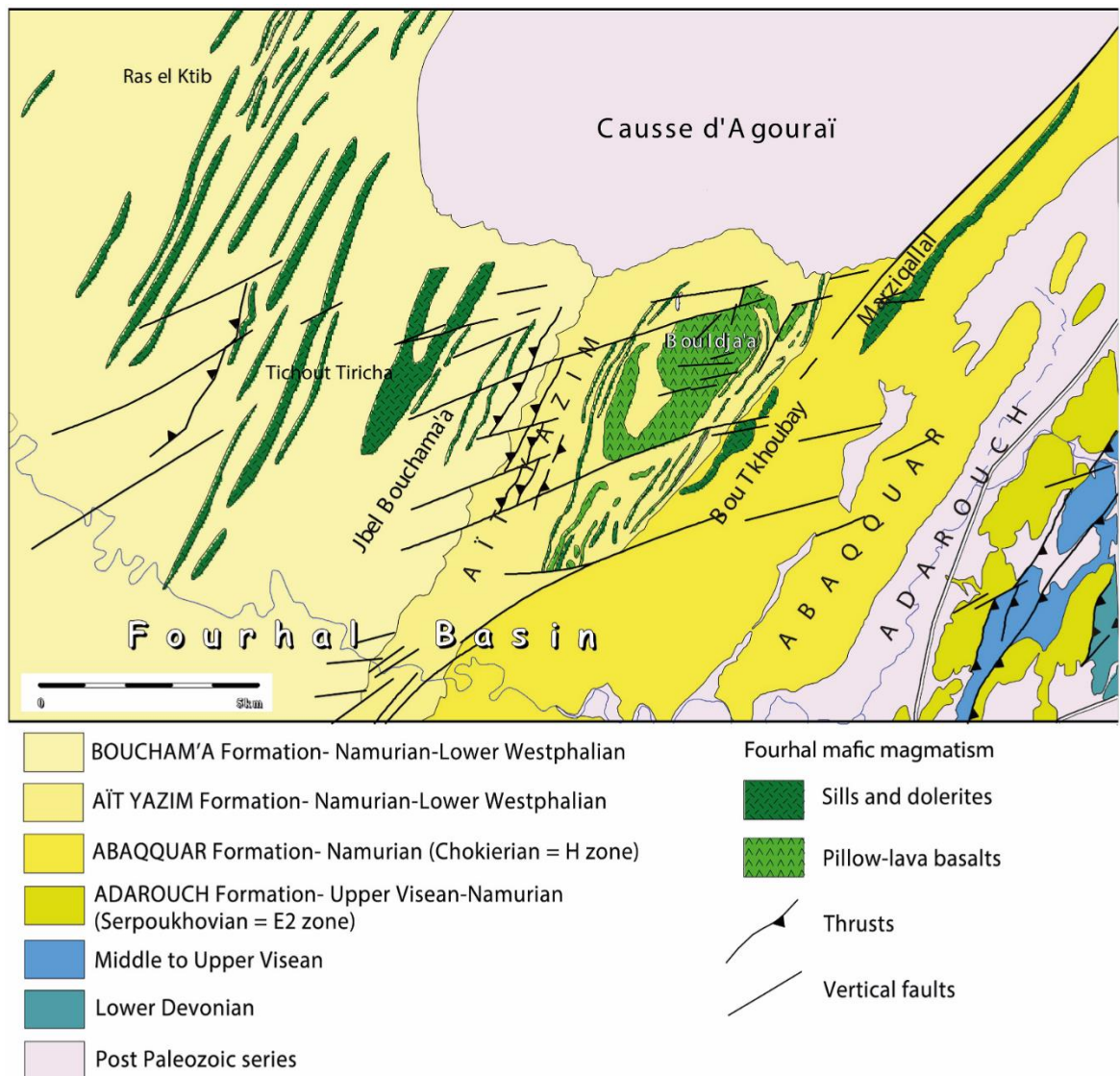


Figure 5. 7. Geological map of the Carboniferous Fourhal Basin (Moroccan Central Massif) showing the occurrences of the mafic intrusions (dykes and sills). (Moutbir et al., 2024)

In the case of the Eastern High Atlas in the Tamlalt Plain, one of the most relevant Sb deposits corresponds to the Jbel Haouanite (Fig. 5.8: Addi et al., 2019; Michard et al., 2008; Pelleter et al., 2010). The Jbel Haouanite Au-Sb mineralization can be found at the northern part of the Tamlalt plain (Fig. 5.7) within Paleozoic rocks (Azza, 2019; Azza et al., 2019). Azza et al. (2019) suggested a late Variscan age for the Au-Sb mineralization and proposed several similarities with the Au-Sb deposits of the Western Variscan Belt in Europe. These include the metamorphic host rocks and the formation age, among other characteristics (Azza, 2019; Azza et al., 2019). According to Azza et al. (2019), the formation of the Au-Sb mineralization in Morocco occurred during the extensional collapse of the chain at the end of the Variscan orogeny. This is consistent with the “Or 300” event proposed by Bouchot et al. (2005) for the formation of Au-Sb deposits in the French Massif Central. A geochronological study of these mineralization would clarify the genetic processes at their origin and possible links with Sb mineralization of the Ibero-Armorican Arc

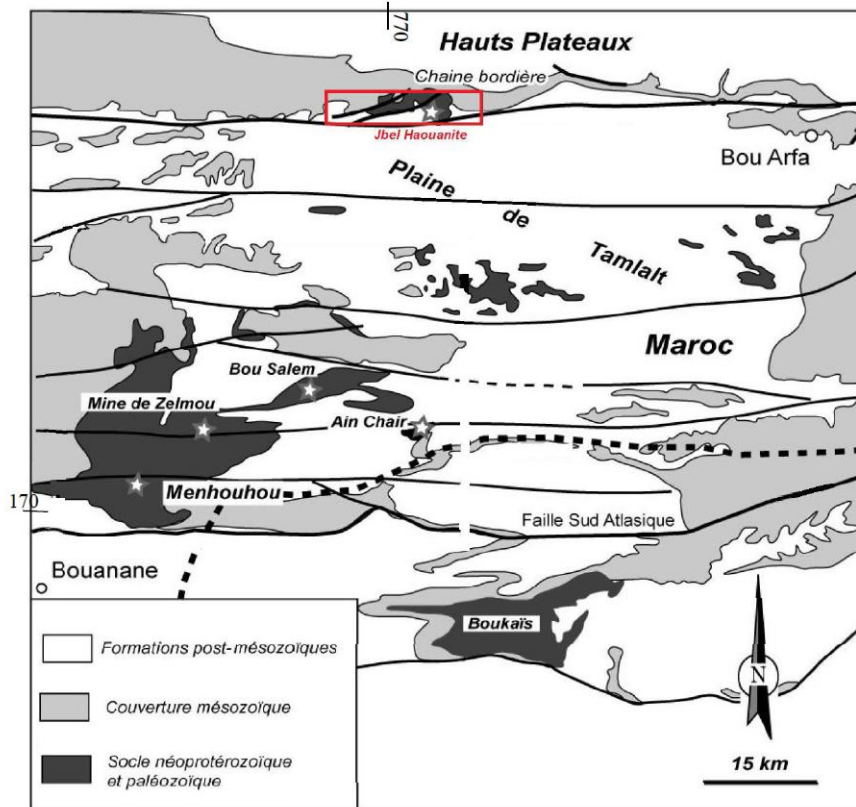


Figure 5. 8. Location of the Jbel Haouanite Au-Sb mineralization in the Tamlalt Plain (Azza, 2019).

CONCLUSIONS

MAFIC MAGMATISM IN THE CIZ

The LA-ICP-MS dating of apatite together with geochemistry analyses enhanced the understanding of the geochronological and geochemical characteristics of several intrusive mafic rocks across five different localities of the CIZ (GS, AS, SUM, NZM and CS). The alkaline basalts from the NZM, SUM, GS and AS were emplaced during at least three distinct events, the first one occurring approximately 480 Ma, the second at around 420 Ma ago and the third one between 387 ± 18 Ma and 360 ± 22 Ma. The basalts from the CS were emplaced between 359 ± 21 Ma and 332 ± 17 Ma and are related to a magmatism with transitional affinity. The Lower Ordovician age in the NZM is coeval within uncertainty with the beginning of the opening of the Rheic ocean. The Silurian to Lower Devonian age in the GS is consistent with the final stage of the same extensive event. The Lower Devonian to Carboniferous ages in the GS, AS, SUM and CS span from the subduction/closure of the Rheic ocean to the onset of the Variscan orogeny. This magmatism is related to local extensional settings, which has been documented at the southern part of the CIZ during the initial stage of the C1 collisional setting of the Variscan orogeny. The AS, GS and SUM rocks are also coeval with Hg mineralization events documented in the AS during Silurian and Devonian periods (Higueras, 1995; Higueras et al., 2013; Higueras & Oyarzun, 2005; Palero-Fernández et al., 2015).

The Upper Devonian to early Carboniferous mafic suites in the GS, AS and CS coincide with the emplacement ages of several mafic rocks in the Armorican Massif (Pochon et al., 2016b), allowing us to propose widespread mafic magmatism that took place in both domains (CIZ, Armorican Massif) at ca. 360-350 Ma.

Conclusions

According to this study, the alkaline mafic magmatism in the AS, GS, SUM and NZM may be related to a garnet bearing enriched mantle source with no evidence of crustal recycling or contamination and a low degree of partial melting. The Upper Devonian to Carboniferous mafic magmatism in the CS seems to be associated with a more hydrous metasomatized garnet-bearing source similar to the mafic suites of the Armorican Massif (Pochon et al., 2016). This interpretation is compatible with the high Pb anomalies related to the suggested devolatilization of the Rheic slab at the first stages of the Variscan orogeny. Furthermore, the lower LREE/HREE of the CS compared to GS, AS, SUM and NZM, might imply the highest degree of partial melting among all of the studied samples in this study. Additional geochemical analyses (e.g. isotope geochemistry) are crucial in order to better constrain the sources and the evolution of the Upper Devonian-lower Carboniferous mafic magmatism in the CIZ.

Implications of the mafic magmatism on Sb mineralization

The mafic samples from the CS, GS, SUM and, NZM are spatially associated to Sb deposits. Furthermore, as shown in Chapter 3, some of our mafic rocks are temporally related to mafic intrusions and Sb deposits in the Armorican Massif. In the CS, a hydrothermal event associated with mafic volcanism was proposed as a possible source for the mineralizing fluids that lead to the formation of Sb deposits in the area (Arribas & Gumiel, 1984). However, the lack of geochronological data for the Sb deposits in the CS makes the temporal and genetical link difficult to prove in this area.

Exsolution of magmatic volatile phases

Primary fluid inclusions (FI) were observed in ilmenite crystals within two samples of the CS, suggesting the occurrence of a fluid phase in the magma at the time of ilmenite crystallization (Chatelin, 2022; Pochon et al., 2024). LA-ICP-MS analyses performed on the ilmenites show that the FI are characterized by a solute composition dominated by Na-Ca-Cl-

Conclusions

S, with Sb, Cu, Sn, Mo, W and Pb as metals and metalloids (Chatelin, 2022; Pochon et al., 2023, 2024) (Chatelin, 2022; Pochon et al., 2023, 2024). The LA-ICP-MS traverses evidence an increase of incompatible trace elements contents (*e.g.* Sb, As, Cu, Sr) in the FI-bearing areas (Fig. 3.20, Chatelin, 2022; Pochon et al., 2024).

The primary fluid inclusions (FI) in ilmenite in the mafic rocks of the Armorican Massif and the CIZ might represent a good example of magma degassing and volatile saturation at the magmatic-hydrothermal transition in highly crystallized mafic magmas (Chatelin, 2022; Pochon et al., 2023, 2024). The study of these FI could help to understand metal enrichment processes related to magmatic fluids (Chatelin, 2022; Pochon et al., 2023, 2024). Further studies are needed in order to better understand this phenomenon.

GEOCHEMICAL AND PALEOTHERMAL CHARACTERIZATION OF SEDIMENTS AND METASEDIMENTS AT THE CS.

RSCM temperatures in the CS

According to the Raman study, the thermal changes across the CS are dependent on the age of the metasediments and their sampling location within the structure.

The maximum temperatures attained by the Precambrian Schist Greywacke Complex and the Ordovician-Silurian Sierra Fría Unit are 365-390°C. The temperatures of the Carboniferous Gévora Formation (GF) seem to be higher at south-eastern part of the structure (370°C) and lower at the western part of the CS (210-340°C, increasing from S to N).

Although the Sierra Fría Unit of Ordovician to Silurian age show relatively higher temperatures compared to the Gévora Formation of Carboniferous age, the overall temperature range is consistent with the low metamorphic degree previously reported for the CS syncline and in this part of the CIZ

Conclusions

Only two anomalous values (575°C and 557°C) were observed in the SFU rocks and attributed to the contact metamorphic effect, due to the close spatial proximity to the Albuquerque granite and a mafic body (with a width of approximately 1 km).

Sb distribution in the CS

In the CS, the highest Sb values are found in the GF at the western and eastern part of the structure. The samples with high Sb values taken at the western part come from the San Antonio Mine (Sb $\pm$ W), therefore the Sb contents might be related to Sb the presence of Sb sulfides or oxides. At the eastern part, the samples with high Sb come from the Villar del Rey Quarry, here no Sb mineralization has been reported and no Sb sulphides or oxides were observed. These samples present the highest amounts of sulfur, which could be related with the Sb-S correlation observed for the GF rocks. No Sb-bearing phase was identified with SEM observations and analyses. Electron probe microanalyses indicate that the Sb contents of pyrite and its sphalerite inclusions are lower than 300ppm in these samples, suggesting that pyrite cannot be the main Sb-bearing mineral. The organic carbon in this part of the structure is also high, nevertheless no hypothesis can be proposed in this case since there is no clear correlation between Sb and organic carbon.

Comparison between Sb values in the CS and Sb global contents in black shales

Overall, the CS rocks, especially the ones coming from the GF, seem to be slightly more enriched compared to global data of Pre and post-Cambrian shales from Canada, China, USA and India (*e.g.* Fan et al., 2004; Goodfellow et al., 2009; Manikyamba et al., 2008; Manikyamba & Kerrich, 2006; Orberger et al., 2007; Pašava et al., 2008; Turner & Kamber, 2012; Xu et al., 2013). The median value for the GF rocks (Med=2.85) is higher compared to the SGC-SFU (Med=2.02) and the global black shales (Med=2.01).

Conclusions

As no Sb-bearing minerals were identified in La Codosera samples, it is impossible to assess if the Sb-enrichment of these rocks is pristine and therefore predates magma emplacement or is due to metamorphic processes that occurred after magma intrusion.

Implications of the RSCM metamorphic temperatures in the apatite dating of mafic rocks in the CIZ

The RSCM temperatures found for most the metasedimentary rocks of the CS (ranging between 212-370°C) together with the low-grade metamorphism reported in the studied area, support the hypothesis that the isotopic system of the dated apatites was not reset after the intrusion of the mafic sills.

Implications for Sb mineralization: Thermal devolatilization during magma emplacement

The metasedimentary sequences of the CS show a temperature range between 210-370°C, this would imply that the Sb was redistributed within the sulfide phases in the rock, without mobilizing it efficiently. Higher temperatures, like those attained in the contact aureoles of the mafic sills, would improve Sb mobilization. An adequate sampling of the metasediments perpendicular to the contact with the sill would be essential to evaluate this devolatilization effect. Moreover, such a sampling should be performed within the same stratigraphic horizon, to avoid differences due to original stratigraphic variations (Svensen et al., 2023). The sampling used in this thesis had the objective of studying the maximum temperatures reached during regional metamorphism and only occasionally regarded contact aureoles.

MINERAL SYSTEMS APPROACH-Sb DEPOSITS IN THE IBERO-ARMORICAN ARC

The Ibero-Armorican Arc illustrated a perfect example for the application of the mineral system concept to the study of Sb mineralization. At the continental, province, camp and deposit scales, several critical elements for the formation of Sb deposits were identified. Favorable

Conclusions

geodynamics and architecture are represented by the opening of the Rheic Ocean at the continental scale (Ibero-Armorican Arc), which triggered extensional processes, mantle melting, sedimentation in basins and the emplacement of mafic magma in these basins at the provincial scale (CIZ or Armorican Massif). At the camp scale (La Codosera, Almadén or Guadalmez synclines), the favorable geodynamics consisted in extensional and compressional tectonics leading to magma ascent and storage at upper crustal levels, which led to the emplacement of mafic sills within Sb-rich sediments and their devolatilization, accompanied by volatile degassing induced by the crystallization of the mafic intrusions. At the scale of the deposit, lithological and structural influences on the hydrothermal flows resulted in Sb-enriched fluids being trapped in favorable strata that facilitated the deposition of Sb mineralization. The closure of the Rheic Ocean and the collision between Gondwana and Larussia later resulted in the Variscan orogeny, which helped to the preservation of the Sb mineralization within the Variscan belt.

In terms of fertility, the presence of an Sb-enriched mantle source was not demonstrated in this study, but is a possible feature to be investigated at the continental or province scale. At the camp scale, two critical elements were identified: (i) Sb enrichment of the metasedimentary rocks of the CS suggesting possible primary enrichment of the sedimentary rocks in which the mafic magma emplaced, and (ii) Sb enrichment of the magmatic volatile phases exsolved during the last crystallization stages of these mafic magmas (observed at the CS, but also at the Armorican Massif).

More detailed studies are needed to quantify the respective contributions of these processes to the formation of Sb mineralization in the Ibero-Armorican Arc.

Conclusions

REFERENCES

- Agricola, G. (1556). *De Re Metallica: Translation from the original in Latin into English* (H. C. Hoover & L. H. Hoover (eds.)). New York, Dover Publications.
- Albert, R., Arenas, R., Gerdes, A., Sánchez Martínez, S., Fernández-Suárez, J., & Fuenlabrada, J. M. (2015). Provenance of the Variscan Upper Allochthon (Cabo Ortegal Complex, NW Iberian Massif) R. *Gondwana Research*, 28, 1434–1448.
- Alcock, J. E., Martínez Catalán, J. R., Arenas, R., & Montes, A. D. (2009). Use of thermal modeling to assess the tectono-metamorphic history of the Lugo and Sanabria gneiss domes, Northwest Iberia. *Bulletin de La Societe Geologique de France*, 180(3), 179–197. <https://doi.org/10.2113/gssgfbull.180.3.179>
- Alcock, J. E., Martínez Catalán, J. R., Rubio Pascual, F. J., Montes, A. D., Fernández, R. D., Barreiro, J. G., Arenas, R., Dias da Silva, Í., & Clavijo, E. G. (2015). 2-D thermal modeling of HT-LP metamorphism in NW and Central Iberia: Implications for Variscan magmatism, rheology of the lithosphere and orogenic evolution. *Tectonophysics*, 657, 21–37. <https://doi.org/10.1016/j.tecto.2015.05.022>
- Almela, A., Alvarado, M., Coma, E., Felgueroso, C., & Quintero, L. (1962). Estudio geológico de la región de Almadén. *Boletín Geológico y Minero de España*, 73, 193–327.
- Alonso, J. L., Marcos, A., & Suárez, A. (2009). Paleogeographic inversion resulting from large out of sequence breaching thrusts: The León Fault (Cantabrian zone, NW Iberia). A new picture of the external Variscan thrust belt in the Ibero-Armorican arc. *Geologica Acta*, 7(4), 451–473. <https://doi.org/10.1344/105.000001449>
- Andrade, A. A. S. (1985). Les deux associations basiques-ultrabasiques de Beja (Portugal m´eridional) sont-elles des ophiolites hercyniennes? *Ofioliti*, 10, 147–160.
- Arenas, R., & Martínez Catalán, J. R. (2002). Prograde development of corona textures in metagabbros of the Sobrado unit (Ordenes Complex, northwestern Iberian Massif). In J. R. Martinez-Catalán, J. Hatcher, R. Arenas, & F. Díaz García (Eds.), *Special Paper of the Geological Society of America* (Vol. 364, pp. 73–88). <https://doi.org/10.1130/0-8137-2364-7.73>

References

- Arenas, R., & Martínez Catalán, J. R. (2003). Low-P metamorphism following a Barrovian-type evolution. Complex tectonic controls for a common transition, as deduced in the Mondoñedo thrust sheet (NW Iberian Massif). *Tectonophysics*, 365(1–4), 143–164. [https://doi.org/10.1016/S0040-1951\(03\)00020-9](https://doi.org/10.1016/S0040-1951(03)00020-9)
- Arenas, R., Martínez Catalán, J. R., Sánchez Martínez, S., Fernández-Suárez, J., Andonaegui, P., Pearce, J. A., & Corfu, F. (2007). The Vila de Cruces ophiolite: A remnant of the early Rheic Ocean in the Variscan suture of Galicia (northwest Iberian Massif). *Journal of Geology*, 115(2), 129–148. <https://doi.org/10.1086/510645>
- Arenas, R., Sánchez Martínez, S., Díez Fernández, R., Gerdes, A., Abati, J., Fernández-Suárez, J., Andonaegui, P., González Cuadra, P., López Carmona, A., Albert, R., Fuenlabrada, J. M., & Rubio Pascual, F. J. (2016). Allochthonous terranes involved in the Variscan suture of NW Iberia: A review of their origin and tectonothermal evolution. *Earth-Science Reviews*, 161, 140–178. <https://doi.org/10.1016/j.earscirev.2016.08.010>
- Armendáriz, M., López-Guijarro, R., Quesada, C., Pin, C., & Bellido, F. (2008). Genesis and evolution of a syn-orogenic basin in transpression: Insights from petrography, geochemistry and Sm-Nd systematics in the Variscan Pedroches basin (Mississippian, SW Iberia). *Tectonophysics*, 461(1–4), 395–413. <https://doi.org/10.1016/j.tecto.2008.02.007>
- Arribas, & Gumiel, P. (1984). First Occurrence of a Strata-Bound Sb-W-Hg Deposit in the Spanish Hercynian Massif. In A. Wauschkuhn, C. Kluth, & R. H. Zimmerman (Eds.), *Syngeneses and epigenesis in the formation of mineral deposits* (pp. 469–481). Springer-Verlag.
- Audétat, A., Günther, D., & Heinrich, C. A. (2000). Magmatic-hydrothermal evolution in a fractionating granite: A microchemical study of the Sn-W-F-mineralized mole granite (Australia). *Geochimica et Cosmochimica Acta*, 64(19), 3373–3393. [https://doi.org/10.1016/S0016-7037\(00\)00428-2](https://doi.org/10.1016/S0016-7037(00)00428-2)
- Azor, A., Dias da Silva, Í., Gómez Barreiro, J., González-Clavijo, E., Martínez Catalán, J. R., Simancas, J. F., Martínez Poyatos, D., Pérez-Cáceres, I., González Lodeiro, F., Expósito, I., Casas, J. M., Clariana, P., García-Sansegundo, J., & Margalef, A. (2019). *Deformation and Structure* (Issue September). Springer International Publishing. https://doi.org/10.1007/978-3-030-10519-8_10
- Azor, A., Rubatto, D., Simancas, J. F., González Lodeiro, F., Martínez Poyatos, D., Martín

References

- Parra, L. M., & Matas, J. (2008). Rheic Ocean ophiolitic remnants in southern Iberia questioned by SHRIMP U-Pb zircon ages on the Beja-Acebuches amphibolites. *Tectonics*, 27(5), 1–11. <https://doi.org/10.1029/2008TC002306>
- Azza, A. (2019). *Géologie et métallogénie des minéralisations à or et antimoine du Jbel Haouanite (Haut Atlas oriental , Maroc)*. Université Sidi Mohamed ben Abdellah.
- Azza, A., Abdellah, B., & Ali, M. (2019). Gold and Antimony Mineralizations of Jbel Haouanite (High Atlas, Morocco) in Their Geodynamic Context. *European Scientific Journal ESJ*, 15(18), 336–354. <https://doi.org/10.19044/esj.2019.v15n18p336>
- Bailly, L., Bouchot, V., Bény, C., & Milési, J. P. (2000). Fluid inclusion study of stibnite using infrared microscopy: An example from the Brouzils antimony deposit (Vendee, Armorican massif, France). *Economic Geology*, 95(1), 221–226. <https://doi.org/10.2113/gsecongeo.95.1.221>
- Balé, P., & Brun, J.-P. (1986). Les complexes métamorphiques du Leon (NW Bretagne); un segment du domaine eo-hercynien sud armoricain translate au Devonien. *Bulletin de La Societe Geologique de France*, 2(3), 471–477. <https://doi.org/10.2113/gssgfbull.II.3.471>
- Ballèvre, M., Bosse, V., Ducassou, C., & Pitra, P. (2009). Palaeozoic history of the Armorican Massif: Models for the tectonic evolution of the suture zones. *Comptes Rendus - Geoscience*, 341(2–3), 174–201. <https://doi.org/10.1016/j.crte.2008.11.009>
- Ballèvre, M., Martínez-Catalán, J. R., López-Carmona, A., Pitra, P., Abati, J., Fernández, R. D., Ducassou, C., Arenas, R., Bosse, V., Castiñeiras, P., Fernández-Suárez, J., Gómez Barreiro, J., Paquette, J.-L., Peucat, J.-J., Poujol, M., Ruffet, G., & Sánchez-Martínez, S. (2014). Correlation of the nappe stack in the Ibero-Armorican arc across the Bay of Biscay: a joint French–Spanish project. *Geological Society, London, Special Publications*, 405(1), 77–113. <https://doi.org/10.1144/SP405.13>
- Ballèvre, M., Paris, F., & Robardet, M. (1992). Ibero-Armorican correlations during the Palaeozoic: confrontation of palaeobiogeographic and tectonometamorphic data[Correlations ibero-armoricaines au Paleozoique: une confrontation des donnees paleobiogeographiques et tectonometamorphiques]. *Comptes Rendus - Academie Des Sciences, II*(315), 1783–1789. https://doi.org/10.20595/jjbf.19.0_3
- Ballouard, C., Poujol, M., Boulvais, P., & Zeh, A. (2017). Crustal recycling and juvenile

References

- addition during lithospheric wrenching: The Pontivy-Rostrenen magmatic complex, Armorican Massif (France), Variscan belt. *Gondwana Research*, 49, 222–247. <https://doi.org/10.1016/j.gr.2017.06.002>
- Bandrés, A., Eguíluz, L., Pin, C., Paquette, J. L., Ordóñez, B., Le Fèvre, B., Ortega, L. A., & Gil Ibarguchi, J. I. (2004). The northern Ossa-Morena Cadomian batholith (Iberian Massif): Magmatic arc origin and early evolution. *International Journal of Earth Sciences*, 93(5), 860–885. <https://doi.org/10.1007/s00531-004-0423-6>
- Barbero, L. (1995). Granulite-facies metamorphism in the Anatectic Complex of Toledo, Spain: late Hercynian tectonic evolution by crustal extension. *Journal - Geological Society (London)*, 152(2), 365–382. <https://doi.org/10.1144/gsjgs.152.2.0365>
- Barbero, L., & Villaseca, C. (2000). Eclogite facies relics in metabasites from the Sierra de Guadarrama (Spanish Central System): P-T estimations and implications for the Hercynian evolution. *Mineralogical Magazine*, 64, 815–836.
- Barboni, M., Schoene, B., Ovtcharova, M., Bussy, F., Schaltegger, U., & Gerdes, A. (2013). Timing of incremental pluton construction and magmatic activity in a back-arc setting revealed by ID-TIMS U/Pb and Hf isotopes on complex zircon grains. *Chemical Geology*, 342, 76–93. <https://doi.org/10.1016/j.chemgeo.2012.12.011>
- Barquero, J. I., Lorenzo, S., Esbri, J. M., Rivera, S., González-Valoys, A. C., García-Ordiales, E., & Higuera, P. (2022). *Geochemical Assessment of Mineral Resource Potential in a Hg-Sb-Pb-Zn Mining Area: The Almadén and Guadalmez Synclines (South-Central Spain)*. 1–17.
- Barrois, C. (1899). Sketch of the Geology of central Brittany: With special reference to the Whitsuntide excursion for 1899. *Proceedings of the Geologists' Association*, 16(3), 101–132. [https://doi.org/10.1016/S0016-7878\(99\)80010-8](https://doi.org/10.1016/S0016-7878(99)80010-8)
- Bea, F., Montero, P. G., Gonzalez-Lodeiro, F., Talavera, C., Molina, J. F., Scarrow, J. H., Whitehouse, M. J., & Zinger, T. (2006). Zircon thermometry and U-Pb ion-microprobe dating of the gabbros and associated migmatites of the Variscan Toledo Anatectic Complex, Central Iberia. *Journal of the Geological Society*, 163(5), 847–855. <https://doi.org/10.1144/0016-76492005-143>
- Bea, F., Montero, P., & Molina, J. F. (1999). Mafic precursors, peraluminous granitoids, and

References

- late lamprophyres in the Avila batholith: A model for the generation of variscan batholiths in Iberia. *Journal of Geology*, 107(4), 399–419. <https://doi.org/10.1086/314356>
- Bea, F., Montero, P., & Zinger, T. (2003). The nature, origin, and thermal influence of the granite source layer of Central Iberia. *Journal of Geology*, 111(5), 579–595. <https://doi.org/10.1086/376767>
- Beaudoin, G., & Pitre, D. (2005). Stable isotope geochemistry of the Archean Val-d'Or (Canada) orogenic gold vein field. *Mineralium Deposita*, 40(1), 59–75. <https://doi.org/10.1007/s00126-005-0474-z>
- Béchenec, F., Audru, J. C., Corbier, P., Bourgon, J., Guyomard, Y., & Cardoso, J. D. S. (2006). *Carte géologique de la France n° 348 au 1/50 000, feuille Plouay*.
- Beyssac, O., Goffé, B., Chopin, C., & Rouzaud, J. N. (2002). Raman spectra of carbonaceous material in metasediments: a new geothermometer. *Journal of Metamorphic Geology*, 20(9), 859–871.
- Beyssac, O., Negro, F., Simoes, M., Chan, Y. C., & Chen, Y. G. (2008). High-pressure metamorphism in Taiwan: From oceanic subduction to arc-continent collision? *Terra Nova*, 20(2), 118–125. <https://doi.org/10.1111/j.1365-3121.2008.00796.x>
- Blatrix, P., & Burg, J. P. (1981). ⁴⁰Ar-³⁹Ar dates from Sierra Morena (southern Spain): Variscan metamorphism and Cadomian orogeny. *Neues Jahrbuch Fur Mineralogie, Monatshefte*, 470–478.
- Bloomstein, E. I., & Clark, J. B. (1989). Geochemistry of the Ordovician High-Calcium Black Shales Hosting Major gold Deposits of the Getchell Trend in Nevada. In *METALLIFEROUS BLACK SHALES AND RELATED ORE DEPOSITS PROCEEDINGS, 1989 UNITED STATES WORKING GROUP MEETING, INTERNATIONAL GEOLOGICAL CORRELATION PROGRAM PROJECT 254* (p. 254).
- Blouin, J. P. (1991). District antimonifère de Vendée. Rappel sur les réserves démontrées à l'intérieur des divers P.E.R. *Rapport BRGM DMM/DL/NANTES RVL/FD92-04*.
- Bonatti, E., Lawrence, J. R., & Morandi, N. (1984). Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content. *Earth and Planetary Science Letters*, 70(1), 88–94. [https://doi.org/10.1016/0012-821X\(84\)90211-5](https://doi.org/10.1016/0012-821X(84)90211-5)
- Bosse, V., Balleve, M., & Vidal, O. (2002). Ductile thrusting recorded by the garnet isograd

References

- from blueschist-facies metapelites of the Ile de Groix, Armorican Massif, France. *Journal of Petrology*, 43(3), 485–510. <https://doi.org/10.1093/petrology/43.3.485>
- Bosse, V., Feraud, G., Ruffet, G., Ballèvre, M., Peucat, J.-J., & DeJong, K. (2000). Late Devonian subduction and early-orogenic exhumation of eclogite-facies rocks from the Champtoceaux Complex (Variscan belt, France). *Geological Journal*, 35, 297–325. <https://doi.org/10.1016/j.physc.2005.01.050>
- Bouchot, V., Ledru, P., Lerouge, C., Lescuyer, J. L., & Milesi, J. P. (2005). 5: Late Variscan mineralizing systems related to orogenic processes: The French Massif Central. *Ore Geology Reviews*, 27(1–4), 169–197. <https://doi.org/10.1016/j.oregeorev.2005.07.017>
- Boudreau, A. E. (1995). Fluid evolution in layered intrusions: evidence from the chemistry of the halogen-bearing minerals. In J. F. H. Thompson (Ed.), *Magma, Fluids and Ore Deposits*. (23rd ed., pp. 25–46). Geological Society of Canada Short Course.
- Boyle, R. W., & Jonasson, I. R. (1984). The geochemistry of antimony and its use as an indicator element in geochemical prospecting. *Journal of Geochemical Exploration*, 20(3), 223–302. [https://doi.org/10.1016/0375-6742\(84\)90071-2](https://doi.org/10.1016/0375-6742(84)90071-2)
- Braid, J. A., Brendan Murphy, J., Quesada, C., & Mortensen, J. (2011). Tectonic escape of a crustal fragment during the closure of the Rheic Ocean: U-Pb detrital zircon data from the late Palaeozoic Pulo do Lobo and South Portuguese zones, Southern Iberia. *Journal of the Geological Society*, 168(2), 383–392. <https://doi.org/10.1144/0016-76492010-104>
- BRGM. (1987). Plan minier breton, exercice 1985, rapport de fin de travaux, les recherches minières. *BRGM Report 87-DAM-018-OP4*, 12.
- BRGM. (1990). Plan minier breton, convention 1988, rapport de fin de travaux, les recherches minières. *BRGM Report RR-30413-FR*, 10.
- Brobst, D. A., & Pratt, W. P. (1981). United States Mineral Resources. In D. A. Brobst & W. P. Pratt (Eds.), *GEOLOGICAL SURVEY PROFESSIONAL PAPER 820*. United States Government Printing Office.
- Brun, J. P., Guennoc, P., Truffert, C., & Vairon, J. (2001). Cadomian tectonics in northern Brittany: A contribution of 3-D crustal-scale modelling. *Tectonophysics*, 331(1–2), 229–246. [https://doi.org/10.1016/S0040-1951\(00\)00244-4](https://doi.org/10.1016/S0040-1951(00)00244-4)
- Buchholz, P., Oberthür, T., Lüders, V., & Wilkinson, J. (2007). Multistage Au-As-Sb

References

- mineralization and crustal-scale fluid evolution in the Kwekwe District, Midlands Greenstone Belt, Zimbabwe: A combined geochemical, mineralogical, stable isotope, and fluid inclusion study. *Economic Geology*, 102(3), 347–378. <https://doi.org/10.2113/gsecongeo.102.3.347>
- Burrows, D. R., & Spooner, E. T. C. (1988). Relationships between Archean Gold Quartz Vein-Shear Zone Mineralization and Igneous Intrusions in the Val d’Or and Timmins Areas, Abitibi Subprovince, Canada. *Economic Geology Monograph*, 6, 424–445.
- Cambeses, A., Scarrow, J. H., Montero, P., Molina, J. F., & Moreno, J. A. (2015). SHRIMP U-Pb zircon dating of the Valencia del Ventoso plutonic complex, Ossa-Morena Zone, SW Iberia: Early Carboniferous intra-orogenic extension-related “calc-alkaline” magmatism. *Gondwana Research*, 28(2), 735–756. <https://doi.org/10.1016/j.gr.2014.05.013>
- Campos Rodríguez, H. R., Gloaguen, E., Pochon, A., Tuduri, J., Sizaret, S., Higuera, P., Iacono-Marziano, G., Lorenzo, S., Esbri, J. M., Poujol, M., & Mollé, V. (2023). Mafic magmatism in the Central Iberian Zone: Towards a better understanding of Sb mineralization? In *Proceedings of the 17th SGA Biennial Meeting, 28 August – 1 September 2023* (Vol. 3, pp. 121–125). <https://e-sga.org/nc/publications/sga-biennial-meetings-abstract-volumes/2023-zurich/>
- Capdevila, R. (1969). *Le métamorphisme régional progressif et les granites dans le segment hercynien de Galice Nord Orientale (NW de l’Espagne)* [Université de Montpellier]. <https://pascal-francis.inist.fr/vibad/index.php?action=getRecordDetail&idt=GEODEBRGM6907017104>
- Carbonell, R., Simancas, F., Juhlin, C., Pous, J., Pérez-Estaún, A., Gonzalez-Lodeiro, F., Munoz, G., Heise, W., & Ayarza, P. (2004). Geophysical evidence of a mantle derived intrusion in SW Iberia. *Geophysical Research Letters*, 31(11), 2–5. <https://doi.org/10.1029/2004GL019684>
- Carlin, J. F. (1994). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (1995). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>

References

and-information

- Carlin, J. F. (1996). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
- Carlin, J. F. (1997). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (1998). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (1999). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2000). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2001). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2002). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2003). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2004). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2005). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
<http://minerals.usgs.gov/minerals/pubs/country/2005/limyb05.pdf>
- Carlin, J. F. (2006). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.

References

- <http://minerals.usgs.gov/minerals/pubs/commodity/myb/>
- Carlin, J. F. (2007). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2009). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <http://minerals.usgs.gov/minerals/pubs/commodity/myb/>
- Carlin, J. F. (2010). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2011). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2012). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Carlin, J. F. (2013). Antimony. In *U.S. Geological Survey Mineral Commodity Summaries 2013* (Issue b, pp. 18 – 19).
- Carnicero, A., & Castro, A. (1983). El plutón de Higuera-Táliga y su haz de diques básicos (Badajoz, Sierra Morena occidental). *Estudios Geológicos (Madrid)*, 39, 141–150.
- Cartier, C., & Faure, M. (2004). The Saint-Georges-sur-Loire olistostrome, a key zone to understand the Gondwana-Armorica boundary in the Variscan belt (Southern Brittany, France). *International Journal of Earth Sciences*, 93(6), 945–958. <https://doi.org/10.1007/s00531-004-0398-3>
- Casetta, F., Ickert, R. B., Mark, D. F., Bonadiman, C., Giacomoni, P. P., Ntaflos, T., & Coltorti, M. (2019). The alkaline lamprophyres of the dolomitic area (Southern Alps, Italy): Markers of the late triassic change from orogenic-like to anorogenic magmatism. *Journal of Petrology*, 60(6), 1263–1298. <https://doi.org/10.1093/petrology/egz031>
- Catchpole, H., Kouzmanov, K., Fontboté, L., Guillong, M., & Heinrich, C. (2011). Fluid evolution in zoned Cordilleran polymetallic veins – insights from microthermometry and LA-ICP-MS of fluid inclusions. *Chemical Geology*, 281, 293–304.

References

- <https://doi.org/10.1016/j.chemgeo.2010.12.016>0AFluid
- Cebriá, J. M., López-Ruiz, J., Doblas, M., Martins, L. T., & Munha, J. (2003). Geochemistry of the early Jurassic Messejana- Plasencia dyke (Portugal-Spain): Implications on the origin of the Central Atlantic magmatic province. *Journal of Petrology*, 44(3), 547–568. <https://doi.org/10.1093/petrology/44.3.547>
- Chantraine, J., Chauvel, J. . J., & Rabu, D. (1994). Lithostratigraphy. In J. Chantraine, J. Rolet, D. S. Santallier, A. Piqué, & J. D. Keppie (Eds.), *Pre-Mesozoic Geology in France and Related Areas* (pp. 81–95). Springer.
- Chatelin, T. (2022). *Transition Magmatique-Hydrothermale : Compréhension des processus à travers la caractérisation des ilménites dans les roches mafiques*. Université d'Orléans.
- Chauris, L., Fouquet, Y., & Moëlo, Y. (1977). Les occurrences antimonifères de l'île de Sein et du cap Sizun (Finistère). Leur place dans la métallogénie armoricaine. *Bulletin de La Société Française de Minéralogie et de Cristallographie*, 100(3), 208–213. <https://doi.org/10.3406/bulmi.1977.7138>
- Chauris, L., Houlgatte, E., Laforêt, C., & Picot, P. (1985). Un district antimonoaurifère à gangue quartzo-carbonatée: Le Semnon (Ille-et-Vilaine, Massif Armoricaïn, France). *Hercynica*, 1, 111–119.
- Chauris, L., & Marcoux, E. (1994). Metallogeny of the Armorican Massif. In J. D. Keppie (Ed.), *Pre-Mesozoic Geology in France and Related Areas*. Springer-Verlag Berlin Heidelberg.
- Chauvel, C., Lewin, E., Carpentier, M., Arndt, N. T., & Marini, J. C. (2008). Role of recycled oceanic basalt and sediment in generating the Hf-Nd mantle array. *Nature Geoscience*, 1(1), 64–67. <https://doi.org/10.1038/ngeo.2007.51>
- Cherniak, D. J., Lanford, W. A., & Ryerson, F. J. (1991). Lead diffusion in apatite and zircon using ion implantation and Rutherford Backscattering techniques. *Geochimica et Cosmochimica Acta*, 55(6), 1663–1673. [https://doi.org/10.1016/0016-7037\(91\)90137-T](https://doi.org/10.1016/0016-7037(91)90137-T)
- Cheval-Garabédian, F. (2016). *Les minéralisations à Sb et Au tardi-varisques : vers un modèle génétique unifié ? Exemples du Massif Armoricaïn et du Massif Central*. Université d'Orléans.
- Cheval-Garabédian, F., Marcoux, E., Raimbourg, H., & Faure, M. (2023). The La Lucette Sb-Au-(W) vein-deposit (Armorican Massif, France): New time and genetic constraints to

References

- decipher the 310–295 Ma Sb-Au metallogenic peak in the Variscan Belt. *Ore Geology Reviews*, 163(October). <https://doi.org/10.1016/j.oregeorev.2023.105728>
- Chew, D. M., Petrus, J. A., & Kamber, B. S. (2014). U-Pb LA-ICPMS dating using accessory mineral standards with variable common Pb. *Chemical Geology*, 363, 185–199. <https://doi.org/10.1016/j.chemgeo.2013.11.006>
- Cocherie, A. (2001). Datations à la SHRIMP II dans le cadre du projet carte 1/50 000 des zircons magmatiques de l'Orthogneiss du Loc'h et du Granite d'Odet. *Rapport Interne BRGM AC/02.01*, 8.
- Cochrane, R., Spikings, R. A., Chew, D., Wotzlaw, J. F., Chiaradia, M., Tyrrell, S., Schaltegger, U., & Van der Lelij, R. (2014). High temperature (>350°C) thermochronology and mechanisms of Pb loss in apatite. *Geochimica et Cosmochimica Acta*, 127, 39–56. <https://doi.org/10.1016/j.gca.2013.11.028>
- Conolly, H. J. C. (1936). A contour method of revealing some ore structures. *Economic Geology*, 31(3), 259–271. <https://doi.org/10.2113/gsecongeo.31.3.259>
- Corretgé, L. G., & Suárez, O. (1990). Cantabrian and Palentian Zones. Igneous Rocks. *Pre-Mesozoic Geology of Iberia*, 72–79.
- Cotrim, B., Bento dos Santos, T., Mata, J., Benoit, M., & Jesus, A. P. (2021). Lower Paleozoic rifting event in Central Iberian Zone (central-north Portugal): Evidence from elemental and isotopic geochemistry of metabasic rocks. *Geochemistry*, 81(3), 125768. <https://doi.org/10.1016/j.chemer.2021.125768>
- Couto, H., Roger, G., Moëlo, Y., & Bril, H. (1990). Le district à antimoine-or Dúrico-Beirão (Portugal): évolution paragénetique et géochimique; implications métallogéniques. *Mineralium Deposita*, 25(1). <https://doi.org/10.1007/BF00205252>
- Cunha, P. P., Martins, A. A., Gomes, A., Stokes, M., Cabral, J., Lopes, F. C., Pereira, D., de Vicente, G., Buylaert, J. P., Murray, A. S., & Antón, L. (2019). Mechanisms and age estimates of continental-scale endorheic to exorheic drainage transition: Douro River, Western Iberia. *Global and Planetary Change*, 181, 102985. <https://doi.org/10.1016/J.GLOPLACHA.2019.102985>
- Dabard, M. P., Loi, A., Pavanetto, P., Meloni, M. A., Hauser, N., Matteini, M., & Funedda, A. (2021). Provenance of Ediacaran-Ordovician sediments of the Medio Armorican Domain,

References

- Brittany, West France: Constraints from U/Pb detrital zircon and Sm–Nd isotope data. *Gondwana Research*, 90, 63–76. <https://doi.org/10.1016/j.gr.2020.11.004>
- Dallmeyer, R. D., Martínez Catalán, J. R., Arenas, R., Gil Ibarguchi, J. I., Gutiérrez Alonso, G., Farias, P., Bastida, F., & Aller, J. (1997). Diachronous Variscan tectonothermal activity in the NW Iberian Massif: Evidence from $^{40}\text{Ar}/^{39}\text{Ar}$ dating of regional fabrics. *Tectonophysics*, 277(4), 307–337. [https://doi.org/10.1016/S0040-1951\(97\)00035-8](https://doi.org/10.1016/S0040-1951(97)00035-8)
- Dallmeyer, R. D., & Quesada, C. (1992). Cadomian vs. Variscan evolution of the Ossa-Morena zone (SW Iberia): field and $^{40}\text{Ar}/^{39}\text{Ar}$ mineral age constraints. *Tectonophysics*, 216(3–4), 339–364. [https://doi.org/10.1016/0040-1951\(92\)90405-U](https://doi.org/10.1016/0040-1951(92)90405-U)
- de Almeida Coelho, C. M. (2021). *O Campo Lamprofírico de Labruge: Petrologia e Geoquímica*. Universidade do Porto.
- De La Rosa, J. D., Jenner, G. A., & Castro, A. (2002). A study of inherited zircons in granitoid rocks from the South Portuguese and Ossa-Morena Zones, Iberian Massif: Support for the exotic origin of the South Portuguese Zone. *Tectonophysics*, 352(1–2), 245–256. [https://doi.org/10.1016/S0040-1951\(02\)00199-3](https://doi.org/10.1016/S0040-1951(02)00199-3)
- De Vicente, G., Cloetingh, S., Van Wees, J. D., & Cunha, P. P. (2011). Tectonic classification of Cenozoic Iberian foreland basins. *Tectonophysics*, 502(1–2), 38–61. <https://doi.org/10.1016/j.tecto.2011.02.007>
- De Vicente, G., Olaiz, A., Muñoz-Martín, A., & Cunha, P. P. (2021). Longest and still longer: The Messejana-Plasencia dyke and its links with later Alpine deformation belt in Iberia. *Tectonophysics*, 815(July). <https://doi.org/10.1016/j.tecto.2021.229009>
- Dee, S. J., & Roberts, S. (1993). Late-kinematic gold mineralisation during regional uplift and the role of nitrogen: an example from the La Codosera area, W. Spain. *Mineralogical Magazine*, 57(388), 437–450. <https://doi.org/10.1180/minmag.1993.057.388.07>
- Deschamps, F., Godard, M., Guillot, S., Chauvel, C., Andreani, M., Hattori, K., Wunder, B., & France, L. (2012). Behavior of fluid-mobile elements in serpentines from abyssal to subduction environments: Examples from Cuba and Dominican Republic. *Chemical Geology*, 312–313, 93–117. <https://doi.org/10.1016/j.chemgeo.2012.04.009>
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., & Hattori, K. (2010). In situ characterization of serpentinites from forearc mantle wedges: Timing of

References

- serpentinization and behavior of fluid-mobile elements in subduction zones. *Chemical Geology*, 269(3–4), 262–277. <https://doi.org/10.1016/j.chemgeo.2009.10.002>
- Dias da Silva, Í., Díez Fernández, R., Díez-Montes, A., González Clavijo, E., & Foster, D. A. (2016). Magmatic evolution in the N-Gondwana margin related to the opening of the Rheic Ocean—evidence from the Upper Parautochthon of the Galicia-Trás-os-Montes Zone and from the Central Iberian Zone (NW Iberian Massif). *International Journal of Earth Sciences*, 105(4), 1127–1151. <https://doi.org/10.1007/s00531-015-1232-9>
- Dias da Silva, Í., González Clavijo, E., & Martínez-Catalán, J. R. (2010). Evolução tectono-térmica de um sector da Zona Centro Ibérica na região de Palaçoulo (leste do Maciço de Morais, NE Portugal). *Revista Electrónica de Ciências Da Terra Geosciences On-Line Journal*, 11(4).
- Dias da Silva, Í., Valverde-Vaquero, P., Gonzálezclavijo, E., Díez-Montes, A., & Catalán, J. R. M. (2014). Structural and stratigraphical significance of U-Pb ages from the Mora and Saldanha volcanic complexes (NE Portugal, Iberian Variscides). *Geological Society Special Publication*, 405(1), 115–135. <https://doi.org/10.1144/SP405.3>
- Dias, G., Leterrier, J., Mendes, A., Simões, P. P., & Bertrand, J. M. (1998). U-Pb zircon and monazite geochronology of post-collisional Hercynian granitoids from the Central Iberian Zone (Northern Portugal). *Lithos*, 45(1–4), 349–369. [https://doi.org/10.1016/S0024-4937\(98\)00039-5](https://doi.org/10.1016/S0024-4937(98)00039-5)
- Días, R., & Ribeiro, A. (1995). The Ibero-Armorican Arc: A collision effect against an irregular continent? *Tectonophysics*, 246(1–3), 113–128. [https://doi.org/10.1016/0040-1951\(94\)00253-6](https://doi.org/10.1016/0040-1951(94)00253-6)
- Dias, R., Ribeiro, A., Coke, C. Pereira, E., Rodrigues, J. F., Castro, P., Moreira, N., & Rebelo, J. A. (2013). Evolução estrutural dos sectores setentrionais do Autóctone da Zona Centro-Ibérica. In R. Dias, A. Araújo, P. Terrinha, & J. C. Kullberg (Eds.), *Geologia de Portugal* (Vol. 5, p. 2013).
- Díez Balda, M. ., Vegas, R., & González Lodeiro, F. (1990). Structure. In R. D. Dallmeyer & E. Martinez García (Eds.), *Pre-Mesozoic Geology of Iberia* (pp. 172–188). Springer-Verlag.
- Díez Fernández, R., & Arenas, R. (2015). The Late Devonian Variscan suture of the Iberian Massif: A correlation of high-pressure belts in NW and SW Iberia. *Tectonophysics*, 654,

References

- 96–100. <https://doi.org/10.1016/j.tecto.2015.05.001>
- Díez Fernández, R., & Pereira, M. F. (2016). Extensional orogenic collapse captured by strike-slip tectonics: Constraints from structural geology and U–Pb geochronology of the Pinhel shear zone (Variscan orogen, Iberian Massif). *Tectonophysics*, 691, 290–310. <https://doi.org/10.1016/j.tecto.2016.10.023>
- Díez Montes, A. (2007). La geología del Dominio “Ollo de Sapo” en las comarcas de Sanabria y Terra do Bolo. In *Nova Terra* (34th ed.). Instituto Universitario de Geología “Isidro Parga Pondal”—Área de Xeoloxía e Minería do Seminario de Estudos Galegos.
- Díez Montes, A., & Gallastegui, G. (1992). The geology of the Ciperez-Garcirrey granitic pluton (Prov. Salamanca, Spain). *Cuadernos Do Laboratorio Xeoloxico de Laxe*, 17, 279–292.
- Dill, H. G. (2010). The “chessboard” classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. *Earth-Science Reviews*, 100(1–4), 1–420. <https://doi.org/10.1016/j.earscirev.2009.10.011>
- Dodson, M. H. (1973). Closure temperature in cooling geochronological and petrological systems. *Contributions to Mineralogy and Petrology*, 40(3), 259–274. <https://doi.org/10.1007/BF00373790>
- Dostal, J., Murphy, J. B., Shellnutt, J. G., Ulrych, J., & Fediuk, F. (2019). Neoproterozoic to Cenozoic magmatism in the central part of the Bohemian Massif (Czech Republic): Isotopic tracking of the evolution of the mantle through the Variscan orogeny. *Lithos*, 326–327, 358–369. <https://doi.org/10.1016/j.lithos.2018.12.028>
- Dubé, B., & Gosselin, P. (2007). Greenstone-hosted quartz-carbonate vein deposits. In W. D. Goodfellow (Ed.), *Mineral deposits of Canada: A synthesis of major deposit types, district metallogeny, the evolution of geological provinces, and exploration methods* (pp. 49–73). Geological Association of Canada, Mineral Deposits Division.
- Dudek, A. (1980). The crystalline basement block of the Outer Carpathians in Moravia. In Ľ. Cs. Rozpr. & V. Akad. (Eds.), *Academia nakladatelství Československé akademie věd* (Vol. 90, Issue 8).
- Dunn, A. M., Reynolds, P. H., Clarke, D. B., & Ugidos, J. M. (1998). A comparison of the age and composition of the Shelburne dyke, Nova Scotia, and the Messejana dyke, Spain.

References

- Canadian Journal of Earth Sciences*, 35(10), 1110–1115. <https://doi.org/10.1139/e98-058>
- Edel, J. B., Schulmann, K., Lexa, O., & Lardeaux, J. M. (2018). Late Palaeozoic palaeomagnetic and tectonic constraints for amalgamation of Pangea supercontinent in the European Variscan belt. *Earth-Science Reviews*, 177(December 2017), 589–612. <https://doi.org/10.1016/j.earscirev.2017.12.007>
- Einaudi, M. T., Hedenquist, J. W., & Inan, E. (2003). Sulfidation State of Fluids in Active and Extinct Hydrothermal Systems: Transitions from Porphyry to Epithermal Environments. In S. T. Simmons & I. Graham (Eds.), *Volcanic, geothermal and ore-forming fluids: Rulers and witnesses of processes within the Earth* (Special Pu, Issue November, pp. 285–313). Society of Economic Geologist. <https://doi.org/10.5382/sp.10.15>
- Errandonea-Martin, J., Sarrionandia, F., Janoušek, V., Carracedo-Sánchez, M., & Gil Ibarguchi, J. I. (2019). Origin of cordierite-bearing monzogranites from the southern Central Iberian Zone – Inferences from the zoned Sierra Bermeja Pluton (Extremadura, Spain). *Lithos*, 342–343, 440–462. <https://doi.org/10.1016/j.lithos.2019.06.009>
- Escuder Viruete, J., Indares, A., & Arenas, R. (1997). P–T path determinations in the Tormes Gneissic Dome, NW Iberian Massif, Spain. *Journal of Metamorphic Geology*, 645–663.
- European Commission. (2020). *Study on the EU 's list of Critical Raw Materials, Factsheets on Critical Raw Materials*. <https://doi.org/10.2873/92480>
- European Commission. (2023). *Study on the EU 's list of Critical Raw Materials, Factsheets on Critical Raw Materials* (M. Grohol, C. Veeh, D. GROW, & European Comission (eds.)). European Comission. <https://doi.org/10.2873/725585>
- Expósito, I., Simancas Cabrera, J., & González Lodeiro, F. (2002). Estructura de la mitad septentrional de la zona de Ossa-Morena: Deformación en el bloque inferior de un cabalgamiento cortical de evolución compleja: Deformación en el bloque inferior de un cabalgamiento cortical de evolución compleja. *Revista de La Sociedad Geológica de España*, 15(1), 3–14.
- Fan, D., Zhang, T., & Ye, J. (2004). The Xikuangshan Sb deposit hosted by the Upper Devonian black shale series, Hunan, China. *Ore Geology Reviews*, 24(1–2), 121–133. <https://doi.org/10.1016/j.oregeorev.2003.08.005>
- Farias, P., Gallastegui, G., González Lodeiro, F., Marquínez, J., Martín Parra, L. M., Martínez

References

- Catalán, J. R., de Pablo Macía, J. G., & Rodríguez Fernández, L. R. (1987). Aportaciones al conocimiento de la litoestratigrafía y estructura de Galicia Central. *Memórias Da Faculdade de Ciências, Universidade Do Porto 1*, 411–413.
- Fernández-Suárez, J., Corfu, F., Arenas, R., Marcos, A., Martínez Catalán, J. R., Díaz García, F., Abati, J., & Fernández, F. J. (2002). U-Pb evidence for a polyorogenic evolution of the HP-HT units of the NW Iberian Massif. *Contributions to Mineralogy and Petrology*, 143(2), 236–253. <https://doi.org/10.1007/s00410-001-0337-2>
- Fouad, L., & Mustapha, C. (2024). Occurrences antimonifères du Massif Hercynien Central Marocain: Essai comparatif, hypothèse génétique et perspectives d’exploration. *International Journal of Innovation and Applied Studies*, 42(3), 437–447. <https://doi.org/ISSN 2028-9324>
- Fouquet, Y. (1980). *Les districts antimonifères de Quimper et du Cap Sizun (Finistère): leur placedans la métallogénie de l’antimoine dans le massif armoricain (France)*. Université de Clermont II.
- Franke, W. (2000). The mid-European segment of the Variscides: Tectonostratigraphic units, terrane boundaries and plate tectonic evolution. *Geological Society Special Publication*, 179, 35–56. <https://doi.org/10.1144/GSL.SP.2000.179.01.05>
- Franke, W., Cocks, L. R. M., & Torsvik, T. H. (2017). The Palaeozoic Variscan oceans revisited. *Gondwana Research*, 48, 257–284. <https://doi.org/10.1016/j.gr.2017.03.005>
- Ganino, C., & Arndt, N. T. (2009). Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology*, 37(4), 323–326. <https://doi.org/10.1130/G25325A.1>
- García Alcalde, J. L., Carls, P., Pardo Alonso, M. V., Sanz López, J., Soto, F., Truyols-Massoni, M., & Valenzuela-Ríos, J. L. (2002). Devonian. In W. Gibbons & T. Moreno (Eds.), *The Geology of Spain* (pp. 67–91). The Geological Society of London.
- García Casquero, J. L., Boelrijk, N. A. I. M., Chacón, J., & Priem, H. N. A. (1985). Rb-Sr evidence for the presence of Ordovician gsrnites in the deformed basement of the Badajoz-Córdoba belt, SW Spain. *Geologische Rundschau*, 74(2), 379–384. <https://doi.org/10.1007/BF01824904>
- García de Figuerola, L. C., Corretge, L. G., & Bea, F. (1974). El dique de Alentejo-Plasencia y

References

- haces de diques básicos de Extremadura. *Boletín Geológico y Minero de España*, 85, 40–69.
- García San Segundo, J., Lorenzo Álvarez, S., Martínez Rius, A., Vergés Masip, J., & Quesada, C. (1985). Mapa geológico & memoria explicativa de la hoja num. 808, Almadén. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 62). IGME.
- Ghienne, J., Le Heron, D. P., Moreau, J., Denis, M., & Deynoux, M. (2007). The Late Ordovician Glacial Sedimentary System of the North Gondwana Platform. *Glacial Sedimentary Processes and Products*, 295–319. <https://doi.org/10.1002/9781444304435.ch17>
- Gibson, R. I. (1998). Type cast - Antimony, the metallic sidekick, sets the world on fire and puts it out. *Earth Magazine, February*, 58. <http://www.gravmag.com/antimony.shtml>.
- Gloaguen, E., Pochon, A., Branquet, Y., Poujol, M., Boulvais, P., Gumiaux, C., Cagnard, F., & Gapais, D. (2024). Comment on : The La Lucette Sb-Au- (W) vein-deposit (Armorican Massif , France): New time and genetic constraints to decipher the 310 – 295 Ma Sb-Au metallogenic peak in the Variscan Belt by Cheval-Garab ´ edian. *Ore Geology Reviews*, 171(February), 106185. <https://doi.org/10.1016/j.oregeorev.2024.106185>
- Gloaguen, E., Tourlière, B., & Angel, J. M. (2016). Revalorisation du potentiel minier français : le district à antimoine-or du Semnon (Ille-et-Vilaine, France). BRGM report. *BRGM/RP-66200-FR*, 71.
- Goldfarb, R. J., Bradley, D., & Leach, D. L. (2010). Secular variation in economic geology. *Economic Geology*, 105, 459–465.
- Goldfarb, R. J., & Groves, D. I. (2015). Orogenic gold: Common or evolving fluid and metal sources through time. *Lithos*, 233, 2–26. <https://doi.org/10.1016/j.lithos.2015.07.011>
- Goldfarb, R. J., Groves, D. I., & Gardoll, S. (2001). Orogenic gold and geologic time: A global synthesis. *Ore Geology Reviews*, 18(1–2), 1–75. [https://doi.org/10.1016/S0169-1368\(01\)00016-6](https://doi.org/10.1016/S0169-1368(01)00016-6)
- Goldoff, B., Webster, J. D., & Harlov, D. E. (2012). Characterization of fluor-chlorapatites by electron probe microanalysis with a focus on time-dependent intensity variation of halogens. *American Mineralogist*, 97(7), 1103–1115. <https://doi.org/10.2138/am.2012.3812>

References

- Gonçalves, F. (1971). Subsídios para o Conhecimento Geológico do Nordeste Alentejano. In *Mem. Servo Geol. Portugal* (Vol. 18, pp. 1–62).
- Gonçalves, F. (1973). *Carta Geológica de Portugal. E. 1:50.000. Notícia Explicativa da Folha 32-B (Portalegre)*. Servo Geol. Portugal.
- Gonçalves, F., & Perdigao, J. C. (1978). *Carta Geológica de Portugal. E. 1:50.000. Notícia Explicativa da Folha 33-A (Assumar)*. Servo Geol. Portugal.
- González Clavijo, E., Dias da Silva, Í. F., Gutiérrez-Alonso, G., & Díez Montes, A. (2016). U/Pb age of a large dacitic block locked in an Early Carboniferous synorogenic mélange in the Parautochthon of NW Iberia: New insights on the structure/sedimentation Variscan interplay. *Tectonophysics*, 681, 159–169. <https://doi.org/10.1016/j.tecto.2016.01.001>
- Goodfellow, B. W., Fredin, O., Derron, M. H., & Stroeve, A. P. (2009). Weathering processes and quaternary origin of an alpine blockfield in arctic Sweden. *Boreas*, 38(2), 379–398. <https://doi.org/10.1111/j.1502-3885.2008.00061.x>
- Gore, B., & Le Corre, C. (1987). Cinématique hercynienne du cisaillement nord-armoricain à la bordure du granite syntectonique de Saint Renan-Kersaint (Finistère). *Bulletin de La Societe Geologique de France*, 3, 811–819.
- Gorichon, A., & Kerjean, M. (1979). Reconnaissance par travaux miniers des indices d'antimoine de Quimper (PER de l'Odet). Résultats au 31 mai 1979. *BRGM Report 79-RDM-035-FE*, 13.
- Grant, J. A. (1986). The isocon diagram; a simple solution to Gresens' equation for metasomatic alteration. *Economic Geology*, 81(8), 1976–1982.
- Grant, J. A. (2005). Isocon analysis: A brief review of the method and applications. *Physics and Chemistry of the Earth*, 30(17-18 SPEC. ISS.), 997–1004. <https://doi.org/10.1016/j.pce.2004.11.003>
- Gregory, D. D., Large, R. R., Halpin, J. A., Baturina, E. L., Lyons, T. W., Wu, S., Danyushevsky, L., Sack, P. J., Chappaz, A., Maslennikov, V. V., & Bull, S. W. (2015). Trace element content of sedimentary pyrite in black shales. *Economic Geology*, 110(6), 1389–1410. <https://doi.org/10.2113/econgeo.110.6.1389>
- Groves, D. I., Condie, K. C., Goldfarb, R. J., Hronsky, J. M. A., & Vielreicher, R. M. (2005). Secular changes in global tectonic processes and their influence on the temporal

References

- distribution of gold-bearing mineral deposits. *Economic Geology*, 100, 203–224.
- Groves, D. I., Goldfarb, R. J., Gebre-Mariam, M., Hagemann, S. G., & Robert, F. (1998). Orogenic gold deposits: a proposed classification in the context of their crustal distribution and relationship to other gold deposit types. *Ore Geology Reviews*, 13(1–5), 7–27. [https://doi.org/10.1016/S0169-1368\(97\)00012-7](https://doi.org/10.1016/S0169-1368(97)00012-7)
- Guberman, D. E. (2013). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <http://minerals.usgs.gov/minerals/pubs/country/2013/myb3-2013-gy.pdf>
- Guberman, D. E. (2014). Antimony. In *USGS Minerals Yearbook*. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Guilloard, P. C. (2009). *L'industrie minière de l'antimoine et du tungstène : émergence, prospérité et disparition des exploitations de France métropolitaine aux XIXe et XX siècles*. Université de Haute-Alsace Mulhouse-Colmar.
- Gumiaux, C., Brun, J. P., & Gapais, D. (2004). Strain removal within the Hercynian Shear Belt of Central Brittany (western France): Methodology and tectonic implications. *Geological Society Special Publication*, 224, 287–305. <https://doi.org/10.1144/GSL.SP.2004.224.01.18>
- Gumiaux, C., Gapais, D., Brun, J. P., Chantaine, J., & Ruffet, G. (2004). Tectonic history of the hercynian armorican shear belt (brittany, France). *Geodinamica Acta*, 17(4), 289–307. <https://doi.org/10.3166/ga.17.289-307>
- Gumiel, P. (1982). *METALOGENIA DE LOS YACIMIENTOS DE ANTIMONIO DE LA PENINSULA IBERICA*. Universidad de Salamanca.
- Gumiel, P., Antón-Pacheco, C., Campos, R., Pérez-Cerdán, F., Nesbitt, R. W., Roberts, S., & Sanderson, D. J. (1990). Alburquerque-La Codosera Area (Extremadura-Spain). In *DEVELOPMENT OF NEW MULTI-DISCIPLINARY TECHNIQUES FOR MINERAL EXPLORATION IN SEVERAL AREAS OF THE WESTERN IBERIAN PENINSULA* (p. 178).
- Gumiel, P., & Arribas, A. (1987). Antimony deposits in the Iberian Peninsula. *Economic Geology*, 82(6), 1453–1463. <https://doi.org/10.2113/gsecongeo.82.6.1453>
- Gumiel, P., Arribas, A., & Saavedra-Alonso, J. (1976). Geología y metalogénia del yacimiento

References

- de estibina-scheelita de “San Antonio” Alburquerque (Badajoz). *STVDIA GEOLOGICA*, X, 61–93.
- Gumiel, P., Campos, R., Monteserín, V., & Bellido, F. (2002). *Memoria y mapa geológico y de recursos minerales del sector centro-occidental de Extremadura (escala 1:100.000)*. Junta de Extremadura.
- Gutiérrez-Alonso, G., Collins, A. S., Fernández-Suárez, J., Pastor-Galán, D., González-Clavijo, E., Jourdan, F., Weil, A. B., & Johnston, S. T. (2015). Dating of lithospheric buckling: $^{40}\text{Ar}/^{39}\text{Ar}$ ages of syn-oroclinal strike-slip shear zones in northwestern Iberia. *Tectonophysics*, 643, 44–54. <https://doi.org/10.1016/j.tecto.2014.12.009>
- Gutiérrez-Alonso, G., Murphy, J. B., Fernández-suárez, J., & Hamilton, M. . . (2008). Rifting along the northern Gondwana margin and the evolution of the Rheic Ocean : A Devonian age for the El Castillo volcanic rocks (Salamanca , Central Iberian Zone). *Tectonophysics*, 461(1–4), 157–165.
- Gutiérrez-Marco, J. C., Ghienne, J. F., Bernárdez, E., & Hacar, M. P. (2010). Did the late Ordovician African ice sheet reach Europe? *Geology*, 38(3), 279–282. <https://doi.org/10.1130/G30430.1>
- Gutiérrez-Marco, J. C., Piçarra, J. M., Meireles, C. A., Cózar, P., García-Bellido, D. C., Pereira, Z., Vaz, N., Pereira, S., Lopes, G., Oliveira, J. T., Quesada, C., Zamora, S., Esteve, J., Colmenar, J., Bernárdez, E., Coronado, I., Lorenzo, S., Sá, A. A., Dias da Silva, Í., ... Gómez-Barreiro, J. (2019). *Early Ordovician–Devonian Passive Margin Stage in the Gondwanan Units of the Iberian Massif. November*, 75–98. https://doi.org/10.1007/978-3-030-10519-8_3
- Hall, C. M., Higuera, P. L., Kesler, S. E., Lunar, R., Dong, H., & Halliday, A. N. (1997). Dating of alteration episodes related to mercury mineralization in the Almadén district, Spain. *Earth and Planetary Science Letters*, 148(1–2), 287–298. [https://doi.org/10.1016/S0012-821X\(97\)00041-1](https://doi.org/10.1016/S0012-821X(97)00041-1)
- Harrison, W. J. (1981). Partitioning REE between minerals and coexisting melts during partial melting of a garnet lherzolite. *American Mineralogist*, 66(3–4), 242–259. <http://ammin.geoscienceworld.org/cgi/content/abstract/66/3-4/242>
- Hart, C. . J. R. (2007). REDUCED INTRUSION-RELATED GOLD SYSTEMS. In W. D.

References

- Goodfellow (Ed.), *Mineral deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods* (Special Pu, Issue Special Publication No. 5, pp. 95–112). Geological Association of Canada, Mineral Deposits Division.
- Hedenquist, J. W., Arribas, A., & Gonzalez-Urien, E. (2000). Exploration for Epithermal Gold Deposits. *SEG Reviews*, 13, 245–277. <https://doi.org/10.5382/rev.13.07>
- Hedenquist, J. W., John, F. H., Thompson, J. F. H., Goldfarb, R. J., & Richards, J. P. (2005). *Economic Geology 100th Anniversary Volume* (J. W. Hedenquist, F. H. John, J. F. H. Thompson, R. J. Goldfarb, & J. P. Richards (eds.)). Society of Economic Geologist. <https://doi.org/10.1177/002205742911001810>
- Hedenquist, J. W., & Lowenstern, J. B. (1994). The role of magmas in the formation of hydrothermal ore deposits. *Nature*, 370, 519–527.
- Hellgren, U., Ericsson, O., & Gustafsson, L. L. (1995). *Handbook of Drugs for Tropical Parasitic Infections*. CRC Press. <https://doi.org/https://doi.org/10.1201/9781482272536>
- Henriques, S. B. A., Neiva, A. M. R., Ribeiro, M. L., Dunning, G. R., & Tajčmanová, L. (2016). Erratum: Corrigendum to “Evolution of a Neoproterozoic suture in the Iberian Massif, Central Portugal: New U-Pb ages of igneous and metamorphic events at the contact between the Ossa Morena Zone and Central Iberian Zone” (*Lithos* (2015) 220–223 (43–59) (S0. *Lithos*, 264, 595. <https://doi.org/10.1016/j.lithos.2016.08.032>
- Henry, J. L., Nion, J., Paris, F., & Thadeu, D. (1974). Chitinozoaires, Ostracodes et Trilobites de l’Ordovicien du Portugal (Serra de Buçaco) et du Massif Armoricaín: essai de comparaison et signification paléogéographique. *Comunicações Dos Serviços Geológicos de Portugal*, 57, 303–345.
- Hernández, A., Jébrak, M., Higuera, P., Oyarzun, R., Morata, D., & Munhá, J. (1999). The Almaden mercury mining district, Spain. *Mineralium Deposita*, 34(5–6), 539–548. <https://doi.org/10.1007/s001260050219>
- Hiess, J., Condon, D. J., McLean, N., & Noble, S. R. (2012). 238U/235U systematics in terrestrial uranium-bearing minerals. *Science*, 335(6076), 1610–1614. <https://doi.org/10.1126/science.1215507>
- Higuera, P. (1995). *Procesos petrogenéticos y de alteración de las rocas magmáticas*

References

- asociadas a las mineralizaciones de mercurio del distrito de Almadén*. Universidad de Castilla-La Mancha.
- Higuera, P. (2000). The Almadén mercury metallogenic cluster (Ciudad Real, Spain): alkaline magmatism leading to mineralization processes at an intraplate tectonic setting: alkaline magmatism leading to mineralization processes at an intraplate tectonic setting. *Revista de La Sociedad Geológica de España*, 13(1), 105–119.
- Higuera, P., Esbri, J. M., Campos Rodríguez, H., & Gloaguen, E. (2022). Antimony mineralizations in the Guadalmez syncline – relationships with Almadén mercury deposits, South-Central Spain. In A. B. Christie (Ed.), *Proceeding of the 16th SGA Biennial meeting, 28-31 March 2022, Rotorua, New Zealand* (Vol. 2, p. 72).
- Higuera, P., Morata, D., & Munha, J. (1995). Metamorfismo de bajo grado en facies prehnita-pumpellyita en las metabasitas del Sinclinal de Almadén. *Boletín de La Sociedad Española de Mineralogía*, 18, 111–125.
- Higuera, P., & Oyarzun, R. (2005). First lead isotopic data for cinnabar in the Almadén district (Spain): implications for the genesis of the mercury deposits. *Geogaceta*, 37, 67–70.
- Higuera, P., Oyarzun, R., Lillo, J., & Morata, D. (2013). Intraplate mafic magmatism, degasification, and deposition of mercury: The giant Almadén mercury deposit (Spain) revisited. *Ore Geology Reviews*, 51, 93–102. <https://doi.org/10.1016/j.oregeorev.2012.12.004>
- Higuera, P., Oyarzun, R., Munha, J., & Morata, D. (2000). The Almadén mercury metallogenic cluster (Ciudad Real, Spain): alkaline magmatism leading to mineralization process at an intraplate tectonic setting. *Revista de La Sociedad Geológica de España*, 13(1), 105–119.
- Hubbert, J. J. M. W. (1973). *Petrology of the Mellid area, a Precambrian polymetamorphic rock complex, Galicia, NW Spain*. Rijksuniversiteit te Leiden.
- Hughes, J. M., & Rakovan, J. F. (2015). Structurally robust, chemically diverse: Apatite and apatite supergroup minerals. *Elements*, 11(3), 165–170. <https://doi.org/10.2113/gselements.11.3.165>
- Insua Marquez, M., Santos García, J. A., Opatalegui Isasa, O., Carvajal Menéndez, A., & Gracia Prieto, F. J. (1990). *Mapa geológico & memoria explicativa de la hoja num. 750, Botoa*. Instituto Geológico y Minero de España.

References

- Jegouzo, P. (1980). The South Armorican Shear Zone. *Journal of Structural Geology*, 2, 39–47.
- Jochum, K. P., Hofmann, A. W., & Seufert, H. M. (1993). Tin in mantle-derived rocks: Constraints on Earth evolution. *Geochimica et Cosmochimica Acta*, 57(15), 3585–3595. [https://doi.org/10.1016/0016-7037\(93\)90141-I](https://doi.org/10.1016/0016-7037(93)90141-I)
- Jones, K. A., & Brown, M. (1990). High-temperature ‘clockwise’ P-T paths and melting in the development of regional migmatites: An example from southern Brittany, France. *Journal of Metamorphic Geology*, 8, 551–578.
- Julivert, M., Fontboté, J. M., Ribeiro, A., & Conde, L. (1974). *Mapa Tectónico de la Península Ibérica y Baleares*. Instituto Geológico y Minero de España.
- Kamenetsky, V. S., & Eggins, S. M. (2012). Systematics of metals, metalloids, and volatiles in MORB melts: Effects of partial melting, crystal fractionation and degassing (a case study of Macquarie Island glasses). *Chemical Geology*, 302–303, 76–86. <https://doi.org/10.1016/j.chemgeo.2011.04.008>
- Kerrick, R. (1983). Geochemistry of gold deposits in the Abitibi greenstone belt. *Canadian Institute of Mining and Metallurgy Special Paper*, 27–75.
- Kerrick, R., Goldfarb, R. J., & Richards, J. P. (2005). Metallogenic provinces in an evolving geodynamic framework. *Economic Geology*, 100, 1097–1136.
- Klochko, K. (2015). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. http://minerals.usgs.gov/minerals/pubs/commodity/soda_ash/myb1-2015-sodaa.pdf
- Klochko, K. (2016). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov/centers/national-minerals-information-center/antimony-statistics-and-information>
- Klochko, K. (2017). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
- Klochko, K. (2018). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey. <https://www.usgs.gov>
- Klochko, K. (2019). Antimony. In *USGS Minerals Yearbook*. U.S. Geological Survey.
- Klochko, K. (2020). Antimony. In *Mineral Commodity Summaries*. U.S. Geological Survey.

References

- Klochko, K. (2021). Antimony. In *Mineral Commodity Summaries*. U.S. Geological Survey.
- Klochko, K. (2022). Antimony. In *Mineral Commodity Summaries*. U.S. Geological Survey.
- Klochko, K. (2024). Antimony. In *Mineral Commodity Summaries*. U.S. Geological Survey.
- Knox-Robinson, C. M., & Wyborn, L. A. I. (1997). Towards a holistic exploration strategy: Using Geographic Information Systems as a tool to enhance exploration. *Australian Journal of Earth Sciences*, 44(4), 453–463. <https://www.tandfonline.com/doi/abs/10.1080/08120099708728326>
- Kossmat, F. (1927). *Gliederung des varistischen Gebirgsbaues. Abhandlungen des Sächsischen Geologuschen Landesamts* (Heft 1).
- Kroner, U., & Romer, R. L. (2013). Two plates - Many subduction zones: The Variscan orogeny reconsidered. *Gondwana Research*, 24(1), 298–329. <https://doi.org/10.1016/j.gr.2013.03.001>
- Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., & Goffé, B. (2010). Evolution of the Raman spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland). *Terra Nova*, 22(5), 354–360. <https://doi.org/10.1111/j.1365-3121.2010.00956.x>
- Lardeaux, J. M., Schulmann, K., Faure, M., Janoušek, V., Lexa, O., Skrzypek, E., Edel, J. B., & Štípská, P. (2014). The moldanubian zone in the French Massif Central, Vosges/Schwarzwald and Bohemian Massif revisited: Differences and similarities. *Geological Society Special Publication*, 405(1), 7–44. <https://doi.org/10.1144/SP405.14>
- Lardeux, H., & Cavet, P. (1994). Paleozoic of the Ligerian Domain, the Variscan Orogeny in the Armorican Massif. In J. D. Keppie (Ed.), *Pre-Mesozoic Geology in France and Related Areas* (pp. 152–156). Springer-Verlag.
- Large, R. R. (2001). The Alteration Box Plot: A Simple Approach to Understanding the Relationship between Alteration Mineralogy and Lithogeochemistry Associated with Volcanic-Hosted Massive Sulfide Deposits. *Economic Geology*, 96(5), 957–971. <https://doi.org/10.2113/96.5.957>
- Large, R., Thomas, H., Craw, D., Henne, A., & Henderson, S. (2012). Diagenetic pyrite as a source for metals in orogenic gold deposits, Otago Schist, New Zealand. *New Zealand Journal of Geology and Geophysics*, 55(2), 137–149.

References

- <https://doi.org/10.1080/00288306.2012.682282>
- Laznicka, P. (2010). *Giant Metallic Deposits, 2nd edition*. Springer-Verlag.
- Laznicka, P. (2014). Giant metallic deposits-A century of progress. *Ore Geology Reviews*, 62(2012), 259–314. <https://doi.org/10.1016/j.oregeorev.2014.03.002>
- Le Bas, M. J., Maitre, R. W. L., Streckeisen, A., & Zanettin, B. (1986). A chemical classification of volcanic rocks based on the total alkali-silica diagram. *Journal of Petrology*, 27(3), 745–750. <https://doi.org/10.1093/petrology/27.3.745>
- Le Gall, J. (1999). Les dolérites et basaltes tholéiitiques varisque du domaine nord-est armoricain. In *Géologie de la France* (Vol. 4, pp. 3–26).
- Linnemann, U., Pereira, M. F., Jeffries, T. E., Drost, K., & Gerdes, A. (2008). The Cadomian Orogeny and the opening of the Rheic Ocean: The diachrony of geotectonic processes constrained by LA-ICP-MS U-Pb zircon dating (Ossa-Morena and Saxo-Thuringian Zones, Iberian and Bohemian Massifs). *Tectonophysics*, 461(1–4), 21–43. <https://doi.org/10.1016/j.tecto.2008.05.002>
- Linnemann, U., Pidal, A. P., Hofmann, M., Drost, K., Quesada, C., Gerdes, A., Marko, L., Gärtner, A., Zieger, J., Ulrich, J., Krause, R., Vickers-Rich, P., & Horak, J. (2018). A ~565 Ma old glaciation in the Ediacaran of peri-Gondwanan West Africa. *International Journal of Earth Sciences*, 107(3), 885–911. <https://doi.org/10.1007/s00531-017-1520-7>
- López-Moro, F. J., Murciego, A., & López-Plaza, M. (2007). Silurian/Ordovician asymmetrical sill-like bodies from La Codosera syncline, W Spain: A case of tholeiitic partial melts emplaced in a single magma pulse and derived from a metasomatized mantle source. *Lithos*, 96(3–4), 567–590. <https://doi.org/10.1016/j.lithos.2006.12.006>
- López-Moro, F. J., Murciego, A., López-Plaza, M., Romer, R. L., & de Rafélis, M. (2020a). Sequential crystal overproduction triggering Mg-Cr-Ti-V-P-MREE- enrichment in a single-pulse tholeiitic mafic sill in the Central Iberian Zone, Spain. *Lithos*, 362–363. <https://doi.org/10.1016/j.lithos.2020.105464>
- López-Moro, F. J., Murciego, A., López-Plaza, M., Romer, R. L., & de Rafélis, M. (2020b). Sequential crystal overproduction triggering Mg-Cr-Ti-V-P-MREE- enrichment in a single-pulse tholeiitic mafic sill in the Central Iberian Zone, Spain. *Lithos*, 362–363, 105464. <https://doi.org/10.1016/j.lithos.2020.105464>

References

- López-Moro, F. J., Murciego, A., Rodríguez-González, M. A., Suárez Barrios, M., & Martín Pozas, J. M. (2005). Estudio de la potencialidad como roca ornamental de los sills de diabasa en Alburquerque-Villar del Rey-La Roca de la Sierra-Puebla de Obando, NO de Babajoz. *Boletín Geológico y Minero*, 116(1), 53–64.
- López-Moro, F. J., Romer, R. L., López-Plaza, M., & González Sánchez, M. (2017). Zircon and allanite U-Pb ID-TIMS ages of vaugnerites from the Calzadilla Pluton, Salamanca (Spain): Dating mantle-derived magmatism and post-magmatic subsolidus overprint. *Geologica Acta*, 15(4), 395–408. <https://doi.org/10.1344/GeologicaActa2017.15.4.9>
- López Díaz, F., Monteserín López, V., Pineda Velasco, A., Gil Serrano, G., Rubio Pascual, F. J., & Martín-Serrano García, A. (1989). Mapa geológico & memoria explicativa de la hoja num. 728, Puebla de Obando. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 63). IGME.
- Lorenzo Álvarez, S., Martín Herrero, D., Valverde Hernández, M. F., & Monteserín López, V. (1995). Mapa geológico & memoria explicativa de la hoja num. 807, Chillón. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 116). IGME.
- Lotze, F. (1945). Zur Gliederung der Varisziden der Iberischen Meseta. *Geotekt*, 6, 78–92. https://doi.org/10.1007/978-3-663-02849-9_1
- Lotze, F. (1956). Über sardischen Bewegungen im Spanien und ihre Beziehungen zur assynthischen Faltung, in , 128 – 139, Stuttgart. In *Geotektonische Symposium zu Ehren von Hans Stille* (pp. 128–139).
- Loughlin, G. F., & Behre, C. H. (1933). Classification of ore deposits. In J. W. Finch, A. M. Bateman, B. S. Butler, G. F. Loughlin, D. H. McLaughlin, & J. T. Singewald (Eds.), *Ore deposits of the western states (Lindgren volume)* (pp. 17–55). <http://repositorio.unan.edu.ni/2986/1/5624.pdf%0Ahttp://fiskal.kemenkeu.go.id/ejournal%0Ahttp://dx.doi.org/10.1016/j.cirp.2016.06.001%0Ahttp://dx.doi.org/10.1016/j.powtec.2016.12.055%0Ahttps://doi.org/10.1016/j.ijfatigue.2019.02.006%0Ahttps://doi.org/10.1>
- Manikyamba, C., & Kerrich, R. (2006). Geochemistry of black shales from the Neoarchaeon Sandur Superterrane, India: First cycle volcanogenic sedimentary rocks in an intraoceanic arc-trench complex. *Geochimica et Cosmochimica Acta*, 70(18), 4663–4679. <https://doi.org/10.1016/j.gca.2006.07.015>

References

- Manikyamba, C., Kerrich, R., Khanna, T. C., Keshav Krishna, A., & Satyanarayanan, M. (2008). Geochemical systematics of komatiite-tholeiite and adakitic-arc basalt associations: The role of a mantle plume and convergent margin in formation of the Sandur Superterrane, Dharwar craton, India. *Lithos*, 106(1–2), 155–172. <https://doi.org/10.1016/j.lithos.2008.07.003>
- Marcoux, E., Serment, R., & Allon, A. (1984). Les gîtes d'antimoine de Vendée (Massif Armoricaín, France). Historique des recherches et synthèse métallogénique. *Chronique de La Recherche Minière*, 476, 3–30.
- Martín-Parra, L. M., Gonzalez-Lodeiro, F., Martínez Poyatos, D., Matas, J., & Salazar Rincón, A. (1996). Mapa geológico & memoria explicativa de la hoja num. 863, Aldeaquemada. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA*.
- Martín Herrero, D., Valverde Hernández, M. F., & Lorenzo Álvarez, S. (1994). Mapa geológico & memoria explicativa de la hoja num. 780, Puebla de Alcocer. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 82).
- Martínez-Catalán, J. R., González Clavijo, E., Meireles, C., Díez Fernández, R., & Bevis, J. (2016). Relationships between syn-orogenic sedimentation and nappe emplacement in the hinterland of the Variscan belt in NW Iberia deduced from detrital zircons. *Geological Magazine*, 153(1), 38–60. <https://doi.org/10.1017/S001675681500028X>
- Martínez-Catalán, J. R., Martínez Poyatos, D., & Bea, F. (2004). Zona Centroibérica: Introducción. In: Vera, J.A. (Ed.), *Geología de España*, SGE-IGME, Madrid, Cap. 2, pp. 68 – 69. In J. A. Vera (Ed.), *Geología de España* (pp. 68–69). SGE-IGME.
- Martínez Catalán, J. R., Arenas, R., Abati, J., Martínez, S. S., García, F. D., Suárez, J. F., Cuadra, P. G., Castiñeiras, P., Barreiro, J. G., Montes, A. D., Clavijo, E. G., Pascual, F. J. R., Andonaegui, P., Jeffries, T. E., Alcock, J. E., Fernández, R. D., & Carmona, A. L. (2009). A rootless suture and the loss of the roots of a mountain chain: The Variscan belt of NW Iberia. *Comptes Rendus - Geoscience*, 341(2–3), 114–126. <https://doi.org/10.1016/j.crte.2008.11.004>
- Martínez Catalan, J. R., Arenas, R., Diágarcía, F., Cuadra, P. G., Gómez-Barreiro, J., Abati, J., Castiñeiras, P., Fernández-Suárez, J., Martínez, S. S., Andonaegui, P., Clavijo, E. G., Montes, A. D., Rubio Pascual, F. J., & Aguado, B. V. (2007). Space and time in the tectonic evolution of the northwestern Iberian Massif: Implications for the Variscan belt.

References

- Memoir of the Geological Society of America*, 200(January), 403–423.
[https://doi.org/10.1130/2007.1200\(21\)](https://doi.org/10.1130/2007.1200(21))
- Martínez Catalán, J. R., Arenas, R., & Díez Balda, M. A. (2003). Large extensional structures developed during emplacement of a crystalline thrust sheet: The Mondoñedo nappe (NW Spain). *Journal of Structural Geology*, 25(11), 1815–1839. [https://doi.org/10.1016/S0191-8141\(03\)00038-5](https://doi.org/10.1016/S0191-8141(03)00038-5)
- Martínez Catalán, J. R., Rubio Pascual, F. J., Díez Montes, A., Díez Fernández, R., Gómez Barreiro, J., Dias Da Silva, Í., González Clavijo, E., Ayarza, P., & Alcock, J. E. (2014). The late variscan HT/LP metamorphic event in NW and Central Iberia: Relationships to crustal thickening, extension, orocline development and crustal evolution. *Geological Society Special Publication*, 405(1), 225–247. <https://doi.org/10.1144/SP405.1>
- Martínez Catalán, J. R., Schulmann, K., & Ghienne, J. F. (2021). The Mid-Variscan Allochthon: Keys from correlation, partial retrodeformation and plate-tectonic reconstruction to unlock the geometry of a non-cylindrical belt. *Earth-Science Reviews*, 220. <https://doi.org/10.1016/j.earscirev.2021.103700>
- Martínez Poyatos, D., Carbonell, R., Palomeras, I., Simancas, J. F., Ayarza, P., Martí, D., Azor, A., Jabaloy, A., González Cuadra, P., Tejero, R., Martín Parra, L. M., Matas, J., González Lodeiro, F., Pérez-Estaún, A., García Lobón, J. L., & Mansilla, L. (2012). Imaging the crustal structure of the Central Iberian Zone (Variscan Belt): The ALCUDIA deep seismic reflection transect. *Tectonics*, 31(3), 1–21. <https://doi.org/10.1029/2011TC002995>
- Martínez Poyatos, D., Gutierrez Marco, J. C., Pardo Alonso, M. V., Rábano, I., & Sarmiento, G. (2004). Dominio del Complejo Esquisto-grauváquico: La secuencia paleozoica postcámbrica. In J. A. Vera (Ed.), *Geología de España* (pp. 81–83). SGE-IGME.
- Matte, P. (2001). The Variscan collage and orogeny (480-290 Ma) and the tectonic definition of the Armorica microplate: A review. *Terra Nova*, 13(2), 122–128. <https://doi.org/10.1046/j.1365-3121.2001.00327.x>
- McCuaig, T. C., Beresford, S., & Hronsky, J. (2010). Translating the mineral systems approach into an effective exploration targeting system. *Ore Geology Reviews*, 38(3), 128–138. <https://doi.org/10.1016/j.oregeorev.2010.05.008>
- McCuaig, T. C., & Hronsky, J. (2014). The mineral systems concept: the key to exploration

References

- targeting. *Economic Geology*, 18, 153–175.
<https://doi.org/10.1080/03717453.2017.1306274>
- McDougall, N., Brenchley, P. J., Rebelo, J. A., & Romano, M. (1987). Fans and fan deltas - precursors to the Armorican Quartzite (Ordovician) in western Iberia. *Geological Magazine*, 124(4), 347–359. <https://doi.org/10.1017/S0016756800016678>
- McDowell, F. W., McIntosh, W. C., & Farley, K. A. (2005). A precise ⁴⁰Ar-³⁹Ar reference age for the Durango apatite (U-Th)/He and fission-track dating standard. *Chemical Geology*, 214(3–4), 249–263. <https://doi.org/10.1016/j.chemgeo.2004.10.002>
- McKeith, T. D., Schodde, R. C., & Baltis, E. J. (2010). Gold Discovery Trends. *SEG Discovery*, 81, 1–26. <https://doi.org/10.5382/segnews.2010-81.fea>
- McKinstry, H. E. (1941). Structural control of ore deposition in fissure veins: American Institute of Mining Engineers Transactions. *Economic Geology*, 144(1), 65–95.
- McKinstry, H. E. (1955). Structure of hydrothermal ore deposits. *Economic Geology*, 50(1), 170–225.
- Medeiros, A., Pereira, M. F., & Moreira, A. (1981). *Carta Geológica de Portugal Folha 9-D (PENAFIEL)*. LNEG.
- Michard, A., Hoepffner, C., Soulaïmani, A., & Baidder, L. (2008). The variscan belt. In *Continental Evolution: The Geology of Morocco. Lecture Notes in Earth Sciences* (Vol. 116, pp. 65–132). Springer-Verlag. https://doi.org/10.1007/978-3-540-77076-3_3
- Mira López, M., Ortega Gironés, E., & Rodríguez Pevida, L. (1983). Mapa geológico & memoria explicativa de la hoja num. 834, San Benito. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 53). IGME.
- Mira López, M., Ortega Gironés, E., Rodríguez Pevida, L., Soubrier, J., & Quesada, C. (1983). Mapa geológico & memoria explicativa de la hoja num. 833, Hinojosa del Duque. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 58). IGME.
- Montero, P., Bea, F., Zinger, T., Scarrow, J. H., Molina, J. F., & Whitehouse, M. (2004). 55 million years of continuous anatexis in Central Iberia: Single-zircon dating of the Peña Negra Complex. *Journal of the Geological Society*, 161(2), 255–263. <https://doi.org/10.1144/0016-764903-024>

References

- Montero, P., Zinger, T., & Bea, F. (2004). Edad “207” Pb/206 Pb en cristal único de circón de las rocas máficas y ultramáficas del sector de Gredos, Batolito de Ávila (Sistema Central Español). *Revista de La Sociedad Geológica de España*, 17(3), 157–167.
- Montmartin, C., Faure, M., & Raimbourg, H. (2021). Paleotemperature investigation of the Variscan southern external domain: The case of the Montagne Noire (France). *BSGF - Earth Sciences Bulletin*, 192. <https://doi.org/10.1051/bsgf/2020043>
- Moutbir, O., Aarab, E. M., Youbi, N., Lahna, A. A., Tassinari, C. C. G., Mata, J., Mitchell, R. N., Gärtner, A., Soesoo, A., Bensalah, M. K., Soulimani, A., Boumehdi, M. A., & Linnemann, U. (2024). Evidence of a large igneous province at ca. 347–330 Ma along the northern Gondwana margin linked to the assembly of Pangea: Insights from U Pb zircon geochronology and geochemistry of the South-Western Branch of the Variscan Belt (Morocco). *Earth-Science Reviews*, 258(August), 104905. <https://doi.org/10.1016/j.earscirev.2024.104905>
- Moyroud, B., Féraud, J., Bornuat, M., & Ziserman, A. (1979). Ressources minières françaises. Tome 6, les gisements d’Antimoine (Situation en 1979). *BRGM Report RR-41430-FR-06*, 6, 121.
- Munoz, M., Courjault-Radé, P., & Tollon, F. (1992). The massive stibnite veins of the French Palaeozoic basement: a metallogenic marker of Late Variscan brittle extension. *Terra Nova*, 4(2), 171–177. <https://doi.org/10.1111/j.1365-3121.1992.tb00468.x>
- Murphy, J. B., Eguiluz, L., & Zulauf, G. (2002). Cadomian Orogens, peri-Gondwanan correlatives and Laurentia–Baltica connections. *Tectonophysics*, 352(1–2), 1–9. [https://doi.org/10.1016/s0040-1951\(02\)00186-5](https://doi.org/10.1016/s0040-1951(02)00186-5)
- Murphy, P. J., & Roberts, S. (1997). Evolution of a metamorphic fluid and its role in lode gold mineralisation in the Central Iberian Zone. *Mineralium Deposita*, 32(5), 459–474. <https://doi.org/10.1007/s001260050115>
- Nance, R. D., Gutiérrez-Alonso, G., Keppie, J. D., Linnemann, U., Murphy, J. B., Quesada, C., Strachan, R. A., & Woodcock, N. H. (2012). A brief history of the Rheic Ocean. *Geoscience Frontiers*, 3(2), 125–135. <https://doi.org/10.1016/j.gsf.2011.11.008>
- Obolensky, A. A., Gushchina, L. V., Borisenko, A. S., Borovikov, A. A., & Pavlova, G. G. (2007). Antimony in hydrothermal processes: solubility, conditions of transfer, and metal-

References

- bearing capacity of solutions. *Russian Geology and Geophysics*, 48(12), 992–1001. <https://doi.org/10.1016/j.rgg.2007.11.006>
- Onézime, J., Charvet, J., Faure, M., Chauvet, A., & Panis, D. (2002). Structural evolution of the southernmost segment of the West European variscides: The South Portuguese zone (SW Iberia). *Journal of Structural Geology*, 24(3), 451–468. [https://doi.org/10.1016/S0191-8141\(01\)00079-7](https://doi.org/10.1016/S0191-8141(01)00079-7)
- Orberger, B., Vymazalova, A., Wagner, C., Fialin, M., Gallien, J. P., Wirth, R., Pasava, J., & Montagnac, G. (2007). Biogenic origin of intergrown Mo-sulphide- and carbonaceous matter in Lower Cambrian black shales (Zunyi Formation, southern China). *Chemical Geology*, 238(3–4), 213–231. <https://doi.org/10.1016/j.chemgeo.2006.11.010>
- Ordóñez Casado, B., Gebauer, D., Schäfer, H. J., Ibarguchi, J. I. G., & Peucat, J. J. (2001). A single Devonian subduction event for the HP/HT metamorphism of the Cabo Ortegal complex within the Iberian Massif. *Tectonophysics*, 332(3), 359–385. [https://doi.org/10.1016/S0040-1951\(00\)00210-9](https://doi.org/10.1016/S0040-1951(00)00210-9)
- Orejana, D., Villaseca, C., & Kristoffersen, M. (2020). Geochemistry and geochronology of mafic rocks from the Spanish Central System: Constraints on the mantle evolution beneath central Spain. *Geoscience Frontiers*, 11(5), 1651–1667. <https://doi.org/10.1016/j.gsf.2020.01.002>
- Orejana, D., Villaseca, C., & Merino Martínez, E. (2017). Basic Ordovician magmatism of the Spanish Central System: Constraints on the source and geodynamic setting. *Lithos*, 284–285, 608–624. <https://doi.org/10.1016/j.lithos.2017.05.012>
- Orejana, D., Villaseca, C., Pérez-Soba, C., López-García, J., & Billström, K. (2009). The Variscan gabbros from the Spanish Central System: A case for crustal recycling in the sub-continental lithospheric mantle? *Lithos*, 110(1–4), 262–276. <https://doi.org/10.1016/j.lithos.2009.01.003>
- Ortega, E., & Gonzalez-Lodeiro, F. (1986). La Discordancia Intra-Alcudiense en el Dominio Meridional de la Zona Centroiberica. *Breviora Geol Asturica*, 27, 27–32.
- Ortega, L., Oyarzun, R., & Gallego, M. (1996). The Mari Rosa late Hercynian Sb-Au deposit, western Spain Geology and geochemistry of the mineralizing processes L. *Mineralium Deposita*, 31(3), 172–187.

References

- Ortega, L., & Vindel, E. (1995). Evolution of ore-forming fluids associated with late Hercynian antimony deposits in Central/Western Spain: case study of Mari Rosa and El Juncalón. *European Journal of Mineralogy*, 7(3), 655–674. <https://doi.org/10.1127/ejm/7/3/0655>
- Palero-Fernández, F. J., Martín-Izard, A., Prieto, M. Z., & Mansilla-Plaza, L. (2015). Geological context and plumbotectonic evolution of the giant Almadén mercury deposit. *Ore Geology Reviews*, 64(1), 71–88. <https://doi.org/10.1016/j.oregeorev.2014.06.013>
- Palero, F. (1993). Tectónica pre-hercínica de las series infraordovícicas del anticlinal de Alcudia y la discordancia intraprecámbrica en su parte oriental (Sector meridional de la Zona Centroibérica). *Boletín Geológico y Minero*, 104(3), 227–242.
- Palero, F., & Lorenzo, S. (2009). Mercury mineralization in the region of Almadén. In A. García-Cortés, J. Agueda-Villar, J. Palacio Suarez-Valgrande, & C. I. Salvador González (Eds.), *Spanish Geological Frameworks and Geosites: An Approach to Spanish Geological Heritage of International Relevance* (pp. 65–72). Instituto Geológico y Minero de España.
- Palomeras, I., Carbonell, R., Ayarza, P., Fernández, M., Simancas, J. F., Poyatos, D. M., González Lodeiro, F., & Pérez-Estaún, A. (2011). Geophysical model of the lithosphere across the Variscan Belt of SW-Iberia: Multidisciplinary assessment. *Tectonophysics*, 508(1–4), 42–51. <https://doi.org/10.1016/j.tecto.2010.07.010>
- Palomeras, I., Villaseñor, A., Thurner, S., Levander, A., Gallart, J., & Harnafi, M. (2017). Lithospheric structure of Iberia and Morocco using finite-frequency Rayleigh wave tomography from earthquakes and seismic ambient noise. *Geochemistry Geophysics Geosystems*, 18, 1824–1840. <https://doi.org/10.1002/2016GC006657>. Received
- Paquette, J. L., Ballèvre, M., Peucat, J. J., & Cornen, G. (2017). From opening to subduction of an oceanic domain constrained by LA-ICP-MS U-Pb zircon dating (Variscan belt, Southern Armorican Massif, France). *Lithos*, 294–295, 418–437. <https://doi.org/10.1016/j.lithos.2017.10.005>
- Pardo, M. V., & García-Alcarde, J. L. (1984). Bioestratigrafía del Devónico de la región de Almadén (Ciudad Real, España). *Trabajos de Geología*, 14.
- Paris, F., & Robardet, M. (1977). Paléogéographie et relations ibéro-armoricaines au Paléozoïque. *Bulletin de La Societe Geologique de France*, 14(5), 1121–1126.

References

- Pašava, J., Kříbek, B., Vymazalová, A., Sýkorová, I., Žák, K., & Orberger, B. (2008). Multiple sources of metals of mineralization in Lower Cambrian black shales of South China: Evidence from geochemical and petrographic study. *Resource Geology*, 58(1), 25–42. <https://doi.org/10.1111/j.1751-3928.2007.00042.x>
- Paton, C., Woodhead, J. D., Hellstrom, J. C., Hergt, J. M., Greig, A., & Maas, R. (2010). Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction. *Geochemistry, Geophysics, Geosystems*, 11(3). <https://doi.org/10.1029/2009GC002618>
- Pearce, J. A. (1983). Role of the sub-continental lithosphere in magma genesis at active continental margins. *Continental Basalts and Mantle Xenoliths*, 250, 230–249.
- Pearce, J. A. (1996). A user's guide to basalt discrimination diagrams. *Geological Association of Canada, Short Course Notes 12*, 79–113.
- Pearce, J. A. (2008). Geochemical fingerprinting of oceanic basalts with applications to ophiolite classification and the search for Archean oceanic crust. *Lithos*, 100(1–4), 14–48. <https://doi.org/10.1016/j.lithos.2007.06.016>
- Pelleter, E., Cheilletz, A., Gasquet, D., Mouttaqi, A., Annich, M., & El Hakour, A. (2010). The Tamlalt-Menhouhou Polyphase Gold Deposit (High-Atlas, Morocco): IOCG-type Mineralisation Overprinted by Shear-Zone Related Gold. *Hydrothermal Iron Oxide Copper-Gold & Related Deposits: A Global Perspective, Vol. 3, Advances in the Understanding of IOCG Deposits, July 2015*, 600p. <https://hal.archives-ouvertes.fr/halsde-00871808>
- Pereira Gómez, M. D., & Shaw, D. M. (1997). Behaviour of boron in the generation of an anatectic complex: The Peña Negra complex, central Spain. *Lithos*, 40(2–4), 179–188. [https://doi.org/10.1016/S0024-4937\(97\)00009-1](https://doi.org/10.1016/S0024-4937(97)00009-1)
- Pereira, M. F., Ribeiro, A., & Meireles, C. (1993). Cisalhamentos hercínicos e controlo das mineralizações de Sn-W, Au e U na Zona Centro-Iberica, em Portugal. *Cuadernos Laboratorio Xeoloxico de Laxe*, 18(1980), 89–119.
- Pereira, M. F., Solá, A. R., Chichorro, M., Lopes, L., Gerdes, A., & Silva, J. B. (2012). North-Gondwana assembly, break-up and paleogeography: U-Pb isotope evidence from detrital and igneous zircons of Ediacaran and Cambrian rocks of SW Iberia. *Gondwana Research*,

References

- 22(3–4), 866–881. <https://doi.org/10.1016/j.gr.2012.02.010>
- Pereira, M. Francisco, Fernández, C., Rodríguez, C., & Castro, A. (2022). Ordovician tectonics and crustal evolution at the Gondwana margin (Central Iberian Zone). *Journal of the Geological Society*, 179(5). <https://doi.org/10.1144/jgs2021-168>
- Pérez-Estaún, A., Bastida, F., Alonso, J. L., Aller, J., Alvarez-Marrón, J., Marcos, A., & Pulgar, J. A. (1988). A thin-skinned tectonics model for an arcuate fold and thrust belt: the Cantabrian Zone (Variscan Ibero-Armorican Arc). *Tectonics*, 7(3), 517–537.
- Pérez-Estaún, A., Bastida, F., Martínez-Catalán, J. R., Gutierrez Marco, J. C., & Pulgar, J. A. (1990). West Asturian-Leonese Zone. Stratigraphy. In R. D. Dallmeyer & E. Martínez García (Eds.), *Pre-Mesozoic Geology of Iberia* (pp. 72–79). Springer-Verlag.
- Pfiffner, A. O. (2014). *Geology of the Alps* (Issue 1). WILEY-Blackwell. <https://doi.org/10.1007/s13398-014-0173-7.2>
- Phillips, G. N., & Powell, R. (2009). Formation of gold deposits: Review and evaluation of the continuum model. *Earth-Science Reviews*, 94(1–4), 1–21. <https://doi.org/10.1016/j.earscirev.2009.02.002>
- Piccoli, P. M., & Candela, P. A. (2002). Apatite in Igneous Systems. *Reviews in Mineralogy and Geochemistry*, 48(1), 255–292. <https://doi.org/10.2138/rmg.2002.48.0>
- Pin, C., Fonseca, P. E., Paquette, J. L., Castro, P., & Matte, P. (2008). The ca. 350 Ma Beja Igneous Complex: A record of transcurrent slab break-off in the Southern Iberia Variscan Belt? *Tectonophysics*, 461(1–4), 356–377. <https://doi.org/10.1016/j.tecto.2008.06.001>
- Pitcairn, I. K., Craw, D., & Teagle, D. (2014a). Metabasalts as sources of metals in orogenic gold deposits. *Mineralium Deposita*, 50. <https://doi.org/10.1007/s00126-014-0547-y>
- Pitcairn, I. K., Craw, D., & Teagle, D. A. H. (2014b). The gold conveyor belt: Large-scale gold mobility in an active orogen. *Ore Geology Reviews*, 62, 129–142. <https://doi.org/10.1016/j.oregeorev.2014.03.006>
- Pitcairn, I. K., Teagle, D. A. H., Craw, D., Olivo, G. R., Kerrich, R., & Brewer, T. S. (2006). Sources of metals and fluids in orogenic gold deposits: Insights from the Otago and Alpine schists, New Zealand. *Economic Geology*, 101(8), 1525–1546. <https://doi.org/10.2113/gsecongeo.101.8.1525>

References

- Pitcairn, I. K., Teagle, D. A. H., Kerrich, R., Craw, D., & Brewer, T. S. (2005). The behavior of nitrogen and nitrogen isotopes during metamorphism and mineralization: Evidence from the Otago and Alpine Schists, New Zealand. *Earth and Planetary Science Letters*, 233(1–2), 229–246. <https://doi.org/10.1016/j.epsl.2005.01.029>
- Pochon, A. (2018). *Magmatisme mafique et minéralisations Sb-Au dans le domaine Centre Armoricaïn : contrôles spatio-temporels et implications métallogéniques*. Université de Rennes 1.
- Pochon, A., Branquet, Y., Gloaguen, E., Ruffet, G., Poujol, M., Boulvais, P., Gumiaux, C., Cagnard, F., Baele, J. M., Kéré, I., & Gapais, D. (2019). A Sb ± Au mineralizing peak at 360 Ma in the Variscan belt. *BSGF - Earth Sciences Bulletin*, 190. <https://doi.org/10.1051/bsgf/2019004>
- Pochon, A., Gapais, D., Gloaguen, E., Gumiaux, C., Branquet, Y., Cagnard, F., & Martelet, G. (2016). Antimony deposits in the Variscan Armorican belt, a link with mafic intrusives? *Terra Nova*, 28(2), 138–145. <https://doi.org/10.1111/ter.12201>
- Pochon, A., Gloaguen, E., Branquet, Y., Poujol, M., Ruffet, G., Boiron, M. C., Boulvais, P., Gumiaux, C., Cagnard, F., Gouazou, F., & Gapais, D. (2018). Variscan Sb-Au mineralization in Central Brittany (France): A new metallogenic model derived from the Le Semnon district. *Ore Geology Reviews*, 97(January), 109–142. <https://doi.org/10.1016/j.oregeorev.2018.04.016>
- Pochon, A., Kontak, D., Gloaguen, E., Tuduri, J., Iacono-marziano, G., Campos-Rodríguez, H. R., Mollé, V., & Chatelin, T. (2023). Ilmenite-hosted fluid inclusions : Snapshot of magmatic fluid chemistry in mafic rocks. *Proceedings of the 17th SGA Biennial Meeting, 28 August – 1 September 2023*, 3, 196–199. <https://e-sga.org/nc/publications/sga-biennial-meetings-abstract-volumes/2023-zurich/>
- Pochon, A., Kontak, D., Iacono-Marziano, G., Gloaguen, E., Tuduri, J., Chatelin, T., Précigout, J., Campos Rodríguez, H. R., Mollé, V., Gourcerol, B., & Monnier, L. (2024). Primary fluid inclusions in magmatic ilmenite: a window into the volatile saturation of mafic intrusions. *Communications Earth & Environment*.
- Pochon, A., Poujol, M., Gloaguen, E., Branquet, Y., Cagnard, F., Gumiaux, C., & Gapais, D. (2016). U-Pb LA-ICP-MS dating of apatite in mafic rocks: Evidence for a major magmatic event at the Devonian-Carboniferous boundary in the Armorican Massif (France).

References

- American Mineralogist*, 101(11), 2430–2442. <https://doi.org/10.2138/am-2016-5736>
- Pohl, W. L. (2011). *Economic Geology Principles and Practice*. Wiley-Blackwell. <https://doi.org/10.5962/bhl.title.18736>
- Poujol, M. (2001). U-Pb isotopic evidence for episodic granitoid emplacement in the Murchison greenstone belt, South Africa. *Journal of African Earth Sciences*, 33(1), 155–163. [https://doi.org/10.1016/S0899-5362\(01\)90096-X](https://doi.org/10.1016/S0899-5362(01)90096-X)
- Rajič, K., Raimbourg, H., Famin, V., Moris-Muttoni, B., Fisher, D. M., Morell, K. D., & Canizarés, A. (2023). Exhuming an Accretionary Prism: A Case Study of the Kodiak Accretionary Complex, Alaska, USA. *Tectonics*, 42(10). <https://doi.org/10.1029/2023TC007754>
- Research and Markets. (2023). *Antimony Market: Global Industry Trends, Share, Size, Growth, Opportunity and Forecast 2023-2028*. https://www.researchandmarkets.com/report/antimony?gclid=CjwKCAjw-eKpBhAbEiwAqFL0mqGCCVHN9S0LWK0BKTbceebByxaUmKFjzPTP_5yRLkZoV-YIWOil-xoCKCAQAvD_BwE#product--adaptive
- Ribeiro, A. (1974). Contribution à l'étude tectonique de Trás-os-Montes Oriental Ribeiro,. In *Memória dos Serviços Geológicos de Portugal* (Vol. 24).
- Rice, C. M., Harmon, R. S., & Shepherd, T. J. (1985). Central City, Colorado: the upper part of an alkaline porphyry molybdenum system. *Economic Geology*, 80(7), 1769–1796. <https://doi.org/10.2113/gsecongeo.80.7.1769>
- Ridley, J. (2013a). Ore Deposit Geology. In *American Mineralogist* (Vol. 99, Issue 10). Cambridge University Press. <https://doi.org/10.2138/am-2014-651>
- Ridley, J. (2013b). *Ore Deposit Geology* (Vol. 25, Issue 2). Cambridge University Press. [https://doi.org/10.1016/0016-7142\(88\)90013-0](https://doi.org/10.1016/0016-7142(88)90013-0)
- Robardet, M., & Gutiérrez-Marco, J. C. (1990). Ossa-Morena Zone. Stratigraphy. Passive margin phase (Ordovician-Silurian-Devonian). In R. D. Dallmeyer & E. Martínez-García (Eds.), *Pre-Mesozoic Geology of Iberia* (pp. 267–272). Springer-Verlag. <https://www.unhcr.org/publications/manuals/4d9352319/unhcr-protection-training-manual-european-border-entry-officials-2-legal.html?query=excom> 1989
- Roberts, S., Sanderson, D. J., Dee, S., & Gumiel, P. (1991). Tectonic setting and fluid evolution

References

- of auriferous quartz veins from the La Codosera Area, western Spain. *Economic Geology*, 86(5), 1012–1022. <https://doi.org/10.2113/gsecongeo.86.5.1012>
- Rodriguez, B., Chew, D. M., Jorge, R. C. G. S., Fernandes, P., Veiga-Pires, C., & Oliveira, J. T. (2015). Detrital zircon geochronology of the Carboniferous Baixo Alentejo Flysch Group (South Portugal); constraints on the provenance and geodynamic evolution of the South Portuguese Zone. *Journal - Geological Society (London)*, 172, 294–308.
- Rodríguez, C., Castro, A., Gómez-Frutos, D., Gutiérrez-Alonso, G., Francisco Pereira, M., & Fernández, C. (2022). The unique Cambro-Ordovician silicic large igneous province of NW Gondwana: Catastrophic melting of a thinned crust. *Gondwana Research*, 106, 164–173. <https://doi.org/10.1016/j.gr.2022.01.011>
- Rodríguez González, R., Medina Varea, P., González Lodeiro, F., Martín-Parra, L. M., Martínez Poyatos, D., & Matas, J. (2007). Microflora y conodontos del Mississippense en la Fm Gévora (núcleo del Sinforme LaCodosera-Puebla de Obando, SO de la Zona Centroibérica). *Revista de La Sociedad Geológica de España*, 20(1), 71–88.
- Ross, P. S., & Bédard, J. H. (2009). Magmatic affinity of modern and ancient subalkaline volcanic rocks determined from trace-element discriminant diagrams Magmatic affinity of modern and ancient subalkaline volcanic rocks determined from trace element discriminant diagrams. *Canadian Journal of Earth Sciences*, 46, 823–839. <https://doi.org/10.1139/E09-054>
- Rubio-Ordóñez, A., Valverde-Vaquero, P., Corretgé, L. G., Cuesta-Fernández, A., Gallastegui, G., Fernández-González, M., & Gerdes, A. (2012). An early Ordovician tonalitic-granodioritic belt along the Schistose-Greywacke Domain of the Central Iberian Zone (Iberian Massif, Variscan belt). *Geological Magazine*, 149(5), 927–939. <https://doi.org/10.1017/S0016756811001129>
- Rubio Pascual, F. J., Arenas, R., Martinez-Catalán, J. R., Rodríguez Fernández, L. R., & Wijbrans, J. R. (2013). Thickening and exhumation of the Variscan roots in the Iberian Central System: Tectonothermal processes and $40\text{Ar}/39\text{Ar}$ ages. *Tectonophysics*, 587, 207–221.
- Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., & Pöschl, U. (2005). Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon*, 43(8), 1731–1742.

References

- <https://doi.org/10.1016/j.carbon.2005.02.018>
- San José, M. A., Piere, A. P., García Hidalgo, J. F., Villas, L., Herranz, P., Peláez, J. R., & Perejón, A. (1990). Central-Iberian zone. Ante-Ordovician stratigraphy. In R. D. Dallmeyer & E. Martínez-García (Eds.), *Pre-Mesozoic Geology of Iberia* (pp. 147–159). Springer-Verlag.
- Sánchez-García, T., Chichorro, M., Solá, A. R., Álvaro, J. J., Díez-Montes, A., Bellido, F., Ribeiro, M. L., Quesada, C., Lopes, J. C., Dias da Silva, Í., González-Clavijo, E., Gómez Barreiro, J., & López-Carmona, A. (2019). *The Cambrian-Early Ordovician Rift Stage in the Gondwanan Units of the Iberian Massif*. 27–74. https://doi.org/10.1007/978-3-030-10519-8_2
- Sanderson, D. J., Roberts, S., McGowan, J. A., & Gumiel, P. (1991). Hercynian transpressional tectonics at the southern margin of the Central Iberian Zone, west Spain. *Journal of the Geological Society*, 148(5), 893–898. <https://doi.org/10.1144/gsjgs.148.5.0893>
- Sangine, E. (2023). Antimony. In *Mineral Commodity Summaries*. U.S. Geological Survey.
- Santos García, J. A., Apatalegue Isasa, O., Carvajal Menéndez, A., Insua Marquez, M., & Gracia Prieto, F. J. (1990). Mapa geológico & memoria explicativa de la hoja num. 751, Villar del Rey. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 63). IGME. <http://www.nber.org/papers/w16019>
- Santos Garcia, J. A., & Casas Ruiz, J. (1979). Geologia del sinclinorio de Sao Mamede-La Codosera, zona espanola (provincias de Caceres y Badajoz). *Boletin Geologico y Minero*, 90(5), 420–431.
- Santos Garcia, J. A., & Casas Ruiz, J. (1982). Mapa geológico & memoria explicativa de la hoja num. 727, Albuquerque. In *Mapa Geológico de España, escala 1:50.000, 2a serie, plan MAGNA* (p. 33). IGME.
- Santos García, J. A., & Casas Ruiz, J. (1982). Mapa geológico & memoria explicativa de la hoja num. 727, Albuquerque. In *Mapa Geológico de España E. 1:50.000* (p. 35). Instituto Geológico y Minero de España.
- Sarrionandia, F., Errandonea-Martin, J., Larrondo, E., Carracedo-Sánchez, M., Ábalos, B., & Gil Ibarguchi, J. I. (2023). Low-Ti Continental Tholeiite Origin of Magmas With Calc-Alkaline Signature in Transcurrent Settings: The Mississippian Matachel Volcanic Field

References

- (SW Iberian Massif). *Geochemistry, Geophysics, Geosystems*, 24(11), 1–39. <https://doi.org/10.1029/2023GC011139>
- Saupe, F. (1973). Le geologie du gisement de mercure d'Almaden (Ciudad Real, Espagne). *BRGM Science Terre*, 29, 342.
- Saupé, F. (1990). Geology of the Almaden mercury deposit, province of Ciudad Real, Spain. *Economic Geology*, 85(3), 482–510. <https://doi.org/10.2113/gsecongeo.85.3.482>
- Saupé, F., & Arnold, M. (1992). Sulphur isotope geochemistry of the ores and country rocks at the Almadén mercury deposit, Ciudad Real, Spain. *Geochimica et Cosmochimica Acta*, 56(10), 3765–3780. [https://doi.org/10.1016/0016-7037\(92\)90169-J](https://doi.org/10.1016/0016-7037(92)90169-J)
- Scambelluri, M., Rampone, E., & Piccardo, G. B. (2001). Fluid and element cycling in subducted serpentinite: A trace-element study of the Erro-Tobbio high-pressure ultramafites (Western Alps, NW Italy). *Journal of Petrology*, 42(1), 55–67. <https://doi.org/10.1093/petrology/42.1.55>
- Scarrow, J. H., Molina, J. F., Bea, F., & Montero, P. (2009). Within-plate calc-alkaline rocks: Insights from alkaline mafic magma-peraluminous crustal melt hybrid appinites of the Central Iberian Variscan continental collision. *Lithos*, 110(1–4), 50–64. <https://doi.org/10.1016/j.lithos.2008.12.007>
- Schoene, B., & Bowring, S. A. (2006). U-Pb systematics of the McClure Mountain syenite: Thermochronological constraints on the age of the $^{40}\text{Ar}/^{39}\text{Ar}$ standard MMhb. *Contributions to Mineralogy and Petrology*, 151(5), 615–630. <https://doi.org/10.1007/s00410-006-0077-4>
- Schoene, B., & Bowring, S. A. (2007). Determining accurate temperature-time paths from U-Pb thermochronology: An example from the Kaapvaal craton, southern Africa. *Geochimica et Cosmochimica Acta*, 71(1), 165–185. <https://doi.org/10.1016/j.gca.2006.08.029>
- Schulmann, K., Edel, J. B., Martínez Catalán, J. R., Mazur, S., Guy, A., Lardeaux, J. M., Ayarza, P., & Palomeras, I. (2022). Tectonic evolution and global crustal architecture of the European Variscan belt constrained by geophysical data. *Earth-Science Reviews*, 234(June). <https://doi.org/10.1016/j.earscirev.2022.104195>
- Schwarz-Schampera, U. (2014). Antimony. In G. Gunn (Ed.), *Critical Metals Handbook* (First

References

- Edit, Vol. 121, pp. 70–98). John Wiley & Sons, Ltd.
- Schwarz-Schampera, U., Terblanche, H., & Oberthür, T. (2010). Volcanic-hosted massive sulfide deposits in the Murchison greenstone belt, South Africa. *Mineralium Deposita*, 45(2), 113–145. <https://doi.org/10.1007/s00126-009-0266-y>
- Seal II, R. R., Schulz, K. J., DeYoung, J. H., Sutphin, D. M., Drew, L. J. ., Carlin, J. F., & Berger, B. R. (2017). Antimony. In K. J. Schulz, J. H. DeYoung, R. R. Seal, & D. C. Bradley (Eds.), *Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply* (pp. C1–C17). U.S. Geological Survey Professional Paper. <https://doi.org/https://doi.org/10.3133/pp1802C>. ISSN
- Serment, R. (1978). La mine d’antimoine et or de la Lucette (Mayenne, France) : Historique – Etat des connaissances sur les travaux d’exploitation (1900-1934). *Chronique de La Recherche Minière*, 442, 35–52.
- Sillitoe, R. H., & Hedenquist, J. W. (2003). Linkages between Volcanotectonic Settings, Ore-Fluid Compositions, and Epithermal Precious Metal Deposits. In S. F. Simmons & I. Graham (Eds.), *Volcanic, geothermal and ore-forming fluids: Rulers and witnesses of processes within the Earth* (Special Pu, pp. 315–343). Society of Economic Geologist. <https://doi.org/10.5382/sp.10.16>
- Simancas, J. F. (2019). The Variscan Cycle. In C. Quesada & J. T. Oliveira (Eds.), *The Geology of Iberia: A Geodynamic Approach* (Vol. 2). Springer International Publishing. <https://doi.org/10.1007/978-3-030-10519-8>
- Simancas, J. F., Carbonell, R., González Lodeiro, F., Pérez Estaun, A., Juhlin, C., Ayarza, P., Kashubin, A., Azor, A., Martínez Poyatos, D., Almodóvar, G. R., Pascual, E., Sáez, R., & Expósito, I. (2003). Crustal structure of the transpressional Variscan orogen of SW Iberia: SW Iberia deep seismic reflection profile (IBERSEIS). *Tectonics*, 22(6). <https://doi.org/10.1029/2002TC001479>
- Simancas, J. F., Carbonell, R., González Lodeiro, F., Pérez Estaún, A., Juhlin, C., Ayarza, P., Kashubin, A., Azor, A., Martínez Poyatos, D., Sáez, R., Almodóvar, G. R., Pascual, E., Flecha, I., & Martí, D. (2006). Transpressional collision tectonics and mantle plume dynamics: The Variscides of southwestern Iberia. *Geological Society Memoir*, 32, 345–354. <https://doi.org/10.1144/GSL.MEM.2006.032.01.21>

References

- Simpson, M. P., & Mauk, J. L. (2007). The Favona epithermal gold-silver deposit, Waihi, New Zealand. *Economic Geology*, 102(5), 817–839. <https://doi.org/10.2113/gsecongeo.102.5.817>
- Solá, A. R., Neiva, A. M. R., & Ribeiro, M. L. (2010). Geocronologia, petrologia e geoquímica dos granitóides do ne alentejano (transição zci/zom): significado geodinâmico. *Ciências Geológicas – Ensino e Investigação e Sua História*, 1(2), 281–290.
- Solá, A. R., Neiva, A. M. R., Ribeiro, M. L., & Moreira, M. E. (2003). Geochemistry of igneous rocks from Carrascal Massif (Central Portugal) - A preliminary approach. *Journal of the Czech Geological Society*, 48(1–2), 115–116.
- Solá, A. R., Williams, I. S., Neiva, A. M. R., & Ribeiro, M. L. (2009). U-Th-Pb SHRIMP ages and oxygen isotope composition of zircon from two contrasting late Variscan granitoids, Nisa-Albuquerque batholith, SW Iberian Massif: Petrologic and regional implications. *Lithos*, 111(3–4), 156–167. <https://doi.org/10.1016/j.lithos.2009.03.045>
- Soldevila Bartolí, J. (1992). La sucesión paleozoica en el sinforme de la Codosera-Puebla de Obando (provincias de Cáceres y Badajoz, SO de España). *Estudios Geológicos (Madrid)*, 48, 353–362.
- Song, X. Y., Keays, R. R., Xiao, L., Qi, H. W., & Ihlenfeld, C. (2009). Platinum-group element geochemistry of the continental flood basalts in the central Emeishan Large Igneous Province, SW China. *Chemical Geology*, 262(3–4), 246–261. <https://doi.org/10.1016/j.chemgeo.2009.01.021>
- Stampfli, G. M., & Borel, G. D. (2002). A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. *Earth and Planetary Science Letters*, 196(1–2), 17–33. [https://doi.org/10.1016/S0012-821X\(01\)00588-X](https://doi.org/10.1016/S0012-821X(01)00588-X)
- Stormer, J. C., Pierson, M. L., & Tacker, R. C. (1993). Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. *American Mineralogist*, 78(5–6), 641–648.
- Sun, S.-S., & McDonough, W. F. (1989). Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. *Geological Society Special Publication*, 42(1), 313–345. <https://doi.org/10.1144/GSL.SP.1989.042.01.19>

References

- Svensen, H. H., Fristad, K. E., Polozov, A. G., & Planke, S. (2015). Volatile generation and release from continental large igneous provinces. In A. Schmidt, K. E. Fristad, & L. Elkins-Tanton (Eds.), *Volcanism and Global Environmental Change* (pp. 177–192). Cambridge University Press.
- Svensen, H. H., Jones, M. T., Percival, L. M. E., Grasby, S. E., & Mather, T. A. (2023). Release of mercury during contact metamorphism of shale: Implications for understanding the impacts of large igneous province volcanism. *Earth and Planetary Science Letters*, 619, 118306. <https://doi.org/10.1016/j.epsl.2023.118306>
- Talavera, C., Martínez Poyatos, D., & González Lodeiro, F. (2015). SHRIMP U–Pb geochronological constraints on the timing of the intra-Alcudian (Cadomian) angular unconformity in the Central Iberian Zone (Iberian Massif, Spain). *International Journal of Earth Sciences*, 104(7), 1739–1757. <https://doi.org/10.1007/s00531-015-1171-5>
- Tappe, S., Graham Pearson, D., Kjarsgaard, B. A., Nowell, G., & Dowall, D. (2013). Mantle transition zone input to kimberlite magmatism near a subduction zone: Origin of anomalous Nd-Hf isotope systematics at Lac de Gras, Canada. *Earth and Planetary Science Letters*, 371–372, 235–251. <https://doi.org/10.1016/j.epsl.2013.03.039>
- Tartèse, R., Poujol, M., Ruffet, G., Boulvais, P., Yamato, P., & Košler, J. (2011). New U-Pb zircon and ⁴⁰Ar/³⁹Ar muscovite age constraints on the emplacement of the Lizio syn-tectonic granite (Armorican Massif, France). *Comptes Rendus - Geoscience*, 343(7), 443–453. <https://doi.org/10.1016/j.crte.2011.07.005>
- Taylor, B. E. (2007). Epithermal gold deposits. In W. D. Goodfellow (Ed.), *Mineral deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods* (5th ed., Issue 5, pp. 113–139). Geological Association of Canada, Mineral Deposits Division.
- Teal, L., & Benavides, A. (2010). History and Geologic Overview of the Yanacocha Mining District, Cajamarca, Peru. *Economic Geology*, 105(7), 1173–1190.
- Teixeira, C. (1955). *Notas sobre Geologia de Portugal: O Complexo xisto-grauvácico anteordeviciano*. Empresa Literaria Fluminense.
- Thompson, J. F. H., Abidin, H. Z., Both, R. A., Martosuroyo, S., Rafferty, W. J., & T, A. J. B. (1994). Alteration and epithermal mineralization in the Masupa Ria volcanic center,

References

- Central Kalimantan, Indonesia. *Journal of Geochemical Exploration*, 50, 429–456.
- Thomson, S. N., Gehrels, G. E., Ruiz, J., & Buchwaldt, R. (2012). Routine low-damage apatite U-Pb dating using laser ablation-multicollector- ICPMS. *Geochemistry, Geophysics, Geosystems*, 13(1), 1–23. <https://doi.org/10.1029/2011GC003928>
- Tomkins, A. G. (2010). Windows of metamorphic sulfur liberation in the crust: Implications for gold deposit genesis. *Geochimica et Cosmochimica Acta*, 74(11), 3246–3259. <https://doi.org/10.1016/j.gca.2010.03.003>
- Tomkins, A. G. (2013). On the source of orogenic gold. *Geology*, 41(12), 1255–1256. <https://doi.org/10.1130/focus122013.1>
- Triboulet, C. L., & Audren, C. (1988). Controls on P–T–t deformation path from amphibole zonation during progressive metamorphism of basic rocks (estuary of the River Vilaine, South Brittany, France). *Journal of Metamorphic Geology*, 6(2), 117–133. <https://doi.org/10.1111/j.1525-1314.1988.tb00412.x>
- Turner, E. C., & Kamber, B. S. (2012). Arctic Bay Formation, Borden Basin, Nunavut (Canada): Basin evolution, black shale, and dissolved metal systematics in the Mesoproterozoic ocean. *Precambrian Research*, 208–211, 1–18. <https://doi.org/10.1016/j.precamres.2012.03.006>
- U.S. Geological Survey. (2023). *Mineral Commodity Summaries 2023: U.S. Geological Survey*. <https://doi.org/https://doi.org/10.3133/mcs2023>.
- U.S. Geological Survey. (2024). *Mineral Commodity Summaries 2024: U.S. Geological Survey*. <http://pubs.er.usgs.gov/publication/mcs2023>
- Valverde-Vaquero, P., & Dunning, G. R. (2000). New U-Pb ages for Early Ordovician magmatism in Central Spain. *Journal of the Geological Society*, 157(1), 15–26. <https://doi.org/10.1144/jgs.157.1.15>
- Vearncombe, J. R., Barton, J. M., Cheshire, P. E., De Beer, J. H., Stettler, E. H., & Brandl, G. (1992). Geology, geophysics and mineralisation of the Murchison Schist Belt, Rooiwater Complex and surrounding granitoids. *Memoir- Geological Survey of South Africa*, 81, 1992.
- Vermeesch, P. (2018). IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers*, 9(5), 1479–1493. <https://doi.org/10.1016/j.gsf.2018.04.001>

References

- Vielreicher, N. M., Groves, D. I., & McNaughton, N. J. (2016). The giant Kalgoorlie Gold Field revisited. *Geoscience Frontiers*, 7(3), 359–374. <https://doi.org/10.1016/j.gsf.2015.07.006>
- Villas, E., Lorenzo, S., & Gutiérrez-Marco, J. C. (1999). First record of a Hirnantia Fauna from Spain, and its contribution to the Late Ordovician palaeogeography of northern Gondwana. *Transactions of the Royal Society of Edinburgh, Earth Sciences*, 89(3), 187–197. <https://doi.org/10.1017/s0263593300007124>
- Villaseca, C., Castiñeiras, P., & Orejana, D. (2015). Early Ordovician metabasites from the Spanish Central System: A remnant of intraplate HP rocks in the Central Iberian Zone. *Gondwana Research*, 27(1), 392–409. <https://doi.org/10.1016/j.gr.2013.10.007>
- Villaseca, C., Martín Romera, C., & Barbero, L. (2002). Estimaciones termobarométricas en los metagabros coroníticos de la región de Segovia (Sierra de Guadarrama). *Geogaceta*, 32, 11–14.
- Villaseca, C., Orejana, D., Higuera, P., Pérez-Soba, C., García Serrano, J., & Lorenzo, S. (2022). The evolution of the subcontinental mantle beneath the Central Iberian Zone: Geochemical tracking of its mafic magmatism from the Neoproterozoic to the Cenozoic. *Earth-Science Reviews*, 228(October 2021), 103997. <https://doi.org/10.1016/j.earscirev.2022.103997>
- Vils, F., Müntener, O., Kalt, A., & Ludwig, T. (2011). Implications of the serpentine phase transition on the behaviour of beryllium and lithium-boron of subducted ultramafic rocks. *Geochimica et Cosmochimica Acta*, 75(5), 1249–1271. <https://doi.org/10.1016/j.gca.2010.12.007>
- Virtanen, V. J., Heinonen, J. S., Märki, L., Galvez, M. E., & Molnár, F. (2024). Sedimentary and metamorphic processes priming black shale for magmatic assimilation of sulfur: an example from the Virginia Formation, Minnesota, United States. *Mineralium Deposita*. <https://doi.org/10.1007/s00126-024-01268-1>
- Vogel, D. E. (1967). acquired a flaser of major Vogel : Polymetamorphic Ortegál Non-eclogitic Metamorphic facies. *Leidse. Geol. Meded.*, 40, 121–213.
- Webster, J. D., & Piccoli, P. M. (2015). Magmatic apatite: A powerful, yet deceptive, mineral. *Elements*, 11(3), 177–182. <https://doi.org/10.2113/gselements.11.3.177>
- Weil, A., Gutiérrez-Alonso, G., & Conan, J. (2010). New time constraints on lithospheric-scale

References

- oroclinal bending of the Ibero-Armorican Arc: A palaeomagnetic study of earliest Permian rocks from Iberia. *Journal of the Geological Society*, 167(1), 127–143. <https://doi.org/10.1144/0016-76492009-002>
- Williams, N. C., & Davinson, G. J. (2004). Possible submarine advanced argillic alteration at the basin lake prospect, Western Tasmania, Australia. *Economic Geology*, 99, 987–1002. [https://doi.org/10.1016/S0361-1124\(78\)80358-X](https://doi.org/10.1016/S0361-1124(78)80358-X)
- Wyborn, L. A. I., Heinrich, C., & Jaques, A. L. (1994). Australian Proterozoic mineral systems: Essential ingredients and mappable criteria: Australasian Institute of Mining and Metallurgy. *Darwin Conference, Abstract Series*, 5(January 2015), 94.
- Xu, L., Lehmann, B., & Mao, J. (2013). Seawater contribution to polymetallic Ni-Mo-PGE-Au mineralization in Early Cambrian black shales of South China: Evidence from Mo isotope, PGE, trace element, and REE geochemistry. *Ore Geology Reviews*, 52, 66–84. <https://doi.org/10.1016/j.oregeorev.2012.06.003>
- Yang, D. S., Shimizu, M., Shimazaki, H., Li, X. H., & Xie, Q. L. (2006). Sulfur isotope geochemistry of the supergiant Xikuangshan Sb deposit, central Hunan, China: Constraints on sources of ore constituents. *Resource Geology*, 56(4), 385–396. <https://doi.org/10.1111/j.1751-3928.2006.tb00291.x>
- Žák, J., Verner, K., Finger, F., Faryad, S. W., Chlupáková, M., & Veselovský, F. (2011). The generation of voluminous S-type granites in the Moldanubian unit, Bohemian Massif, by rapid isothermal exhumation of the metapelitic middle crust. *Lithos*, 121(1–4), 25–40. <https://doi.org/10.1016/j.lithos.2010.10.002>
- Žák, J., Verner, K., Janoušek, V., Holub, F. V., Kachlík, V., Finger, F., Hajná, J., Tomek, F., Vondrovic, L., & Trubač, J. (2014). A plate-kinematic model for the assembly of the Bohemian Massif constrained by structural relationships around granitoid plutons. In K. Schulmann, J. R. Martínez-Catalán, J. M. Lardeaux, V. Janoušek, & G. Oggiano (Eds.), *The Variscan Orogeny: Extent, Timescale and the Formation of the European Crust* (Vol. 405, pp. 169–196). Geological Society of London. <https://doi.org/10.1144/SP405.9>
- Zeck, H. P., Wingate, M. T. D., & Pooley, G. (2007). Ion microprobe U-Pb zircon geochronology of a late tectonic granitic-gabbroic rock complex within the Hercynian Iberian belt. *Geological Magazine*, 144(1), 157–177. <https://doi.org/10.1017/S0016756806002652>

References

- Zeh, A., & Gerdes, A. (2010). Baltica- and Gondwana-derived sediments in the Mid-German Crystalline Rise (Central Europe): Implications for the closure of the Rheic ocean. *Gondwana Research*, 17(2–3), 254–263. <https://doi.org/10.1016/j.gr.2009.08.004>
- Zhao, Z., Mo, X., Dilek, Y., Niu, Y., DePaolo, D. J., Robinson, P., Zhu, D., Sun, C., Dong, G., Zhou, S., Luo, Z., & Hou, Z. (2009). Geochemical and Sr-Nd-Pb-O isotopic compositions of the post-collisional ultrapotassic magmatism in SW Tibet: Petrogenesis and implications for India intra-continental subduction beneath southern Tibet. *Lithos*, 113(1–2), 190–212. <https://doi.org/10.1016/j.lithos.2009.02.004>
- Zotov, A. V., Shikina, N. D., & Akinfiev, N. N. (2003). Thermodynamic properties of the Sb(III) hydroxide complex $\text{Sb}(\text{OH})_3(\text{aq})$ at hydrothermal conditions. *Geochimica et Cosmochimica Acta*, 67(10), 1821–1836. [https://doi.org/10.1016/S0016-7037\(00\)01281-4](https://doi.org/10.1016/S0016-7037(00)01281-4)

LIST OF FIGURES

CHAPTER 1

Figure 1. 1. Current major uses of antimony (Carlin, 2013).	32
Figure 1. 2. Average antimony prices per ton from 1994-2024 in USD\$. All values were taken from the Minerals Yearbook and the Mineral Commodities Summary from the US Geological Survey (Carlin, 1994, 1995, 2004, 2005, 2006, 2007, 2009, 2010, 2011, 2012, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003; Guberman, 2013, 2014; Klochko, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2024; Sangine, 2023).....	35
Figure 1. 3. Global antimony market forecast, 2022-2028. CAGR: Compound Annual Growth Rate. (Research and Markets, 2023)	36
Figure 1. 4. Ore variation of orogenic-gold deposits based on depth. (Goldfarb & Groves, 2015).....	39
Figure 1. 5. Processes and scenarios in subduction settings that could lead to the mobilization and formation of Sb deposits (Goldfarb & Groves, 2015). These scenarios are related to the devolatilization of oceanic rocks accreted along a continental margin in regions where the crust has been thickened (A); the generation of extensional structures related to the ascension of a mantellic plume (B), subduction roll back (C) and the subduction of an oceanic ridge (D). ..	40
Figure 1. 6. Temperature zonation of the depletion of the ore-forming elements from the metamorphic rocks of the Otago and Alpine schists (Pitcairn et al., 2006)	42
Figure 1. 7. Emplacement of the mafic magmatism in the Armorican Massif related to a slab roll back at ca. 360Ma. This event led to the partial melting of the sub-continental lithospheric mantle under the Armorica plate and the generation of important amounts of mafic magmas	

List of figures

that contributed to the heating, rising and mobilization of several crustal fluids related to the Sb deposits in the Central Armorican Domain (Pochon, 2018).	43
Figure 1. 8. Sb mineralization model for La Lucette deposit at late Variscan times (Cheval-Garabédian et al., 2023).	45
Figure 1. 9. Distribution of several Sb deposits, mines and occurrences. (Schwarz-Schampera, 2014).....	46
Figure 1. 10. Schematic representation of crustal environments of several hydrothermal deposits (where Sb is present) in terms of depth of formation and structural setting within a convergent plate margin. (Groves et al., 1998)	47
Figure 1. 11. Schematic cross section through a LS epithermal ore system showing a hypothetical composite system containing different styles of ore: vein ore, disseminated ore and hot spring ore, together with the distribution of alteration assemblages. (Einaudi et al., 2003; Hedenquist et al., 2000; Ridley, 2013b).....	48
Figure 1. 12. Model of a reduced magmatic/intrusion related ore deposit. The mineralized system shows an important zonation starting with Au-W-As at the proximal parts of the intrusion; As-Sb-Au at the intermediate part; and Ag-Pb-Zn at the most distal part (Hart, 2007; Schwarz-Schampera, 2014).....	49
Figure 1. 13. Cross-section showing the ore bodies in the Xikouangshan deposit. The mineralization presents an important structural and stratigraphic control. (Yang et al., 2006).	52
Figure 1. 14. Simplified geological map of the Murchinson greenstone belt showing the antimony line. (Poujol, 2001; Schwarz-Schampera et al., 2010).....	53
Figure 1. 15. Model proposed by Pochon et al. (2018) for explaining the main formation stages of the Le Semnon Sb-Au deposit in the Armorican Massif.	54

CHAPTER 2

Figure 2. 1. Reconstruction of the European Variscan Belt from Late-Carboniferous-early Permian. **Variscan domains (VD):** CVD, Central; NVD, North-eastern; SVD, South-western. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Trás-os-Montes; MSZ, Moravo-Silesian Zone; MZ, Moldanubian; OMZ, Ossa-Morena; RHZ, Rhenohercynian; SPZ, South Portuguese; STZ, Saxothuringian; TBZ, Teplá-Barrandian; WALZ, West Asturian-Leonese. **Armorican Domains (AD):** CAD, Central; NAD, North; SAD, South. **Shear zones (SZ), faults (F) and fault zones (FZ):** BBSZ, Baden-Baden; BCSZ, Badajoz-Córdoba; BrF, Bray; EFZ, Elbe; JPSZ, Juzbado-Penalva; LLSZ, Lalaye-Lubine; MT, Moldanubian Thrust; NASZ, North Armorican; NEF, Nort-sur-Erdre; NPF, North Pyrenean; PASZ, Posada-Asinara; Pf, Pfahl-Danubian fault system; PTSZ, Porto-Tomar; SASZ, South Armorican (N and S, northern and southern branches); SHF, Sillon Houiller; SISZ, Southern Iberian; SFS, Sudetic fault system; VF, Variscan Front. **Other:** MT, Moldanubian thrust; BM, Basque Massifs; CIA, Central Iberian Arc; Co, Corsica; FMC, French Massif Central; IAA, Ibero- Armorican Arc; Lo, Lizard ophiolites; MTM, Maures-Tanneron Massif; MGCR, Mid-German Crystalline Rise; MN, Montagne Noire; Sa, Sardinia; SWM, Schwarzwald Massif; VM, Vosges Massif. Modified after (Martínez Catalán et al., 2021; Schulmann et al., 2022)..... 59

Figure 2. 2. Simplified map of the different domains in the Armorican Massif. After (Ballèvre et al., 2009)..... 60

Figure 2. 3. (a) Geological map of the Iberian Peninsula showing the Variscan massifs and the zones of the Iberian Massif, continued into the Pyrenees, Iberian Chain and Catalonia Coast Ranges. Based on the Geological map of Spain and Portugal to scale 1:1000 000 (IGME-LNEG, 2015) and in Martínez Catalán (2012). The most important structures are shown, including early and late folds, thrust faults, and the main ductile strike-slip shear zones. **(b)** Detail of the geology of the Galicia allochthonous complexes showing the distribution of the three

List of figures

Allochthons and the Parautochthon. **(c)** Detail of the geology of the Portuguese allochthonous complexes. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Trás-os-Montes; OMZ, Ossa-Morena; SPZ, South Portuguese; WALZ, West Asturian- Leonese. **Domains of the CIZ (D):** DRF, of Recumbent Folds; DUF, of Upright Folds; OSD, Ollo de Sapo; OVD, Obejo-Valsequillo; SGD, Schist-Greywacke. **Allochthonous complexes:** B, Bragança; CO, Cabo Ortegal; M, Morais; MT, Malpica-Tui; O, Órdenes. **Other units:** BAU, Beja-Acebuches; CU, Central Unit; EAMB, Évora-Aracena Metamorphic Belt; NSSB, Northern Sierra de Sevilla Batholith; PL, Pulo do Lobo Unit. **Shear zones (SZ) and faults (F):** BCSZ, Badajoz-Córdoba; JPSZ, Juzbado-Penalva; NPF, North Pyrenean; PTSZ, Porto-Tomar; SISZ, Southern Iberian. **Arcs (A):** CIA, Central Iberian; IAA, Ibero-Armorican. **Pyrenees:** AZ, Axial Zone; NM, Northern Massifs; Basque Massifs: CV, Cinco Villas; QR, Quinto Real; UB, Ursuya-Baygura. **Balearic Islands:** Ma, Majorca; Me, Menorca; Ib, Ibiza. **Allochthonous groups:** LA, Lower Allochthon; MA, Middle Allochthon; PA, Parautochthon; UA, Upper Allochthon (IP, Intermediate-P; HP-HT, High-P/ High-T). After Martínez Catalán et al, (2021). 63

Figure 2. 4. Cross sections representative of the structure of the Iberian Massif including the Variscan sutures. **(a)** Northwest Iberian section A-A'', modified from Martínez Catalán et al. (2014). **(b)** Central Iberian section B-B', based on Martínez Poyatos et al. (2012). **(c)** Southwest Iberian section C-C', based on Simancas et al. (2003) and partly on Rubio Pascual et al. (2013b). The sections are built from field geology and partly using deep seismic reflection profiles. For section A-A'', these are ESCIN-1 (Pérez-Estaún et al., 1994, 1995), ESCIN-3.2 (Alvarez-Marrón, 1995, 1996) and ESCIN-3.3 (Martínez Catalán et al., 1995; Ayarza et al., 1998). The two latter were acquired offshore, while section A-A'' derives from onshore geology. In the parts of section A-A'' roughly corresponding to these two profiles, (GTMZ, CIZ and WALZ), the seismic reflections have been placed approximately. Section B-B' roughly follows the seismic line ALCUDIA (Martínez Poyatos et al., 2012). Section C-C' follows the

List of figures

seismic line IBERSEIS (Simancas et al., 2003). Whrench faults are continued at depth avoiding to cross low-dipping reflections. Colors corresponding to zones or groups are superposed to frames or grey shades indicating lithologies or units. **Zones (Z):** CZ, Cantabrian; CIZ, Central Iberian; GTMZ, Galicia-Tr´as-os- Montes; OMZ, Ossa-Morena; SPZ, South Portuguese; WALZ, West Asturian-Leonese. **Domains of the CIZ (D):** DRF, of Recumbent Folds; DUF, of Upright Folds; OSD, Ollo de Sapo; OVD, Obejo-Valsequillo; SGD, Schist-Greywacke. **Other units:** BAU, Beja-Acebuches; EAMB, ´Evora-Aracena Metamorphic Belt; IRB, Iberian Reflective Body. **Other:** Upper Allochthon: IP, Intermediate-P; HP-HT, High-P/High-T. See Fig. 2 for location of the sections. After Martínez Catalán et al. (2021) and references therein.

..... 64

Figure 2. 5. Evolution of the Variscan deformation, metamorphism and magmatism in the GTMZ, CIZ, WALZ and CZ. Modified after Azor et al. (2019) based on the work performed by Dallmeyer et al. (1997); Martínez-Catalán et al. (2016); Martínez Catalán et al. (2014)... 82

Figure 2. 6. Distribution of the Variscan Gneiss domes with published ages of migmatization. Ce: Celanova; Gd: Guadarrama; Gr: Gredos; Gu: Guitiriz; Lu: Lugo; Ma: Martinamor; Pa: Padrón; Pe: Peares; Sa: Sanabria; So: Somosierra; To: Toledo; Tr: Tormes. Modified after Martínez Catalán et al. (2014) and references therein..... 83

Figure 2. 7. A) Geological sketch of the Variscan Belt showing the main terranes and domains, modified after Martínez Catalán et al. (2014); B) Simplified geological map of the Iberian Massif showing mafic rocks in the studied areas and the mafic suites reported in the Central Iberian Zone (CIZ) from Ordovician times to the late stages of the Variscan orogeny. The map was designed based on the studies made by Julivert et al. (1974) and Simancas (2019). Abbreviations: OMZ: Ossa Morena Zone; GTMZ: Galicia-Tras-Os Montes-Zone; WALZ: West Asturian Leonese Zone (WALZ); CZ: Cantabrian Zone; MN: Montagne Noire; ECM: External Crystalline Massifs of the Alps; VM: Vosges Massif; BF: Black Forest; CP: Calzadilla

List of figures

Plutón (López-Moro et al., 2017); LA: Praia de Labruga (de Almeida Coelho, 2021); GD: Godomar (Medeiros et al., 1981); F: Farminhao (Cotrim et al., 2021); AP: Appinites (Montero, Bea, et al., 2004; Montero, Zinger, et al., 2004; Scarrow et al., 2009); TAC: Toledo Anatetic Complex (Bea et al., 2006); C: Caloco Sector (Orejana et al., 2017; Villaseca et al., 2015); R: Revenga Sector (Orejana et al., 2017; Villaseca et al., 2015); TM: Tenzuela Massif; MMC: Mérida Montoro Complex (Bandrés et al., 2004); SB: Sierra Bermeja (Errandonea-Martin et al., 2019); CM: Carrascal Massif (Solá et al., 2010); MG : Microgabbros (Orejana et al., 2020) ; CS: Codosera Syncline (López-Moro et al., 2007); AS: Almadén Syncline (Higueras, 1995; Higueras et al., 2013); GS: Guadalmez Syncline (Gumiel & Arribas, 1987; Lorenzo Álvarez et al., 1995); SUM: Susana Mine (Gumiel, 1982); NZM: Nazarena Mine (Gumiel, 1982).	85
Figure 2. 8. Location of the Tenzuela Massif, the Revenga and El Caloco sectors in the Spanish Central System. (Orejana et al., 2017).	86
Figure 2. 9. Geology and metallogenic activity of the Almadén district taken from Higueras et al. (2013) and modified from Higueras (1995); Higueras et al. (2013); Palero & Lorenzo (2009).	88
Figure 2. 10. Simplified geological map of the Valongo-Tamames syncline showing the location of El Castillo basalts. Modified from Gutiérrez-Alonso et al. (2008) and references therein.	89
Figure 2. 11. Simplified geological map of the Iberian Massif showing the southern part of the CIZ. Modified after López-Moro et al. (2020) and references therein ; B) Location of La Codosera syncline (CS) in the Southern part of the CIZ. Modified after López-Moro et al. (2020)	90
Figure 2. 12. Geological simplified map showing the location of the Avila batholith and the mafic rocks in it. After (Montero et al., 2004)	92

Figure 2. 13. Geological map showing other outcrops of mafic/intermediate rocks located in the Spanish Central System. Modified after (Orejana et al., 2009)	92
Figure 2. 14. Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline (CS). Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the mafic samples studied in this work. Reference (c): Sampling points from Rodríguez González (2007). The map was redesigned based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).	95
Figure 2. 15. A) Simplified geological map of the Iberian Massif showing the studied area of the Almadén (AS) and Guadalmez (GS) synclines. Modified after López-Moro et al. (2020) ; B) Geological map of the of the Almadén (AS) and Guadalmez (GS) synclines showing the location of the Sb mines as well as the Almadén Hg district. The map was designed based on the Geological Maps (scale 1:50000) of Chillón (Lorenzo Álvarez et al., 1995), Almadén (García San Segundo et al., 1985), Hinojosa del Duque (Mira López, Ortega Gironés, Rodríguez Pevida, et al., 1983) and San Benito (Mira López, Ortega Gironés, & Rodríguez Pevida, 1983).	100
Figure 2. 16. Simplified geological map of the Armorican Massif showing several Sb and Au mineralization located in the Southern Armorican Domain (SAD), the Central Armorican Domain (CAD) and the North Armorican Domain (NAD). Legend: LU: Sb-Au district of La Lucette, S: Sb-Au Semnon-La Coëfferie district, V : Sb-(Au) Vendée district, Q : Sb Quimper-Cap Sizun CG district ; Au district of Château-Gontier, P : Au district of Pontivy-Loudéac, L : Lizio granite, PR : Pontivy-Rostrenen Complex, Pe : granite of Pertre and Cr : granite of Craon. Modified after Pochon (2018) and references therein.....	103

Figure 2. 17. Distribution of the antimony deposits and occurrences in the Iberian Peninsula (Gumiel & Arribas, 1987).	112
Figure 2. 18. Isometric section of the San Antonio Sb-deposit. After Gumiel (1982).	115

CHAPTER 3

Figure 3. 1. A) Geological sketch of the Variscan Belt showing the main terranes and domains, modified after Martínez Catalán et al. (2014); B) Simplified geological map of the Iberian Massif showing mafic rocks in the studied areas and the mafic suites reported in the Central Iberian Zone (CIZ) from Ordovician times to the late stages of the Variscan orogeny. The map was designed based on the studies made by Julivert et al. (1974) and Simancas (2019). Abbreviations: OMZ: Ossa Morena Zone; GTMZ: Galicia-Tras-Os Montes-Zone; WALZ: West Asturian Leonese Zone (WALZ); CZ: Cantabrian Zone; MN: Montagne Noire; ECM: External Crystalline Massifs of the Alps; VM: Vosges Massif; BF: Black Forest; CP: Calzadilla Plutón (López-Moro et al., 2017); LA: Praia de Labruga (de Almeida Coelho, 2021); GD: Godomar (Medeiros et al., 1981); F: Farminhao (Cotrim et al., 2021); AP: Appinites (Montero, Bea, et al., 2004; Montero, Zinger, et al., 2004; Scarrow et al., 2009); TAC: Toledo Anatetic Complex (Bea et al., 2006); C: Caloco Sector (Orejana et al., 2017; Villaseca et al., 2015); R: Revenga Sector (Orejana et al., 2017; Villaseca et al., 2015); TM: Tenzuela Massif; MMC: Mérida Montoro Complex (Bandrés et al., 2004); SB: Sierra Bermeja (Errandonea-Martin et al., 2019); CM: Carrascal Massif (Solá et al., 2010); MG : Microgabbros (Orejana et al., 2020) ; CS: Codosera Syncline (López-Moro et al., 2007); AS: Almadén Syncline (Higueras, 1995; Higueras et al., 2013); GS: Guadalmez Syncline (Gumiel & Arribas, 1987; Lorenzo Álvarez et al., 1995); SUM: Susana Mine (Gumiel, 1982); NZM: Nazarena Mine (Gumiel, 1982).	123
--	-----

Figure 3. 2. A) Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the mafic samples studied in this work. Reference (c): Sampling points from Rodríguez González (2007). The map was redesigned based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).	125
Figure 3. 3. A) Simplified geological map of the Iberian Massif showing the studied area of the Almadén (AS) and Guadalmez (GS) synclines. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the of the Almadén (AS) and Guadalmez (GS) synclines showing the mafic samples studied in this work. The map was redesigned based on the Geological Maps (scale 1:50000) of Chillón (Lorenzo Álvarez et al., 1995), Almadén (García San Segundo et al., 1985), Hinojosa del Duque (Mira López et al., 1983) and San Benito (Mira López et al., 1983).....	126
Figure 3. 4. Simplified geological map of the Iberian Massif showing the studied area of the Susana Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Susana Mine (SUM) showing the mafic samples studied in this work. The map was redesigned based on the Geological Map (scale 1:50000) of Puebla de Alcocer (Martín Herrero et al., 1994).....	127
Figure 3. 5. Simplified geological map of the Iberian Massif showing the studied area of the Nazarena Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Nazarena Mine (NZM) showing the mafic samples studied in this work. The map was redesigned based on the Geological Map (scale 1:50000) of Aldeaquemada (Martín-Parra et al., 1996).....	127

Figure 3. 6. Structural data of the mafic sills and metasedimentary sequence in the studied areas.....	132
Figure 3. 7. Thin section micro-photographs showing the least altered samples A-B) plagioclase (Pg) and clinopyroxene (Cpx) showing their primary features in sample SA2014 from CS. C-D) typical mineralogical assemblage from AS dolerites with plagioclase, Cpx, and secondary chlorite (Chl); E-F) typical mineralogical assemblage from GS dolerites with plagioclase, apatite (ap), and secondary calcite (Cal) and chlorite.	134
Figure 3. 8. Thin section micro-photographs showing the most altered samples: A-B) amphibole and plagioclase altered to epidote (Amph-Ep), as well as ilmenite (Fe-Ti Oxides), in sample SA2042 from CS; H-I) chlorite (Chl) and Plagioclase (Pg) in sample AL2077B from AS; H-I) plagioclase altered to Chlorite (Chl) and ilmenite in sample AL2073 from GS.....	135
Figure 3. 9. Selected thin section micro-photographs illustrating the studied apatite crystals. A) Optical image showing apatite associated to primary ilmenite; B) BSE image showing apatite associated to primary ilmenite; C-D) cathodoluminescence micro-photographs of the studied apatite crystals, E-F) Thin section micro-photographs showing apatite related to primary clinopyroxene. The apatite appears as acicular crystals (Ap) associated to the primary plagioclases, clinopyroxene (Cpx) and ilmenite (Ilm).	136
Figure 3. 10. Hydrothermal alteration diagrams for the samples in this study. A) Alteration box plot diagram of Large (2001). AI: Alteration Index, CCPI: Chlorite-Carbonate-Pyrite-Index; B) Alteration diagram of Williams and Davinson (2004), AAI: Advanced-Argilic-Alteration-Index.....	139
Figure 3. 11. Isocon diagrams for metasomatic alteration of Grant (2005), showing samples from CS (A) and (AS-GS). These diagrams allow to determine the alteration degree of all samples by plotting an altered composition against an original composition. A) Samples from CS plotted against the least altered sample from CS (SA2026); B) Samples from AS-GS plotted	

List of figures

against the least altered sample from AS (AL2088), both synclines present the same stratigraphic succession and are found in the same region which is why GS samples were plotted against an AS sample.	141
Figure 3. 12. Total Alkali Silica diagram (TAS) from Le Bas et al. (1986) showing the samples studied in this work and in previous studies done by Higuera (1995); Higuera et al. (2013); López-Moro et al. (2007).	143
Figure 3. 13. Discrimination diagrams for the mafic samples of the CS, AS, GS, SUM and NZM. A) Nb/Y vs Zr/Ti diagram with field boundaries taken from Pearce (1996); B) Zr/Y vs Th/Yb diagram with field boundaries taken from Ross and Bedard (2009).	144
Figure 3. 14. A-B) Chondrite normalized spider diagram for samples from CS (A) and AS-GS-SUM-NZM (B); C-D) primitive mantle normalized spider diagrams for samples from CS (C) and the AS-GS-SUM-NZM (D). Primitive mantle normalizing values are from Sun & McDonough (1989).	145
Figure 3. 15. Cathodoluminescence micro-photographs of the studied apatite crystals for samples A) SA2022C; B) SA2026; C) AL2075; D) AL2076. In cathodoluminescence images, the apatite crystals do not show any oscillatory zoning. The lack of any zoning along fractures suggests the lack of hydrothermal dissolution/recrystallization processes and supports their main primary character. The apatites exhibit homogeneous colours ranging from yellow, green, violet and blue	146
Figure 3. 16. X-ray maps showing P (A), Ca (B), F (C) and Cl (D) distribution within an apatite crystal from sample AL2075 in the GS. The Ca and the P seem to be less enriched in the rim. The F distribution in the crystal is homogeneous whereas the Cl present a heterogeneous distribution.	148
Figure 3. 17. Average electron microprobe analyses of apatite for the dolerite samples dated in this study, compared to the apatites from the Armorican massif dolerites (field in green) by	

List of figures

Pochon et al. (2016b). The halogens content plot has been modified from Boudreau (1995).	149
Figure 3. 18. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks of the CS.	150
Figure 3. 19. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks coming from GS (A-C) and AS (D).	151
Figure 3. 20. Tera-Wasserbourg diagram showing the obtained dates for the mafic rocks coming from SUM (A) and NZM (B).	152
Figure 3. 21. LA-ICP-MS analyses of ilmenite from the Armorican Massif showing the enrichment in incompatible trace elements in FI-bearing areas. Modified after Pochon et al. (in review).....	153
Figure 3. 22. Synthesis of the ages of the mafic samples studied in this work and comparison with previous data on mafic magmatism in the Armorican Massif. References in the figure: ¹ (Pochon et al., 2016b); ² (Barboni et al., 2013); ³ (Paquette et al., 2017).	157
Figure 3. 23. Th/Yb vs Ta/Yb diagram from Pearce (1983, 2008) showing the mafic rocks studied in this work and those reported for the CIZ and the Armorican Massif. The rocks from CS show a less enriched and less metasomatized mantle source compared to the rocks from AS, GS, SUM and NZM. The CS is consistent with the data reported for the Armorican Massif (Pochon et al. 2016). References in the figure: ¹ (Orejana et al., 2009); ² (Scarrow et al., 2009); ³ (López-Moro et al., 2007); ⁴ (Pochon et al., 2016).	161
Figure 3. 24. A) La/Sm vs Gd/Yb diagram (Kamenetsky & Eggins, 2012) showing samples coming from CS, GS, AS, SUM and NZM. The data is consistent with the presence of garnet in the source, which also matches with the enrichment in LREE.	164
Figure 3. 25. Simplified model for the possible mantle sources of the mafic rocks from the CS, GS , AS, SUM and NZM. A) Simplified geological map of the Iberian Massif (Julivert et al.,	

List of figures

1974; Simancas, 2019). Section traces, A-A^I and B-B^I, are those of Palomeras et al. (2017), and only the part of section associated with our studies areas have been retain. B) AS and GS as well as their inferred mantle sources projected on a schematic cross section along the trace A-A^I. C) Inferred mantle source of the CS projected on a schematic cross section along the trace B-B^I. The high and low velocity zones in the mantle are based on the seismic velocity models from Palomeras et al. (2017). The crustal architecture is inspired on the IBERSEIS and ALCUDIA seismic profiles from Simancas et al. (2003; 2006) and Martínez Poyatos et al. (2012), respectively. Mantle plumes, and slabs inspired from the studies done by Azor et al. (2019); Cambeses et al. (2015); Martínez Catalán et al. (2009); Pereira et al. (2022); Rodríguez et al. (2022); Sarrionandia et al. (2023). The intrusions on the Spanish Central System were reported by Orejana et al. (2009) and Scarrow et al. (2009). 166

CHAPTER 4

Figure 4. 1. Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the Raman and mafic samples studied in this work. This map was designed based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990). 178

Figure 4. 2. Simplified stratigraphic column showing the Palaeozoic sequence of la Codosera Syncline and the samples studied by RAMAN spectroscopy in this chapter. This column was designed based on the sedimentary and stratigraphic studies done by Gumiel (1982); Rodríguez González et al. (2007); Santos Garcia & Casas Ruiz (1979); Soldevila Bartolí (1992). 180

Figure 4. 3. Thin section micro-photographs in reflected light showing the distribution of the carbonaceous material (CM) and the main characteristics of the samples from the Sierra Fría Unit (SFU). All of the samples present OM and Fe-Oxides evenly distributed in the groundmass. A-B) Sample SA21016B (PPL-XPL); C-D) Sample SA21018B (PPL-XPL); E-F) Sample SA21020A (PPL-XPL).	185
Figure 4. 4. Thin section micro-photographs in reflected light showing the distribution of the organic material (OM) and the main characteristics of the samples from the Gévora Formation (GF). All of the samples present OM, Fe-Oxides and sulfides evenly distributed in the groundmass. A-B) Sample SA2007 (PPL); C) Sample SA21023A (PPL); D) Sample SA21024A (PPL); E) Sample SA21029G (PPL); F) Sample SA2033A (PPL); G-H) Sample SA2033C (PPL-XPL).....	186
Figure 4. 5. SEM imaging showing the main phases found for the rocks of: A) SFU: Fe oxides, muscovite and quartz; B) SFU: Fe oxides, Rutile and muscovite; C) SFU: Fe oxides, muscovite, quartz and monazite; D) GF: Calcite, galena, quartz, muscovite and monazite; E) GF: Quartz, chlorite, apatite, muscovite and rutile; F) GF: Quartz, chlorite and apatite. CM=Carbonaceous Material	188
Figure 4. 6. Whisker plots showing the data distribution of SiO ₂ (A), Al ₂ O ₃ (B), Fe ₂ O ₃ (C), CaO (D), Log ₁₀ S (E) and C organic (F) for the SGC-SFU and the GF samples in this study. Legend: SGC = Schist Greywacke Complex; SFU = Sierra Fría Unit; GF = Gévora Formation; n = number of measurements; AVG = average; Mdn = Median; Q1 = first quartile; Q3 = third quartile; Max = maximum value; Min = Minimum value; Out = outlier.....	192
Figure 4. 7. Sb distribution in the CS. The higher values of Sb are found at the western (San Antonio Mine, Sb-W) and eastern part (Villar del Rey Quarry) of the CS.....	193
Figure 4. 8. Sb correlation diagrams with SiO ₂ (A), Al ₂ O ₃ (B), Fe ₂ O ₃ (C), CaO (D), S (E) and C organic (F), for the SGC-SFU and GF samples in this study.	194

List of figures

Figure 4. 9. Sb correlation diagrams with W, As, Hg, Cu, Pb and Co for the SGC-SFU and GF samples in this study.	195
Figure 4. 10. Representative Raman spectra of the SGC and the Sierra Fría Unit samples shown together with the approximate positions of the G, D1 and D2 peaks. The temperatures were calculated using the high temperature method from Beyssac et al. (2002).....	199
Figure 4. 11. Representative Raman spectra of the GF samples shown together with the approximate positions of the G, D1, D2, D3 and D4 peaks. The temperatures were calculated using the low temperature method from Lahfid et al. (2010).	200
Figure 4. 12. Representative Raman spectra of the GF samples shown together with the approximate positions of the G, D1, D2, D3 and D4 peaks. The temperatures were calculated using the high temperature method from Beyssac et al. (2002).....	201
Figure 4. 13. Whisker plots showing the Sb data distribution for the SGC-SFU, the GF compared to global data of Pre and post-Cambrian shales (Fig. 4.13). These data include shales from Canada, China, USA and India, and derives from 8 publications (Fan et al., 2004; Goodfellow et al., 2009; Manikyamba et al., 2008; Manikyamba & Kerrich, 2006; Orberger et al., 2007; Pašava et al., 2008; Turner & Kamber, 2012; Xu et al., 2013).	203
Figure 4. 14. Simplified geological map of the Iberian Massif showing the Codosera syncline, the distribution of the temperatures obtained for the metasediments (yellow circles) and the mafic samples studied in this tesis (back triangles). Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the Raman and mafic samples studied in this work. This map was designed based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).	206

Figure 4. 15. Distribution of the late Variscan Gneiss domes and the location of the Codosera syncline within an area (green zone) where the highest metamorphic degree reported goes up to greenschist facies. Legend: Ce: Celanova; Gd: Guadarrama; Gr: Gredos; Gu: Guitiriz; Lu: Lugo; Ma: Martinamor; Pa: Padrón; Pe: Peares; Sa: Sanabria; So: Somosierra; To: Toledo; Tr: Tormes. Modified after *Martínez Catalán et al. (2014); Azor et al. (2019); Barbero & Villaseca (2000).	207
--	-----

CHAPTER 5

Figure 5. 1. A) Sample SA2033C at the eastern part of the CS, with more than 250ppm of Sb. B) LA-ICP-MS analyses show that pyrite is not the main Sb-bearing phase in the CS.	217
---	-----

Figure 5. 2. Presence of primary fluid inclusions on ilmenite in the mafic rocks from the CS. A) Sample SA2022; B) Sample SA2042. Modified after Chatelin (2022).	220
--	-----

Figure 5. 3. Schematic diagram illustrating the conceptual model of entrapment of magmatic volatile phases within ilmenite from Pochon et al. (2024). (a) General geometry (not to scale) of a gabbroic intrusion with the location of insets (b), (c) and (d). (b-d) Back-scattered electron (BSE) images of ilmenite (Ilm) texture from the lower (b), central (c) and upper (d) parts of the basic intrusion that records magma degassing from the base to the top. White scale bar represents 20 μm . (e) Onset of volatile exsolution in the residual melt (RM) of the mush and release of a magmatic volatile phase (MVP) via 2 nd boiling. Ilmenite may act as a preferential site for nucleation of bubbles during its growth or ilmenite crystallization may act as the trigger of exsolution of bubbles at the growing crystal-melt interface. (f) Ilmenite grain crystallizes more or less quickly and may easily traps abundant MVP as fluid inclusions (FI) during its progressive crystallization and magma cooling. (g) Following ilmenite formation, trapped FI likely undergo re-equilibration via necking, whereas the untrapped MVP likely escapes via capillary fracturing or others processes and probably coalesce towards the surface. The latter	
---	--

MVP interacts with and modifies earlier crystallized silicate phases. Interaction of ilmenite with fluids saturated in Si and Ca (due to alteration of calcic plagioclase (Pl) and mafic minerals) causes ilmenite breakdown. This fracture-controlled subsolidus alteration is responsible for the formation of FI-free ilmenite and the development of secondary titanite (Ttn) $\pm$ rutile (Rt).
Abbreviation: Cpx – clinopyroxene, Amph – amphibole, Low T – low temperature. 220

Figure 5. 4. NE-SW Cross-section of the Carboniferous sequence showing the main sampling location of: (A) Samples SA21024A and SA21024B; (B) SA21023C and SA21023I. 223

Figure 5. 5. Simplified model for explaining the formation of Sb deposits such as the San Antonio district (SA) at the Codosera Syncline (CS) of the Central Iberian Zone (CIZ). This model considers the accommodation of the Variscan deformation by left transtensional kinematics at the Badajoz Cordoba Shear Zone (BCSZ, (Azor et al., 2019; Gutiérrez-Marco et al., 2019; Martínez-Catalán et al., 2016) and the emplacement ages of the mafic sills in this thesis between ca. 360-340 Ma. The mafic intrusions would have acted either as a metal source for the Sb deposits (by magmatic degassing) or as a heating source allowing the devolatilization of Sb-rich metasediments and therefore the mobilization of Sb and other elements within the CS. 225

Figure 5. 6. Simplified geological map of the Moroccan Variscides showing the location of the main units and the mafic intrusions. Modified after Moutbir et al. (2024) and references therein.

Abbreviations: MMFZ, Middle Meseta Fault Zone; RTFZ, Rabat–Tiflet Fault Zone; SAF, South Atlas Fault; SMFZ, Southern Meseta Fault Zone; WMSZ, Western Meseta Shear Zone; MCM, Moroccan Central Massif; SBB, Sidi Bettache Basin; FB, Fourhal Basin; AKB, Azrou–Khenifra Basin, Camb: Cambrian; Silu: Silurian; Dev: Devonian. 229

Figure 5. 7. Geological map of the Carboniferous Fourhal Basin (Moroccan Central Massif) showing the occurrences of the mafic intrusions (dykes and sills). (Moutbir et al., 2024) ... 230

List of figures

Figure 5. 8. Location of the Jbel Haouanite Au-Sb mineralization in the Tamlalt Plain (Azza, 2019).....	232
--	-----

LIST OF TABLES

CHAPTER 1

Table 1. 1. World mine production and reserves of antimony. (U.S. Geological Survey, 2024).

..... 34

CHAPTER 2

Table 2. 1. Main minerals present in the paragenetic sequences of the Sb districts in the Armorican Massif. (Blouin, 1991; BRGM, 1987; Chauris et al., 1985; Chauris & Marcoux, 1994; Fouquet, 1980; Gloaguen et al., 2016; Gorichon & Kerjean, 1979; Marcoux et al., 1984; Moyroud et al., 1979; Serment, 1978). Po: Pyrrhotite; Sch: Scheelite; Gn: Galena; Sl: Sphalerite; Stbn: Stibnite; Btr: Berthierite. 105

Table 2. 2. Main data for the Sb districts in the Armorican Massif 106

Table 2. 3. Antimony deposits in the Iberian Massif. (Gumiel & Arribas, 1987)..... 113

Table 2. 4. Main minerals present in the paragenetic sequences of the Sb districts in the CIZ. (Gumiel, 1982; Gumiel & Arribas, 1987 and references therein)..... 117

Table 2. 5. Main data available for the most relevant Sb deposits in the CIZ..... 118

CHAPTER 3

Table 3. 1. Whole-rock geochemistry data for studied mafic samples from la Codosera syncline-Central Iberian Zone. 137

Table 3. 2. Whole-rock geochemistry data for studied mafic samples from Guadalmez and Almadén synclines-Central Iberian Zone.....	138
--	-----

Table 3. 3. Average electron microprobe analyses and corresponding structural formulas of apatite for the mafic samples dated in this study.	147
--	-----

CHAPTER 4

Table 4. 1. Whole-rock geochemistry for the studied sedimentary/metasedimentary rocks from the Codosera syncline. SGC: Schist Greywacke Complex; SFU: Sierra Fría Unit; GF: Gévora Formation.	189
---	-----

Table 4. 2. Whole-rock geochemistry for the studied sedimentary/metasedimentary rocks from the Codosera syncline. GF: Gévora Formation.	190
---	-----

Table 4. 3. EMPA of pyrite and sphalerite in samples SA2033A and SA2033C	196
---	-----

Table 4. 4. RSCM temperatures results obtained with Beyssac et al. (2002) and Lahfid et al. (2010). HT: High temperature; LT: Low temperature; SD: Standard Deviation; SGC: Schist Greywacke Complex; SFU: Sierra Fría Unit; GF: Gévora Formation.....	197
---	-----

CHAPTER 5

Table 5. 1. Critical elements for the mineral systems concept applied to the study of Sb mineralization in the CIZ. This table was created based on the critical elements table in the formation of gold deposits from McCuaig & Hronsky (2014).	227
--	-----

ANNEXES

MAFIC MAGMATISM

Supplementary material 1. Operating conditions for the LA-ICP-MS equipment used for the U-Pb dating of apatite in mafic rocks.

Laboratory & Sample Preparation	
Laboratory name	GeOHeLiS Analytical Platform, OSUR, Univ of Rennes , France
Sample type/mineral	Apatite
Sample preparation	Thin section and separated grain in epoxy pucks
Imaging	Cathodyne-OPEA cold cathode instrument (ISTO-BRGM facilities)
Laser ablation system	
Make, Model & type	ESI NWR193UC, Excimer
Ablation cell	ESI NWR TwoVol2
Laser wavelength	193 nm
Pulse width	< 5 ns
Fluence	6.5 J/cm ²
Repetition rate	5Hz
Spot size	30x40 µm or 25x50 µm or rond spot of 40 µm
Sampling mode / pattern	Single spot
Carrier gas	100% He, Ar make-up gas and N2 (3 ml/mn) combined using in-house smoothing device
Background collection	20 seconds
Ablation duration	60 seconds
Wash-out delay	15 seconds
Cell carrier gas flow (He)	0.75 l/min
ICP-MS Instrument	
Make, Model & type	Agilent 7700x, Q-ICP-MS
Sample introduction	Via conventional tubing
RF power	1350W
Sampler, skimmer cones	Ni
Extraction lenses	X type
Make-up gas flow (Ar)	0.85 l/min
Detection system	Single collector secondary electron multiplier
Data acquisition protocol	Time-resolved analysis
Scanning mode	Peak hopping, one point per peak
Detector mode	Pulse counting, dead time correction applied, and analog mode when signal intensity > ~ 10 ⁶ cps
Masses measured	²⁰⁴ (Hg + Pb), ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³² Th, ²³⁸ U + ⁴³ Ca (Ap)
Integration time per peak	10-30 ms
Sensitivity / Efficiency	21000 cps/ppm Pb (50µm, 10Hz)
Data Processing	
Gas blank	20 seconds on-peak
Calibration strategy	Madagascar apatite standard used as primary reference material, McClure and Durango standards used as secondary reference material (quality control)

Annexes

Common-Pb correction, composition and uncertainty	No common-Pb correction.
Reference Material info	Madagascar (Cochrane <i>et al.</i> , 2014) McClure (Schoene and Bowring, 2006) Durango (McDowell <i>et al.</i> , 2005)
Data processing package used	Iolite (Paton <i>et al.</i> , 2010), VizualAge_UcomPbine (Chew <i>et al.</i> , 2014) More information on the procedure in Pochon <i>et al.</i> (2016)
Quality control / Validation	McClure: First session: 528 ± 5 Ma (n=31, MSWD=0.5); second session: 509 ± 12 Ma (n=26, MSWD=3) Durango: First session: 32 ± 0.5 Ma (n=33, MSWD=1.1); second session: 30.6 ± 0.6 Ma (n=16, MSWD=1.1)

Supplementary material 2. Representative LA-ICP-MS U-Pb apatite data for studied mafic samples.

Sample	U (ppm)	Pb (ppm)	$^{238}\text{U}/^{206}\text{Pb}$	Error (2se%)	$^{207}\text{Pb}/^{206}\text{Pb}$	Error (2se%)
SA2014A						
SA2014A-1	3.2	2.6	8.3	9.7	0.5	11.8
SA2014A-2	1.5	2.1	4.9	8.5	0.7	10.3
SA2014A-3	2.3	2.2	7.0	11.6	0.5	10.7
SA2014A-4	2.1	0.9	12.0	10.0	0.3	14.8
SA2014A-5	1.6	1.0	14.3	21.2	0.3	27.6
SA2014A-6	1.2	1.4	6.9	9.9	0.5	11.1
SA2014A-7	1.3	0.9	12.6	10.3	0.3	22.4
SA2014A-8	1.7	2.1	9.9	12.3	0.5	19.8
SA2014A-9	0.6	0.6	6.9	11.9	0.5	15.4
SA2014A-10	1.2	1.5	5.5	7.8	0.6	9.5
SA2014A-11	1.6	0.9	13.4	9.5	0.3	15.8
SA2014A-12	1.3	0.8	11.2	12.3	0.3	15.0
SA2014A-13	1.4	0.7	14.1	9.6	0.2	18.4
SA2014A-14	1.2	0.7	13.4	15.5	0.2	19.3
SA2014A-15	0.6	0.4	11.2	20.7	0.3	32.3
SA2014A-16	1.1	0.5	12.3	8.4	0.3	16.3
SA2014A-17	1.2	0.4	14.7	14.0	0.2	28.8
SA2014A-18	0.3	0.2	7.7	21.3	0.3	40.0
SA2014A-19	0.8	0.4	9.9	11.0	0.3	20.6
SA2014A-20	0.8	0.4	12.4	18.8	0.4	25.6
SA2014A-21	1.5	0.7	14.1	8.5	0.2	19.4
SA2014A-22	1.5	0.9	12.4	10.6	0.2	19.2
SA2014A-23	1.4	0.7	13.1	11.7	0.2	25.6
SA2014A-24	1.2	0.8	11.5	11.6	0.3	19.6
SA2014A-25	0.9	0.4	10.9	10.1	0.3	24.6
SA2014A-26	1.6	0.6	13.8	11.5	0.2	20.3
SA2014A-27	1.6	0.7	14.9	8.6	0.2	20.3
SA2014A-28	1.2	0.5	14.5	12.3	0.3	23.2
SA2014A-29	1.8	0.9	13.0	9.3	0.2	15.6
SA2014A-30	2.2	1.0	14.0	9.6	0.3	24.0

Annexes

SA2014A-31	0.7	0.4	12.3	14.8	0.3	28.5
SA2014A-32	1.2	0.7	12.7	22.2	0.3	35.6
SA2014A-33	1.7	1.0	14.1	11.7	0.2	21.5
SA2022C	U (ppm)	Pb (ppm)	²³⁸U/²⁰⁶Pb	Error (2se%)	²⁰⁷Pb/²⁰⁶Pb	Error (2se%)
SA2022C-1	1.3	1.2	6.9	4.4	0.5	4.7
SA2022C-2	1.3	0.6	10.1	4.1	0.4	5.4
SA2022C-3	1.3	0.6	9.9	4.2	0.4	5.0
SA2022C-4	1.3	0.7	9.3	4.1	0.4	5.2
SA2022C-5	1.2	0.6	9.5	4.3	0.4	5.1
SA2022C-6	1.8	1.4	7.0	4.2	0.6	4.2
SA2022C-7	1.8	1.6	6.2	4.4	0.6	4.4
SA2022C-8	1.7	1.2	7.9	3.9	0.5	4.1
SA2022C-9	1.8	1.4	7.9	3.9	0.5	3.5
SA2022C-10	1.4	1.3	6.5	4.5	0.6	4.4
SA2022C-11	1.5	1.5	6.4	4.7	0.6	4.6
SA2022C-12	1.5	1.4	7.0	4.0	0.5	4.3
SA2022C-13	1.4	1.7	5.0	4.3	0.6	4.2
SA2022C-14	1.3	1.0	7.5	4.0	0.5	4.3
SA2022C-15	1.4	1.2	6.8	4.2	0.5	4.0
SA2022C-16	1.7	1.1	8.4	3.9	0.5	4.4
SA2022C-17	1.4	1.0	8.3	3.9	0.5	4.0
SA2022C-18	1.7	1.0	8.9	4.5	0.4	6.6
SA2022C-19	1.1	0.6	9.1	5.0	0.5	7.2
SA2022C-20	1.6	1.5	6.3	3.9	0.6	3.4
SA2022C-21	1.4	1.0	7.6	4.7	0.5	5.5
SA2022C-22	1.5	0.9	8.2	4.1	0.5	4.1
SA2022C-23	1.4	1.2	6.3	4.8	0.6	4.2
SA2022C-24	3.7	2.2	10.4	4.2	0.4	4.5
SA2022C-25	1.3	0.9	7.8	4.2	0.5	4.4
SA2022C-26	1.3	1.3	6.1	4.0	0.6	3.8
SA2022C-27	1.4	1.2	6.9	4.2	0.6	3.8
SA2022C-28	1.5	1.3	7.0	4.0	0.6	3.8
SA2022C-29	1.7	1.3	7.3	4.3	0.5	3.4
SA2022C-30	1.6	1.5	6.7	4.4	0.6	5.4
SA2022C-31	1.5	1.2	6.9	4.2	0.5	4.1
SA2022C-32	1.4	1.2	7.0	4.4	0.6	5.3
SA2022C-33	1.4	1.1	7.2	4.6	0.5	4.6
SA2022C-34	1.2	0.7	9.5	4.4	0.5	5.4
SA2022C-35	1.3	0.7	9.6	4.6	0.5	5.3
SA2026	U (ppm)	Pb (ppm)	²³⁸U/²⁰⁶Pb	Error (2se%)	²⁰⁷Pb/²⁰⁶Pb	Error (2se%)
SA2026-1	2.2	1.4	9.3	5.3	0.4	4.8
SA2026-2	1.9	1.0	10.6	5.2	0.4	6.5
SA2026-3	2.0	1.3	8.8	6.5	0.4	6.9
SA2026-4	1.7	1.0	9.7	5.2	0.4	5.7
SA2026-5	2.0	1.3	9.1	8.0	0.5	9.3
SA2026-6	1.9	1.2	8.4	6.1	0.4	7.9
SA2026-7	1.7	1.1	8.3	7.4	0.5	9.8

Annexes

SA2026-8	2.6	1.5	9.5	6.1	0.4	7.2
SA2026-9	2.3	1.5	8.8	6.4	0.4	6.6
SA2026-10	1.6	0.8	11.1	7.4	0.4	10.8
SA2026-11	1.6	0.9	10.8	6.6	0.4	8.8
SA2026-12	1.7	1.7	6.6	7.3	0.6	7.2
SA2026-13	1.5	1.1	8.1	10.5	0.5	12.9
SA2026-14	1.8	1.0	10.1	5.5	0.4	6.2
SA2026-15	1.6	1.1	8.8	5.3	0.5	5.3
SA2026-16	1.8	1.0	9.7	5.2	0.4	5.8
SA2026-17	1.9	1.3	8.9	5.2	0.5	5.4
SA2026-18	1.6	1.3	6.5	10.6	0.5	10.1
SA2026-19	2.0	1.1	8.5	7.4	0.5	7.3
SA2026-20	1.6	1.1	8.2	6.4	0.5	7.1
SA2026-21	1.7	1.3	7.5	5.9	0.5	5.8
SA2026-22	3.8	2.0	10.0	5.3	0.4	6.2
SA2026-23	3.8	1.8	10.2	5.9	0.4	6.6
SA2026-24	2.8	1.6	9.7	5.9	0.4	7.6
SA2026-25	2.2	1.3	8.4	6.1	0.4	9.4
SA2026-26	2.2	4.0	3.6	5.7	0.7	4.7
SA2026-27	3.5	2.2	9.6	5.9	0.4	7.2
SA2026-28	3.5	2.3	10.4	5.8	0.4	7.0
SA2026-29	3.3	1.7	11.1	6.0	0.4	6.3
SA2026-30	3.9	2.1	11.0	7.2	0.4	7.0
SA2026-31	2.6	1.4	10.3	5.7	0.4	6.4
SA2026-32	2.3	1.4	9.5	6.8	0.4	7.8
SA2026-33	2.1	1.3	9.0	7.5	0.5	8.1
SA2026-34	1.8	1.0	10.7	5.1	0.4	5.9
SA2026-35	2.2	1.6	9.0	5.7	0.5	6.1
SA2026-36	1.8	1.4	8.3	5.3	0.5	5.9
SA2026-37	1.8	1.1	10.1	5.1	0.4	6.8
SA2026-38	2.6	1.6	9.3	5.3	0.5	5.9
SA2026-39	2.3	1.5	8.5	4.8	0.5	5.2
SA2026-40	3.4	1.9	9.8	6.9	0.5	9.7
SA2026-41	3.0	1.6	10.7	4.6	0.4	5.5
SA2026-42	2.1	1.5	8.5	5.6	0.5	6.0
SA2026-43	2.7	1.7	9.8	4.4	0.4	4.5
SA2026-44	3.1	1.9	9.7	4.8	0.4	4.8
SA2026-45	1.9	1.1	9.5	5.7	0.4	7.2
SA2026-46	1.8	1.2	9.3	5.1	0.4	5.4
SA2026-47	1.7	1.0	9.6	4.8	0.5	5.5
SA2026-48	2.3	1.4	9.8	4.8	0.4	6.3
SA2026-49	2.2	1.5	8.5	4.9	0.5	4.4
SA2026-50	2.1	1.9	6.9	5.9	0.5	4.9
SA2026-51	2.2	1.2	10.0	6.7	0.5	8.5
SA2026-52	1.9	1.0	10.0	6.6	0.4	8.0
SA2026-53	1.7	1.2	8.3	7.1	0.5	8.7
SA2026-54	2.6	1.4	9.9	5.4	0.4	5.8
SA2026-55	2.4	1.9	9.8	5.6	0.4	6.5

Annexes

SA2026-56	1.9	1.0	10.1	5.2	0.4	5.8
SA2026-57	2.1	1.1	10.5	5.1	0.4	5.5
AL2072	U (ppm)	Pb (ppm)	²³⁸U/²⁰⁶Pb	Error (2se%)	²⁰⁷Pb/²⁰⁶Pb	Error (2se%)
AL2072-1	4.4	2.2	9.2	10.2	0.4	7.2
AL2072-2	5.7	3.4	10.7	8.9	0.3	6.1
AL2072-3	3.2	2.1	9.8	9.0	0.4	8.5
AL2072-4	5.8	3.4	11.1	9.0	0.3	6.7
AL2072-5	6.8	4.0	11.9	9.2	0.3	8.7
AL2072-6	5.5	4.4	8.8	9.5	0.4	8.0
AL2072-7	3.4	3.1	8.2	9.5	0.4	7.4
AL2072-8	1.1	1.2	7.0	17.1	0.4	28.6
AL2072-9	1.3	1.1	7.8	12.0	0.5	13.3
AL2072-10	1.4	2.1	6.7	9.7	0.5	8.2
AL2072-11	2.5	2.4	10.1	11.4	0.4	13.9
AL2072-12	1.5	23.4	0.5	16.7	0.8	4.7
AL2072-13	5.4	3.4	9.6	9.4	0.3	7.0
AL2072-14	3.0	2.4	8.4	10.1	0.4	8.4
AL2072-15	2.4	1.7	8.3	8.8	0.4	6.0
AL2072-16	2.6	2.0	9.1	9.7	0.4	11.1
AL2072-17	2.6	2.2	9.4	9.1	0.4	7.8
AL2072-18	0.3	4.5	0.4	13.2	0.8	8.2
AL2072-19	1.0	1.7	4.8	10.6	0.6	9.0
AL2072-20	4.4	3.3	8.1	9.8	0.4	7.9
AL2072-21	0.2	0.4	3.2	16.5	0.7	22.9
AL2073	U (ppm)	Pb (ppm)	²³⁸U/²⁰⁶Pb	Error (2se%)	²⁰⁷Pb/²⁰⁶Pb	Error (2se%)
AL2073-1	4.4	1.9	13.1	5.5	0.2	8.3
AL2073-2	2.3	1.3	10.4	6.2	0.4	6.5
AL2073-3	2.9	1.8	10.0	6.0	0.4	5.9
AL2073-4	3.8	3.6	10.8	5.4	0.4	6.3
AL2073-5	1.2	1.1	6.7	9.7	0.5	15.0
AL2073-6	1.2	1.4	5.5	7.0	0.6	7.3
AL2073-7	3.0	2.1	8.3	6.8	0.4	6.7
AL2073-8	2.0	1.5	8.6	6.1	0.4	6.7
AL2073-9	2.0	1.4	8.5	6.5	0.4	7.7
AL2073-10	2.3	1.3	9.9	7.5	0.3	9.1
AL2073-11	2.2	2.8	5.2	5.9	0.6	6.6
AL2073-12	0.7	6.9	1.0	18.4	0.8	9.2
AL2073-13	2.5	1.4	10.9	5.7	0.4	6.7
AL2073-14	3.2	1.6	11.5	5.6	0.3	7.2
AL2073-15	2.7	1.7	9.5	7.5	0.4	8.2
AL2073-16	2.6	2.0	8.4	5.3	0.5	5.6
AL2073-17	3.7	2.1	11.1	4.1	0.3	6.4
AL2073-18	2.7	1.5	10.9	4.0	0.3	4.7
AL2073-19	2.5	1.7	9.8	4.2	0.4	4.6
AL2073-20	3.1	2.6	7.6	6.1	0.4	5.8
AL2073-21	2.5	2.3	8.3	4.4	0.4	4.6
AL2073-22	3.1	2.3	9.1	4.3	0.4	4.9

Annexes

AL2073-23	2.3	1.7	8.4	7.0	0.4	8.2
AL2073-24	2.8	2.4	9.0	3.7	0.4	3.7
AL2073-25	2.9	2.4	9.3	3.9	0.4	3.8
AL2073-26	2.6	1.9	8.8	4.5	0.4	4.8
AL2073-27	3.8	3.4	9.9	4.2	0.4	4.6
AL2073-28	3.1	1.9	10.3	4.1	0.4	4.1
AL2073-29	3.3	2.4	9.6	5.3	0.4	7.9
AL2073-30	2.8	1.6	10.4	4.9	0.3	6.9
AL2073-31	1.9	1.4	8.2	6.3	0.5	8.1
AL2073-32	3.0	1.7	11.1	4.2	0.4	5.0
AL2073-33	4.8	4.6	8.1	4.5	0.5	5.5
AL2073-34	2.0	1.1	10.6	4.7	0.3	6.2
AL2075	U (ppm)	Pb (ppm)	$^{238}\text{U}/^{206}\text{Pb}$	Error (2se%)	$^{207}\text{Pb}/^{206}\text{Pb}$	Error (2se%)
AL2075-1	4.1	3.3	10.3	6.7	0.3	12.6
AL2075-2	2.4	3.0	5.5	5.7	0.5	6.0
AL2075-3	2.0	2.2	6.7	5.0	0.5	6.4
AL2075-4	3.9	4.3	7.6	5.3	0.4	5.4
AL2075-5	2.5	3.3	5.0	5.0	0.6	4.3
AL2075-6	2.9	3.9	5.2	4.4	0.6	4.4
AL2075-7	2.3	3.8	5.1	4.8	0.6	5.1
AL2075-8	2.1	2.6	4.9	5.0	0.5	6.2
AL2075-9	12.3	15.0	9.9	3.1	0.3	3.2
AL2075-10	2.1	11.8	1.2	4.4	0.8	2.0
AL2075-11	0.2	0.9	1.2	12.3	0.8	11.0
AL2075-12	2.2	16.9	0.9	4.8	0.8	1.8
AL2075-13	2.2	3.0	5.2	8.2	0.6	8.7
AL2075-14	3.2	2.8	9.5	7.4	0.4	12.5
AL2075-15	1.1	2.7	2.8	7.4	0.7	8.2
AL2075-16	1.1	1.7	4.5	7.1	0.6	7.1
AL2075-17	1.3	2.1	3.8	7.1	0.6	5.6
AL2075-18	0.2	1.9	0.7	9.2	0.8	10.6
AL2075-19	1.0	1.9	3.9	5.1	0.7	5.0
AL2075-20	2.5	2.7	6.2	4.8	0.5	4.6
AL2075-21	3.3	2.6	8.7	6.2	0.4	8.5
AL2075-22	5.4	5.9	9.1	3.9	0.4	5.8
AL2075-23	1.1	2.6	3.0	4.4	0.7	4.1
AL2075-24	4.8	5.3	6.7	4.6	0.5	4.9
AL2075-25	8.5	8.7	9.1	3.7	0.3	4.4
AL2075-26	1.3	2.5	3.2	7.9	0.7	7.5
AL2075-27	0.4	2.2	1.2	8.3	0.8	7.8
AL2075-28	1.5	3.6	3.2	6.0	0.7	6.0
AL2075-29	1.2	2.0	4.5	6.9	0.7	9.8
AL2075-30	1.1	3.8	2.0	5.7	0.7	4.5
AL2075-31	0.8	1.5	3.2	8.3	0.6	10.1
AL2075-32	0.7	3.1	1.6	7.0	0.8	7.8
AL2075-33	5.7	5.4	8.5	6.7	0.4	6.8
AL2076	U (ppm)	Pb (ppm)	$^{238}\text{U}/^{206}\text{Pb}$	Error (2se%)	$^{207}\text{Pb}/^{206}\text{Pb}$	Error (2se%)

Annexes

AL2076-1	4.7	3.6	8.0	4.9	0.5	4.7
AL2076-2	1.7	3.6	3.3	5.5	0.7	4.3
AL2076-3	0.8	1.8	3.0	8.8	0.7	7.7
AL2076-4	1.1	1.8	3.5	10.2	0.7	9.6
AL2076-5	2.3	1.7	7.4	6.0	0.5	8.5
AL2076-6	2.7	2.6	6.2	8.9	0.5	9.6
AL2076-7	2.9	2.6	6.8	9.3	0.5	14.1
AL2076-8	3.9	7.0	3.5	5.9	0.7	3.7
AL2076-9	2.8	2.4	7.3	5.6	0.5	6.2
AL2076-10	2.0	1.5	9.0	4.1	0.4	4.9
AL2076-11	4.6	3.1	8.8	5.6	0.5	7.5
AL2076-12	1.7	1.8	5.5	7.1	0.6	9.7
AL2076-13	8.4	5.0	9.9	4.6	0.4	5.0
AL2076-14	6.9	2.4	12.0	7.7	0.3	10.9
AL2076-15	4.5	1.8	12.6	5.6	0.3	10.3
AL2076-16	14.3	3.9	13.2	5.4	0.3	8.1
AL2076-17	4.6	5.0	5.5	14.4	0.6	11.3
AL2076-18	1.8	2.3	4.9	5.3	0.6	4.3
AL2076-19	1.8	1.9	6.3	4.7	0.6	4.4
AL2076-20	3.2	2.4	9.8	4.1	0.4	5.5
AL2076-21	5.3	1.6	12.5	5.4	0.3	6.9
AL2076-22	2.7	2.7	7.2	6.7	0.5	8.9
AL2076-23	1.5	1.6	6.2	5.1	0.6	5.4
AL2076-24	3.9	3.7	6.6	4.7	0.5	4.2
AL2076-25	2.5	2.2	7.7	4.2	0.5	4.5
AL2076-26	1.8	0.9	10.2	6.4	0.3	9.9
AL2076-27	3.6	3.1	7.3	7.9	0.5	11.3
AL2076-28	2.4	2.3	6.3	4.6	0.5	4.0
AL2076-29	2.3	2.1	7.5	4.2	0.5	4.5
AL2076-30	1.8	1.5	7.5	5.2	0.5	6.3
AL2076-31	2.3	2.2	6.5	5.4	0.5	7.7
AL2076-32	2.1	1.5	8.0	5.9	0.4	9.8
AL2076-33	2.0	2.8	5.9	4.8	0.6	4.8
AL2076-34	1.3	1.9	4.7	6.7	0.6	8.2

Supplementary material 3. Electron microprobe analyses and corresponding structural formulas of plagioclase
for the mafic samples SA2022C.

Plagioclase	SiO2	Al2O3	TiO2	Na2O	CaO	K2O	MgO	FeO	MnO	Total sonde
	68.08	19.48	0.00	11.05	0.47	0.16	0.00	0.00	0.00	99.25
	65.50	16.97	0.00	0.43	0.00	16.14	0.00	1.05	0.00	100.09
SA2022CM1.	64.14	21.41	0.00	10.22	3.13	0.00	0.00	0.00	0.00	98.89

Annexes

SA2022CM1.	65.79	21.41	0.00	9.70	2.63	0.00	0.00	0.00	0.00	99.54
SA2022CM1.	64.68	22.55	0.00	9.20	3.65	0.00	0.00	0.00	0.00	100.09
SA2022CM1.	65.01	21.86	0.00	9.44	2.94	0.24	0.00	0.00	0.00	99.49
SA2022CM1.	63.78	22.63	0.00	8.82	3.63	0.21	0.00	0.00	0.00	99.07
SA2022CM1.	65.09	21.80	0.00	9.43	3.17	0.00	0.00	0.23	0.00	99.72
SA2022CM1.	65.91	21.45	0.00	9.70	2.53	0.00	0.00	0.00	0.00	99.59
SA2022CM1.	60.87	24.29	0.00	7.63	6.32	0.13	0.00	0.28	0.00	99.52
SA2022CM1.	63.85	22.03	0.00	8.28	3.23	0.00	0.00	0.00	0.00	97.48
SA2022CM1.	65.01	22.41	0.00	9.34	3.66	0.00	0.00	0.36	0.00	100.80
SA2022CM1.	63.82	17.25	0.00	8.18	3.60	0.00	2.35	2.61	0.00	97.82
SA2022CM1.	58.55	26.37	0.00	6.54	8.37	0.41	0.06	0.37	0.00	100.67
SA2022CM1.	66.66	20.69	0.00	10.38	1.46	0.00	0.51	0.48	0.00	100.18
SA2022CM1.	67.55	21.16	0.00	10.07	1.85	0.00	0.00	0.00	0.00	100.63
SA2022CM1.	67.46	21.66	0.00	10.25	2.18	0.00	0.00	0.19	0.00	101.74
SA2022CM1.	65.54	20.91	0.00	8.91	1.98	0.00	0.00	0.24	0.00	97.95
SA2022CM1.	57.54	28.63	0.00	5.00	1.47	5.13	0.20	0.90	0.00	98.88
SA2022CM1.	63.94	21.83	0.00	9.04	3.27	0.00	0.00	0.00	0.00	98.12
SA2022CM1.	62.82	25.17	0.00	7.42	1.23	2.99	0.56	0.63	0.00	100.83
SA2022CM1.	67.25	20.85	0.00	10.17	1.54	0.00	0.00	0.00	0.00	99.81
SA2022CM1.	66.62	20.96	0.00	10.43	2.14	0.11	0.00	0.00	0.00	100.27
SA2022CM1.	67.56	20.58	0.00	9.98	1.71	0.00	0.00	0.00	0.00	99.83
SA2022CM1.	66.17	21.41	0.00	9.65	2.93	0.00	0.00	0.00	0.00	100.16
SA2022CM1.	66.53	21.64	0.00	9.98	2.27	0.00	0.00	0.26	0.00	100.68
SA2022CM1.	67.51	21.81	0.00	10.28	1.86	0.00	0.00	0.26	0.00	101.72
SA2022CM1.	66.98	21.80	0.00	10.09	2.16	0.00	0.00	0.00	0.00	101.02
SA2022CM1.	66.49	21.39	0.00	10.17	2.16	0.00	0.00	0.00	0.00	100.21
SA2022CM1.	67.67	21.31	0.00	10.14	1.77	0.00	0.00	0.00	0.00	100.89
SA2022CM1.	58.28	26.31	0.00	6.33	8.45	0.36	0.00	0.62	0.00	100.35
SA2022CM1.	65.22	22.04	0.00	9.24	2.95	0.46	0.06	0.43	0.00	100.40
SA2022CM1.	64.79	23.50	0.00	9.09	3.87	0.13	0.00	0.22	0.00	101.60
SA2022CM1.	63.09	25.64	0.00	8.05	1.51	2.49	0.12	0.27	0.00	101.17
SA2022CM1.	67.60	21.49	0.00	10.16	1.97	0.00	0.00	0.00	0.00	101.22
SA2022CM1.	66.83	21.42	0.00	10.07	2.18	0.00	0.00	0.00	0.00	100.50
SA2022CM1.	65.93	22.27	0.00	9.22	2.86	0.14	0.00	0.32	0.00	100.74
SA2022CM1.	65.48	20.22	0.00	10.71	1.20	0.00	0.00	0.27	0.13	98.01
SA2022CM1.	57.41	26.82	0.00	6.14	9.20	0.17	0.00	0.88	0.00	100.61
SA2022CM1.	65.63	21.54	0.00	9.43	1.66	0.76	0.00	0.00	0.00	99.03
SA2022CM1.	65.14	19.14	0.00	9.15	2.77	0.19	1.17	2.24	0.00	99.80
SA2022CM1.	64.32	22.24	0.00	9.34	3.26	0.00	0.00	0.47	0.00	99.63

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Ca	K	Mg	Fe	Mn	Total
	2.99	1.01	0.00	4.00	0.94	0.02	0.01	0.00	0.00	0.00	0.97
	3.04	0.93	0.00	3.96	0.04	0.00	0.95	0.00	0.04	0.00	1.03
SA2022CM1.	2.86	1.13	0.00	3.99	0.88	0.15	0.00	0.00	0.00	0.00	1.03
SA2022CM1.	2.90	1.11	0.00	4.01	0.83	0.12	0.00	0.00	0.00	0.00	0.95
SA2022CM1.	2.84	1.17	0.00	4.01	0.78	0.17	0.00	0.00	0.00	0.00	0.96
SA2022CM1.	2.87	1.14	0.00	4.01	0.81	0.14	0.01	0.00	0.00	0.00	0.96
SA2022CM1.	2.83	1.18	0.00	4.02	0.76	0.17	0.01	0.00	0.00	0.00	0.94

Annexes

SA2022CM1.	2.87	1.13	0.00	4.00	0.81	0.15	0.00	0.00	0.01	0.00	0.96
SA2022CM1.	2.90	1.11	0.00	4.01	0.83	0.12	0.00	0.00	0.00	0.00	0.95
SA2022CM1.	2.72	1.28	0.00	4.00	0.66	0.30	0.01	0.00	0.01	0.00	0.98
SA2022CM1.	2.87	1.17	0.00	4.03	0.72	0.16	0.00	0.00	0.00	0.00	0.88
SA2022CM1.	2.84	1.16	0.00	4.00	0.79	0.17	0.00	0.00	0.01	0.00	0.98
SA2022CM1.	2.91	0.93	0.00	3.83	0.72	0.18	0.00	0.16	0.10	0.00	1.16
SA2022CM1.	2.61	1.38	0.00	3.99	0.56	0.40	0.02	0.00	0.01	0.00	1.01
SA2022CM1.	2.92	1.07	0.00	3.99	0.88	0.07	0.00	0.03	0.02	0.00	1.00
SA2022CM1.	2.93	1.08	0.00	4.02	0.85	0.09	0.00	0.00	0.00	0.00	0.93
SA2022CM1.	2.91	1.10	0.00	4.01	0.86	0.10	0.00	0.00	0.01	0.00	0.96
SA2022CM1.	2.92	1.10	0.00	4.03	0.77	0.09	0.00	0.00	0.01	0.00	0.87
SA2022CM1.	2.61	1.53	0.00	4.14	0.44	0.07	0.30	0.01	0.03	0.00	0.86
SA2022CM1.	2.86	1.15	0.00	4.01	0.78	0.16	0.00	0.00	0.00	0.00	0.94
SA2022CM1.	2.76	1.30	0.00	4.07	0.63	0.06	0.17	0.04	0.02	0.00	0.92
SA2022CM1.	2.94	1.08	0.00	4.02	0.86	0.07	0.00	0.00	0.00	0.00	0.93
SA2022CM1.	2.92	1.08	0.00	4.00	0.88	0.10	0.01	0.00	0.00	0.00	0.99
SA2022CM1.	2.95	1.06	0.00	4.01	0.85	0.08	0.00	0.00	0.00	0.00	0.93
SA2022CM1.	2.90	1.10	0.00	4.00	0.82	0.14	0.00	0.00	0.00	0.00	0.96
SA2022CM1.	2.90	1.11	0.00	4.01	0.84	0.11	0.00	0.00	0.01	0.00	0.96
SA2022CM1.	2.91	1.11	0.00	4.01	0.86	0.09	0.00	0.00	0.01	0.00	0.95
SA2022CM1.	2.90	1.11	0.00	4.02	0.85	0.10	0.00	0.00	0.00	0.00	0.95
SA2022CM1.	2.91	1.10	0.00	4.01	0.86	0.10	0.00	0.00	0.00	0.00	0.96
SA2022CM1.	2.93	1.09	0.00	4.02	0.85	0.08	0.00	0.00	0.00	0.00	0.93
SA2022CM1.	2.60	1.39	0.00	3.99	0.55	0.40	0.02	0.00	0.02	0.00	1.00
SA2022CM1.	2.86	1.14	0.00	4.00	0.79	0.14	0.03	0.00	0.02	0.00	0.97
SA2022CM1.	2.81	1.20	0.00	4.01	0.76	0.18	0.01	0.00	0.01	0.00	0.96
SA2022CM1.	2.76	1.32	0.00	4.08	0.68	0.07	0.14	0.01	0.01	0.00	0.91
SA2022CM1.	2.92	1.09	0.00	4.02	0.85	0.09	0.00	0.00	0.00	0.00	0.94
SA2022CM1.	2.91	1.10	0.00	4.01	0.85	0.10	0.00	0.00	0.00	0.00	0.95
SA2022CM1.	2.87	1.14	0.00	4.02	0.78	0.13	0.01	0.00	0.01	0.00	0.93
SA2022CM1.	2.93	1.07	0.00	4.00	0.93	0.06	0.00	0.00	0.01	0.00	1.00
SA2022CM1.	2.57	1.41	0.00	3.98	0.53	0.44	0.01	0.00	0.03	0.00	1.02
SA2022CM1.	2.90	1.12	0.00	4.03	0.81	0.08	0.04	0.00	0.00	0.00	0.93
SA2022CM1.	2.90	1.00	0.00	3.90	0.79	0.13	0.01	0.08	0.08	0.00	1.09
SA2022CM1.	2.84	1.16	0.00	4.00	0.80	0.15	0.00	0.00	0.02	0.00	0.97

Supplementary material 4. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples SA2026.

Plagioclase	Na2O	MgO	Al2O3	SiO2	K2O	CaO	TiO2	MnO	FeO	Total
SA2026 Pg	11.58	0.00	19.72	70.04	0.00	0.19	0.00	0.00	0.00	101.63
SA2026 Pg	11.69	0.00	20.01	69.51	0.00	0.32	0.00	0.00	0.00	101.61
SA2026 Pg	11.60	0.00	19.50	70.16	0.00	0.16	0.00	0.00	0.00	101.57
SA2026 Pg	11.40	0.00	19.67	69.65	0.10	0.44	0.00	0.00	0.00	101.34
SA2026 Pg	11.48	0.00	19.84	69.52	0.00	0.36	0.00	0.00	0.00	101.33
SA2026 Pg	11.51	0.00	19.55	69.80	0.12	0.26	0.00	0.00	0.00	101.33

Annexes

SA2026 Pg	11.50	0.00	19.61	69.81	0.15	0.24	0.00	0.00	0.00	101.31
SA2026 Pg	11.56	0.00	19.67	69.62	0.00	0.14	0.00	0.00	0.00	101.27
SA2026 Pg	11.32	0.00	20.00	69.00	0.31	0.42	0.00	0.00	0.00	101.22
SA2026 Pg	11.78	0.00	19.52	69.59	0.00	0.21	0.00	0.00	0.00	101.20
SA2026 Pg	11.56	0.00	19.44	69.59	0.00	0.26	0.00	0.00	0.00	101.14
SA2026 Pg	11.18	0.00	19.95	69.27	0.00	0.37	0.00	0.00	0.00	100.87
SA2026 Pg	11.44	0.00	19.77	69.29	0.00	0.22	0.00	0.00	0.00	100.87
SA2026 Pg	11.38	0.00	19.64	69.13	0.23	0.25	0.00	0.00	0.21	100.85
SA2026 Pg	11.52	0.00	19.56	69.15	0.00	0.25	0.00	0.00	0.00	100.71
SA2026 Pg	10.43	0.00	19.84	69.47	0.24	0.19	0.00	0.00	0.24	100.43
SA2026 Pg	10.45	0.00	19.77	68.93	0.20	0.51	0.00	0.00	0.00	100.10
SA2026 Pg	10.63	0.24	19.12	69.42	0.00	0.34	0.00	0.00	0.00	100.04
SA2026 Pg	11.56	0.00	19.87	68.31	0.00	0.16	0.00	0.00	0.00	100.02
SA2026 Pg	10.77	0.00	19.33	69.50	0.14	0.18	0.00	0.00	0.00	99.99
SA2026 Pg	9.98	0.00	19.39	70.07	0.00	0.29	0.00	0.00	0.00	99.90
SA2026 Pg	10.72	1.13	19.58	66.71	0.00	0.32	0.00	0.00	1.35	99.88
SA2026 Pg	11.00	0.00	19.56	68.85	0.00	0.25	0.00	0.00	0.00	99.85
SA2026 Pg	9.77	0.00	19.56	69.91	0.00	0.16	0.00	0.00	0.00	99.75
SA2026 Pg	10.51	0.00	19.31	69.52	0.00	0.11	0.00	0.00	0.00	99.70
SA2026 Pg	9.69	0.00	19.41	70.05	0.00	0.29	0.00	0.00	0.00	99.63
SA2026 Pg	11.08	0.00	19.25	68.48	0.00	0.37	0.00	0.00	0.00	99.55
SA2026 Pg	10.51	0.00	19.51	69.13	0.00	0.29	0.00	0.00	0.00	99.54
SA2026 Pg	10.65	0.00	19.29	69.10	0.00	0.29	0.00	0.00	0.00	99.50
SA2026 Pg	9.79	0.00	19.41	69.78	0.00	0.29	0.00	0.00	0.00	99.47
SA2026 Pg	10.51	1.04	19.04	67.43	0.32	0.36	0.00	0.00	0.70	99.47
SA2026 Pg	9.68	0.00	19.34	69.83	0.00	0.35	0.00	0.00	0.00	99.43
SA2026 Pg	8.86	0.32	20.31	68.09	0.98	0.32	0.00	0.00	0.44	99.41
SA2026 Pg	10.03	0.00	19.26	69.57	0.00	0.31	0.00	0.00	0.00	99.25
SA2026 Pg	9.56	0.00	19.30	69.88	0.00	0.16	0.00	0.00	0.00	98.98
SA2026 Pg	8.43	0.59	19.51	68.18	0.82	0.36	0.00	0.00	0.76	98.72
SA2026 Pg	9.53	0.00	19.35	68.58	0.38	0.31	0.00	0.00	0.00	98.22
SA2026 Pg	8.72	0.00	19.27	69.71	0.00	0.20	0.00	0.00	0.00	98.12

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Ca	K	Mg	Fe	Mn	Total
SA2026 Pg	3.01	1.00	0.00	4.00	0.48	0.01	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	2.99	1.01	0.00	4.00	0.49	0.01	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	3.01	0.99	0.00	4.00	0.48	0.01	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	3.00	1.00	0.00	4.00	0.48	0.02	0.01	0.00	0.00	0.00	0.50
SA2026 Pg	3.00	1.01	0.00	4.00	0.48	0.02	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	3.01	0.99	0.00	4.00	0.48	0.01	0.01	0.00	0.00	0.00	0.50
SA2026 Pg	3.01	1.00	0.00	4.00	0.48	0.01	0.01	0.00	0.00	0.00	0.50
SA2026 Pg	3.00	1.00	0.00	4.00	0.48	0.01	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	2.98	1.02	0.00	4.00	0.47	0.02	0.02	0.00	0.00	0.00	0.51
SA2026 Pg	3.00	0.99	0.00	4.00	0.49	0.01	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	3.01	0.99	0.00	4.00	0.48	0.01	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	2.99	1.02	0.00	4.01	0.47	0.02	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	3.00	1.01	0.00	4.01	0.48	0.01	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	3.00	1.00	0.00	4.00	0.48	0.01	0.01	0.00	0.01	0.00	0.51

Annexes

SA2026 Pg	3.00	1.00	0.00	4.00	0.48	0.01	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	3.01	1.01	0.00	4.02	0.44	0.01	0.01	0.00	0.01	0.00	0.47
SA2026 Pg	3.00	1.02	0.00	4.02	0.44	0.02	0.01	0.00	0.00	0.00	0.48
SA2026 Pg	3.02	0.98	0.00	4.01	0.45	0.02	0.00	0.02	0.00	0.00	0.48
SA2026 Pg	2.98	1.02	0.00	4.01	0.49	0.01	0.00	0.00	0.00	0.00	0.50
SA2026 Pg	3.02	0.99	0.00	4.01	0.45	0.01	0.01	0.00	0.00	0.00	0.47
SA2026 Pg	3.04	0.99	0.00	4.03	0.42	0.01	0.00	0.00	0.00	0.00	0.43
SA2026 Pg	2.94	1.02	0.00	3.96	0.46	0.02	0.00	0.07	0.05	0.00	0.60
SA2026 Pg	3.01	1.01	0.00	4.01	0.47	0.01	0.00	0.00	0.00	0.00	0.48
SA2026 Pg	3.04	1.00	0.00	4.04	0.41	0.01	0.00	0.00	0.00	0.00	0.42
SA2026 Pg	3.03	0.99	0.00	4.02	0.44	0.01	0.00	0.00	0.00	0.00	0.45
SA2026 Pg	3.04	0.99	0.00	4.04	0.41	0.01	0.00	0.00	0.00	0.00	0.42
SA2026 Pg	3.01	1.00	0.00	4.00	0.47	0.02	0.00	0.00	0.00	0.00	0.49
SA2026 Pg	3.02	1.00	0.00	4.02	0.44	0.01	0.00	0.00	0.00	0.00	0.46
SA2026 Pg	3.02	0.99	0.00	4.02	0.45	0.01	0.00	0.00	0.00	0.00	0.47
SA2026 Pg	3.04	1.00	0.00	4.04	0.41	0.01	0.00	0.00	0.00	0.00	0.43
SA2026 Pg	2.97	0.99	0.00	3.96	0.45	0.02	0.02	0.07	0.03	0.00	0.58
SA2026 Pg	3.04	0.99	0.00	4.04	0.41	0.02	0.00	0.00	0.00	0.00	0.43
SA2026 Pg	2.98	1.05	0.00	4.03	0.38	0.02	0.05	0.02	0.02	0.00	0.48
SA2026 Pg	3.04	0.99	0.00	4.03	0.42	0.01	0.00	0.00	0.00	0.00	0.44
SA2026 Pg	3.05	0.99	0.00	4.04	0.40	0.01	0.00	0.00	0.00	0.00	0.41
SA2026 Pg	3.01	1.01	0.00	4.02	0.36	0.02	0.05	0.04	0.03	0.00	0.49
SA2026 Pg	3.03	1.01	0.00	4.04	0.41	0.01	0.02	0.00	0.00	0.00	0.44
SA2026 Pg	3.06	1.00	0.00	4.06	0.37	0.01	0.00	0.00	0.00	0.00	0.38
SA2026 Pg	3.01	1.00	0.00	4.01	0.37	0.01	0.00	0.00	0.00	0.00	0.38

Supplementary material 5. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples SA2042.

Plagioclase	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO	MnO	Total
SA2042 M1 Pg	5.03	0.00	53.77	29.63	0.00	11.64	0.00	0.58	0.00	100.84
SA2042 M1 Pg	7.22	0.00	58.59	26.20	0.00	7.82	0.00	0.39	0.00	100.37
SA2042 M1 Pg	9.69	0.00	64.26	22.65	0.05	3.60	0.00	0.00	0.00	100.31
SA2042 M1 Pg	6.60	0.00	57.16	26.86	0.00	9.14	0.00	0.00	0.00	99.87
SA2042 M1 Pg	6.73	0.00	56.91	26.54	0.00	8.77	0.33	0.43	0.00	99.86
SA2042 M1 Pg	7.47	0.77	57.92	24.69	0.00	7.46	0.00	1.29	0.00	99.70
SA2042 M1 Pg	6.54	0.34	56.75	25.90	0.27	8.41	0.32	0.96	0.00	99.64
SA2042 M1 Pg	8.53	0.00	61.29	23.64	0.00	5.76	0.00	0.00	0.00	99.54
SA2042 M1 Pg	7.78	0.00	59.32	24.90	0.00	7.00	0.00	0.00	0.00	99.39
SA2042 M1 Pg	7.47	0.34	59.90	23.78	0.00	6.51	0.00	0.88	0.00	98.99
SA2042 M1 Pg	8.22	0.00	60.21	23.82	0.00	5.97	0.00	0.31	0.00	98.68
SA2042 M1 Pg	6.76	0.00	56.51	25.88	0.05	8.79	0.00	0.22	0.00	98.47
SA2042 M1 Pg	10.32	0.00	64.62	20.79	0.06	2.17	0.00	0.00	0.00	98.34
SA2042 M1 Pg	7.60	0.00	58.51	24.82	0.06	7.09	0.00	0.00	0.00	98.34
SA2042 M1 Pg	6.80	0.00	57.54	25.60	0.00	8.14	0.00	0.00	0.00	98.31
SA2042 M1 Pg	6.33	0.07	56.43	26.65	0.95	7.39	0.00	0.25	0.00	98.22

Annexes

SA2042 M1 Pg	10.94	0.00	65.81	19.87	0.00	1.12	0.00	0.00	0.00	98.10
SA2042 M1 Pg	8.98	0.58	61.71	22.24	0.00	3.71	0.00	0.58	0.00	97.94
SA2042 M1 Pg	6.42	0.06	56.16	26.07	0.09	7.54	0.00	0.59	0.00	97.05

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Mg	K	Ca	Fe	Mn	Total
SA2042 M1 Pg	2.42	1.57	0.00	3.99	0.44	0.00	0.00	0.56	0.02	0.00	1.02
SA2042 M1 Pg	2.62	1.38	0.00	3.99	0.62	0.00	0.00	0.37	0.01	0.00	1.01
SA2042 M1 Pg	2.83	1.17	0.00	4.00	0.83	0.00	0.00	0.17	0.00	0.00	1.00
SA2042 M1 Pg	2.57	1.42	0.00	3.99	0.58	0.00	0.00	0.44	0.00	0.00	1.02
SA2042 M1 Pg	2.56	1.41	0.01	3.99	0.59	0.00	0.00	0.42	0.02	0.00	1.03
SA2042 M1 Pg	2.62	1.32	0.00	3.93	0.65	0.05	0.00	0.36	0.05	0.00	1.12
SA2042 M1 Pg	2.57	1.38	0.01	3.96	0.57	0.02	0.02	0.41	0.04	0.00	1.06
SA2042 M1 Pg	2.74	1.25	0.00	3.99	0.74	0.00	0.00	0.28	0.00	0.00	1.02
SA2042 M1 Pg	2.67	1.32	0.00	3.99	0.68	0.00	0.00	0.34	0.00	0.00	1.02
SA2042 M1 Pg	2.70	1.26	0.00	3.97	0.65	0.02	0.00	0.31	0.03	0.00	1.02
SA2042 M1 Pg	2.72	1.27	0.00	3.99	0.72	0.00	0.00	0.29	0.01	0.00	1.02
SA2042 M1 Pg	2.58	1.39	0.00	3.98	0.60	0.00	0.00	0.43	0.01	0.00	1.04
SA2042 M1 Pg	2.90	1.10	0.00	4.00	0.90	0.00	0.00	0.10	0.00	0.00	1.00
SA2042 M1 Pg	2.66	1.33	0.00	3.99	0.67	0.00	0.00	0.35	0.00	0.00	1.02
SA2042 M1 Pg	2.62	1.37	0.00	3.99	0.60	0.00	0.00	0.40	0.00	0.00	1.00
SA2042 M1 Pg	2.58	1.44	0.00	4.02	0.56	0.01	0.06	0.36	0.01	0.00	0.99
SA2042 M1 Pg	2.95	1.05	0.00	4.00	0.95	0.00	0.00	0.05	0.00	0.00	1.01
SA2042 M1 Pg	2.79	1.19	0.00	3.98	0.79	0.04	0.00	0.18	0.02	0.00	1.03
SA2042 M1 Pg	2.59	1.42	0.00	4.01	0.57	0.00	0.01	0.37	0.02	0.00	0.98

Supplementary material 6. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples AL2073.

Plagioclase	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO	MnO	Total
AL2073	5.30	0.00	54.63	28.33	0.33	10.77	0.08	0.65	0.00	100.18
AL2073	8.59	0.27	61.25	23.38	0.40	4.74	0.00	0.58	0.00	99.75
AL2073	5.26	0.07	54.52	27.96	0.31	10.85	0.06	0.58	0.00	99.75
AL2073	3.86	0.08	51.10	29.81	0.25	13.69	0.09	0.70	0.00	99.62
AL2073	5.20	0.15	54.54	27.90	0.34	10.73	0.10	0.63	0.00	99.60
AL2073	5.22	0.10	54.32	28.04	0.31	10.82	0.07	0.59	0.00	99.58
AL2073	5.34	0.07	55.00	27.21	0.56	10.13	0.00	0.39	0.00	99.41
AL2073	3.82	0.12	50.90	29.87	0.35	13.19	0.09	0.77	0.00	99.28
AL2073	11.38	0.00	67.69	19.57	0.11	0.27	0.04	0.00	0.00	99.25
AL2073	5.20	0.42	54.03	27.71	0.28	10.55	0.07	0.88	0.00	99.21
AL2073	5.36	0.32	56.35	27.44	4.19	2.80	0.00	1.03	0.00	98.69
AL2073	5.06	0.39	53.42	27.52	0.30	10.56	0.06	1.02	0.00	98.36
AL2073	4.22	2.53	50.25	26.38	0.25	9.79	0.07	4.35	0.00	98.03
AL2073	5.98	0.99	56.38	25.26	1.87	4.65	0.00	2.21	0.00	97.78
AL2073	8.00	0.49	60.98	23.22	1.87	1.95	0.00	0.71	0.00	97.77

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Mg	K	Ca	Mn	Fe	Total
-------------	----	----	----	-------	----	----	---	----	----	----	-------

Annexes

AL2073	2.47	1.51	0.00	3.98	0.23	0.00	0.02	0.52	0.00	0.02	0.80
AL2073	2.74	1.23	0.00	3.98	0.37	0.02	0.02	0.23	0.00	0.02	0.66
AL2073	2.48	1.50	0.00	3.98	0.23	0.00	0.02	0.53	0.00	0.02	0.80
AL2073	2.35	1.61	0.00	3.96	0.17	0.01	0.01	0.67	0.00	0.03	0.89
AL2073	2.48	1.49	0.00	3.98	0.23	0.01	0.02	0.52	0.00	0.02	0.81
AL2073	2.47	1.50	0.00	3.98	0.23	0.01	0.02	0.53	0.00	0.02	0.81
AL2073	2.51	1.46	0.00	3.98	0.24	0.00	0.03	0.50	0.00	0.01	0.78
AL2073	2.35	1.62	0.00	3.97	0.17	0.01	0.02	0.65	0.00	0.03	0.88
AL2073	2.98	1.02	0.00	4.00	0.49	0.00	0.01	0.01	0.00	0.00	0.51
AL2073	2.47	1.49	0.00	3.96	0.23	0.03	0.02	0.52	0.00	0.03	0.83
AL2073	2.59	1.49	0.00	4.08	0.24	0.02	0.25	0.14	0.00	0.04	0.68
AL2073	2.46	1.50	0.00	3.96	0.23	0.03	0.02	0.52	0.00	0.04	0.83
AL2073	2.37	1.47	0.00	3.84	0.19	0.18	0.02	0.50	0.00	0.17	1.05
AL2073	2.61	1.38	0.00	3.99	0.27	0.07	0.11	0.23	0.00	0.09	0.76
AL2073	2.78	1.25	0.00	4.03	0.35	0.03	0.11	0.10	0.00	0.03	0.62
AL2073	2.54	1.43	0.00	3.98	0.26	0.03	0.05	0.41	0.00	0.04	0.78

Supplementary material 7. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples AL2075.

Plagioclase	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO	MnO	Total sonde
AL2075M1.	5.71	0.00	56.43	26.37	0.41	9.22	0.00	0.52	0.00	98.66
AL2075M1.	6.16	0.00	56.91	25.94	0.63	8.27	0.00	0.36	0.00	98.27
AL2075M1.	4.35	0.08	52.73	28.15	0.33	11.44	0.00	0.72	0.00	97.80
AL2075M1.	6.01	0.07	56.09	26.01	0.37	8.95	0.00	0.64	0.00	98.14
AL2075M1.	10.48	0.00	67.49	19.23	0.55	0.39	0.00	0.00	0.00	98.14
AL2075M1.	8.74	0.00	65.27	20.87	1.59	2.63	0.00	0.35	0.00	99.45
AL2075M1.	5.79	0.00	56.08	26.96	0.33	9.92	0.00	0.57	0.00	99.64
AL2075M1.	4.32	0.00	52.18	28.85	0.30	12.18	0.00	0.57	0.00	98.39
AL2075M1.	10.97	0.00	69.48	19.38	0.10	0.20	0.00	0.27	0.00	100.40
AL2075M1.	9.33	0.49	65.52	21.00	0.84	1.64	0.00	0.76	0.00	99.57
AL2075M1.	5.43	0.00	54.89	27.18	0.19	10.27	0.00	0.44	0.00	98.41
AL2075M1.	6.47	0.00	57.36	25.74	0.34	8.28	0.00	0.41	0.00	98.60
AL2075M1.	10.46	0.00	66.67	20.19	0.25	1.04	0.00	0.00	0.00	98.62
AL2075M1.	7.43	0.00	60.30	24.75	0.71	6.45	0.00	0.43	0.00	100.06
AL2075M1.	9.08	0.08	64.19	21.00	0.00	3.24	0.41	0.37	0.00	98.38
AL2075M1.	7.35	0.15	60.87	23.87	1.17	4.32	0.00	0.72	0.00	98.45
AL2075M1.	9.34	0.00	64.41	22.34	0.66	1.30	0.00	0.48	0.00	98.52
AL2075M1.	5.59	0.08	56.60	26.13	0.36	9.29	0.00	0.40	0.00	98.45
AL2075M1.	6.07	0.06	56.48	26.11	0.43	8.99	0.00	0.40	0.00	98.53
AL2075M1.	6.12	0.13	56.15	25.45	0.38	8.82	0.00	0.71	0.00	97.76
AL2075M1.	5.97	0.00	56.53	25.81	0.36	8.99	0.20	0.38	0.00	98.24

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Ca	K	Mg	Fe	Mn	Total
AL2075M1.	2.57	1.42	0.00	3.99	0.50	0.45	0.02	0.00	0.02	0.00	1.00
AL2075M1.	2.60	1.40	0.00	3.99	0.55	0.40	0.04	0.00	0.01	0.00	1.00

Annexes

AL2075M1.	2.44	1.54	0.00	3.98	0.39	0.57	0.02	0.01	0.03	0.00	1.01
AL2075M1.	2.57	1.41	0.00	3.98	0.53	0.44	0.02	0.00	0.02	0.00	1.02
AL2075M1.	3.00	1.01	0.00	4.01	0.90	0.02	0.03	0.00	0.00	0.00	0.95
AL2075M1.	2.90	1.09	0.00	3.99	0.75	0.13	0.09	0.00	0.01	0.00	0.98
AL2075M1.	2.54	1.44	0.00	3.98	0.51	0.48	0.02	0.00	0.02	0.00	1.03
AL2075M1.	2.41	1.57	0.00	3.98	0.39	0.60	0.02	0.00	0.02	0.00	1.03
AL2075M1.	3.01	0.99	0.00	4.01	0.92	0.01	0.01	0.00	0.01	0.00	0.95
AL2075M1.	2.90	1.09	0.00	3.99	0.80	0.08	0.05	0.03	0.03	0.00	0.99
AL2075M1.	2.52	1.47	0.00	3.98	0.48	0.50	0.01	0.00	0.02	0.00	1.01
AL2075M1.	2.61	1.38	0.00	3.99	0.57	0.40	0.02	0.00	0.02	0.00	1.01
AL2075M1.	2.96	1.06	0.00	4.01	0.90	0.05	0.01	0.00	0.00	0.00	0.96
AL2075M1.	2.69	1.30	0.00	3.99	0.64	0.31	0.04	0.00	0.02	0.00	1.01
AL2075M1.	2.87	1.11	0.01	3.99	0.79	0.16	0.00	0.01	0.01	0.00	0.96
AL2075M1.	2.75	1.27	0.00	4.02	0.64	0.21	0.07	0.01	0.03	0.00	0.96
AL2075M1.	2.87	1.17	0.00	4.04	0.81	0.06	0.04	0.00	0.02	0.00	0.92
AL2075M1.	2.58	1.40	0.00	3.98	0.49	0.45	0.02	0.01	0.02	0.00	0.99
AL2075M1.	2.58	1.40	0.00	3.98	0.54	0.44	0.02	0.00	0.02	0.00	1.02
AL2075M1.	2.59	1.38	0.00	3.97	0.55	0.44	0.02	0.01	0.03	0.00	1.04
AL2075M1.	2.58	1.39	0.01	3.98	0.53	0.44	0.02	0.00	0.01	0.00	1.01

Supplementary material 8. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples AL2077B.

Plagioclase	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO	MnO	Total	
AL2077BPg	6.23	0.00	56.85	27.48	0.47	9.26	0.00	0.80	0.00	101.21	
AL2077BPg	6.32	0.09	58.81	26.33	0.50	8.44	0.00	0.52	0.00	101.11	
AL2077BPg	7.32	0.00	59.77	25.36	0.49	7.02	0.00	0.63	0.00	100.66	
AL2077BPg	5.82	0.08	56.34	27.37	0.32	9.54	0.00	0.62	0.00	100.31	
AL2077BPg	5.75	0.07	56.45	27.43	0.27	9.58	0.00	0.51	0.00	100.23	
AL2077BPg	5.16	0.07	54.95	27.74	0.16	10.69	0.19	0.66	0.00	99.68	
AL2077BPg	5.92	0.09	56.11	27.24	0.66	8.78	0.00	0.69	0.00	99.52	
AL2077BPg	5.76	0.10	55.50	27.19	0.33	9.76	0.00	0.53	0.00	99.33	
AL2077BPg	5.95	0.00	55.61	27.54	0.35	9.06	0.00	0.63	0.00	99.29	
AL2077BPg	6.51	0.00	57.69	25.57	0.50	8.17	0.00	0.63	0.00	99.22	
AL2077BPg	5.05	0.09	54.26	28.09	0.24	10.93	0.00	0.35	0.00	99.16	
AL2077BPg	5.81	0.28	55.05	26.83	0.29	9.98	0.00	0.72	0.00	99.15	
AL2077BPg	5.06	0.11	53.74	27.99	0.25	11.31	0.00	0.49	0.00	99.07	
AL2077BPg	5.39	0.10	54.52	27.50	0.38	10.47	0.00	0.59	0.00	99.04	
AL2077BPg	5.06	0.09	53.38	28.16	0.20	11.17	0.00	0.65	0.00	98.90	
AL2077BPg	4.83	0.09	53.41	28.35	0.23	11.31	0.00	0.45	0.00	98.78	
AL2077BPg	4.81	0.10	52.96	28.50	0.23	11.43	0.00	0.55	0.00	98.74	
AL2077BPg	5.73	0.00	54.88	27.35	0.34	9.57	0.00	0.47	0.00	98.57	
AL2077BPg	5.42	0.08	54.46	27.21	0.31	10.23	0.00	0.59	0.00	98.46	
Structural formula on the basis of an 8 oxygen equivalent											
Plagioclase	Si	Al	Ti	Total	Na	Ca	K	Mg	Fe	Mn	Total
AL2077BPg	2.54	1.45	0.00	3.98	0.27	0.44	0.03	0.00	0.03	0.00	0.77

Annexes

AL2077BPg	2.61	1.38	0.00	3.99	0.27	0.40	0.03	0.01	0.02	0.00	0.73
AL2077BPg	2.66	1.33	0.00	3.99	0.32	0.33	0.03	0.00	0.02	0.00	0.70
AL2077BPg	2.53	1.45	0.00	3.99	0.25	0.46	0.02	0.01	0.02	0.00	0.76
AL2077BPg	2.54	1.45	0.00	3.99	0.25	0.46	0.02	0.00	0.02	0.00	0.75
AL2077BPg	2.49	1.48	0.01	3.98	0.23	0.52	0.01	0.01	0.03	0.00	0.79
AL2077BPg	2.54	1.45	0.00	3.99	0.26	0.43	0.04	0.01	0.03	0.00	0.76
AL2077BPg	2.52	1.46	0.00	3.98	0.25	0.48	0.02	0.01	0.02	0.00	0.78
AL2077BPg	2.53	1.47	0.00	4.00	0.26	0.44	0.02	0.00	0.02	0.00	0.75
AL2077BPg	2.61	1.37	0.00	3.98	0.29	0.40	0.03	0.00	0.02	0.00	0.74
AL2077BPg	2.48	1.51	0.00	3.99	0.22	0.53	0.01	0.01	0.01	0.00	0.79
AL2077BPg	2.52	1.45	0.00	3.96	0.26	0.49	0.02	0.02	0.03	0.00	0.81
AL2077BPg	2.46	1.51	0.00	3.97	0.22	0.55	0.01	0.01	0.02	0.00	0.82
AL2077BPg	2.49	1.48	0.00	3.97	0.24	0.51	0.02	0.01	0.02	0.00	0.80
AL2077BPg	2.45	1.52	0.00	3.97	0.23	0.55	0.01	0.01	0.03	0.00	0.82
AL2077BPg	2.45	1.53	0.00	3.98	0.21	0.56	0.01	0.01	0.02	0.00	0.81
AL2077BPg	2.44	1.54	0.00	3.98	0.21	0.56	0.01	0.01	0.02	0.00	0.82
AL2077BPg	2.52	1.48	0.00	3.99	0.25	0.47	0.02	0.00	0.02	0.00	0.76
AL2077BPg	2.50	1.47	0.00	3.98	0.24	0.50	0.02	0.01	0.02	0.00	0.79

Supplementary material 9. Electron microprobe analyses and corresponding structural formulas of plagioclase for the mafic samples AL2077B.

Plagioclase	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO	MnO	Total sonde
	11.05	0.00	68.08	19.48	0.16	0.47	0.00	0.00	0.00	99.25
	0.43	0.00	65.50	16.97	16.14	0.00	0.00	1.05	0.00	100.09
AL2088M1Pg	10.22	0.00	68.88	20.66	0.00	0.66	0.00	0.00	0.00	100.43
AL2088M1	10.43	0.00	69.57	20.47	0.00	0.65	0.00	0.00	0.00	101.13
AL2088M1	11.07	0.00	68.87	20.90	0.00	0.74	0.00	0.00	0.00	101.58
AL2088M1	11.31	0.00	68.58	20.37	0.00	0.61	0.00	0.00	0.00	100.87
AL2088M1	10.48	0.00	67.50	20.60	0.39	0.56	0.00	0.00	0.00	99.53
AL2088M1	11.21	0.00	69.43	20.40	0.09	0.47	0.00	0.00	0.00	101.60
AL2088M1	10.88	0.00	67.87	20.29	0.00	0.64	0.00	0.00	0.00	99.68
AL2088M1	11.43	0.00	68.95	20.00	0.00	0.52	0.00	0.00	0.00	100.90
AL2088M1	11.13	0.00	68.07	20.46	0.24	0.36	0.00	0.00	0.00	100.25
AL2088M1	11.14	0.00	67.55	20.05	0.00	0.63	0.00	0.26	0.00	99.69
AL2088M1	11.32	0.00	69.20	20.56	0.00	0.54	0.13	0.26	0.00	102.01
AL2088M1	10.65	0.00	67.63	19.64	0.00	0.62	0.00	0.00	0.00	98.60
AL2088M1	11.56	0.00	68.93	20.45	0.00	0.40	0.00	0.00	0.00	101.34
AL2088M1	10.60	0.00	68.65	20.50	0.00	0.65	0.00	0.00	0.00	100.40
AL2088M1.	11.23	0.06	68.83	20.12	0.00	0.44	0.00	0.00	0.00	100.69
AL2088M1.	11.26	0.00	68.72	20.39	0.00	0.67	0.00	0.25	0.00	101.29
AL2088M1.	11.03	0.00	67.73	20.04	0.00	0.70	0.00	0.00	0.00	99.50
AL2088M1.	11.08	0.00	68.93	20.06	0.00	0.74	0.00	0.00	0.00	100.82
AL2088M1.	10.63	0.00	67.17	20.11	0.37	0.61	0.00	0.00	0.00	98.90
AL2088M1.	11.03	0.00	68.62	19.61	0.00	0.54	0.00	0.00	0.00	99.81
AL2088M1.	10.88	0.00	69.00	20.04	0.00	0.71	0.00	0.00	0.00	100.63
AL2088M1.	10.89	0.00	69.14	20.01	0.00	0.35	0.00	0.00	0.00	100.39

Annexes

AL2088M1.	10.77	0.00	67.97	19.97	0.00	0.65	0.00	0.00	0.00	99.35
AL2088M1.	10.90	0.00	68.73	19.44	0.00	0.37	0.00	0.00	0.00	99.48
AL2088M1.	11.03	0.00	68.94	19.86	0.00	0.48	0.00	0.00	0.00	100.32
AL2088M1.	10.84	0.00	68.45	19.92	0.00	0.63	0.00	0.00	0.00	99.84
AL2088M1.	10.93	0.00	67.85	19.86	0.00	0.74	0.00	0.00	0.00	99.39
AL2088M1.	10.89	0.00	68.82	19.72	0.00	0.46	0.00	0.00	0.00	99.88
AL2088M1.	10.88	0.00	66.68	19.44	0.00	0.74	0.00	0.00	0.00	97.75
AL2088M1.	10.62	0.31	66.42	19.31	0.15	0.36	0.00	0.82	0.00	98.00
AL2088M1.	10.79	0.05	67.56	19.59	0.00	0.75	0.00	0.00	0.00	98.75
AL2088M1.	10.72	0.00	67.58	19.57	0.00	0.72	0.00	0.00	0.00	98.59
AL2088M1.	10.42	0.00	68.62	20.02	0.00	0.56	0.00	0.00	0.00	99.63
AL2088M1.	10.52	0.00	67.52	19.45	0.00	0.56	0.00	0.00	0.00	98.06
AL2088M1.	10.51	0.00	67.46	19.62	0.00	0.50	0.00	0.00	0.00	98.25
AL2088M1.	10.71	0.00	67.90	20.07	0.00	0.63	0.00	0.00	0.00	99.42
AL2088M1.	10.92	0.00	68.56	20.15	0.00	0.58	0.00	0.00	0.00	100.20
AL2088M1.	10.60	0.00	68.21	20.35	0.00	0.77	0.00	0.00	0.00	99.92
AL2088M1.	11.06	0.00	68.47	20.51	0.15	0.70	0.00	0.00	0.00	100.88
AL2088M1.	11.56	0.00	69.97	19.70	0.00	0.15	0.00	0.22	0.00	101.60
AL2088M1.	10.77	0.07	67.96	19.85	0.00	0.56	0.00	0.00	0.00	99.21
AL2088M1.	10.98	0.00	67.66	20.15	0.00	0.52	0.00	0.00	0.00	99.31
AL2088M1.	11.26	0.00	68.49	19.93	0.00	0.59	0.00	0.00	0.00	100.27
AL2088M1.	11.42	0.00	69.54	19.83	0.00	0.36	0.00	0.23	0.00	101.37
AL2088M1.	10.22	0.00	67.98	20.39	0.00	0.69	0.00	0.00	0.00	99.29

Structural formula on the basis of an 8 oxygen equivalent

Plagioclase	Si	Al	Ti	Total	Na	Ca	K	Mg	Fe	Mn	Total
	2.99	1.01	0.00	4.00	0.94	0.02	0.01	0.00	0.00		0.00 0.97
	3.04	0.93	0.00	3.96	0.04	0.00	0.95	0.00	0.04		0.00 1.03
AL2088M1	2.98	1.05	0.00	4.03	0.86	0.03	0.00	0.00	0.00		0.00 0.89
AL2088M1	2.99	1.04	0.00	4.03	0.87	0.03	0.00	0.00	0.00		0.00 0.90
AL2088M1	2.96	1.06	0.00	4.02	0.92	0.03	0.00	0.00	0.00		0.00 0.96
AL2088M1	2.97	1.04	0.00	4.01	0.95	0.03	0.00	0.00	0.00		0.00 0.98
AL2088M1	2.96	1.06	0.00	4.02	0.89	0.03	0.02	0.00	0.00		0.00 0.94
AL2088M1	2.98	1.03	0.00	4.01	0.93	0.02	0.01	0.00	0.00		0.00 0.96
AL2088M1	2.97	1.05	0.00	4.02	0.92	0.03	0.00	0.00	0.00		0.00 0.95
AL2088M1	2.98	1.02	0.00	4.00	0.96	0.02	0.00	0.00	0.00		0.00 0.98
AL2088M1	2.97	1.05	0.00	4.02	0.94	0.02	0.01	0.00	0.00		0.00 0.97
AL2088M1	2.97	1.04	0.00	4.00	0.95	0.03	0.00	0.00	0.01		0.00 0.99
AL2088M1	2.96	1.04	0.00	4.01	0.94	0.02	0.00	0.00	0.01		0.00 0.97
AL2088M1	2.99	1.02	0.00	4.01	0.91	0.03	0.00	0.00	0.00		0.00 0.94
AL2088M1.	2.97	1.04	0.00	4.01	0.97	0.02	0.00	0.00	0.00		0.00 0.98
AL2088M1.	2.98	1.05	0.00	4.02	0.89	0.03	0.00	0.00	0.00		0.00 0.92
AL2088M1.	2.98	1.03	0.00	4.01	0.94	0.02	0.00	0.00	0.00		0.00 0.97
AL2088M1.	2.97	1.04	0.00	4.00	0.94	0.03	0.00	0.00	0.01		0.00 0.98
AL2088M1.	2.97	1.04	0.00	4.01	0.94	0.03	0.00	0.00	0.00		0.00 0.97
AL2088M1.	2.98	1.02	0.00	4.01	0.93	0.03	0.00	0.00	0.00		0.00 0.96
AL2088M1.	2.97	1.05	0.00	4.01	0.91	0.03	0.02	0.00	0.00		0.00 0.96
AL2088M1.	3.00	1.01	0.00	4.01	0.93	0.03	0.00	0.00	0.00		0.00 0.96
AL2088M1.	2.99	1.02	0.00	4.01	0.91	0.03	0.00	0.00	0.00		0.00 0.95

Annexes

AL2088M1.	3.00	1.02	0.00	4.02	0.92	0.02	0.00	0.00	0.00	0.00	0.93
AL2088M1.	2.98	1.03	0.00	4.01	0.92	0.03	0.00	0.00	0.00	0.00	0.95
AL2088M1.	3.01	1.00	0.00	4.01	0.93	0.02	0.00	0.00	0.00	0.00	0.94
AL2088M1.	2.99	1.02	0.00	4.01	0.93	0.02	0.00	0.00	0.00	0.00	0.95
AL2088M1.	2.99	1.02	0.00	4.01	0.92	0.03	0.00	0.00	0.00	0.00	0.95
AL2088M1.	2.98	1.03	0.00	4.01	0.93	0.03	0.00	0.00	0.00	0.00	0.97
AL2088M1.	3.00	1.01	0.00	4.01	0.92	0.02	0.00	0.00	0.00	0.00	0.94
AL2088M1.	2.98	1.02	0.00	4.00	0.94	0.04	0.00	0.00	0.00	0.00	0.98
AL2088M1.	2.97	1.02	0.00	3.99	0.92	0.02	0.01	0.02	0.03	0.00	1.00
AL2088M1.	2.98	1.02	0.00	4.00	0.92	0.04	0.00	0.00	0.00	0.00	0.96
AL2088M1.	2.99	1.02	0.00	4.01	0.92	0.03	0.00	0.00	0.00	0.00	0.95
AL2088M1.	2.99	1.03	0.00	4.02	0.88	0.03	0.00	0.00	0.00	0.00	0.91
AL2088M1.	3.00	1.02	0.00	4.01	0.91	0.03	0.00	0.00	0.00	0.00	0.93
AL2088M1.	2.99	1.03	0.00	4.02	0.90	0.02	0.00	0.00	0.00	0.00	0.93
AL2088M1.	2.98	1.04	0.00	4.02	0.91	0.03	0.00	0.00	0.00	0.00	0.94
AL2088M1.	2.98	1.03	0.00	4.01	0.92	0.03	0.00	0.00	0.00	0.00	0.95
AL2088M1.	2.97	1.05	0.00	4.02	0.90	0.04	0.00	0.00	0.00	0.00	0.93
AL2088M1.	2.96	1.05	0.00	4.01	0.93	0.03	0.01	0.00	0.00	0.00	0.97
AL2088M1.	3.00	1.00	0.00	4.00	0.96	0.01	0.00	0.00	0.01	0.00	0.98
AL2088M1.	2.98	1.03	0.00	4.01	0.92	0.03	0.00	0.00	0.00	0.00	0.95
AL2088M1.	2.97	1.04	0.00	4.01	0.94	0.02	0.00	0.00	0.00	0.00	0.96
AL2088M1.	2.98	1.02	0.00	4.00	0.95	0.03	0.00	0.00	0.00	0.00	0.98
AL2088M1.	2.99	1.01	0.00	4.00	0.95	0.02	0.00	0.00	0.01	0.00	0.98
AL2088M1.	2.98	1.05	0.00	4.03	0.87	0.03	0.00	0.00	0.00	0.00	0.90

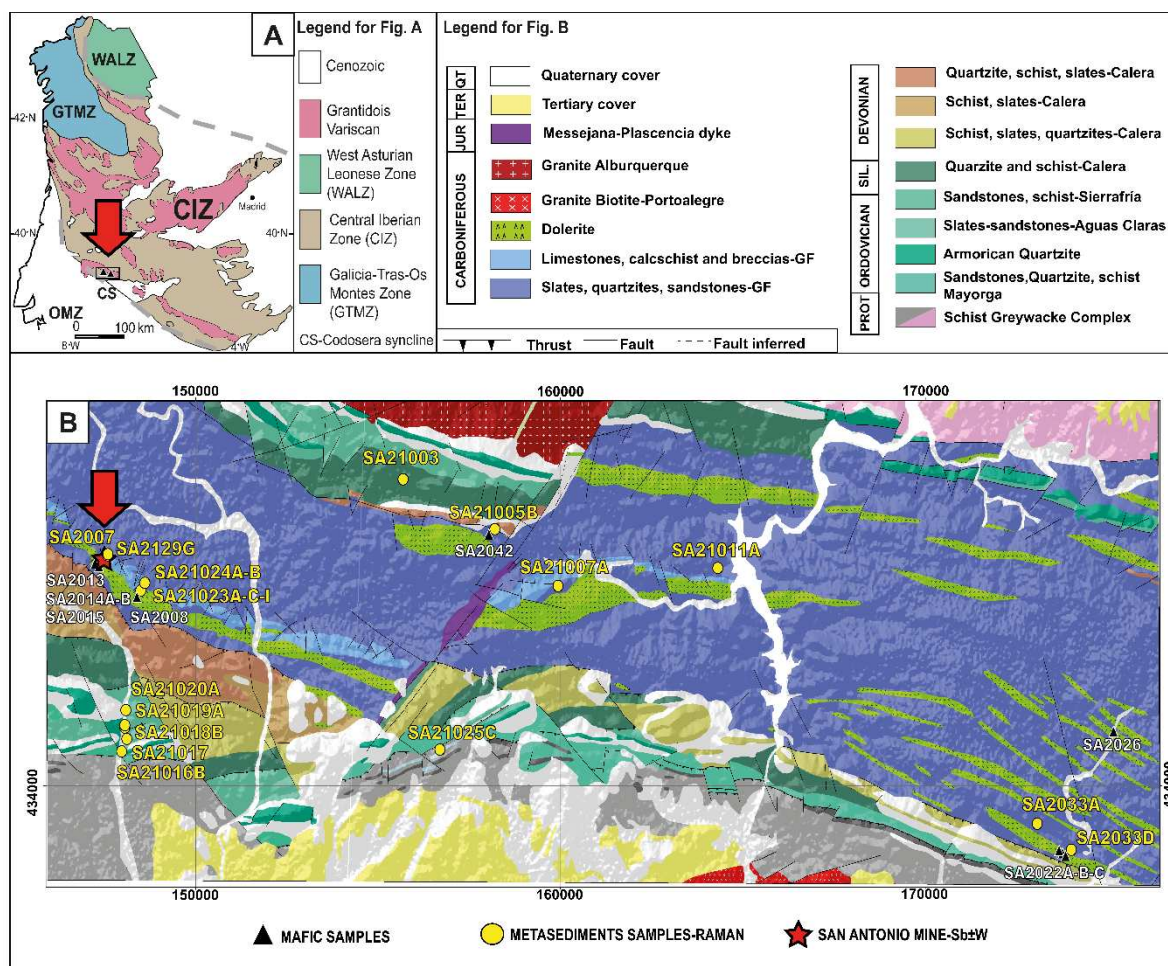
Sb MINERALIZATION IN THE CIZ

As seen in chapter 2, a large number of Sb deposits are scattered across the CIZ. Four of these localities (San Antonio, La Susana, La Balanzona and La Nazarena Mines) were visited during this project in order to better understand their possible link with mafic magmatism and/or metasediments. Nowadays, all of the visited mines are closed reason why all of the samples showed in this chapter were not taken in situ. This section shows all the paragenetic sequences made for the mineralized samples in this study.

San Antonio Mine

Located between the Badajoz and Cáceres provinces, at the center the Extremadura region in Spain. This Sb mineralization is hosted by a level of calcareous rocks (breccia) of the Gévora

Formation (Gumiel, 1982; Rodríguez González et al., 2007) at the western part of the NW-SE trending Codosera Syncline (CS. Supplementary material 10).



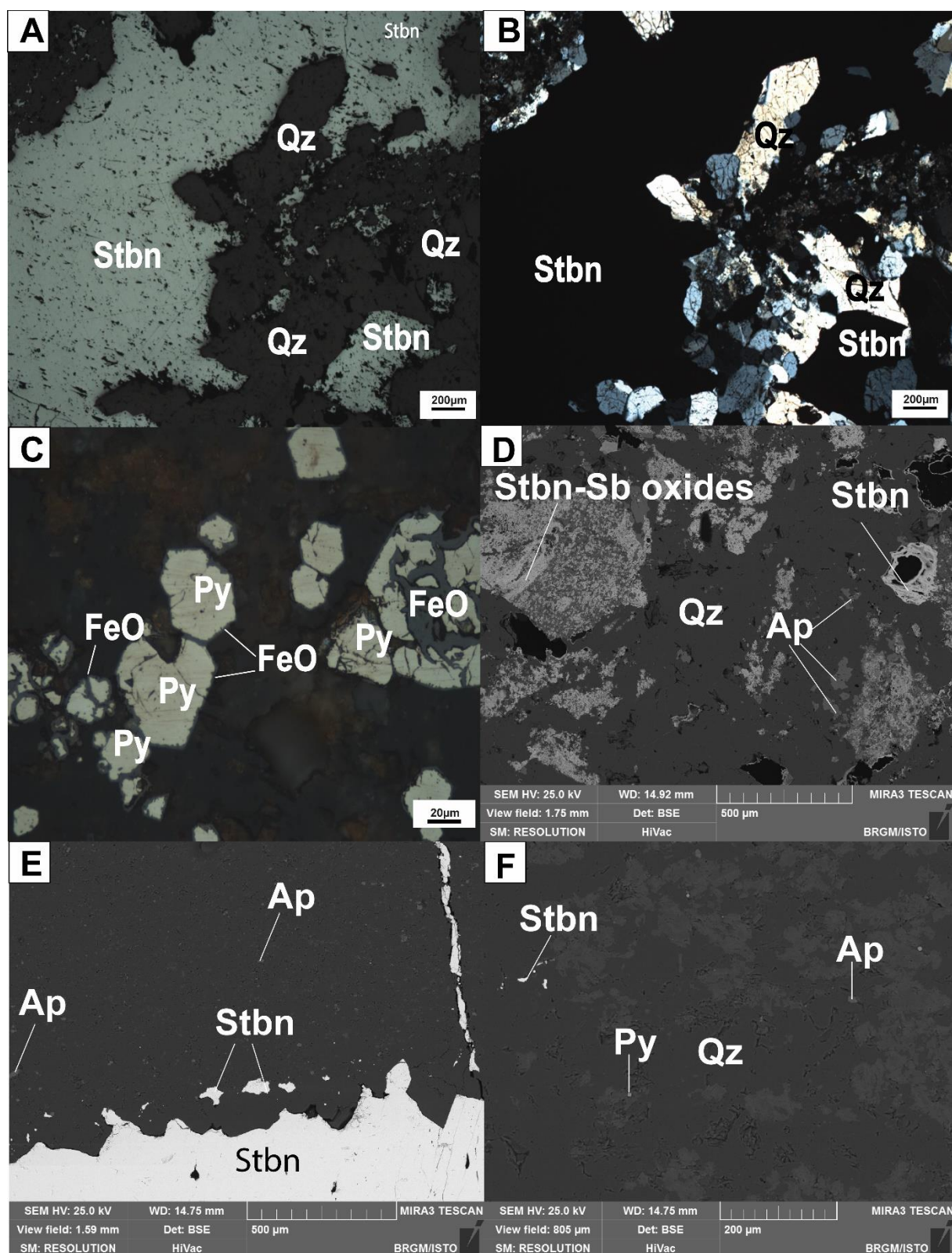
Supplementary material 10. Simplified geological map of the Iberian Massif showing the studied area of La Codosera syncline. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Codosera syncline showing the Raman and mafic samples studied in this work. This map was designed based on the Geological Maps (scale 1:50000) of Alburquerque (Santos García & Casas Ruiz, 1982), Puebla de Obando (López Díaz et al., 1989), Villar del Rey (Santos García et al., 1990) and Botoa (Insua Marquez et al., 1990).

The paragenetic sequence for this locality shows four evolution stages (Supplementary material 11 and 12): i) the first one related to the formation of the calcareous breccia, mainly

marked by the precipitation of calcite and quartz; **ii)** the second one represents the first mineralization stage mostly characterized by disseminated stibnite, arsenopyrite and quartz; **iii)** the third stage is represented by mineralized quartz $\pm$ calcite veins with bethierite and stibnite as main ores; **iv)** the last stage is mainly characterized by a supergene alteration of Sb ores.

Supplementary material 11. Paragenetic sequences for the San Antonio Sb $\pm$ W mineralization in the CIZ.

SAN ANTONIO AND MELITA MINES				
Mineral	Calcareous Breccia	Mineralization stage		Supergene alteration
		Disseminated Stbn	Veins Qz $\pm$ Cal $\pm$ Stbn	
Calcite	██████████			
Quartz	██████████			
Muscovite	_____			
Sericite	_____			
Zircon	_____			
Scheelite-	_____			
Quartz2			██████████	
Calcite2			██████████	
Berthierite-			██	
Stibnite1		██████████		
Stibnite2			██████████	
Arsenopyrite		██████████		
Apatite		██████████		
Stibiconite				_____
Cervantite				_____
Fe Oxides				_____



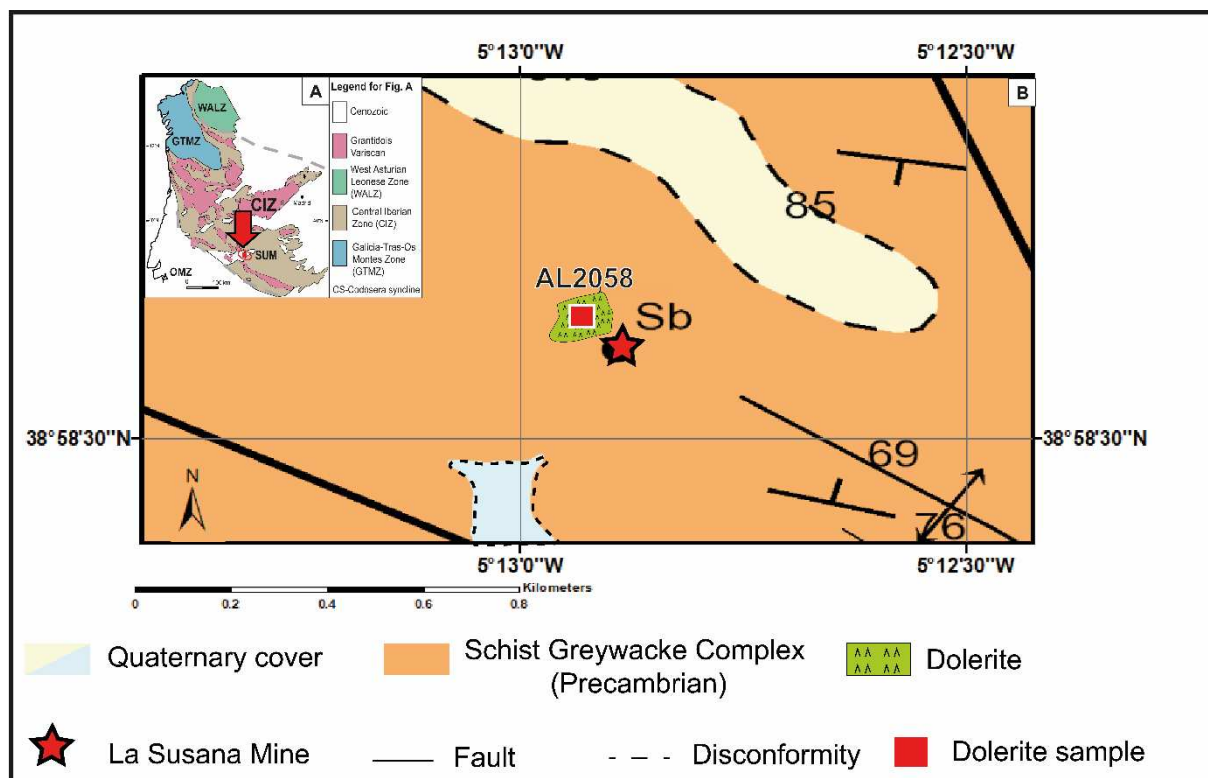
Supplementary material 12. Selected thin section micro-photographs illustrating the studied San Antonio Sb mineralization: A-B) Stibnite and hydrothermal quartz; C) Pyrite altered to Fe-oxides; D-E-F) SEM imaging showing the main phases found for the San Antonio Sb mineralization: D) Disseminated stibnite altered to Sb

Annexes

oxides, hydrothermal apatite and quartz; E) Stibnite veins and disseminated apatite; F) Disseminated stibnite, pyrite apatite in groundmass made of quartz. Legend: Stbn-Stibnite; Qz-Quartz; FeO-Iron oxides; Py- Pyrite; Ap-Apatite.

La Susana Mine

This Sb deposit is located at the Badajoz province and is hosted by the so known Schist Greywacke Complex (SGC, Gumiel, 1982, Supplementary material 13).



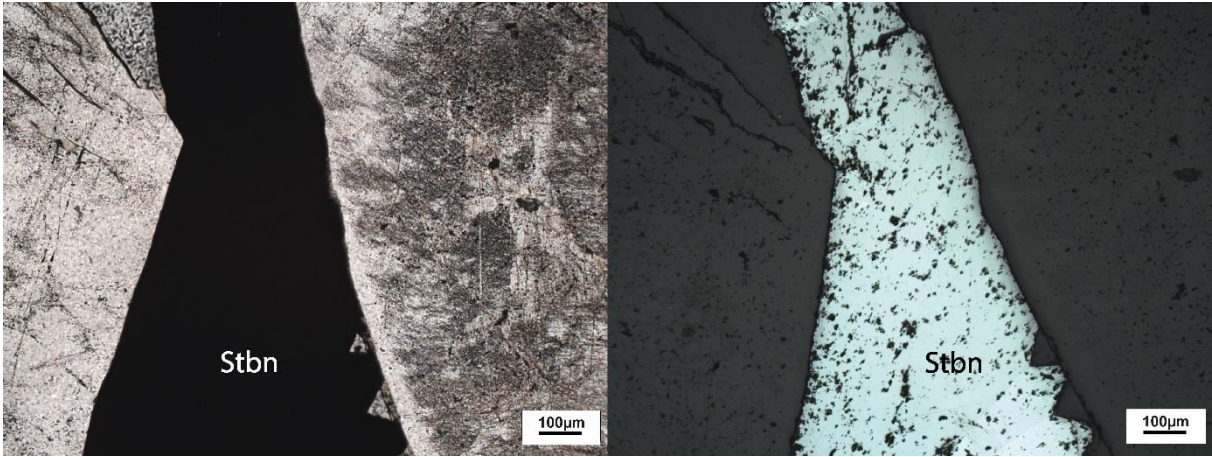
Supplementary material 13. Simplified geological map of the Iberian Massif showing the studied area of the Susana Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Susana Mine (SUM). The map was redesigned based on the Geological Map (scale 1:50000) of Puebla de Alcocer (Martín Herrero et al., 1994).

The paragenetic sequence made for the mineralized samples in this study is represented by three stages (Supplementary material 14 and 15). A first stage characterized by hydrothermal quartz

followed by precipitation of Sb ores (berthierite and Stibnite) and a third stage represented by the alteration of Sb ores into Sb oxides.

LA SUSANA MINE			
Mineral	Early stage	Veins Stbn	Last stage
Quartz			
Berthierite			
Stibinite			
Native As (?)			
Sb Oxides			

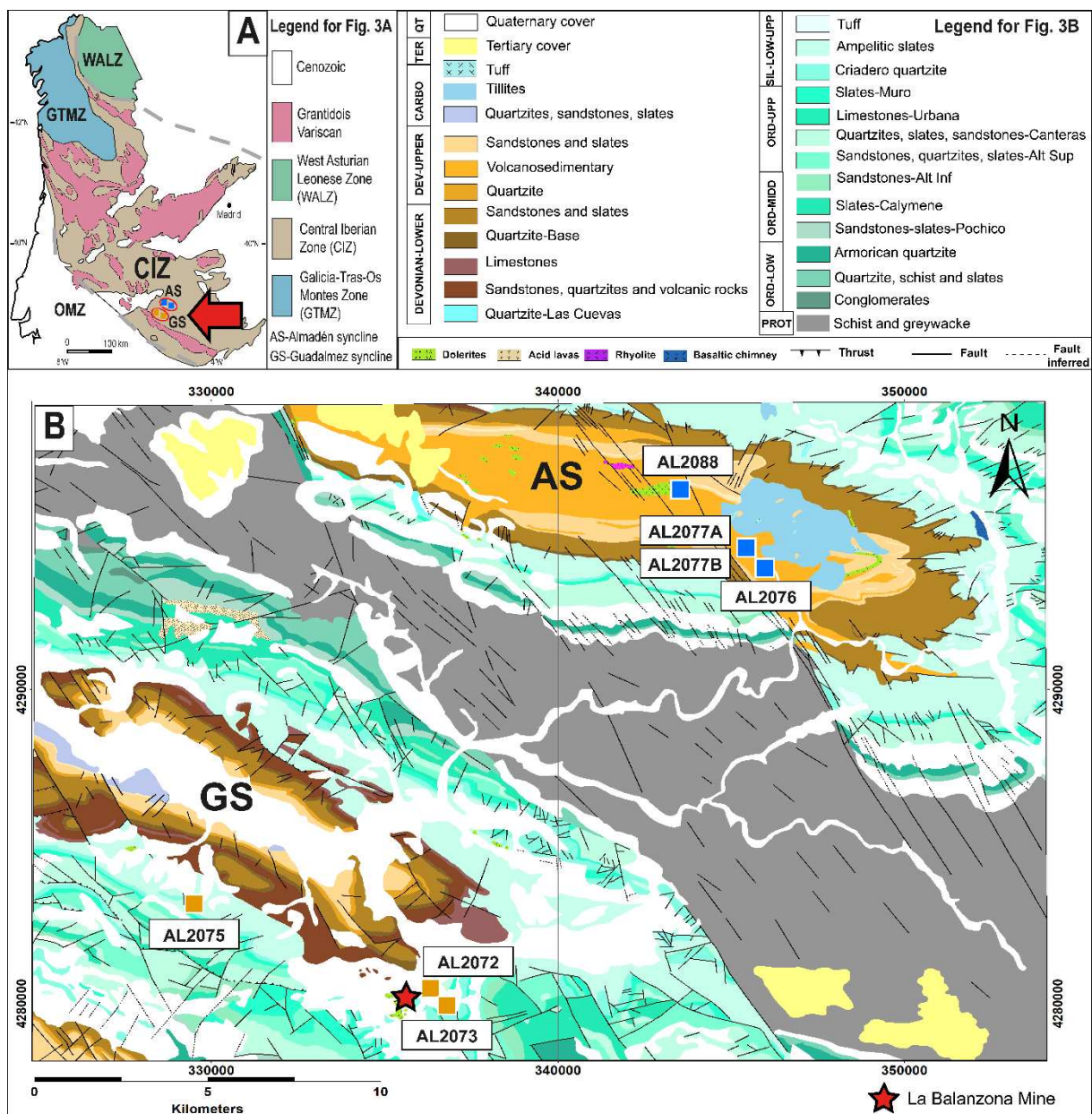
Supplementary material 14. Paragenetic sequences for the La Susana Sb mineralization in the CIZ.



Supplementary material 15. Stibnite vein in the Susana Sb mineralization.

La Balanzona Mine

La Balanzona Mine is located at the northern flank of the Guadalmez syncline in the Cordoba Province (Supplementary material 16). The Sb mineralization is hosted by the upper Ordovician-lower Silurian formation known as the Criadero Quartzite (Gumiel, 1982).



Supplementary material 16. A) Simplified geological map of the Iberian Massif showing the studied area of the Almadén (AS) and Guadalmez (GS) synclines. Modified after López-Moro et al. (2020) and references

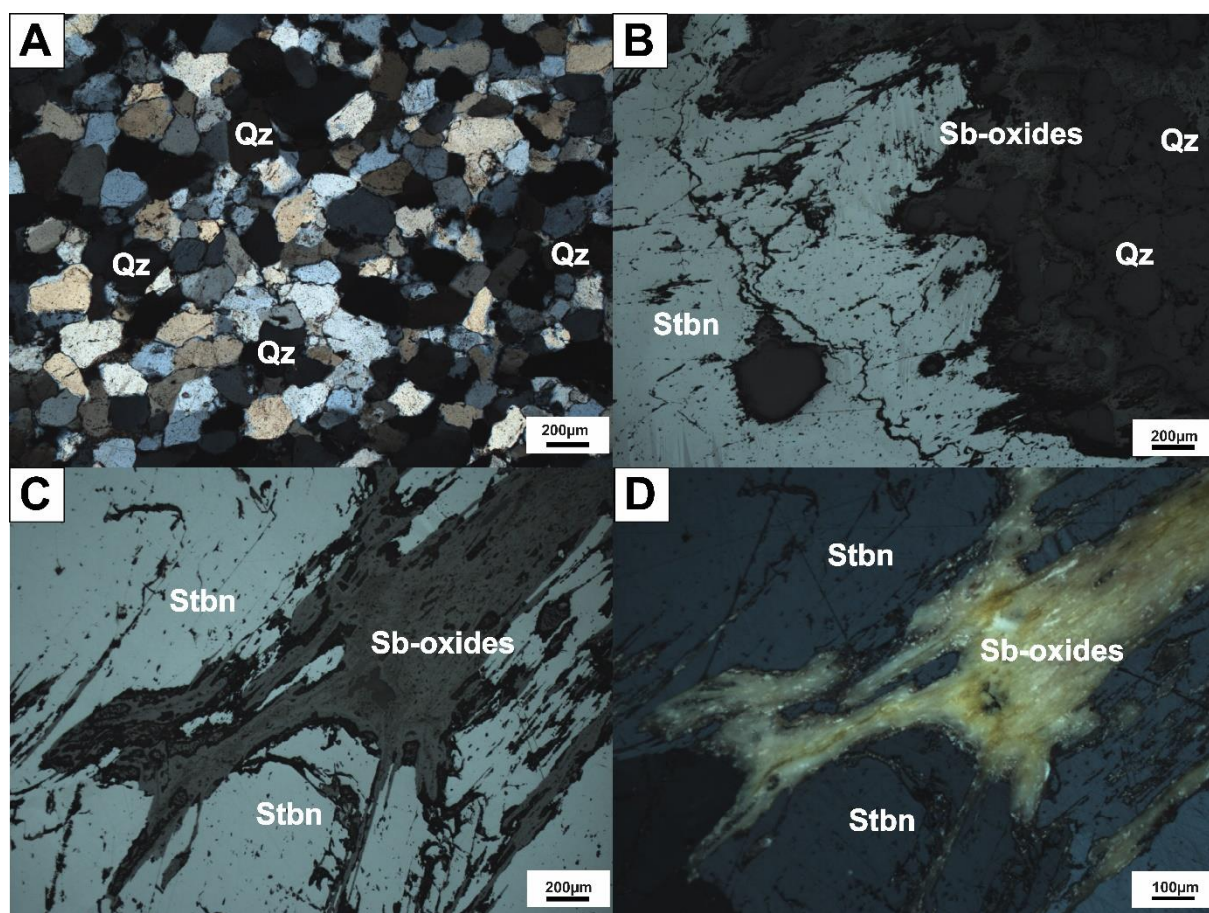
Annexes

therein ; B) Geological map of the of the Almadén (AS) and Guadalmez (GS) synclines showing the mafic samples studied in this work. The map was redesigned based on the Geological Maps (scale 1:50000) of Chillón (Lorenzo Álvarez et al., 1995), Almadén (García San Segundo et al., 1985), Hinojosa del Duque (Mira López et al., 1983) and San Benito (Mira López et al., 1983).

The paragenetic sequence for this locality shows three evolution stages (Figs. 5.8 and 5.9). An early stage represented by quartz and pyrite (Supplementary material 17 and 18). The main mineralization stage is characterized by berthierite and stibnite (Supplementary material 17 and 18). The last stage is marked by the alteration of pyrite and stibnite into Fe-oxides and Sb-oxides, respectively (Supplementary material 17 and 18).

LA BALANZONA MINE			
Mineral	Early stage	Mineralization stage	Last stage
Quartz	—————		
Pyrite	—————		
Berthierite		———	
Stibnite		—————	
Stibiconite			—————
Cervantite			—————
Fe Oxides			—————

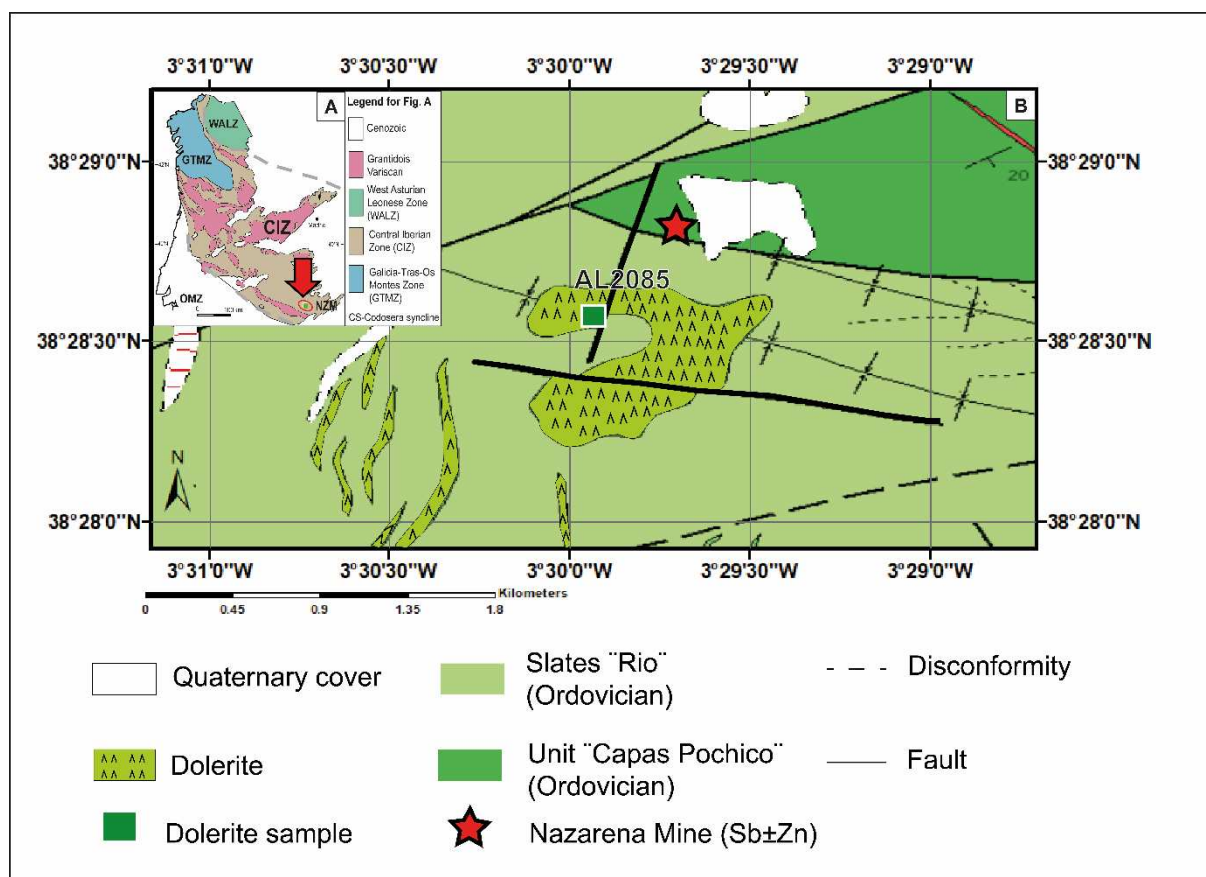
Supplementary material 17. Paragenetic sequence for the La Balanzona Sb mineralization in the CIZ.



Supplementary material 18. Selected thin section micro-photographs illustrating the studied La Balanzona Sb mineralization: A) Groundmass essentially composed by quartz; B) Stibnite, Sb-oxides and quartz; C-D) Stibnite altered to Sb oxides.

La Nazarena Mine

This Sb-Zn stratabound deposit is located in the Almuradiel locality in the Ciudad Real Province (Supplementary material 19). It is hosted within a sequence composed of slates and quartzites known as the “Capas o Alternancias Pochico” of Ordovician age (Gumiel, 1982).



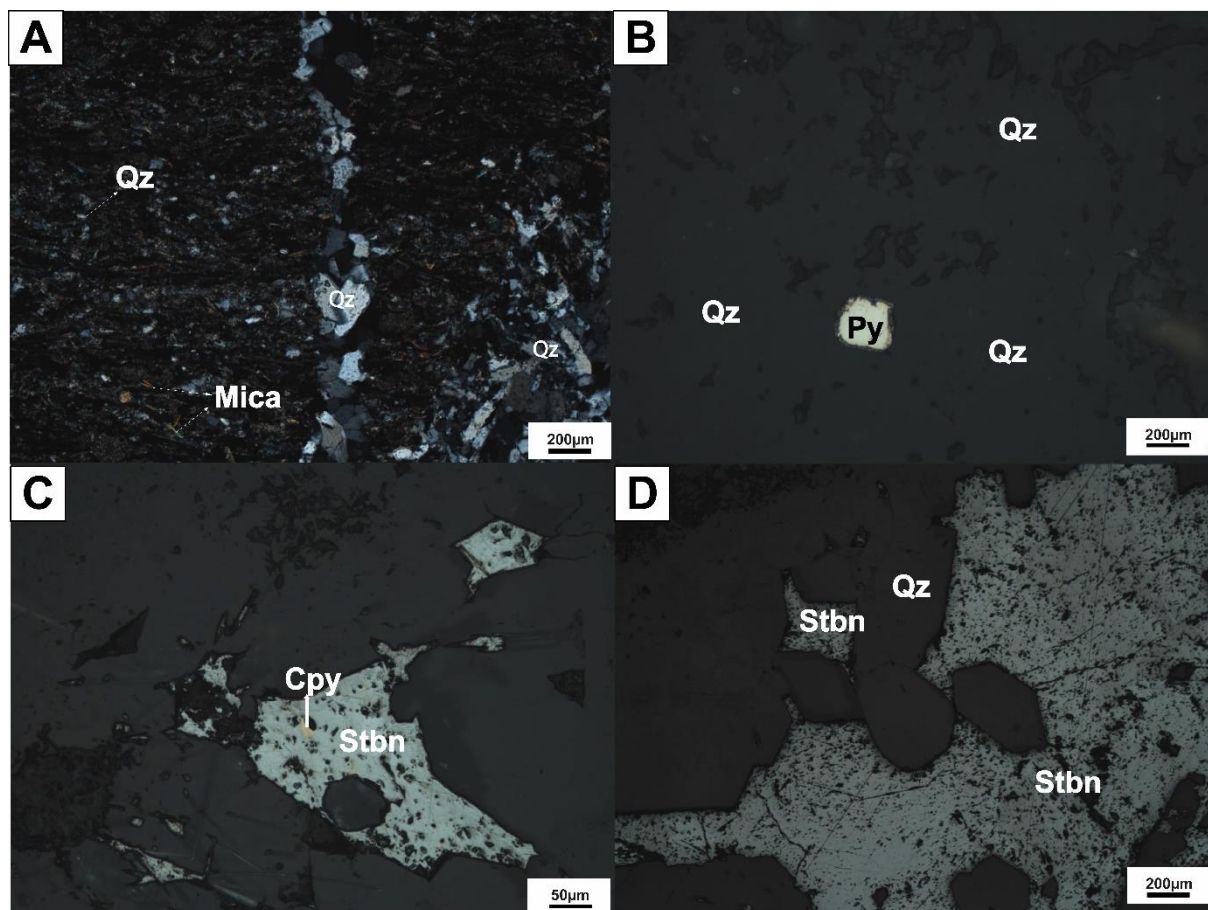
Supplementary material 19. Simplified geological map of the Iberian Massif showing the studied area of the Nazarena Mine. Modified after López-Moro et al. (2020) and references therein ; B) Geological map of the Nazarena Mine (NZM) showing the mafic samples studied in this work. The map was redesigned based on the Geological Map (scale 1:50000) of Aldequemada (Martín-Parra et al., 1996).

Three main stages are observed for the Nazarena Sb mineralization. The first one is represented by the main phases in the groundmass (quartz, muscovite and pyrite, Supplementary material 20 and 21). The second stage is mostly characterized by quartz-stibnite veins, chalcopyrite is also observed associated to the Sb ores (Supplementary material 20 and 21). The last stage is mostly represented by antimony and iron oxides (Supplementary material 20 and 21).

Annexes

NAZARENA MINE			
Mineral	Early stage	Mineralization stage-Qz Stbn veins	Last stage
Quartz	██████████		
Muscovite	██████████		
Pyrite	██████████		
Sphalerite ¹	██████████		
Quartz 2		██████████	
Berthierite		██████████	
Stibinite		████████████████████	
Chalcopyrite			██████████
Marcasite ¹			██████████
Stibiconite			██████████
Cervantite			██████████
Fe oxides			██████████

Supplementary material 20. Paragenetic sequence for the La Nazarena Sb mineralization in the CIZ.



Supplementary material 21. Selected thin section micro-photographs illustrating the studied La Nazarena Sb mineralization: A-B) Groundmass essentially composed by quartz and mica, minor pyrite can be also observed;

C) Stibnite and chalcopyrite; D) Quartz veins mineralized with Sb ores.

PUBLICATIONS AND INTERNATIONAL CONFERENCES

- Article, first author, submitted-BSGF (2024)

Campos-Rodríguez, H. R., Gloaguen, E., Tuduri, J., Pochon, A., Iacono-marziano, G., Poujol, M., Higuera, P., Virtanen, V. J., Lorenzo, S., Esbri, J. M., & Mollé, V. (2024). *Geochemistry and geochronology of the Paleozoic mafic magmatism in the Codosera, Almadén and Guadalmez synclines, Central Iberian Zone, Spain. Peer review.*

- Article, co-author- Communications Earth & Environment (2024)

Pochon, A., Kontak, D. J., Iacono-marziano, G., Gloaguen, E., Tuduri, J., Chatelin, T., Précigout, J., Campos Rodríguez, H., & Mollé, V. (2024). *Fluid inclusions in magmatic ilmenite record degassing in basic magmas. Communications Earth & Environment, 1–12.*
<https://doi.org/10.1038/s43247-024-01788-8>

- Article, co-author-Environmental Science and Pollution Research (2023)

Peco, J. D., Thouin, H., Esbrí, J. M., Campos-Rodríguez, H. R., García-Noguero, E. M., Breeze, D., Villena, J., Gloaguen, E., Higuera, P. L., & Battaglia-Brunet, F. (2023). *Mobility of antimony in contrasting surface environments of a mine site: influence of redox conditions and microbial communities. Environmental Science and Pollution Research.*
<https://doi.org/10.1007/s11356-023-29734-9>

- Geodays, Turku, Finland. First author-abstract- poster (2024)

Campos-Rodríguez, Héctor. Ricardo., Virtanen, V. J., Voipio, T., & Yang, S. (2024). *On the carbonaceous materials and sulfides in the black shales and schists of the Matarakoski Formation: characteristics of the possible sulfur source of the Kevitsa Cu-Ni-(PGE) sulfide deposits. In J. S. Heinonen (Ed.), Abstracts of the 2nd GeoDays, 12th–14th March 2024, Turku, Finland. (Proceedings of the Geological Society of Finland; Vol. 4). (Issue 4, p. 79). Geological Society of Finland.* <https://research.abo.fi/en/publications/abstracts-of-the-2nd-geodays-12th14th-march-2024-turku-finland>

- **17th SGA Biennial Meeting, Zurich, Suisse. First author-extended abstract-presentation (2023)**

Campos Rodríguez, H. R., Gloaguen, E., Pochon, A., Tuduri, J., Sizaret, S., Higuera, P., Iacono-Marziano, G., Lorenzo, S., Esbri, J. M., Poujol, M., & Mollé, V. (2023). Mafic magmatism in the Central Iberian Zone: Towards a better understanding of Sb mineralization? In *Proceedings of the 17th SGA Biennial Meeting, 28 August – 1 September 2023 (Vol. 3, pp. 121–125)*. <https://e-sga.org/nc/publications/sga-biennial-meetings-abstract-volumes/2023-zurich/>

- **École GRANITES “Magmas, volatils et processus métallogéniques”-15 au 18 novembre 2022-presentation**

Mafic magmatism and Sb mineralization: Geochemical insights from the Central Iberian Zone, Spain

- **16th SGA Biennial Meeting Rotorua, New Zealand. First author-extended abstract-presentation (2022)**

Campos Rodríguez, H. R., Gloaguen, E., Pochon, A., Higuera, P., Lorenzo, S., Esbri, J. M., Mollé, V., & Iacono-marziano, G. (2022). Mafic magmatism and Sb mineralization: Geochemical insights from the Central Iberian Zone, Spain. In *Proceedings of the 16th SGA Biennial Meeting, 22-31 March, Rotorua, New Zealand (pp. 22)*.

- **16th SGA Biennial Meeting, Rotorua, New Zealand. Co-author-extended abstract (2022)**

Higuera, P., Esbri, J. M., Campos Rodríguez, H., & Gloaguen, E. (2022). Antimony mineralizations in the Guadalmez syncline –relationships with Almadén mercury deposits, South-Central Spain. In A. B. Christie (Ed.), *Proceeding of the 16th SGA Biennial meeting, 28-31 March 2022, Rotorua, New Zealand (Vol. 2, p. 72)*.

- ***EGU General Assembly 2021, Vienna, Austria. First author-abstract-presentation (2021)***

Campos Rodríguez, H. R., Gloaguen, E., Pochon, A., Higuera, P., Lorenzo, S., Esbri, J. M., Mollé, V., & Iacono-marziano, G. (2021). Unravelling the relationship between mafic magmatism and Sb mineralization through dolerite geochemistry (Central Iberian Zone, Spain). EGU General Assembly 2021



Mobility of antimony in contrasting surface environments of a mine site: influence of redox conditions and microbial communities

Jesús Daniel Peco^{1,2} · Hugues Thouin³ · José María Esbri⁴ · Héctor Ricardo Campos-Rodríguez⁵ · Eva Maria García-Noguero¹ · Dominique Breeze³ · Jaime Villena² · Eric Gloaguen⁵ · Pablo Leon Higuera¹ · Fabienne Battaglia-Brunet⁵

Received: 1 May 2023 / Accepted: 2 September 2023

© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2023

Abstract

Microbial processes can influence the complex geochemical behaviour of the toxic metalloid antimony (Sb) in mining environments. The present study is aimed to evaluate the influence of microbial communities on the mobility of Sb from solid phases to water in different compartments and redox conditions of a mining site in southwest (SW) Spain. Samples of surface materials presenting high Sb concentrations, from two weathered mining waste dumps, and an aquatic sediment were incubated in slurries comparing oxic and anoxic conditions. The initial microbial communities of the three materials strongly differed. Incubations induced an increase of microbial biomass and an evolution of the microbial communities' structures and compositions, which diverged in different redox conditions. The presence of active bacteria always influenced the mobility of Sb, except in the neutral pH waste incubated in oxic conditions. The effect of active microbial activities in oxic conditions was dependent on the material: Sb oxid release was biologically amplified with the acidic waste, but attenuated with the sediment. Different bacterial genera involved in Sb, Fe and S oxidation or reduction were present and/or grew during incubation of each material. The results highlighted the wide diversity of microbial communities and metabolisms at the small geographic scale of a mining site and their strong implication in Sb mobility.

Keywords Antimony mine · Microbial communities · Redox conditions · Microcosms

Introduction

Antimony (Sb) is a strategic element with a large range of applications. It is involved as a flame retardant in the composition of plastics, coatings and electronics, but also utilised in manufacturing batteries, ammunitions, glasses, semiconductors, diodes, infrared detectors, paints, rubbers and Hall effect devices (Krachler et al. 2001; Dupont et al. 2016). The current order of magnitude of annual Sb production is 150,000 tons (USGS 2021). Antimony is mainly extracted from stibnite (Sb_2S_3) mines, but also from Sb oxides and, as a secondary product, from Pb, Au, Ag, Cu, Ni or Zn ores (Anderson 2012; Dupont et al. 2016; Herath et al. 2017). This element, although necessary for the elaboration of many manufactured products, presents health and environmental issues. Acute and chronic toxicity of Sb have been reported (Sundar and Chakravarty 2010). Results from recent studies indicate that Sb might be genotoxic (El Shanawany et al. 2017), and Sb trioxide has been recognised as a potential carcinogen (Schildroth et al. 2021).

Responsible Editor: Robert Duran

✉ Fabienne Battaglia-Brunet
f.battaglia@brgm.fr

¹ Instituto de Geología Aplicada, Escuela Universitaria Politécnica de Almadén, Universidad de Castilla-La Mancha, Plaza Manuel Meca, Ciudad Real, 13400 Almadén, Spain

² Escuela Técnica Superior de Ingenieros Agrónomos de Ciudad Real, Universidad de Castilla-La Mancha, Ronda de Calatrava 7, 13071 Ciudad Real, Spain

³ BRGM, 3 Av. Claude Guillemin, 45060 Orléans, France

⁴ Departamento de Mineralogía y Petrología, Facultad de Ciencias Geológicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

⁵ CNRS, BRGM, ISTO, UMR 7327, Université d'Orléans, 45071 Orléans, France

Antimony concentration in water compartments of mining environments, i.e. porewater, groundwater and surface water, ranges from a few micrograms per liter to more than $10 \mu\text{g L}^{-1}$ (Ashley et al. 2003; Casiot et al. 2007; Filella et al. 2009; Fawcett et al. 2015; Cidu et al. 2018; Radková et al. 2020). In most cases, Sb(V) is the main Sb chemical species detected in solution (Casiot et al. 2007; Fawcett et al. 2015; Cidu et al. 2015), suggesting that the oxidation state is a major driver of Sb mobility. From a geochemical point of view, environmental behaviour of Sb depends on its speciation, redox conditions, pH and the presence of major and trace elements, as Sb can be integrated in a large range of secondary minerals (Roper et al. 2012; Herath et al. 2017). Climatic conditions and mineralogy influence the biogeochemical Sb transfer and soil enzymatic parameters in mining environments (Gallego et al. 2021; Esbrí et al. 2022). Meanwhile, the microbial communities naturally present in most environments may influence Sb mobility through several indirect or direct processes.

Aerobic dissolution of Sb sulphides by S- and Fe-oxidising bacteria classically involved in acid mine drainage generation has been shown to produce high Sb concentrations in acidic liquors (Torma and Gabra 1977; Hafeez et al. 2017). Conversely, in anoxic zones, where microbial sulphate reduction occurs, Sb might be chemically reduced by dissolved sulphide (Polack et al. 2009), precipitated as Sb_2S_3 (Zhang et al. 2016), or forms mobile thioantimonate complexes (Ye et al. 2019). Direct transformations of Sb species by microorganisms include Sb(III) oxidation, Sb(V) reduction and methylation. More than 60 bacterial strains, belonging to 27 genera, presented the ability to enzymatically oxidise Sb(III) into Sb(V) (Deng et al. 2021). They may contribute to increasing the mobility of Sb from solid phases to water, in oxic and neutral pH conditions, as shown by Loni et al. (2020). Anaerobic bioreduction of Sb(V) into Sb(III), involved in respiratory metabolism, has been evidenced with strains of *Sinorhizobium* (Nguyen and Lee 2014), *Desulfuribacillus* (Abin and Hollibaugh 2017), *Dechloromonas* and *Propionivibrio* (Yang et al. 2020) and *Geobacter* (Nguyen et al. 2018; Yamamura et al. 2021). Microbial methylation of Sb has also been shown to occur, particularly in reducing and organic matter-rich environments (Caplette et al. 2021). A few studies have reported microbiologically influenced Sb behaviour in environmental samples. Biotic versus abiotic incubations of sediments impacted by ancient mining activity indicated an effect of the microbial compartment on Sb release (Casiot et al. 2007) that increased in oxygenated conditions and decreased in anoxic conditions. This overview of the state of the art highlights the potential involvement of a large range of microbial processes in either release of Sb from solid phases to water or, conversely, the immobilisation of this toxic element in mineral sinks. However, considering the complexity of Sb geochemical behaviour,

significant gaps still need to be addressed to evaluate the global resulting impact of biogeochemical processes, compared with non-biological mechanisms, in different environmental compartments of mining sites. The objectives of the present study were (1) to compare the mobility of antimony in contrasting surface environments of a mine site, (2) to explore the diversity of microbial communities and metabolisms at the small geographic scale of a mining site and (3) to evaluate the influence of redox conditions on mobility of antimony.

Material and methods

Site description and sampling

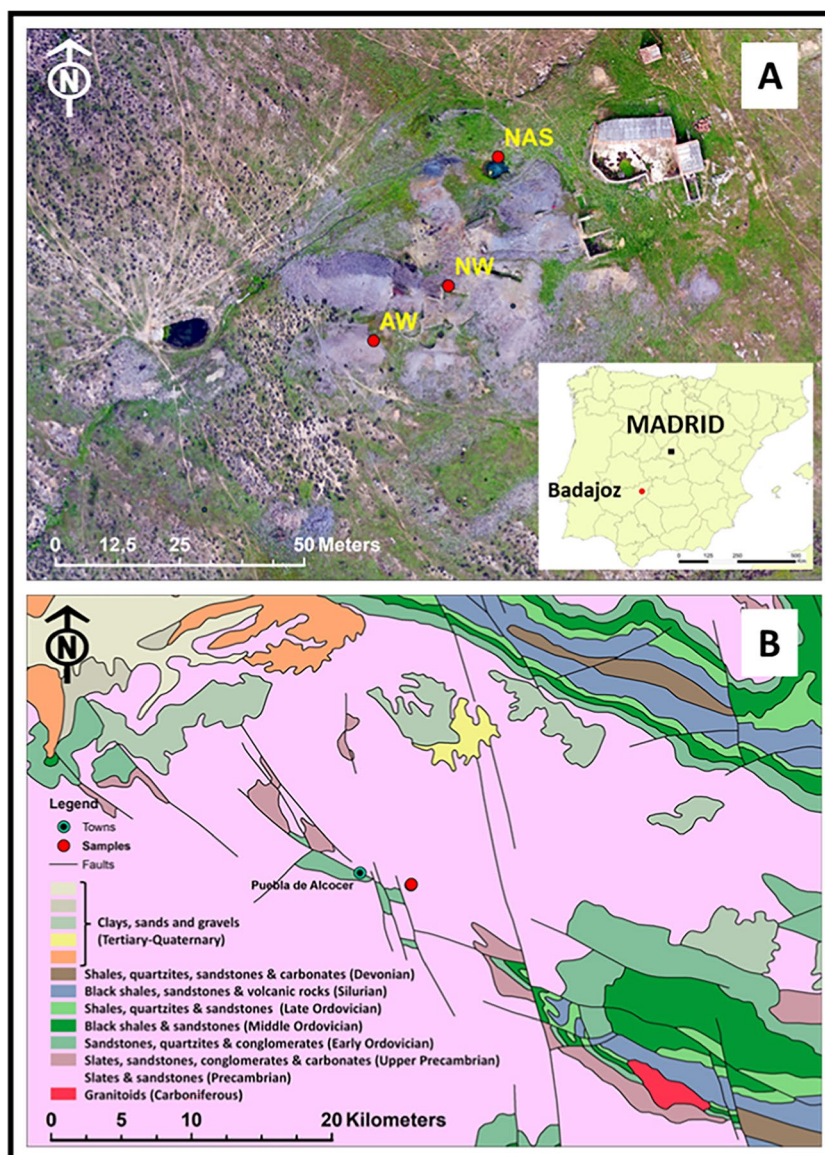
Samples were taken from the abandoned Susana mine, located near La Puebla de Alcocer, Badajoz Province, SW Spain (Fig. 1). Gumiel (1983) described this Sb mineralisation as a small vein-type deposit, exploited through two shallow shafts and galleries, with N 130° E direction, hosted by the Pre-Ordovician “Complejo Esquisto Grauváquico” (Lotze 1956), a monotonous succession of shales/schists and greywackes, where an important number of Sb mineralisations are present (Gumiel and Arribas 1987). The mine ceased exploitation in 1986 (Lorenzo 2015). The area lacks any remediation measures and presents abandoned mine waste dumps. These wastes are very heterogeneous in grain size, with frequent debris containing Sb_2S_3 , the only ore mineral recognised in mineralisation. There is no evidence of in situ ore processing actions; consequently, the wastes correspond exclusively to non-processed materials.

From a climatic point of view, the area corresponds to the BSk Köppen climate (cold semi-arid), which implies a dry area with low precipitation and extreme temperature conditions, particularly during winter. These conditions also imply a low degree of pedogenesis, and very poor vegetal cover, constituted by poor pastures and scattered presence of *Retama sphaerocarpa* bushes and the very occasional presence of acorn trees (*Quercus rotundifolia*).

Different constituents of the local landscape around the mine were sampled. Two samples were taken from a mine waste dump, including acidic pH waste (AW) and neutral pH waste (NW). The third sample corresponded to a sediment (neutral pH aquatic sediment (NAS)) taken from a small, flooded area, some $1 \text{ m} \times 1 \text{ m} \times 1 \text{ m}$ in size, in which reducing conditions were suggested by a black substrate highly enriched in organic matter, supporting an active population of tadpoles when the sampling was performed.

All samples were taken using plastic spoons, after homogenisation of the profile (0–15 cm deep) with a clean geologist's hammer and placed in plastic bags for transportation to the laboratory. Samples were air-dried at ambient

Fig. 1 Presentation of the site, its location (A) and geological context (B)



temperature for 14 days, sieved to remove the < 2 mm fraction and split to obtain three subsamples: one to be stored, one for physicochemical determinations and a last subsample to be milled for analyses. Non-dried samples were kept at 5°C in closed bags for incubation experiments. The respective pH values of these samples, measured 10% slurry of material in model rainwater after 1 h of contact, were 3.91 for AW, 6.40 for NW and 5.51 for NAS.

Microcosms

Four types of microcosms were used: biotic and sterilised (St) in aerobic and anaerobic conditions. To establish the biotic microcosms, fresh samples (equivalent to 20 g dry weight) were mixed in sterile 500-mL glass bottles with 200 mL of sterilised Mont Roucou mineral water

(composition close to rainwater, $\text{pH} = 6.38$, $\text{EC} = 160 \mu\text{S cm}^{-1}$, $\text{Cl}^{-} = 56 \mu\text{M}$, $\text{NO}_3^{-} = 24 \mu\text{M}$, $\text{SO}_4^{2-} = 16 \mu\text{M}$, $\text{Na}^{+} = 109 \mu\text{M}$, $\text{K}^{+} = 7.7 \mu\text{M}$, $\text{Ca}^{2+} = 25 \mu\text{M}$, $\text{Mg}^{2+} = 21 \mu\text{M}$) and covered with cotton plugs (oxic (Ox) conditions) or rubber stoppers (anoxic (AOx) conditions). To create conditions with strongly attenuated microbial activities, bottles were prepared according to the same protocol with St materials. At the beginning of the experiment and every week, $20 \mu\text{L}$ of formaldehyde was added to each St flask to prevent the growth of the microorganisms that were not killed by autoclaving. All conditions were tested in triplicates, except the NAS St conditions, that were prepared in duplicates, due to the limitation of the quantity of material. In anoxic conditions, oxygen was purged from the microcosms with sterile N_2 for 20 min and pressurised with sterile H_2 (1 bar over atmospheric

pressure). All microcosms were incubated for 41 days at 20 °C with rotational shaking (100 rpm) in the dark to prevent photo-induced oxidation of metals. Every week, samples were taken from the bottles and the water that evaporated in oxic conditions was compensated by adding sterile deionised water. For anoxic microcosms, sampling was conducted under strictly anaerobic conditions in an oxygen-free glove box and H_2 pressure was renewed after each sampling event.

Mineralogical and chemical analyses

Mineralogy

Preliminary analysis of the elemental composition of the initial materials was carried out by means of energy-dispersive X-ray fluorescence spectrometry (EDXRF), on milled samples, using an Epsilon 1 (from Malvern Panalytical Ltd., Malvern, UK). Mineralogical characterisation was performed using X-ray diffractometry using a Bruker D8 Advance A25 (Bruker Corp., Billerica, MA, USA) in a 15min work program, on ground and pressed samples. Interpretation was carried out with Match! software for phase analysis using powder diffraction data. Interpretation of diffractograms focused on the identification of the presence of quartz, Fe oxides and mineral phases containing Sb.

For incubation experiments, subsamples of each material were subjected to autoclaving under N_2 atmosphere, three successive times at 120 °C for 20 min, at 24 h intervals, in order to strongly attenuate microbial activity. This treatment did not kill 100% of the microorganisms; however, by convention, the corresponding conditions are thereafter labelled as “St” for “Sterilized”. In order to determine different mineral phases bearing Sb in soil samples and to search for possible differences between autoclaved and non-autoclaved materials, 6 samples (3 autoclaved and 3 non-autoclaved) were analysed using SEM–EDS. The 6 soil samples were compressed using a hydraulic press (10 tons), each sample containing between 70 and 110 g of material. The resulting samples were put into resin and thinly polished in order to be analysed using a Zeiss Merlin Compact Scanning Electron Microscope (SEM, Carl Zeiss Microscopy Deutschland GmbH, Germany). The SEM was operated at 15 kV, and it was provided with an EDXRF spectrum analyser (EDS, Bruker QUANTAX XFlash; 6–30 mm² resolution, 129 eV) and a Bruker (Bruker Corp., Billerica, MA, USA) micro-XRF spectrometer (XTrace-Tube Rh-filters Al, Ti, Ni). The results were analysed using Esprit software 1.9.4.3351 (EdsMrg 1.4.0.38 SmartPI version: V02.01 SP2 SmartSEM 5.6).

Chemical composition of initial solids

Multielemental characterisation of initial materials, including total sulphur, was carried out by EDXRF, using a Bruker S2 Ranger (Bruker Corp., Billerica, MA, USA) with a Pd detector with 10 g of ground and pressed samples. Total organic carbon (TOC) and humic and fulvic acids were analysed according to the protocol described by Schnitzer (1983). For the determination of the TOC, 10 g of soil was added to 50 mL of extractant solution (44.6 g of 0.1 M pyrophosphate and 4 g of NaOH in a total volume of 1 L). Samples were shaken for 2 h and centrifuged for 15 min at 800 g. After that, 0.098 g of $K_2Cr_2O_7$ was added to 1 mL of the supernatant of the samples; then, 4 mL of concentrated H_2SO_4 was added and heated using a Stuart SBH 200D/3 digester at 150 °C for 30 min. After 12 h, 5 mL of ultrapure H_2O was added, finally obtaining the result using a Spectronic Unicam Helios Epsilon spectrophotometer at a wavelength of 590 nm. For the determination of humic and fulvic acids, 10 mL of the extract was taken and acidified with 0.2 mL of H_2SO_4 . The samples were centrifuged for 15 min at 1000 g. The resulting supernatant represents fulvic acids. Ten millilitres of 0.5 M NaOH was added to the resulting precipitate (humic acids). After stirring, 0.098 g of $K_2Cr_2O_7$ was added to 1 mL of the supernatant of the samples, and 4 mL of concentrated H_2SO_4 was added and heated using a Stuart SBH 200D/3 digester at 150 °C for 30 min. After 12 h, 5 mL of ultrapure H_2O was added, and the solution was analysed at 590 nm using a Spectronic Unicam Helios Epsilon spectrophotometer (Profcontrol.de, Schönwalde-Glien, Germany).

Geochemical mobility

Evaluation of geochemical Sb mobility in the initial materials was performed through the following steps. The leachable fraction was evaluated using the modified geological survey field leach test (Hageman 2007): 5 g of soil was mixed with 100 mL of deionised water shaken at 50 rpm for 2 h in a water bath. The supernatant was filtered through 0.45 µm PTFE filters. The available fraction was studied by means of $AcNH_4$ selective extraction: 5 g of soil was mixed with 100 mL of 1 M $AcNH_4$ solution at pH 7, shaken at 50 rpm for 2 h in a shaking water bath. The supernatant was filtered through a 0.45-µm PTFE filter. Modified European Community Bureau of Reference, now the Standards Measurement and Testing Programme (BCR) sequential extraction was carried out according to Quevauviller et al. (1997) in order to obtain data about fractionation of Sb and related elements. This sequential extraction procedure provides information about four fractions: fraction 1 (F1), extracted by a solution of 0.11 M acetic acid, releases the species that are soluble in water, easily leached by weak acids and associated

with soluble carbonates; fraction 2 (F2), extracted by 0.5 M hydroxylamine hydrochloride, consists of easily reducible species associated with Fe and Mn oxyhydroxides; fraction 3 (F3), extracted by 8.8 M hydrogen peroxide and 1 M ammonium acetate solutions, consists in easily oxidisable compounds, mainly associated with organic matter and sulphide minerals; and the residual fraction (RF) was determined by calculating the difference between pseudo-total and mobile fractions. A suitable certified reference material (BCR 701) was used to evaluate Pb recovery (between 95 and 98%). Extractions were filtered using Whatman filters (8 µm). The analysis of Sb, Pb, As, Fe, Mn and Cu in all solutions was performed by high-resolution atomic absorption spectrometry (HR-AAS), using an Analytik Jena contrAA-800D (Analytik Jena AG, Jena, Thuringia, Germany).

Characterisation of water samples

At the beginning of the microcosm experiment and every week, one aliquot of the supernatant was sampled and pH, oxidation–reduction potential (ORP), electric conductivity (EC), Fe(II)/Fe(III) and Sb content were analysed. Additionally, Pb and As contents were determined at the beginning, mid-time and end of the experiment. The pH, EC and ORP parameters were measured immediately in the suspensions using a Consort C3040 apparatus equipped with pH, ORP and EC electrodes. Supernatants were centrifuged at 10,000 g and filtered at 0.45 µm. For dissolved Fe speciation and quantification, a 1.5 mL aliquot was immediately acidified with concentrated HCl. Dissolved Fe(II) was measured using the *ortho*-phenanthroline colorimetric method (Murti et al. 1966; Mamindy-Pajany et al. 2013). For this, 0.5 mL of acetate buffer with pH 4.5, 0.1 mL of 0.5% *ortho*-phenanthroline and 0.9 mL of the filtered sample were added to a spectrophotometer cuvette. The mixture was left at room temperature for 15 min in the dark, and the absorbance was recorded at 510 nm using a UV–vis spectrophotometer. The total dissolved Fe concentration was determined using the same protocol but with the addition of 0.1 mL of 1% hydroquinone prepared in acetate buffer with pH 4.5. Samples for HR-AAS were immediately acidified with 1% of concentrated HNO₃. Concentrations of As, Sb and Pb were quantified by HR-AAS using a contrAA-800 equipment (Analytik Jena, Germany) equipped with a xenon short-arc lamp and using the flame technique. All calibration standard solutions were prepared using 1 g L⁻¹ primary certified standard solutions (Inorganic Ventures).

Speciation of Sb was determined at the end of incubation with the method described by Nguyen and Lee (2015) according to Yu et al. (2002). Samples were diluted in ultrapure water in order to reach a concentration lower than 250 µg L⁻¹. In glass tubes, 1 mL of the sample was mixed with 3.5 mL of ultrapure water and 1 mL of 1% pyrrolidine

dithiocarbamate solution. After 10 min of reaction, the mixture was transferred to an Agilent SampliQ C18ODS (6 mL) solid-phase extraction cartridge, previously conditioned with 1 mL analytical grade methanol then 1 mL ultrapure water and placed above a collection tube. The cartridge was rapidly rinsed with 5 mL of ultrapure water, and Sb(III) was retained in the cartridge. Sb was quantified by oven atomic absorption spectrometry (Varian) in the collection tube that received Sb(V) from the initial sample. The difference between total Sb and Sb(V) was considered to represent Sb(III).

Microbial parameters of microcosms

Microbial growth and viability

The viability of microorganisms in each flask was determined at the beginning, mid-time and end of the incubation process, using a LIVE/DEAD® BacLight Bacterial Viability Kit (Molecular Probes 2004) to stain the bacteria fixed by filtration of 100 µL of incubated slurries diluted in 1 mL of sterile physiological water on GE Whatman™ Nuclepore polycarbonate membrane. Filters were observed under UV light using a Zeiss Imager Z1 optical microscope (DSRED and FITC filters). Twelve images were taken in randomly chosen areas of each filter. Determination of live and dead cells was conducted by counting the number of green (live) and red (dead) points. Points were counted using a recorded macro in ImageJ (National Institutes of Health, USA).

Extraction and quantification of soil DNA

DNA extractions were performed on initial soils and pellets obtained at the middle and end of the experiment after centrifuging the samples at 10,000 g. Pellets of triplicate microcosms were pooled before DNA extraction. Exclusively for the biotic AW in AOx conditions, DNA extraction and 16S fragment sequencing was also performed on individual replicates, because results in terms of Sb concentration strongly differed between these replicates. We used the FastPrep DNA Spin Kit for soil (MP Biomedicals) following the manufacturer's instructions. Total extracted DNA was quantified using a Quantus Fluorometer (Promega) and stored at –20 °C until the next analysis.

16S ribosomal RNA (rRNA) amplification and next-generation sequencing

Bacterial and archaeal diversity was determined by 16S rRNA gene metabarcoding, generated by INRAE Transfert (Narbonne, France). The V4–V5 hypervariable region of the 16S rRNA gene was amplified using the barcoded, universal primer set 515WF/918WR (Wang et al. 2009). PCRs

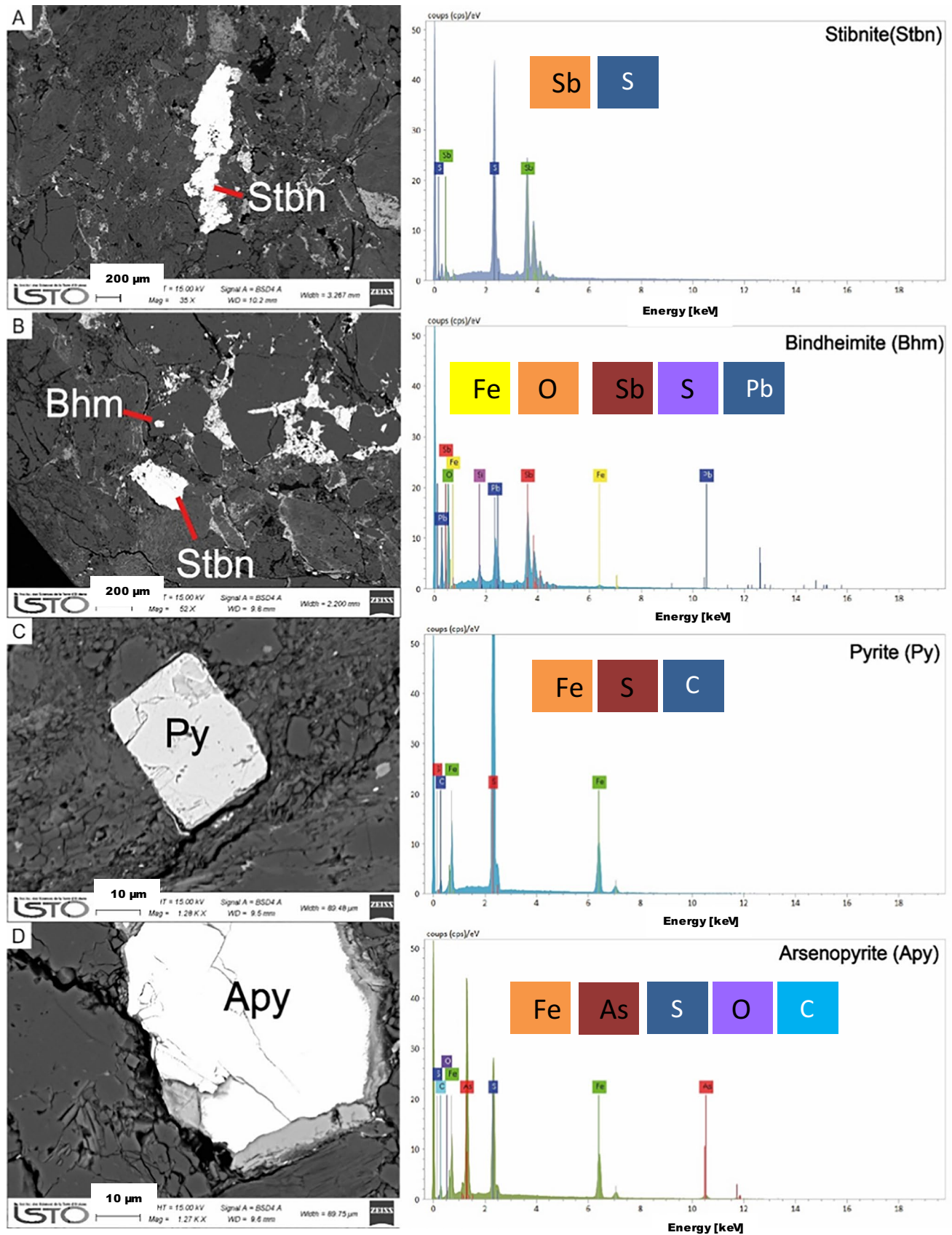


Fig. 2 SEM-EDS observations coupled with μ XRF. Main mineral phases found in the studied samples. **A** AW, stibnite (Stbn); **B** AW St, bindheimite (Bhm, product of the alteration of jamesonite); **C** NW, pyrite (Py); **D** NW St, arsenopyrite (Apy). For more information about mineral phases in each studied sample, see Table S1

were performed using AccuStart II PCR ToughMix kit and cleaned (HighPrep PCR beads, MokaScience). Forward and reverse primers contained the adapter sequences (5'GTG YCAGCMGCCGCGGTA) and (3'ACTYAAAKGAATTG RCGGGG), respectively, used in Illumina sequencing technology. The amplicons were sequenced using an Illumina MiSeq at the GeT-PlaGe platform (Auzeville, France).

Processing of sequencing

The datasets from MiSeq sequencing were processed using the FROGS (Find, Rapidly, OTUs with Galaxy Solution) bioinformatics pipeline (Escudié et al. 2018). FastQ paired reads were merged with VSearch software and clustered into operational taxonomic units (OTUs) with Swarm and an aggregation distance clustering of 1. Chimera and OTU with a proportion less than 0.0005% of all sequences were removed. Taxonomic affiliation was performed using BLAST and the Silva 138.1 database for 16S rRNA gene sequences. The raw datasets can be found on the European Nucleotide Archive system under project accession number ENA PRJEB64667. InvSimpson diversity indexes were calculated based on the Illumina sequence data.

Statistics

Data about the evolution of soil microcosms were tested for homogeneity of variance and normal distribution. In this way, analysis of variance (ANOVA) was carried out using SPSS version 21.0 followed by a Tukey test between means of treatments to determine the significant difference ($P \leq 0.05$).

Redundancy analysis (RDA), using the vegan R package, was performed to identify the effects of environmental variables on bacterial phylum structure, based on the relative abundance of the detected OTUs in pellets at t0, t21 and t41 days. This analysis was calculated based on a Hellinger-transformed phylum abundance basis of 16S rRNA data (Borcard et al. 2011). Non-metric multidimensional scaling (NMDS) of weighted UniFrac distance matrices of microbial beta-diversity between samples was plotted. PERMANOVA was performed to compare the distribution of groups AW, NW and NAS. Environmental explanatory tested variables were standardised, and the function ordiR2step in the vegan package was used to identify the significant environmental explanatory variables. The significance of the RDA model was tested by ANOVA based on the Monte Carlo test with

999 permutations. This analysis helps to determine the most influential factors and the extent to which different environmental parameters affected the bacterial phylum.

Results

Characterisation of solids

Mineralogy

The major Sb phases identified by XRD in rock samples from the site included stibnite (SbS_3) as the primary phase and stibiconite ($\text{Sb}^{3+}(\text{Sb}^{5+})_2\text{O}_6(\text{OH})$) as the oxidised phase. However, in the soil and sediment samples used in this study, XRD analyses revealed only an oxidised phase of Sb and As, stenhuggarite $\text{CaFeSb}(\text{AsO}_3)_2\text{O}$ (5.3% in the NAS sample), in addition to quartz as the majority phase (95–99%) and Fe and Mn oxides (5.6% in the AW sample).

According to the SEM-EDS observations (Fig. 2 and Table S1), the most frequently observed Sb-bearing mineral phases are stibnite (in all samples) and Sb oxides, including cervantite ($\text{Sb}^{3+}\text{Sb}^{5+}\text{O}_4$), bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$) and other Sb oxides that would need further studies to be more precisely determined. Jamesonite ($\text{Pb}_4\text{FeSb}_6\text{S}$) is also present in lesser quantities. Besides these Sb-containing minerals, other important minerals present in both St and non-St samples include quartz, rutile, Fe oxides (hematite), arsenopyrite and monazite. Regarding Sb-bearing minerals, no significant difference was found between St and non-St samples through these qualitative analyses. Nevertheless, a detailed quantitative study of the Sb oxides might lead to some important differentiation.

Chemical composition

All samples are siliceous, with variable contents of Fe (4.6–16.5%), Sb (1.02–4.41%) and As (0.09–0.22%), as shown in Table 1. The NAS sample clearly differs from the other samples, especially in terms of higher concentrations of Fe, As and TOC (Table 1) and P, Mn, Cr and Ca (Table S2).

Geochemical mobility of Sb

A clear differentiation was found in the fractionation between different samples and different considered elements. The first noteworthy finding is the overwhelming proportion of Sb in the residual phase in all samples, although the proportion of Sb in more available phases is very slightly higher than that in the NAS sample (Fig. S1). This is confirmed by the negligible proportion of Sb extracted in a leaching test, or even extracted with AcNH_4 (Fig. S1A).

Table 1 Characteristics of initial materials

	AW	NW	NAS
Fe	4.61	4.67	16.49
Sb	4.41	1.02	1.08
S	0.53	0.13	1.11
As	0.22	0.09	0.98
TOC	2.35	2.43	9.59
Humic acid	0.89 (37.8%)*	1.29 (53.1%)*	2.65 (27.6%)*
Fulvic acid	1.46 (62.1%)*	1.14 (46.9%)*	6.94 (72.3%)*

All data are expressed in %

*Percent of TOC

The fraction extracted with AcNH_4 tends to be higher in the AW sample than in the NAS sample. With the BCR protocol, Fe is extracted in higher proportions (more than 40%) in the soluble/available fractions (Fig. S1B) only in the NAS sample, with the highest values corresponding to the F2 fraction linked to Fe and Mn oxides. However, the low proportion of extracted Sb in F2 suggests that most of the Sb is not associated with oxides in the NAS sample. Iron is only present in very small proportions as oxides in the NW and AW samples.

Microcosms

Evolution of physicochemical parameters

In the AW microcosms, oxidising conditions with microbial growth produced a strong release of Sb ($\approx 495\%$ of the initial concentration, Fig. 3A). However, under anoxic conditions, the three replicates in biotic conditions behaved differently (Fig. 3B): Sb was released more in solution than in the St condition for replicate A, but immobilised between days 6 and 15 in replicate B and immobilised from the beginning of incubation in replicate C. In all replicates, a late release of Sb into water was observed during the last week of incubation. Few changes were observed in the St microcosms. On the other hand, in NW microcosms (Fig. 3C), a release of Sb was observed in all cases (452% Ox, 283% Ox St, 353% AOx St), although it was much less pronounced in the AOx microcosm (92%). Regarding NAS microcosms (Fig. 3D), a release was observed in all cases; however, it was much stronger in the St microcosms than in the biotic microcosms for both Ox and AOx conditions (58% Ox, 122% Ox St, 131% AOx, 152% AOx St). More precisely, in oxic conditions, Sb was released more in biotic than in St conditions during the first week, then the Sb concentration decreased sharply between days 6 and 13. Arsenic had a more homogeneous behaviour within the three studied materials (AW, NW and NAS, Table 1 and Fig. S2). In all cases, the microcosm under anoxic conditions and with microorganisms

produced a release of the metalloid, while in the rest of the microcosms, the release was lower. No release of Fe(III) was observed in any of the microcosms (data not shown). However, under anoxic and biotic conditions, an increase in the content of soluble Fe(II) could be observed mainly with AW and a few with NW, while in the rest of the microcosms, it remained almost unchanged (Fig. 3E, F).

AW microcosms showed lower pH as compared to the other two soil types (NW and NAS, Fig. S3). In the AW microcosm with microorganisms, the pH decreased in Ox conditions and increased in AOx conditions, whereas no change of pH was observed in abiotic conditions. With NW, pH increased in AOx conditions while no major pH change was observed in the other conditions. Similar behaviour was observed in NAS, where an increase in pH was observed only under AOx conditions with microorganisms. The ORP evolved similarly for all materials (AW, NW and NAS, Fig. S4): it reached values of around 200–300 mV (Ref. Ag/AgCl) in microcosms under Ox conditions, while in AOx conditions, it decreased down to -300 mV, with no clear influence of living microbes in any condition. The monitoring of EC showed differences between the studied microcosms (Fig. S5). A very strong increase of EC was observed in AW and NAS incubated in Ox conditions with microorganisms (400% and 162%, AW and NAS, respectively), whereas with NAS, EC tended to decrease in biotic AOx microcosms. In the NW microcosm, there was only a slight increase over the weeks in all conditions.

The final speciation of Sb in the water phase (Table 2) showed the dominance of Sb(V) in all conditions, except in the biotic AOx incubations of NW, in which Sb(V) represented only 20 to 30% of total Sb.

Evolution of the microbial compartment

The cell density increased in all incubation conditions (Fig. 4), the highest cell concentrations being found in the NAS. This result was in accordance with the DNA quantification data (Table S3). For AW microcosms, the AOx conditions gave the highest abundance of live cells; however, in NW, there was a similar abundance of living cells in Ox and AOx, and in NAS, more living cells were found in Ox at the end of incubation (Fig. 4A–C). Considering dead cells, their abundance in AW was similar between Ox and AOx conditions; however, in NW and NAS materials, dead cells were more abundant under AOx conditions (Fig. 4D–F). Cells (live and dead) were observed in St conditions; however, low DNA concentrations confirmed that growth in the presence of St materials was limited.

A total of 382,567 sequences of 16S rRNA gene were obtained from the 21 samples. The highest richness (number of OTUs) was observed in the NAS (Fig. S6). It ranged from 657 OTUs in the soil at the beginning of experiment

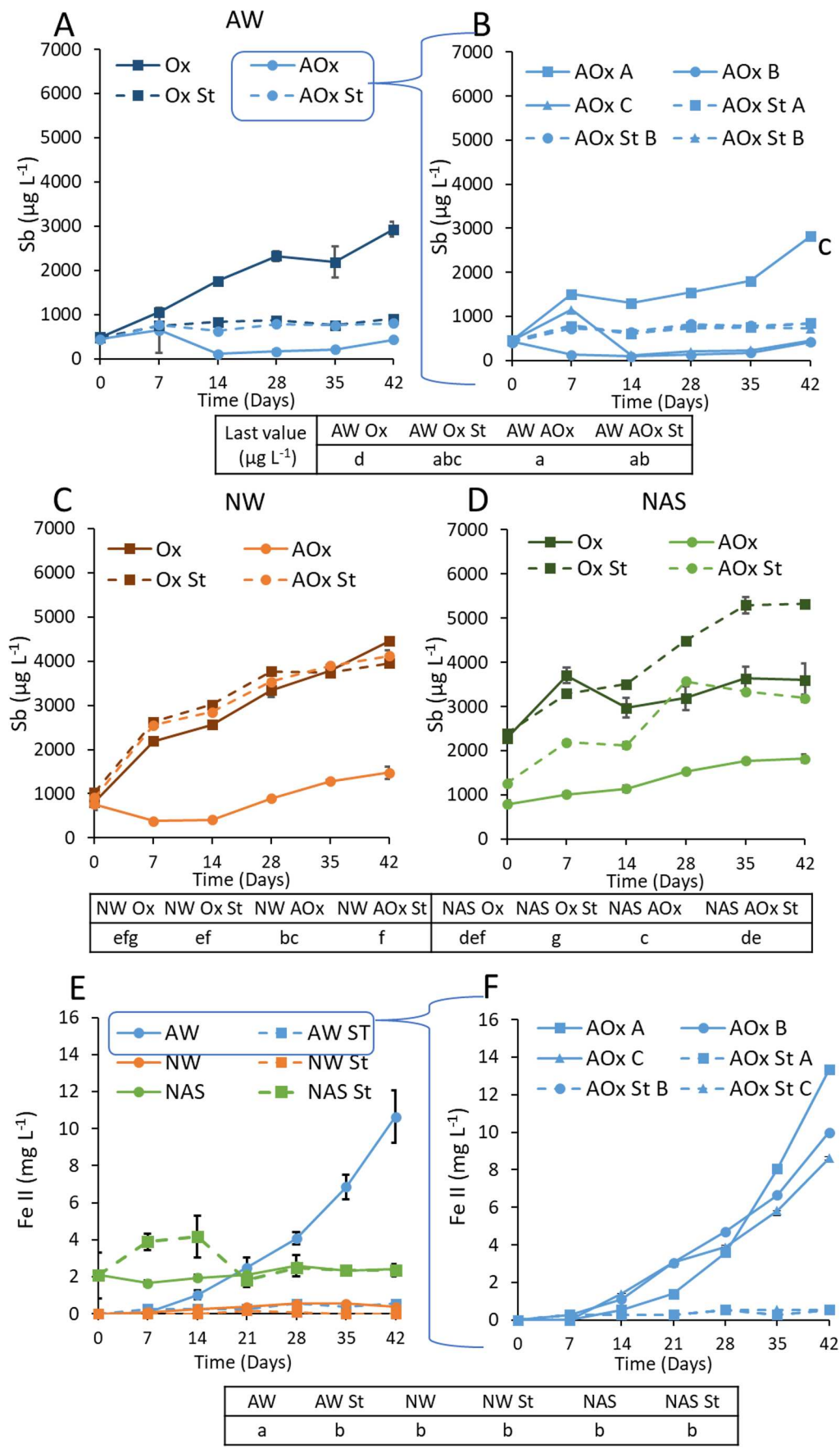


Fig. 3 Evolution of Sb concentration in the liquid phase of acidic pH waste (AW, **A**), individual values for each AW microcosm (**B**), neutral pH waste (NW, **C**) and neutral pH aquatic sediment (NAS, **D**) microcosms. Ox, oxic–biotic conditions; Ox St, oxic–abiotic conditions; AOx, anoxic–biotic conditions; AOx St, anoxic–abiotic conditions. Evolution of Fe(II) concentration in reducing conditions of AW, NW and neutral pH aquatic sediment (**E**) microcosms. Individual values for each AW microcosm (**F**). Except in **B** and **F**, values show the mean of three replicates $\pm$ SE. Values with the same lowercase letters are not significantly different at $P \leq 0.05$ (ANOVA, Tukey test). The Fe(II) concentration did not vary under oxidising conditions

(t0) to 570 OTUs in the Ox condition after 42 days. In NW, 514 OTUs were observed at t0. This sample shows the greatest difference between the Ox and AOx conditions:

after 21 days, in AOx conditions, the richness decreased to 321 OTUs before increasing to 508 OTUs at the end. The lowest richness was observed in AW with a number of OTUs between 300 and 400. OTUs were observed in St conditions: with AW and NAS, few OTUs were present at the end of the St experiment; however, in NW, about 400 OTUs were observed in both St conditions. The diversity based on the InvSimpson index decreased in all conditions between 0 and 21 days, except for NW Ox and AW Ox conditions (Fig. S6A). Between 21 and 42 days, the diversity increased in NW Ox and NAS AOx and decreased in AW Ox. At the end of the experiment, diversity was higher in the Ox condition than in the AOx condition for AW and NAS, but higher in the AOx than in the Ox condition for

Table 2 Speciation of Sb, total Sb and total As in the water phase at the end of the incubation experiment (day 42)

Condition	Replicates	Total Sb ($\mu\text{g L}^{-1}$)	Sb(V) ($\mu\text{g L}^{-1}$)	Sb(V) (%)	Total As ($\mu\text{g L}^{-1}$)
AW Ox	A	2231	2030	91	208
	B	2657	2475	93	217
	C	2693	2253	84	240
AW Ox St	A	1316	1205	92	256
	B	887	768	87	265
	C	1507	1368	91	304
AW AOx	A	3516	3318	94	1337
	B	664	559	84	2955
	C	576	353	61	2963
AW AOx St	A	1049	819	78	360
	B	992	816	82	322
	C	943	752	80	249
NW Ox	A	4596	3981	87	908
	B	4898	4175	85	850
	C	5320	4847	91	892
NW Ox St	A	4030	3691	92	650
	B	3950	3547	90	839
	C	3534	3216	91	854
NW AOx	A	2039	629	31	9764
	B	2199	649	30	10,540
	C	2184	440	20	10,676
NW AOx St	A	4250	3696	87	1146
	B	4552	3960	87	1109
	C	4370	3985	91	1069
NAS Ox	A	3200	3059	96	118
	B	3758	3564	95	116
	C	2652	2424	91	95
NAS Ox St	A	5516	5108	93	1250
	B	4474	4083	91	1764
NAS AOx	A	2021	1453	72	15,045
	B	1808	1539	85	14,986
	C	2155	1482	69	15,515
NAS AOx St	A	3756	3356	89	2285
	B	2816	2561	91	2216

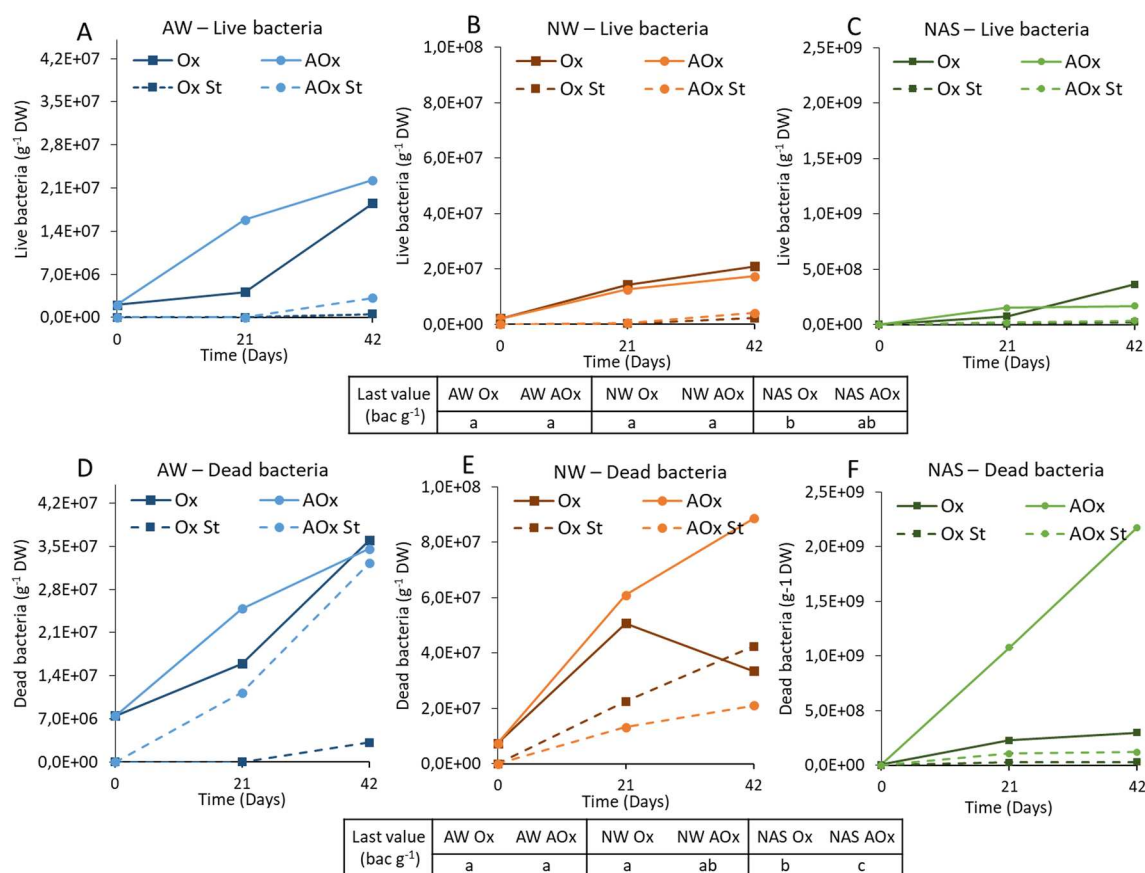


Fig. 4 Evolution of the abundance of live and dead cells (cells g⁻¹ of solid dry weight) in acidic waste (AW, **A** & **D**), neutral waste (NW, **B** & **E**) and neutral aquatic sediment (NAS, **C** & **F**) microcosms. Ox, oxic–biotic conditions; Ox St, oxic–abiotic conditions; AOx, anoxic–

biotic conditions; AOx St, anoxic–abiotic conditions. Values show the mean of three replicates $\pm$ SE. Values with the same lowercase letters are not significantly different at $P \leq 0.05$ (ANOVA, Tukey test)

NAS. Diversity in the St conditions was very low, except for the NAS condition, where it was close to the biotic condition. The NMDS plot of weighted UniFrac distance matrices of microbial beta-diversity between samples (Fig. S6B) shows a clear separation between not St incubated materials. However, no effect of incubation time or condition (AOx versus Ox) on beta-diversity is revealed by this statistical treatment. The relative abundance of the major bacterial and archaeal phyla is shown in Fig. 5. AW was characterised by a predominance of Chloroflexi. Ox conditions favoured the development of Proteobacteria, Bacteroidota, Planctomycetota, Cyanobacteria and WPS-2, while AOx conditions promoted the development of Firmicutes (which became the main phylum) and Acidobacteria. NW was dominated by five phyla: Proteobacteria, Actinobacteriota, Acidobacteriota, Bacteroidota and Crenarchaeota. Ox conditions enhanced the development of Proteobacteria and Bacteroidota, whereas Firmicutes, Desulfobacterota and Myxococcota emerged in AOx conditions. Quite similar compositions at the phylum level were observed in NW and NAS; however, three phyla were

important in this sediment: Desulfobacterota, Myxococcota and Halobacterota. As observed in NW, Proteobacteria and Bacteroidota abundance increased in NAS microcosms with Ox conditions, but a decrease in abundance of Firmicutes, Desulfobacterota and Halobacterota was also observed. In AOx conditions, the NAS phylum composition was very similar during the experiment with no major variations. The main phyla observed in AW and NAS St conditions were Proteobacteria and Actinobacteria, while Firmicutes, Acidobacteriota and Bacteroidota were also observed in proportions greater than 5% in NW.

With the aim of identifying the influence on the microbial community structure of the physicochemical characteristics of the sampled water, an RDA was built (Fig. 6). This model was significant ($R_{adj}^2 = 0.21$, $P = 0.007$). The measured environmental variables (pH, ORP, total dissolved Sb, As and Fe concentrations) explain 40.1% of the variation in the composition of microbial communities at the phylum level. The ordiR2step function indicates that pH and ORP were explanatory variables that significantly influenced the community structure at the phylum level (Table S4). The lowest

Fig. 5 Relative abundance of the major bacterial and archaeal phyla in soils and samples from acidic pH waste (AW), neutral pH waste (NW) and neutral pH aquatic sediment (NAS) microcosms. Ox, oxic–biotic conditions; Ox St, autoclaved oxic–abiotic conditions; AOx, anoxic–biotic conditions; AOx St, autoclaved anoxic–abiotic conditions

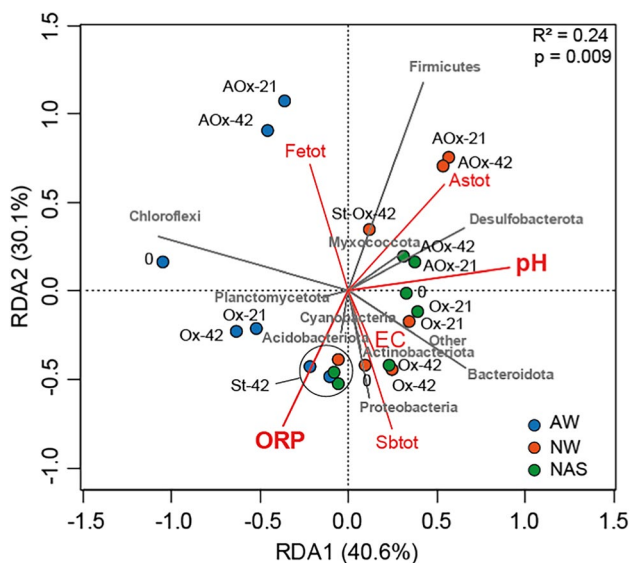
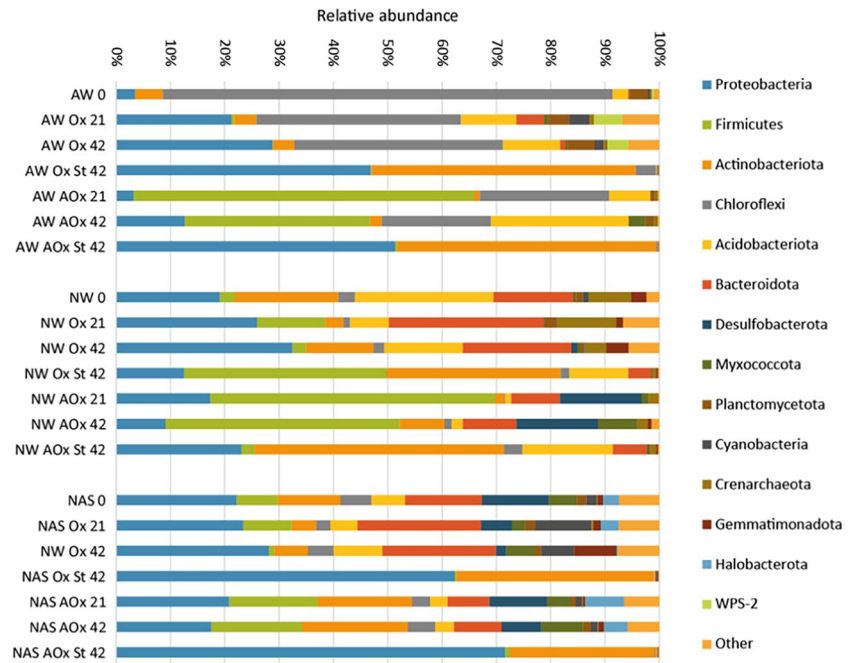


Fig. 6 RDA of sequence abundances assigned at the phylum level of bacterial and archaeal communities in soils and microcosm samples in relation to environmental variables. Red lines represent the environmental variables (significant variables in bold obtained with ordiR2step function), grey lines represent the phyla and circles represent the samples (AW in blue, NW in red and NAS in green). Ox, oxic–biotic conditions; Ox St, autoclaved oxic–abiotic conditions; AOx, anoxic–biotic conditions; AOx St, autoclaved anoxic–abiotic conditions

pH favoured the presence of Chloroflexi, whereas high pH seemed to induce higher proportions of Desulfobacterota and Bacteroidota. Low ORP, in AOx conditions, favoured

the development of Firmicutes. The St conditions had the same community structure, regardless of their conditions, except for the NW Ox condition.

Some of the OTUs identified at the genus level correspond to the genera that were shown to be involved in the metabolisms of Sb, S or Fe (Table 3). Their proportion in the total number of sequences for each sample, grouped by common metabolism, strongly varied between conditions (Fig. 7). With the AW, these metabolic groups represented a very low proportion of the sequences in oxic conditions, whereas in anoxic conditions, Sb(III)-oxidising, sulphate-reducing bacteria (SRB) and Fe(III)-reducing groups emerged during incubation. At the end of the experiment (day 41), the two replicates (AOx B and AOx C), in which Sb was immobilised, counted more Fe(III)-reducing bacteria and SRB and fewer genera including Sb(III)-oxidising strains than the replicate AOx A, in which Sb mobility was higher. This result could be linked to the higher proportion of Sb(V) in AOx A than in AOx B and AOx C (Table 2). With the NW, a high proportion of the Sb(III)-oxidising group was observed in oxic conditions, particularly in the St conditions, linked to the high proportion of sequences affiliated to the genera *Bacillus* and *Novosphingobium* in these samples (Table S5). However, this might not lead to any biogeochemical interpretation, as biomass was very low in the St conditions (Table S3). In anoxic conditions, NW was enriched in Sb(V)-reducing and Fe(III)-reducing metabolic groups, with a major contribution of *Geobacter* in these two groups (Table S5). Sulphate reducers also emerged in the NW biotic AOx incubation,

Table 3 List of genera including strains with known metabolisms related to the biogeochemical cycles of Sb, S or Fe and detected in Susana sample incubations

Genus	Metabolisms	Detected in	Reference
<i>Cupriavidus</i>	Sb(III)-oxidising	NW: AOx, AOx St	Nguyen and Lee (2015)
<i>Pseudomonas</i>	Sb(III)-oxidising	AW: Ox St NW: Ox, Ox St, AOx, AOx St	Nguyen and Lee (2015)
<i>Bacillus</i>	Sb(III)-oxidising	AW: Ox, Ox St, AOx, AOx St NW: Ox, Ox St, AOx, AOx St, NAS: Ox, AOx	Li et al. (2018)
<i>Bosea</i>	Sb(III)-oxidising	NW: Ox, Ox St, AOx, AOx St	Xiang et al. (2022)
<i>Acidithiobacillus</i>	Sb(III)-oxidising	AW: Ox St, AOx, AOx St	Nguyen and Lee (2015)
<i>Flavithiobacillus</i>	Sb(III)-oxidising	NAS: Ox, AOx	Han et al. (2016)
<i>Hydrogenophaga</i>	Sb(III)-oxidising	NAS: Ox, AOx	Terry et al. (2015)
<i>Novosphingobium</i>	Sb(III)-oxidising	NW: Ox, Ox St, AOx, AOx St NAS: Ox, AOx, AOx St	Deng et al. (2021)
<i>Thiobacillus</i>	Sb(III)-oxidising S-oxidising	AW: Ox St NW: Ox NAS: Ox, AOx	Deng et al. (2021)
<i>Roseomonas</i>	Sb(III)-oxidising	AW: Ox St NAS: Ox, AOx	Sun et al. (2020)
<i>Geobacter</i>	Sb(V)-reducing Fe(III)-reducing	AW: Ox St NW: Ox, AOx NAS: Ox, AOx	Nguyen et al. (2018)
<i>Thermithiobacillus</i>	S-oxidising	AW: Ox	Yang et al. (2015)
<i>Acidithiobacillus</i>	S-oxidising Fe(II)-oxidising	AW: Ox St, AOx, AOx St NW: AOx St NAS: AOx St	Quatrini and Johnson (2019)
<i>Sideroxydans</i>	Fe(II)-oxidising	AW: Ox St NAS: Ox, Ox St, AOx	Weiss et al. (2007)
<i>Gallionella</i>	Fe(II)-oxidising	NAS: Ox, AOx	De Vet et al. (2011)
<i>Anaeromyxobacter</i>	Fe(III)-reducing	AW: AOx, Ox St NW: AOx NAS: Ox, AOx	Treude et al. (2003)
<i>Geothermobacter</i>	Fe(III)-reducing	NAS: Ox, AOx, AOx St	Kashefi et al. (2003)
<i>Desulfotomaculum</i>	Fe(III)-reducing, S-reducing	AW: AOx, AOx St NW: Ox, AOx NAS: Ox, Ox St AOx	Finneran et al. (2002)
<i>Desulfosporosinus</i>	S-reducing	AW: Ox, AOx NW: Ox, AOx NAS: Ox, AOx, Ox St	Alazard et al. (2010)
<i>Desulfatirhabdium</i>	S-reducing	NAS: Ox, AOx	Balk et al. (2008)
<i>Desulfotomaculum</i>	S-reducing	NW: AOx NAS: Ox	Kaksonen et al. (2004)
<i>Desulfurivibrio</i>	S-reducing	NAS: AOx	Kaksonen et al. (2004)
<i>Desulfobulbus</i>	S-reducing	NAS: Ox, AOx	Kaksonen et al. (2004)
<i>Desulfovibrio</i>	S-reducing	NAS: Ox, AOx	Deng et al. (2016)
<i>Syntrophobacter</i>	S-reducing	NAS: Ox, AOx	Sánchez-Andrea et al. (2012)

AW acidic pH waste, NW neutral pH waste, NAS neutral pH aquatic sediment, Ox oxic condition, AOx anoxic condition, St sterilised condition

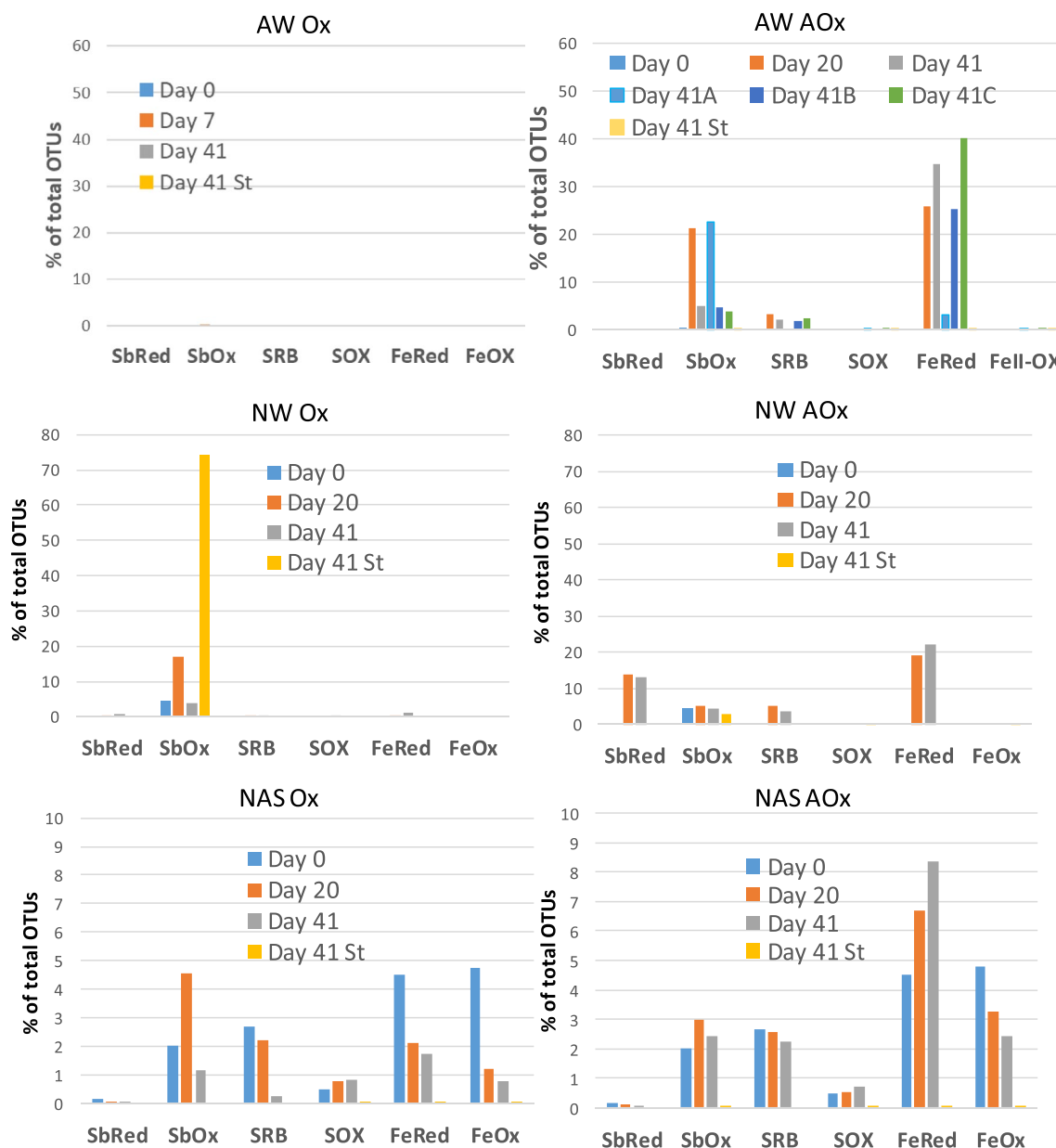


Fig. 7 Proportion in each sample, according to the obtained 16S sequences, of the sum of identified genera including Sb-, S- or Fe-transforming bacterial strains, grouped according to metabolic processes. Incubations of acidic pH waste (AW), neutral pH waste (NW) and neutral pH aquatic sediment (NAS). Ox, oxic condition; AOx, anoxic condition; St, sterilised condition; SbRed, Sb(V)-reducing;

SbOx, Sb(III)-oxidising; SRB, sulphate-reducing bacteria; SOX, sulphur-oxidising; FeRed, Fe(III)-reducing; FeOx, Fe(II)-oxidising. Genera included in each group are detailed in Table 3. The scale of the y-axis was chosen, as a compromise, in order to allow the visibility of the results, while keeping the same scale for each material in Ox and AOx conditions

to a lesser extent. With the NAS, the targeted metabolic groups did not appear in the St conditions, whereas, with the exception of the Sb(V)-reducing group, they were well represented in all the biotic conditions, even at t0. Incubation conditions seemed to favour the development

of Sb(III)-oxidising and SOX groups in oxic conditions and of Sb(III)-oxidising and more clearly Fe(III)-reducing groups in anoxic conditions, with *Anaeromyxobacter* and *Geothermobacter* as the main corresponding putative Fe(III) reducers (Table S5).

Discussion

Evolution of Sb concentrations

Solubility of Sb species

Dissolved Sb concentrations in the present experiments varied from $90 \mu\text{g L}^{-1}$ (in the AW biotic anoxic conditions) to $5400 \mu\text{g L}^{-1}$ (in the NAS St oxic condition). These values are in the range previously found in mining environments, i.e. $2200 \mu\text{g L}^{-1}$ in the adit of Goesdorf mine, Luxembourg (Filella et al. 2009); $1600 \mu\text{g L}^{-1}$ in a pond receiving water from tailings of the Giant gold mine in Yellowknife, Canada (Fawcett et al. 2015); and from $2900 \mu\text{g L}^{-1}$ in surface water to $23,000 \mu\text{g L}^{-1}$ in groundwater from Xikuangshan mine, China (Wen et al. 2016). Whereas sequential extractions showed that most Sb is present in forms that are resistant to dissolution, the high total Sb concentration in our materials explains the dissolved Sb concentrations observed in the microcosms.

The mobility of Sb is linked to its speciation as well as to the pH, redox conditions, type of minerals and microbial processes (Pitman et al. 1957; Filella et al. 2002; Wilson et al. 2010; Hu et al. 2016; Herath et al. 2017). Considering the results of the St microcosms, while in the AW (pH ≈ 4) the dissolved Sb concentration remained unchanged, there was an increase in soluble Sb concentration in NW and NAS (pH ≈ 6.5). Our three materials contained stibnite (Table S1) that dissolves in oxygenated water to form the hydroxide $\text{Sb}(\text{OH})_3$ (Biver and Shotyk 2012). The corresponding dissolution rate is lower at near neutral pH than in acidic or alkaline conditions; thus, this reaction could hardly explain our results in St condition. The resulting hydroxide $\text{Sb}(\text{OH})_3$ presents a low solubility, as it can form a solid species $\text{Sb}(\text{OH})_3(\text{s})$ (Brookins 1986; Shkol'nikov 2010). Our materials also contained Sb oxides that might dissolve in aqueous solutions producing the Sb(V) species $\text{Sb}(\text{OH})_6^-$, which can exist over a wide range of pH (Pitman et al. 1957; Brookins 1986) including our experimental conditions, and the poorly soluble $\text{Sb}(\text{OH})_3$. As a matter of fact, in St conditions, dissolved Sb was mainly present as Sb(V) at the end of incubation (Table 2), even in anaerobic conditions, supporting the hypothesis of the Sb oxide dissolution. Thermodynamic equilibrium data indicate that Sb(V) species should exist in aerobic conditions and Sb(III) species in anoxic and low-redox environments (Pitman et al. 1957; Filella et al. 2002); however, the presence of oxidised Sb species in anaerobic systems has already been observed (Filella et al. 2002; Mitsunobu et al. 2006; Fawcett et al. 2015), suggesting the major role of kinetics in Sb speciation, that could be influenced by microbial catalysis. Indeed, we observed important differences in ORP (Fig. S4) that did not induce

differences in Sb concentrations in St conditions (Fig. 3), whereas the redox conditions significantly influenced Sb behaviour in the presence of microbes (Fig. 6).

Adsorption–desorption mechanisms

Oxyhydroxides of Fe, Mn and Al have strong affinity for Sb; however, adsorption efficiency depends on their type, pH and Sb species (Kong and He 2016; He et al. 2019; Wang et al. 2021). Iron oxides were detected in most of our materials through mineralogical analysis (Table S1) and chemical extractions (Fig. S2). Acidic pH conditions favour the sorption of both Sb(III) and Sb(V) onto Mn (Wang et al. 2021) and Fe (Leuz et al. 2006) oxides. In our study, the most acidic material (AW St) effectively released less Sb in solution than the other two studied materials (NW St and NAS St). The biogeochemical behaviour of Fe is strongly influenced by pH (Emerson and Weiss 2004) and Fe(II) solubility being increased in low pH conditions (Frohne et al. 2011). This fact could explain the increase in soluble Fe concentration under reducing conditions in AW (Fig. 3E, F), since it could be attributed to the bioreduction of Fe hydroxides. However, Sb was rather immobilised than solubilised in the corresponding microcosm, suggesting that adsorption/desorption mechanisms linked to Fe oxides were not the only processes controlling the fate of Sb in our microcosms.

Role of microbial communities

Significance of the comparison biotic vs. St conditions

Through the present experiments, it was possible to evaluate the influence of microbial activities on the mobility of Sb in diverse surface compartments of a mining site, through comparison of complete microbial communities with systems in which microbial activities were greatly weakened. There is no efficient way to completely sterilise environmental samples (Otte et al. 2018). Here, the autoclaving of materials in anoxic conditions did not seem to strongly alter minerals (Table S1), whereas it could have impacted the organic compartment, in particular in the NAS. Monitoring of cell densities by the LIVE/DEAD® BacLight Bacterial Viability Kit showed higher cell concentrations in anoxic conditions than in oxic conditions (Fig. 4). Abundant growth in anoxic conditions could be linked to the availability of H_2 that could be used as an energy source. Dominance of “dead” cells in these samples might simply result from the experimental procedure as filtration and staining were performed in an oxygenated atmosphere. However, “live” cells were also observed in all incubations and their concentration increased, indicating active microbial metabolisms. Conversely, low cell counts, and low final DNA concentrations,

indicated that autoclaving and formaldehyde injections greatly weakened microbial metabolism in the St conditions.

Comparison of environmental compartments

Microbial communities presented very different compositions depending on the type of material, AW, NW or NAS, suggesting a diversity of biological processes depending on environmental compartments at the site. Interestingly, a few OTUs identified at the genus level that were retrieved in most of the samples (Table 3), such as *Bacillus*, *Desulfosporosinus* and *Desulfitobacterium*, correspond to spore-forming microorganisms, able to resist adverse conditions. Not surprisingly, the most acidic environment presented the lowest diversity (Fig. S6), and pH was one of the parameters influencing microbial communities' structure. Previous studies showed that Sb contamination could influence the composition of microbial communities on mining sites (Deng et al. 2020; Duan et al. 2022). In sediments of a watershed contaminated by Sb mining, pH, temperature, ORP and dissolved Sb significantly structured the microbial communities (Sun et al. 2016). Here, we observed strong divergences between communities of surface environments at a small site scale that seemed to be more influenced by pH and redox conditions than by soluble Sb (Fig. 6).

Bio-processes in oxic conditions

Previous studies have already shown that microbial activities could influence the mobility of Sb. Casiot et al. (2007) observed that Sb release from a sediment polluted by mining activities was enhanced by aerobic microbial activity and attenuated in anoxic–biotic conditions. Loni et al. (2020) observed higher Sb solubilisation from mining rock samples, in oxic conditions, by an Sb(III)-oxidising microorganism affiliated to the *Paracoccus* genus. Here, in the presence of oxygen, the overall effect of microbial processes differed between the types of materials: Sb release was enhanced by biological processes in the AW, not influenced in the NW, and attenuated in the NAS (Fig. 3).

In AW, microbial activities in oxic conditions promoted Sb release (Fig. 3) and acidification (Fig. S3); however, these processes could not be clearly related to the analysis and evolution of the microbial community that was largely dominated by OTUs belonging to Chloroflexi of the family of Ktedonobacteraceae, none identified at the genus level (Fig. 5). This family includes filamentous, spore-forming, gram-positive heterotrophic bacteria from soil (Cavalletti et al. 2006). However, although limited (0.6% of total OTUs on day 41), emergence of the known S-oxidising genus *Thermithiobacillus* was observed in these microcosms (Table 3). The observed biologically related release of Sb from AW might be related to the direct or indirect alteration

of Sb-bearing phases, such as sulphides or organic matter. In NW, biological activities did not significantly influence Sb mobility in oxic conditions (Fig. 3), and no known genus with metabolisms based on Sb, S or Fe transformations was identified in the microbial communities (Fig. 7) that seemed dominated by heterotrophic phyla. Conversely, the NAS incubated in oxic conditions showed an overall immobilisation of Sb in biotic compared with St conditions, but only after a strong release of Sb that was observed in both conditions during the first week of incubation (Fig. 3). These results could be explained by the early oxidation of amorphous Fe sulphide, often present in aquatic sediments (Andrade et al. 2010), that would release Fe(II), (bio)-oxidised into Fe(III), that would rapidly precipitate as fresh Fe oxides known to adsorb Sb (Ashley et al. 2003). The increase in the proportion in S-oxidising genus *Thiobacillus* between t0 and t20 days and the presence of the Fe(II)-oxidising genera *Sideroxydans* and *Gallionella* in the sediment appear to be in agreement with this hypothesis (Fig. 7, Table S5). The observation of a colour change, from dark brown (St condition) to ochre brown (biotic condition), also supported this scenario (Fig. S7A). Moreover, the pH values that were lower in NAS than in NAS St (Fig. S3), possibly linked to biologically induced reactions (Fe hydroxide precipitation, oxidation of sulphur compounds, oxidation of organic matter producing CO₂), could favour Sb adsorption onto oxides (Leuz et al. 2006).

Bio-processes in anoxic conditions

In the microcosms, Sb release was nearly always attenuated by living microorganisms in anaerobic conditions (Fig. 3). However, with the AW incubated in AOx conditions, the three replicates behaved differently in terms of Sb mobility and microbial communities (Fig. 3B). In two replicates, Sb was immobilised compared with the St condition, and the proportions of (i) the Fe(III)-reducing *Desulfitobacterium* (25 to 40% of the total sequences) and (ii) the sulphate-reducing *Desulfosporosinus* increased (Table S5E). In the third replicate, Sb was more mobile than in the St condition, the Fe(III) reducer proportion and identity were different (*Anaeromyxobacter*, “only” 3%, Table 3 and Table S5C) and known sulphate reducers were not detected. Conversely, this replicate exhibited a high proportion of sequences affiliated to the *Bacillus* genus (Table 3, Table S5B), which includes known Sb(III) oxidisers (Li et al. 2018) and strains able to grow in either aerobic or anaerobic conditions (Clements et al. 2002). The development of genera including Sb(III) oxidisers in anoxic conditions seems paradoxical; however, some genera of this metabolic group are facultative anaerobic (*Bacillus*, *Acidithiobacillus*, etc.); thus, they could grow in the absence of oxygen and possibly oxidise Sb(III) using alternative electron acceptors such as nitrate (Terry et al.

2015). Other subtle differences between these replicates could be detected: ORP decreased less sharply (Fig. S4), and Fe release was delayed in the microcosm with higher Sb mobility (Fig. 3B). These results show that Sb behaviour cannot be simply inferred from the redox context and could be strongly influenced by the growth sequence of different microorganisms belonging to different metabolic groups. Divergences of biogeochemical reactions linked with subtle differences in the composition of the initial microbial communities have already been observed in microcosms of sediments (Kwon et al. 2016; Battaglia-Brunet et al. 2022).

With the NW, anoxic incubation in the presence of active microbes induced both immobilisation of Sb and a clear increase of the Sb(III) proportion in dissolved Sb (Table 2). Immobilisation of Sb in reducing conditions may be linked to Sb(V) reduction, as Sb(III) hydroxide is less soluble than Sb(V) anions in neutral conditions (Brookins 1986; Shkol'nikov 2010; Herath et al. 2017), or linked to the precipitation of Sb sulphide in the presence of biogenic H_2S (Zhang et al. 2016). Here, NW AOx incubations induced the growth of bacteria belonging to the *Geobacter* genus, whose proportion of 16S sequences rose from being non-detectable in the initial material to 13% on day 20 (Table 3 and Table S5C). A *Geobacter* strain (Yamamura et al. 2021) was shown to be able to grow through dissimilatory Sb(V) reduction with acetate as an electron donor, producing Sb_2O_3 , and this genus was detected as an active member of an Sb(V)-reducing community in incubated paddy soil (Sun et al. 2021). Hydrogen can be used as an energy source by members of the *Geobacter* genus (Caccavo et al. 1994), and this inorganic substrate was also shown to promote Sb(V) bioreduction in soils (Nguyen et al. 2018). Thus, *Geobacter*-affiliated organisms could contribute to attenuating Sb mobility in NW incubations. In NAS microcosms incubated in anoxic conditions, Sb mobility was attenuated, and the Sb(V) proportion was slightly lower than that in St conditions. In these microcosms, SRB were maintained as a major metabolic group identified at the genus level (2–3%), but the main enriched group corresponded to Fe(III) reducers, whose proportion increased continuously during incubation, from 4% (day 0) to 8% (day 41). The main Fe(III) reducers in this group belonged to the genera *Anaeromyxobacter* and *Geothermobacter*. These microcosms contained diverse SRB, and among them, the proportion of *Desulfovibrio*-related sequences slightly increased during incubation. Thus, the biotic stabilisation of Sb in NAS AOx microcosms may have resulted from bio-sulphide precipitation or bioreduction of Sb(V) into Sb(III) by some microorganisms whose Sb(V)-reducing activity has not been yet characterised. These mechanisms could be helped by the generation of Fe(II) by Fe(III)-reducing bacteria, as Fe(II) was shown to accelerate Sb sulphide precipitation by stimulating SRB activity (Xi et al. 2020). In the NAS incubations, the dissolved Fe(II) concentration remained around 2 mg

L^{-1} , probably because Fe(II) also precipitated with hydrogen sulphide as FeS (Fig. 3E). This hypothesis is supported by the darkening of the biotic slurries compared with the St NAS microcosms (Fig. S7B).

Globally, anoxic microbial activities decreased the mobility of Sb; however, they induced a significant release of As in water. The mobilisation of As from mine-contaminated materials in reducing conditions, linked to biological activities, is a well-known phenomenon (Drewniak and Skłodowska 2013; Rajpert et al. 2016), and the antagonist behaviour of Sb and As in mine sediments has previously been described (Casiot et al. 2007).

Conclusions

Microbial communities inhabiting different surface compartments of a small mining area presented very different compositions. The influence of microbial activities on Sb mobility and speciation was proven in nearly all conditions. Whereas Sb was mainly present in mineral phases resistant to chemical extractions, leaching of soils and sediments released several milligrams per liter of dissolved Sb. Several microbial activities could contribute to Sb immobilisation, including Fe(II) oxidation, Sb(V) reduction and sulphate reduction. In aquatic sediments, microbial activities attenuated Sb mobility in both aerobic and anaerobic conditions. Conversely, Sb(III)-oxidising activities could enhance Sb solubilisation from solid phases of mine wastes. The overall results suggest that microbial processes influencing Sb behaviour on mining sites are very diverse. They should be carefully identified and quantified in each environmental compartment in order to avoid unreliable risk assessments. Moreover, the antagonist biogeochemical behaviour of As and Sb deserves specific awareness as these two toxic elements are very often associated in ore bodies. Specific management options, potentially exploiting microbial reactions, aimed to prevent dissemination of these two metalloids in the environment, should be developed.

Abbreviations AOx: Anoxic; As: Arsenic; AW: Acidic pH waste; EC: Electrical conductivity; NAS: Neutral pH aquatic sediment; NW: Neutral pH waste; ORP: Oxidation–reduction potential; Ox: Oxidic; Sb: Antimony; St: Sterilised; SW: South west; TOC: Total organic carbon

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-023-29734-9>.

Author contribution The contributions of each author to this study are as follows: J. D. P. P. and H. T.: methodology, investigation and writing (original draft preparation, editing); H. R. C.-R. and J. M. E.: investigation and writing (original draft preparation, editing); E. M. G.-N., D. B. and J. V.: investigation; E. G.: conceptualisation and resources; P. L. H.:

conceptualisation, writing (original draft), resources and supervision; F. B.-B.: conceptualisation, writing (editing) and supervision.

Funding This work was funded by the ANR (ANR-19-MIN2-0002-01), the AEI (MICIU/AEI/REF.: PCI2019-03779) and author's institutions in the framework of the ERA-MIN2 AUREOLE project. J. D. P. P. is the beneficiary of a grant for the requalification of the Spanish university system from the Ministry of Universities of the Government of Spain, financed by the European Union, NextGenerationEU.

Data availability The authors declare that the data presented and discussed in the present article can be found according to the article information, and extra information can be obtained by request to be addressed to the corresponding author.

Declarations

Ethical approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

References

- Abin CA, Hollibaugh JT (2017) *Desulfuribacillus stibiiarsenatis* sp. nov. an obligately anaerobic, dissimilatory antimonate- and arsenate-reducing bacterium isolated from anoxic sediments, and emended description of the genus *Desulfuribacillus*. Int J Syst Evol Microbiol 67:1011–1017. <https://doi.org/10.1099/ijsem.0.001732>
- Alazard D, Joseph M, Battaglia-Brunet F, Cayol JL, Ollivier B (2010) *Desulfosporosinus acidiphilus* sp. nov.: a moderately acidophilic sulfate-reducing bacterium isolated from acid mining drainage sediments. Extremophiles 14:305–312. <https://doi.org/10.1007/s00792-010-0309-4>
- Anderson CG (2012) The metallurgy of antimony. Geochemistry 72:3–8. <https://doi.org/10.1016/j.chemer.2012.04.001>
- Andrade CF, Jamieson HE, Kyser TK, Praharaj T, Fortin D (2010) Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada. Appl Geochem 25:199–211. <https://doi.org/10.1016/j.apgeochem.2009.11.005>
- Ashley PM, Craw D, Graham BP, Chappell DA (2003) Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. J Geochem Explor 77:1–14. [https://doi.org/10.1016/S0375-6742\(02\)00251-0](https://doi.org/10.1016/S0375-6742(02)00251-0)
- Balk M, Altınbaş M, Rijkstra WIC, Sinninghe D, Jaap S, Stams AJM (2008) *Desulfatirhabdium butyrativorans* gen. nov. sp. nov. a butyrate-oxidizing, sulfate-reducing bacterium isolated from an anaerobic bioreactor. Int J Syst Evol Microbiol 58:110–115. <https://doi.org/10.1099/ijms.0.65396-0>
- Battaglia-Brunet F, Naveau A, Cary L, Bueno M, Biais J, Charron M, Joulain C, Thouin H (2022) Biogeochemical behaviour of geogenic As in a confined aquifer of the Sologne region, France. Chemosphere 304:135252. <https://doi.org/10.1016/j.chemosphere.2022.135252>
- Biver M, Shotyk W (2012) Stibnite (Sb₂S₃) oxidative dissolution kinetics from pH 1 to 11. Geochim Cosmochim Acta 79:127–139. <https://doi.org/10.1016/j.gca.2011.11.033>
- Borcard D, Gillet F, Legendre P (2011) Numerical ecology with R. Springer, New York
- Brookins DG (1986) Geochemical behavior of antimony, arsenic, cadmium and thallium: Eh–pH diagrams for 25°C, 1-bar pressure. Chem Geol 54:271–278. [https://doi.org/10.1016/0009-2541\(86\)90141-5](https://doi.org/10.1016/0009-2541(86)90141-5)
- Caccavo F, Lonergan DJ, Lovley DR, Davis M, Stolz JF, Mc Inerney MJ (1994) *Geobacter sulfurreducens* sp. nov. a hydrogen- and acetate-oxidizing dissimilatory metal-reducing microorganism. Appl Environ Microbiol 60:3752–3759. <https://doi.org/10.1128/aem.60.10.3752-3759.1994>
- Caplette JN, Grob M, Mestrot A (2021) Validation and deployment of a quantitative trapping method to measure volatile antimony emissions. Env Pol 289:117831. <https://doi.org/10.1016/j.envpol.2021.117831>
- Casiot C, Ujevic M, Munoz M, Seidel JL, Elbaz-Poulichet F (2007) Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). Appl Geochem 22:788–798. <https://doi.org/10.1016/j.apgeochem.2006.11.007>
- Cavaletti L, Monciardini P, Bamonte R, Schumann P, Rohde M, Sosio M, Donadio S (2006) New lineage of filamentous, spore-forming, gram-positive bacteria from soil. Appl Environ Microbiol 72:4360–4369. <https://doi.org/10.1128/AEM.00132-06>
- Cidu R, Biddau R, Dore E (2015) Determination of trace of Sb(III) using ASV in Sb-rich water samples affected by mining. Anal Chim Acta 854:34–39. <https://doi.org/10.1016/j.aca.2014.11.020>
- Cidu R, Dore E, Biddau R, Nordstrom DK (2018) Fate of antimony and arsenic in contaminated waters at the abandoned Su Suergiu Mine (Sardinia Italy). Mine Water Environ 37:151–165. <https://doi.org/10.1007/s10230-017-0479-84>
- Clements LD, Miller BS, Streips UN (2002) Comparative growth analysis of the facultative anaerobes *Bacillus subtilis*, *Bacillus licheniformis*, and *Escherichia coli*. System Appl Microbiol 25:284–286. <https://doi.org/10.1078/0723-2020-00108>
- De Vet WWJM, Dinkla IJT, Rietveld LC, van Loosdrecht MCM (2011) Biological iron oxidation by *Gallionella* spp. in drinking water production under fully aerated conditions. Water Res 45:5389–5398. <https://doi.org/10.1016/j.watres.2011.07.028>
- Deng D, Weidhaas JL, Lin LS (2016) Kinetics and microbial ecology of batch sulfidogenic bioreactors for co-treatment of municipal wastewater and acid mine drainage. J Hazard Mater 305:200–208. <https://doi.org/10.1016/j.jhazmat.2015.11.041>
- Deng R, Tang Z, Hou B et al (2020) Microbial diversity in soils from antimony mining sites: geochemical control promotes species enrichment. Environ Chem Lett 18:911–922. <https://doi.org/10.1007/s10311-020-00975-1>
- Deng R, Chen Y, Deng X, Huang Z, Zhou S, Ren B, Jin G, Hursthouse A (2021) A critical review of resistance and oxidation mechanisms of Sb-oxidizing bacteria for the bioremediation of Sb(III) pollution. Front Microbiol 12:2418. <https://doi.org/10.3389/fmicb.2021.738596>
- Drewniak L, Skłodowska A (2013) Arsenic-transforming microbes and their role in biomining processes. Environ Sci Pollut Res 20:7728–7739. <https://doi.org/10.1007/s11356-012-1449-0>
- Duan R, Du Y, Chen Z, Zhang Y, Hu W, Yang L, Xiang G, Luo Y (2022) Diversity and composition of soil bacteria between abandoned and selective-farming farmlands in an antimony mining area. Front Microbiol 13:953624. <https://doi.org/10.3389/fmicb.2022.953624>
- Dupont D, Arnout S, Jones PT, Binnemans K (2016) Antimony recovery from end-of-life products and industrial process residues: a critical review. J Sustain Metall 2:79–103. <https://doi.org/10.1007/s40831-016-0043-y>
- El Shanawany S, Foda N, Hashad DI, Salama N, Sobh Z (2017) The potential DNA toxic changes among workers exposed to antimony trioxide. Environ Sci Pollut Res 24:12455–12461. <https://doi.org/10.1007/s11356-017-8805-z>

- Emerson D, Weiss JV (2004) Bacterial iron oxidation in circumneutral freshwater habitats: findings from the field and the laboratory. *Geomicrobiol J* 21:405–414. <https://doi.org/10.1080/01490450490485881>
- Esbrí JM, Minang CM, Rivera S, Madrid-Illescas M, García-Noguero E, González-Valoys A, Maguregui M, Thoun H, Battaglia-Brunet F, Gloaguen E, Higuera PL (2022) Evaluation of antimony availability in a mining context: impact for the environment, and for mineral exploration and exploitation. *Chemosphere* 311:137086. <https://doi.org/10.1016/j.chemosphere.2022.137086>
- Escudé F, Auer L, Bernard M, Mariadassou M, Cauquil L, Vidal K et al (2018) FROGS: find, rapidly, OTUs with galaxy solution. *Bioinformatics* 34:1287–1294. <https://doi.org/10.1093/bioinformatics/btx791>
- Fawcett SE, Jamieson HE, Nordstrom DK, McCleskey RB (2015) Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. *Appl Geochem* 62:3–17. <https://doi.org/10.1016/j.apgeochem.2014.12.012>
- Filella M, Belzile N, Chen YW (2002) Antimony in the environment: a review focused on natural waters. *I Occurrence Earth-Sci Rev* 57:125–176. [https://doi.org/10.1016/S0012-8252\(01\)00070-8](https://doi.org/10.1016/S0012-8252(01)00070-8)
- Filella M, Philippo S, Belzile N, Chen Y, Quentel F (2009) Natural attenuation processes applying to antimony: a study in the abandoned antimony mine in Goesdorf, Luxembourg. *Sci Total Environ* 407:6205–6216. <https://doi.org/10.1016/j.scitotenv.2009.08.027>
- Finneran KT, Forbush HM, Gaw VanPraagh CV, Lovley DR (2002) *Desulfotobacterium metallireducens* sp. nov. an anaerobic bacterium that couples growth to the reduction of metals and humic acids as well as chlorinated compounds. *Int J Syst Evol Microbiol* 52:1929–1935. <https://doi.org/10.1099/00207713-52-6-1929>
- Frohne T, Rinklebe J, Diaz-Bone RA, Du Laing G (2011) Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony. *Geoderma* 160:414–424. <https://doi.org/10.1016/j.geoderma.2010.10.012>
- Gallego S, Esbrí JM, Campos JA, Peco JD, Martin-Laurent F, Higuera P (2021) Microbial diversity and activity assessment in a 100-year-old lead mine. *J Hazard Mater* 410:124618. <https://doi.org/10.1016/j.jhazmat.2020.124618>
- Gumiel P (1983) Metalogenia de los yacimientos de antimonio de la Península Ibérica. *Tecniterrae* 54:6–120
- Gumiel P, Arribas A (1987) Antimony deposits in the Iberian Peninsula. *Econ Geol* 82:1453–1463. <https://doi.org/10.2113/gsecongeo.82.6.1453>
- Hafeez I, Azam M, Amin A, Mahmood Z, Aamir M, Akram A (2017) Microbial extraction of antimony from stibnite of Qillah Abdullah. *ASRJETS* 28:117–127
- Hageman PL (2007) Geological survey field leach test for assessing water reactivity and leaching potential of mine wastes soils and other geologic and environmental materials. U.S. Geological Survey Techniques and Methods. http://pubs.usgs.gov/tm/2007/05D03/pdf/TM5-D3_508.pdf. Accessed 6 July 2022
- Han Y, Zhang F, Wang Q, Zheng S, Guo W, Feng L, Wang G (2016) *Flaviumibacter stibioxidans* sp. nov. an antimony-oxidizing bacterium isolated from antimony mine soil. *IJSEM* 66:4676–4680. <https://doi.org/10.1099/ijsem.0.001409>
- He M, Wang N, Long X, Zhang C, Ma C, Zhong Q, Shan J (2019) Antimony speciation in the environment: recent advances in understanding the biogeochemical processes and ecological effects. *J Environ Sci* 75:14–39. <https://doi.org/10.1016/j.jes.2018.05.023>
- Herath I, Vithanage M, Bundschuh J (2017) Antimony as a global dilemma: geochemistry, mobility, fate and transport. *Environ Pollut* 223:545–559. <https://doi.org/10.1016/j.envpol.2017.01.057>
- Hu X, Guo X, He M, Li S (2016) pH-dependent release characteristics of antimony and arsenic from typical antimony-bearing ores. *J Environ Sci* 44:171–179. <https://doi.org/10.1016/j.jes.2016.01.003>
- Kaksonen AH, Plumb JJ, Robertson WJ, Franzmann PD, Gibson JAE, Puhakka JA (2004) Culturable diversity and community fatty acid profiling of sulfate-reducing fluidized-bed reactors treating acidic, metal-containing wastewater. *Geomicrobiol J* 21:469–480. <https://doi.org/10.1080/01490450490505455>
- Kashefi K, Holmes DE, Baross JA, Lovley DE (2003) Thermophily in the Geobacteraceae: *Geothermobacter ehrlichii* gen. nov. sp. nov., a novel thermophilic member of the Geobacteraceae from the “Bag City” hydrothermal vent. *Appl Environ Microbiol* 69:2985–2993. <https://doi.org/10.1128/AEM.69.5.2985-2993.2003>
- Kong L, He M (2016) Mechanisms of Sb (III) photooxidation by the excitation of organic Fe(III) complexes. *Environ Sci Technol* 50:6974–6982. <https://doi.org/10.1021/acs.est.6b00857>
- Krachler M, Emons H, Zheng J (2001) Speciation of antimony for the 21st century: promises and pitfalls. *TrAC Trends Anal Chem* 20:79–90. [https://doi.org/10.1016/S0165-9936\(00\)00065-0](https://doi.org/10.1016/S0165-9936(00)00065-0)
- Kwon MJ, O’Loughlin EJ, Boyanov MI, Brulc JM, Johnston ER, Kemner KM, Antonopoulos DA (2016) Impact of organic carbon electron donors on microbial community development under iron- and sulfate-reducing conditions. *PLoS One* 11:e0146689. <https://doi.org/10.1371/journal.pone.0146689>
- Leuz AK, Mönch H, Johnson CA (2006) Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization. *Environ Sci Technol* 40:7277–7282. <https://doi.org/10.1021/es061284b>
- Li J, Yu H, Wu X, Shen L, Liu Y, Qiu G, Zeng W, Yu R (2018) Novel hyper antimony-oxidizing bacteria isolated from contaminated mine soils in China. *Geomicrobiol J* 35:713–720. <https://doi.org/10.1080/01490451.2018.1454556>
- Loni PC, Wu M, Wang W, Wang H, Ma L, Liu C, Song Y, Tuovinen OH (2020) Mechanism of microbial dissolution and oxidation of antimony in stibnite under ambient conditions. *J Haz Mat* 385:121561. <https://doi.org/10.1016/j.jhazmat.2019.121561>
- Lorenzo S (2015) El yacimiento de Sb-W de San Antonio, Alburquerque. <https://info.igme.es/ielig/LIGInfo.aspx?codigo=CI208>. Accessed 27 July 2023
- Lotze F (1956) Das Präkambrium Spaniens. *N Jb Geol Paläont* 8:373–380
- Mamindy-Pajany Y, Bataillard P, Séby F, Crouzet C, Moulin A, Guezennec A-G, Hurel C, Marmier N, Battaglia-Brunet F (2013) Arsenic in marina sediments from the Mediterranean coast: speciation in the solid phase and occurrence of thioarsenates. *Soil Sediment Contam* 22:984–1002. <https://doi.org/10.1080/15320383.2013.770441>
- Mitsunobu S, Harada T, Takahashi Y (2006) Comparison of antimony behavior with that of arsenic under various soil redox conditions. *Environ Sci Technol* 40:7270–7276. <https://doi.org/10.1007/BF02839926>
- Molecular Probes (2004) LIVE/DEAD BacLight Bacterial Viability Kit product information. Handbook of fluorescent probes and research products
- Murti GK, Volk V, Jackson M (1966) Colorimetric determination of iron of mixed valency by orthophenanthroline. *Soil Sci Soc Am J* 30:663–664. <https://doi.org/10.2136/sssaj1966.03615995003000050037x>
- Nguyen VK, Lee JU (2014) Isolation and characterization of antimony-reducing bacteria from sediments collected in the vicinity of an antimony factory. *Geomicrobiol J* 31:855–861. <https://doi.org/10.1080/01490451.2014.901440>
- Nguyen VK, Lee JU (2015) Antimony-oxidizing bacteria isolated from antimony-contaminated sediment – a phylogenetic study.

- Geomicrobiol J 32:50–58. <https://doi.org/10.1080/01490451.2014.925009>
- Nguyen VK, Choi W, Park Y, Yu J, Lee T (2018) Characterization of diversified Sb(V)-reducing bacterial communities by various organic or inorganic electron donors. *Bioresour Technol* 250:239–246. <https://doi.org/10.1016/j.biortech.2017.11.044>
- Otte JM, Blackwell N, Soos V, Rughöft S, Maisch M, Kappler A, Kleindienst S, Schmidt C (2018) Sterilization impacts on marine sediment—are we able to inactivate microorganisms in environmental samples? *FEMS Microbiol Ecol* 94:fiy189. <https://doi.org/10.1093/femsec/fiy189>
- Pitman AL, Pourbaix M, de Zoubov N (1957) Potential-pH diagram of the antimony-water system: its applications to properties of the metal, its compounds, its corrosion, and antimony electrodes. *J Electrochem Soc* 104:594–600. <https://doi.org/10.1149/1.2428423>
- Polack R, Chen YW, Belzile N (2009) Behaviour of Sb(V) in the presence of dissolved sulfide under controlled anoxic aqueous conditions. *Chem Geol* 262:179–185. <https://doi.org/10.1016/j.chemgeo.2009.01.008>
- Quatrini R, Johnson DB (2019) Acidithiobacillus ferrooxidans. *Trends Microbiol* 27:282–283. <https://doi.org/10.1016/j.tim.2018.11.009>
- Quevauviller P, Rauret G, López-Sánchez J, Rubio R, Ure A, Muntau H (1997) Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. *Sci Total Environ* 205:223–234. [https://doi.org/10.1016/S0048-9697\(97\)00205-2](https://doi.org/10.1016/S0048-9697(97)00205-2)
- Radková AB, Jamieson HE, Campbell KM (2020) Antimony mobility during the early stages of stibnite weathering in tailings at the Beaver Brook Sb deposit, Newfoundland. *Appl Geochem* 115:104528. <https://doi.org/10.1016/j.apgeochem.2020.104528>
- Rajpert L, Kolvenbach BA, Ammann EM, Hockmann K, Nachttegaal M, Eichel E, Schäffer A, Corvini PFX, Skłodowska A, Lenz M (2016) Arsenic mobilization from historically contaminated mining soils in a continuously operated bioreactor: implications for risk assessment. *Environ Sci Technol* 50:9124–9132. <https://doi.org/10.1021/acs.est.6b02037>
- Roper AJ, Williams PA, Filella M (2012) Secondary antimony minerals: phases that control the dispersion of antimony in the supergene zone. *Geochemistry* 72:9–14. <https://doi.org/10.1016/j.chemer.2012.01.005>
- Sánchez-Andrea I, Knittel K, Amann R, Amils R, Sanz JL (2012) Quantification of Tinto River sediment microbial communities: importance of sulfate-reducing bacteria and their role in attenuating acid mine drainage. *Appl Environ Microbiol* 78:4638–4645. <https://doi.org/10.1128/AEM.00848-12>
- Schildroth S, Osborne G, Smith AR, Yip C, Collins C, Smith MT, Sandy MS, Zhang L (2021) Occupational exposure to antimony trioxide: a risk assessment. *Occup Environ Med* 78:413–418. <https://oem.bmj.com/content/78/6/413.full.pdf>. Accessed 20 Jan 2022
- Schnitzer M (1983) Organic matter characterization. *Methods Soil Anal Part 2: Chem Microbiol Prop* 2(9):581–594. <https://doi.org/10.2134/agronmonogr9.2.2ed.c30>
- Shkol'nikov EV (2010) Thermodynamic characterization of the amphotericism of oxides M_2O_3 ($M = As, Sb, Bi$) and their hydrates in aqueous media. *Russ J Appl Chem* 83:2121–2127. <https://doi.org/10.1134/S1070427210120104>
- Sun W, Xiao E, Dong Y, Tang S, Krumins V, Ning Z, Sun M, Zhao Y, Wu S, Xiao T (2016) Profiling microbial community in a watershed heavily contaminated by an active antimony (Sb) mine in Southwest China. *Sci Total Environ* 550:297–308. <https://doi.org/10.1016/j.scitotenv.2016.01.090>
- Sun L-N, Guo B, Lyu W-G, Tang X-J (2020) Genomic and physiological characterization of an antimony and arsenite-oxidizing bacterium *Roseomonas rhizosphaerae*. *Env Res* 191:110136. <https://doi.org/10.1016/j.envres.2020.110136>
- Sun W, Sun X, Häggblom MM, Koltun M, Lan L, Li B, Dong Y, Xu R, Li F (2021) Identification of antimonate reducing bacteria and their potential metabolic traits by the combination of stable isotope probing and metagenomic-pangenomic. *Anal Environ Sci Technol* 55:13902–13912. <https://doi.org/10.1021/acs.est.1c03967>
- Sundar S, Chakravarty J (2010) Antimony toxicity. *Int J Environ Res Public Health* 7:4267–4277. <https://doi.org/10.3390/ijerph7124267>
- Terry LR, Kulp TR, Wiatrowski H, Miller LG, Oremland RS (2015) Microbiological oxidation of antimony(III) with oxygen or nitrate by bacteria isolated from contaminated mine sediments. *Appl Environ Microbiol* 81:8478–8488. <https://doi.org/10.1128/AEM.01970-15>
- Torma AE, Gabra GG (1977) Oxidation of stibnite by *Thiobacillus ferrooxidans*. *Antonie Van Leeuwenhoek* 43:1–6. <https://doi.org/10.1007/BF02316204>
- Treude N, Rosencrantz D, Liesack W, Schnell S (2003) Strain FAc12, a dissimilatory iron-reducing member of the Anaeromyxobacter subgroup of Myxococcales. *FEMS Microbiol Ecol* 44:261–269. [https://doi.org/10.1016/S0168-6496\(03\)00048-5](https://doi.org/10.1016/S0168-6496(03)00048-5)
- USGS (2021) Mineral commodity summaries. <https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-antimony.pdf>. Accessed 30 January 2021
- Wang Z, Tollervey J, Briese M et al (2009) CLIP: construction of cDNA libraries for high-throughput sequencing from RNAs cross-linked to proteins in vivo. *Methods* 48:287–293. <https://doi.org/10.1016/j.ymeth.2009.02.021>
- Wang X, Yang Y, Tao L, He M (2021) Antimonite oxidation and adsorption onto two tunnel-structured manganese oxides: implications for antimony mobility. *Chem Geol* 579:120336. <https://doi.org/10.1016/j.chemgeo.2021.120336>
- Weiss JV, Rentz JA, Plaia T, Neubauer SC, Merrill-Floyd MT, Lilburn Bradburne C, Megonigal JP, Emerson D (2007) Characterization of neutrophilic Fe(II)-oxidizing bacteria isolated from the rhizosphere of wetland plants and description of *Ferritrophicum radicola* gen. nov. sp. nov. and *Sideroxydans paludicola* sp. nov. *Geomicrobiol J* 24:559–570. <https://doi.org/10.1080/01490450701670152>
- Wen B, Zhou J, Zhou A, Liu C, Xie L (2016) Sources, migration and transformation of antimony contamination in the water environment of Xikuangshan, China: evidence from geochemical and stable isotope (S, Sr) signatures. *Sci Total Environ* 569:114–122. <https://doi.org/10.1016/j.scitotenv.2016.05.124>
- Wilson SC, Lockwood PV, Ashley PM, Tighe M (2010) The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. *Environ Pollut* 158:1169–1181. <https://doi.org/10.1016/j.envpol.2009.10.045>
- Xi YS, Lan S, Li X, Wu Y, Yuan X, Zhang C, Yunguo L, Huang Y, Quan B, Wu S (2020) Bioremediation of antimony from wastewater by sulfate-reducing bacteria: effect of the coexisting ferrous ion. *I Biodeterior Biodegradation* 148:104912. <https://doi.org/10.1016/j.ibiod.2020.104912>
- Xiang L, Liu C, Liu D, Ma L, Qiu X, Wang H, Lu X (2022) Antimony transformation and mobilization from stibnite by an antimonite oxidizing bacterium *Bosea* sp. AS-1. *J Environ Sci* 111:273–281. <https://doi.org/10.1016/j.jes.2021.03.042>
- Yamamura S, Iida C, Kobayashi Y, Watanabe M, Amachi S (2021) Production of two morphologically different antimony trioxides by a novel antimonate-reducing bacterium, *Geobacter* sp. SVR. *J Hazard Mater* 411:125100. <https://doi.org/10.1016/j.jhazmat.2021.125100>

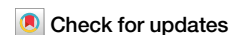
- Yang H, Gao K, Feng S, Zhang L, Wang W (2015) Isolation of sulfide remover strain *Thermithiobacillus tepidarius* JNU-2, and scale-up bioreaction for sulfur regeneration. *Ann Microbiol* 65:553–563. <https://doi.org/10.1007/s13213-014-0891-2>
- Yang Z, Hosokawa H, Sadakane T, Kuroda M, Inoue D, Nishikawa H, Ike M (2020) Isolation and characterization of facultative-anaerobic antimonate-reducing bacteria. *Microorganisms* 8:1435. <https://doi.org/10.3390/microorganisms8091435>
- Ye L, Chen H, Jing C (2019) Sulfate-reducing bacteria mobilize adsorbed antimonate by thioantimonate formation. *Environ Sci Technol Lett* 6:418–422. <https://doi.org/10.1021/acs.estlett.9b00353>
- Yu C, Cai Q, Guo ZX, Yang Z, Khoo SB (2002) Antimony speciation by inductively coupled plasma mass spectrometry using solid phase extraction cartridges. *Analyst* 127:380–385. <https://doi.org/10.1039/B206829J>
- Zhang G, Ouyang X, Li H, Fu Z, Chen J (2016) Bioremoval of antimony from contaminated waters by a mixed batch culture of sulfate-reducing bacteria. *Int Biodeter Biodegradation* 115:148–155. <https://doi.org/10.1016/j.ibiod.2016.08.007>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

<https://doi.org/10.1038/s43247-024-01788-8>

Fluid inclusions in magmatic ilmenite record degassing in basic magmas



Anthony Pochon^{1,2} , Daniel J. Kontak³ , Giada Iacono-Marziano¹, Eric Gloaguen^{1,2,5} , Johann Tuduri^{1,2} , Tom Chatelin¹, Jacques Précigout¹ , Héctor Campos Rodríguez¹, Valentin Mollé¹, Blandine Gourcerol² & Loïs Monnier⁴

Magmatic volatile phases play a major role in igneous systems, but indirect sampling of the magmatic fluid, especially for basic magmas, remains challenging to document. Here, we report compelling evidence of primary fluid inclusions trapped within magmatic ilmenite from two different basic intrusive settings: Armorican Massif (France) and Central Iberian Zone (Spain). Fluid inclusions have a solute chemistry dominated by sodium, calcium, chlorine, sulfur and iron, with detectable contents of metals and metalloids and thus likely record the onset of late-stage magmatic volatile saturation in these basic magmas. Hence, we argue the presence of fluid inclusions in ilmenite may be a good indicator for magma degassing in these settings and importantly records the magmatic-hydrothermal transition. Additionally, this study suggests that the trapping of the magmatic volatile phase during ilmenite (and other opaque minerals) crystallization may be more common but at present an underappreciated phenomenon in basic igneous magmatic systems.

Fluids have played a major role in Earth evolution and its many geological processes. Since the pioneering work of Sorby¹, which provided petrographic evidence of fluid inclusions (FI) in a variety of mineral phases from diverse geological settings, these time capsules of paleo-fluids, the only direct samples of their former presence, have become fundamental tools for studying Earth processes. They have considerably contributed to the understanding of chemistry of the atmosphere and hydrosphere^{2,3}, sedimentary basin evolution⁴, ore-forming processes⁵, deep crustal fluid properties^{6,7}, and mantle volatiles⁸. Originally, FI studies were limited to minerals that transmitted visible light (400–700 nm) with quartz and carbonates among the most widely used. However, the advent of infrared (IR) cameras⁹ revolutionized the application of FI studies by enabling their investigation in some opaque phases that transmit longer wavelengths of light from near infrared to beyond 2000 nm. This breakthrough expanded the scope of FI research to include a broader range of phases, such as oxides (e.g., hematite, wolframite), sulfides (e.g., pyrite, stibnite, Fe-rich sphalerite), and sulfosalts (e.g., tetrahedrite), as comprehensively summarized by Lüders¹⁰.

Despite the progress made in applying the use of FI to numerous geological settings, debates continue about the role and significance of fluids in some geological processes. For instance, volatile saturation leading to magma degassing is critical for understanding magma ascent and eruption¹¹ (e.g., Cashman, 2004) and a prerequisite for many ore-forming

processes^{12–14} whereby fluid circulation associated with intermediate-to-felsic magmatism is considered fundamental to the origin of large hydrothermal metalliferous systems^{5,15}. Conversely, the role of fluids in the formation of mafic-ultramafic intrusion-hosted magmatic sulfide and platinum-group element (PGE) deposits is still debated^{14,16,17}.

Although the former presence of volatiles dissolved in basic magmas is relatively well known due to studies of melt inclusions (MI)^{18–21}, sampling of these exsolved volatiles are rarely preserved in the plutonic settings of such magmas. However, some studies have inferred the former presence of such material preserved as FI in basic and mafic rocks^{22–25}. These investigations were mainly focused on FI hosted in olivine, apatite, plagioclase or quartz in gabbroic rocks and related pegmatoids. In these latter rocks, the presence of early primary FI first indicates the early exsolution of CO₂-rich vapor from the melt which is consistent with solubility data and modeling of basaltic systems²⁶. Subsequently, during progressive crystallization, the later-stage residual evolved melts attained volatile saturation as reflected by the entrapment of either immiscible^{22–24} (i.e., H₂O–CO₂–NaCl ± Fe-rich brines and H₂O–CO₂-rich vapors) or homogeneous^{22,23,27} volatile phases. Two main processes have been suggested to explain the generation of brine variations in gabbroic rocks. The first implies exsolution of magmatic fluids under supercritical conditions with condensation of immiscible droplets of brine in a vapor phase^{24,28–31}. In contrast, the second involves direct exsolution of highly-saline magmatic fluids from residual, evolved, late-stage

¹ISTO, UMR7327, Université d'Orléans, CNRS, BRGM, F-45071 Orléans, France. ²BRGM, F-45060 Orléans, France. ³Harquail School of Earth Sciences, Laurentian University, Sudbury, Ontario, P3C 2E6, Canada. ⁴GET, CNRS/IRD/UPS/CNES, Université de Toulouse, 31400 Toulouse, France. ⁵Deceased: Eric Gloaguen e-mail: a.pochon@brgm.fr

melts in the absence of a discrete vapor phase^{22,23,27,29,32,33}. These gabbroic-hosted FI of magmatic origin may also contain noticeable amounts of Ca, S, and metals²⁵ (e.g., Cu, Zn and Pb). However, the ability to study magmatic FI in basic rocks is not always possible as phases commonly hosting FI are either often lacking (e.g., quartz or olivine) or commonly modified by later fluids (e.g., apatite, plagioclase).

In order to document saturation of a magmatic volatile phase (MVP) in two separate basic (mafic) plutonic settings, we have applied a wide range of analytical methods to test for the preservation of such fluids in ilmenite, as it is a common late-stage magmatic phase in these systems. Here we present compelling evidence arguing for the entrapment of primary FI in magmatic ilmenite during the latter stages of crystallization of the residual melts. Additionally, we also document qualitatively the composition of these trapped fluids, the results of which are consistent with that known and expected for magmatic fluids associated with basic magmas. As ilmenite is common in many reduced, basic-to-intermediate magmas, we propose therefore that ilmenite might be considered as a potential host for FI containing magmatic fluids in such rocks. Therefore, researchers seeking evidence for the former existence of such fluids should consider examining this mineral phase, especially when other hosts for FI are not preserved or subsequently modified by subsolidus processes.

Geological background

The samples used in the study originate from two different basic intrusions: the Saint-Jean-du-Doigt (SJD) intrusion (Armorican Massif, France) and the La Codosera (CS) syncline basic sills (Central Iberian Zone, Spain, Supplementary Fig. 1). The SJD intrusion is a shallow-level, layered basic-silicic intrusive body emplaced at ca. 347 Ma³⁴ within Paleoproterozoic to Carboniferous host rocks. The pluton is mainly composed of underplated subhorizontal gabbroic sills with some sub-parallel felsic layers, subordinate crosscutting dolerite dykes and genetically-related basic amphibole-bearing pegmatoids³⁵. It is exposed along a continuous west-to-east cross-section commencing with the lower part of the intrusion and finishing in its roof zone^{34,36}. The mineralogical composition of the sampled rocks is presented in Supplementary Table 1. It has been demonstrated that an increase of high-temperature alteration occurs eastwards towards the intrusion roof, as evidenced from the complete saussuritization of calcic plagioclase, pervasive replacement of clinopyroxene and primary amphibole by actinolite, and the breakdown of ilmenite to titanite and rutile³⁶. This progressive alteration has been interpreted to result from the interaction of almost solidified gabbro with magmatic fluids posited to have exsolved during its late magmatic stage and thus reflecting the magmatic-hydrothermal transition within the SJD basic intrusive body³⁶.

The basic intrusions from CS consist of a major swarm of sills up to 400 m thickness hosted in Carboniferous slates. These sills are attributed to a single-pulse of tholeiitic basic magma emplaced at 354 ± 5 Ma³⁷. The sills are mainly composed of a floor and a roof sequence of gabbroic and doleritic rocks with interleaved pegmatitic units that are well described by López-Moro et al.^{38,39}. At the base, a pristine mineralogy is preserved in a fine-grained dolerite whereas the central part is coarse-grained gabbro. The intensely altered (e.g., amphibole) roof zone consists of fine-grained dolerite (mineralogical composition in Supplementary Table 1) with abundant pegmatite lenses.

Results

Textural description of ilmenite

Ilmenite crystals are subhedral to anhedral in the gabbroic and doleritic facies of both basic systems. They are mostly intergranular and occur along grain boundaries between plagioclase and amphibole, or clinopyroxene, or between primary amphibole and later low-temperature amphibole. Ilmenite is considered therefore to represent a primary, late-stage magmatic phase^{36,39}. For SJD samples, ilmenite has a grain size ranging between 100 and 2000 μm with smaller grains in the upper part and larger ones in the central part of the complex. It is texturally homogeneous in backscattered electron (BSE) images (Fig. 1A–C) and lacks hematite exsolution textures.

For CS samples, it is again mostly homogeneous in BSE images with similar grain size, but some hematite exsolution textures are observed (Fig. 1D). Ilmenite from SJD is chemically uniform and near end-member composition, whereas for CS samples, its chemistry deviates from that of the end-member and falls along the ilmenite-hematite solid solution (Fig. 2, Supplementary Table 2). These data indicate that slightly more oxidizing conditions prevailed during crystallization of ilmenite from CS versus SJD.

Ilmenites from the SJD intrusion (central and upper part) and the CS basic sills (upper part) are characterized on their exposed surfaces by a high abundance of well-distributed voids with sizes ranging between 0.5 and 7 μm , most of them being lower than 2 μm (Fig. 1B–J); in contrast ilmenite from the lower part of SJD intrusion is noted to lack observable voids (Fig. 1A). The outlines of these voids vary from spherical, equant to multifaceted negative-crystal shapes (Fig. 1I, J). Such negative shapes are commonly observed in FI-bearing transparent phases (e.g., quartz or carbonate) examined in both transmitted (TL) and reflected (RL) light modes, as well as BSE imaging^{40–42}. These voids are thus posited to correspond to breached or opened FI. As the 2D polished cuts of ilmenite studied are presumed to reflect ilmenite grains with random orientations, it is therefore inferred that the FI locally account for up to 15% of the total crystal volume. The opened FI are mostly homogeneous in their distribution throughout the ilmenite grains, but also define sub-parallel trails (Fig. 1C, J) or are concentrically distributed about silicate-rich inclusions (Fig. 1H). In rare cases, opened FI are heterogeneously distributed and may include solids such as gold, barite, and Pt- and Sr-bearing phases (Supplementary Fig. 2).

In most ilmenite crystals, textural observations highlight that rims are devoid of FI (Fig. 1C), and that crack-like channels and irregular-shaped areas barren of FI may also traverse the otherwise FI-rich ilmenite. These latter areas are often spatially linked to titanite, or contain irregular patches of titanite $\pm$ rutile (Fig. 1E–G). Such ilmenite likely records variable amounts of subsolidus replacement post its crystallization (Fig. 1E, F) with some grains replaced via fluid interaction by up to 80% by titanite and/or rutile in the most altered samples (Supplementary Fig. 2). Titanite and rutile are commonly present as reaction rims and also lining thin fractures and cavities in both settings. Additionally, contacts between ilmenite and its alteration products are sharp and irregular.

Electron backscatter diffraction (EBSD) maps reveal that the most misoriented parts of ilmenite grains follow what appear to be fluid-like pathways coincident with fractures and areas barren of FI (Fig. 3A–C). These FI-free cracks are often filled with titanite $\pm$ rutile (Fig. 1G). In contrast, the EBSD patterns for FI-rich areas are relatively uniform and closely resemble the patterns for FI-free ilmenite from the lower part of the SJD intrusion (Supplementary Fig. 3). Chemical maps (Fig. 3D, Supplementary Fig. 3) show that FI-rich and FI-free areas of ilmenite have a similar chemistry, the only subtle differences being due to the presence of FI.

Insight into magmatic fluid chemistry

The chemistry of trapped FI was determined via two indirect methods: (i) LA ICP-MS analyses of distinct FI-free and FI-bearing areas of ilmenite; and (ii) coupled SEM-EDS, EPMA, and LA ICP-MS analyses of evaporate mounds. The LA ICP-MS analyses of ilmenite (Fig. 4A) yield concentrations with a similar order of magnitude for most compatible trace elements^{43,44} (i.e., V, Nb, Ta, Co, Zn, Ni) in both settings (SJD and CS) and both distinct FI-free and FI-bearing areas. Except for Cu concentration in both settings and W concentration in the CS setting that show the same order of magnitude for FI-free and FI-bearing areas, most incompatible trace elements^{43–46} (i.e., Sn, Mo, Sb, W, Pb) are enriched in FI-bearing areas. This observation is corroborated by LA ICP-MS traverses (Fig. 4B) which highlight no sharp differences for Ni and Cu, but clear enrichment in Sb and Mo when crosscutting FI-bearing areas. Again, when LA ICP-MS traverses (Fig. 4C) crosscut FI-free ilmenite from the lower part of the SJD intrusion, Sb and Mo are below the detection limit. These latter observations suggest the incompatible elements are most likely concentrated in FI. The Sb, Mo, Sn, W (for SJD only), and Pb contents generally show larger variability in FI-bearing areas and also have different degrees of enrichment between the two

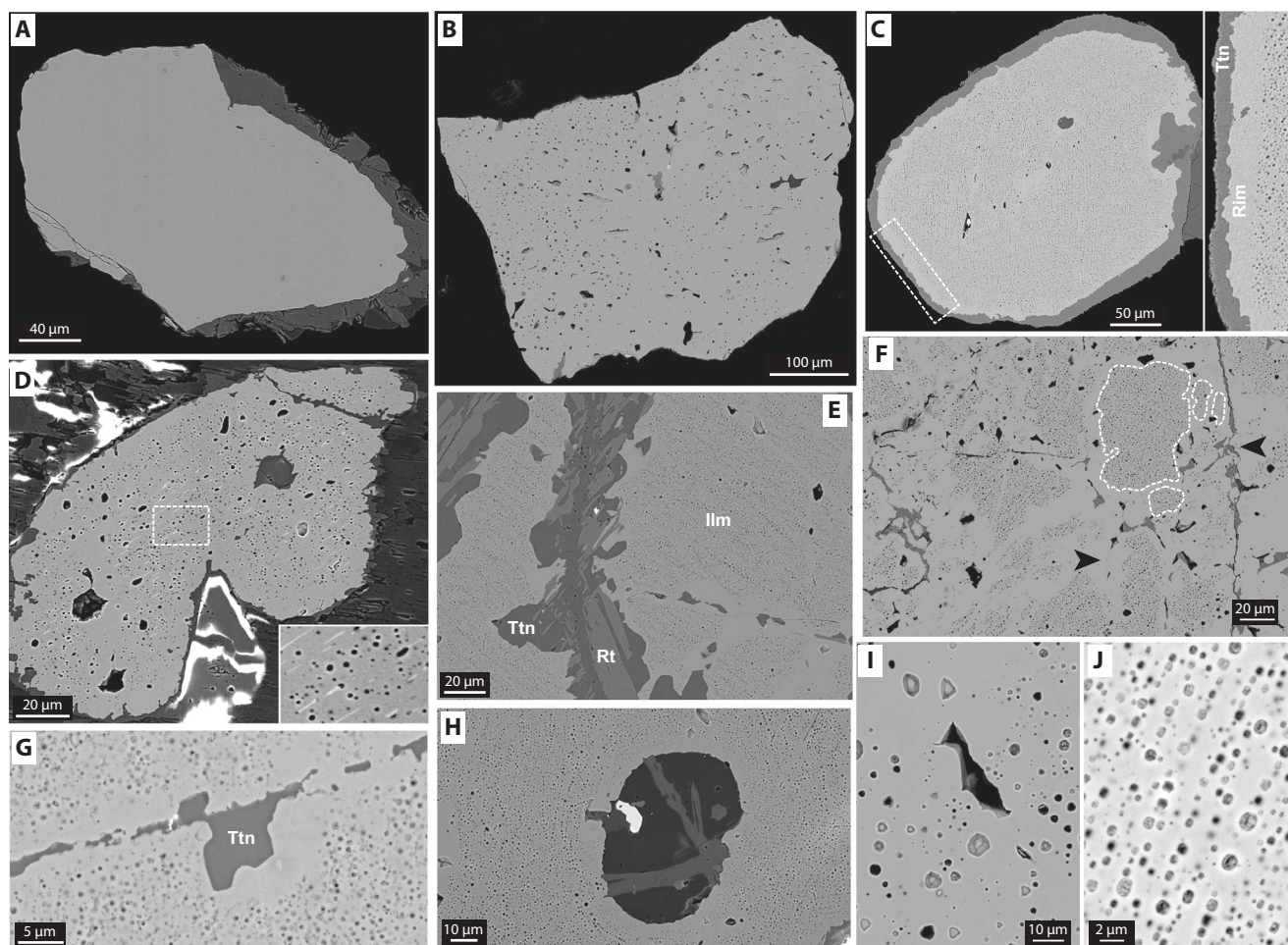


Fig. 1 | Representative back-scattered electron (BSE) images of textural and petrographic features of ilmenite from both settings. Ilmenite from the lower (A), central (B) and upper (C) parts of the Saint-Jean-du-Doigt (SJD) intrusion. The inset in (C) shows the crystal core is full of FI, whereas the rim is FI depleted and replaced by titanite (Ttn). D Ilmenite from La Codosera syncline (CS) showing the presence of FI and hematite exsolution lamellae (see the inset). E Ilmenite (Ilm) from SJD showing and rutile (Rt). F Ilmenite from CS with abundant FI and exhibiting the same secondary texture seen in the SJD samples: cracks are sometimes lined by titanite, and have halos lacking FI (black arrows) which form isolated patches of FI-rich areas (white dashed lines). G Sample from SJD showing a fracture lined by secondary titanite (Ttn) with a halo lacking FI. H Ilmenite from CS displaying the radial distribution of FI around silicate-rich inclusions. I, J Sample from SJD showing opened FI with negative alteration along fractures or fluid pathways with formation of secondary titanite (Ttn)

and rutile (Rt). F Ilmenite from CS with abundant FI and exhibiting the same secondary texture seen in the SJD samples: cracks are sometimes lined by titanite, and have halos lacking FI (black arrows) which form isolated patches of FI-rich areas (white dashed lines). G Sample from SJD showing a fracture lined by secondary titanite (Ttn) with a halo lacking FI. H Ilmenite from CS displaying the radial distribution of FI around silicate-rich inclusions. I, J Sample from SJD showing opened FI with negative alteration along fractures or fluid pathways with formation of secondary titanite (Ttn)

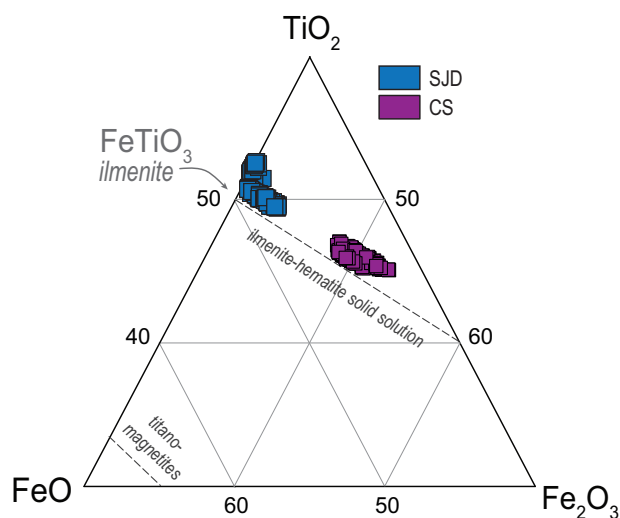


Fig. 2 | Major element composition of ilmenite. Ternary plot of the FeO-Fe₂O₃-TiO₂ system showing the hematite-ilmenite solid solution⁸⁶ and data for Saint-Jean-du-Doigt (SJD) and La Codosera syncline (CS) samples. Data for SJD is from Pochon et al.³⁶.

settings likely reflects distinct fluid chemistries, although heterogeneities related to the FI which are located at different depths below the surface and analytical uncertainties are difficult to assess.

The mounds generated by induced decrepitation of FI (Fig. 5) vary from small isolated features (Fig. 5A, E, F–H) to trails (Fig. 5B–E) in addition to abundant debris that represents splattering of precipitates and projection of fragmented mineral host away from the core areas of the mounds; all these features have shapes from irregular to cubic which are typical mound characteristics⁴². High-resolution X-ray maps show that the major element solute chemistry of the mounds is dominated by Na and Ca, with Fe, as cations, and by Cl and S, as anions (Fig. 6A, B, Supplementary Fig. 4), as is also confirmed by the LA ICP-MS traverses (Fig. 6C, D, Supplementary Fig. 5). The aqueous and non-aqueous volatile or gas content (e.g., H₂O, CO₂ or CH₄) cannot be determined with this protocol. The LA ICP-MS traverses also indicate increasing contents of the incompatible trace element (e.g., Sr, As, Sb, Cu) in mounds from FI-rich areas of ilmenite compared to FI-free areas (Fig. 4).

Discussion

We observed that crystallized ilmenite of magmatic origin from two different settings contain voids that are strikingly similar to FI regularly seen in both transparent and opaque phases via TL and IR observations. As far as we

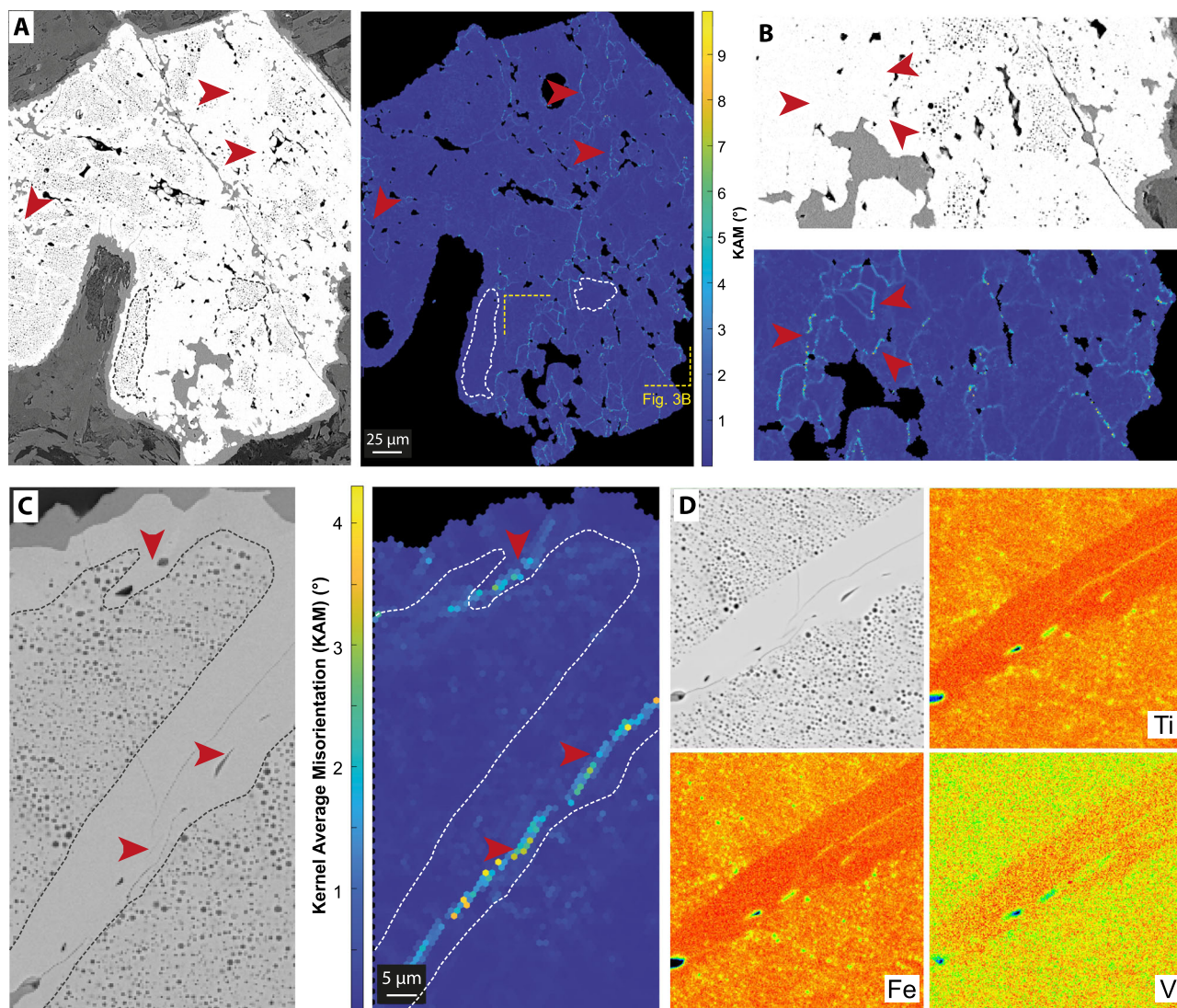


Fig. 3 | Representative electron backscatter diffraction (EBSD) and high-resolution X-rays maps of ilmenite from both Saint-Jean-du-Doigt (SJD) and La Codosera syncline (CS). A, B Back-scattered electron (BSE) images of ilmenite with matching EBSD maps representing the Kernel Average Misorientation (KAM). Sample is from the upper part of the CS intrusion. White dashed line and red arrows, respectively, highlight FI-rich areas and fractures. Yellow dashed line inset

corresponds to the area observed in (B). C BSE image of ilmenite with matching EBSD map representing the KAM. Sample is from the upper part of SJD intrusion. Dashed line and red arrows, respectively, highlight FI-rich areas and fractures. D High-resolution X-ray maps for Ti, V, and Fe of the same ilmenite grain as from (C) with a FI-depleted zone developed around a central fracture.

know, this is the first report of inferred FI in magmatic ilmenite. We therefore reiterate the evidence which shows that these are indeed fluid inclusions⁴⁰: (i) their size and shape are similar to typical FI; (ii) many are negative shaped as is common for FI; (iii) they are mostly homogeneously distributed throughout the host in both two- and three dimensions (Supplementary Fig. 6); and (iv) heating ilmenite up to 600 °C generated Na-Ca salt mounds identical in form and chemistry (i.e., Na-Ca-Cl-S) to those formed from FI hosted in both transparent and opaque phases⁴².

EBSD maps indicate that FI-free areas, often associated with titanite ± rutile, are secondary in origin compared to FI-bearing areas. Thus, whereas FI-bearing areas in ilmenite from both intrusions are posited to represent relics of primary magmatic ilmenite hosting FI, the FI-barren areas are interpreted as post-magmatic in origin and attributed to subsolidus reaction of the host ilmenite with fracture-controlled incursion of a Ca-bearing hydrous phase. The irregular and sharp contacts between ilmenite and titanite ± rutile, the preserved shapes of ilmenite and titanite ± rutile - bearing cracks strongly suggests that the ilmenite breakdown occurred via interface-coupled dissolution-precipitation process (ICDP)^{47–49}, thus post-

dating FI entrapment. All these observations suggest therefore that FI in the magmatic ilmenite are primary and thus likely represent entrapment of an exsolved MVP. Alternatively, the trapped FI might be considered as an ICDP-related porosity⁵⁰ and hence of secondary origin, but this would not corroborate the textural observations and EBSD data presented above. Most important in this regard is that in ICDP the porosity generally characterizes the product phase which thereby implies the ilmenite to be of secondary origin, which is evidently not the case. Furthermore, no relic-clear areas were noted in any studied ilmenite (i.e., about 400 grains examined) and it is very unlikely that such secondary porosity was only filled by fluids with no mineral phase. We conclude therefore that the most reasonable interpretation of the noted features is that they are primary FI trapped during growth of the ilmenite. Their negative shapes are however a secondary feature, as in all FI, and due to the equilibration of the FIs during cooling via dissolution-precipitation processes to minimize surface free energy^{40,41}. In any case, the occurrence of primary FI in magmatic ilmenite demands the presence of a fluid phase that we interpret as an exsolved MVP generated during the latter stage of magma crystallization at the magmatic-hydrothermal transition (Fig. 7) related to second boiling⁵¹. Importantly,

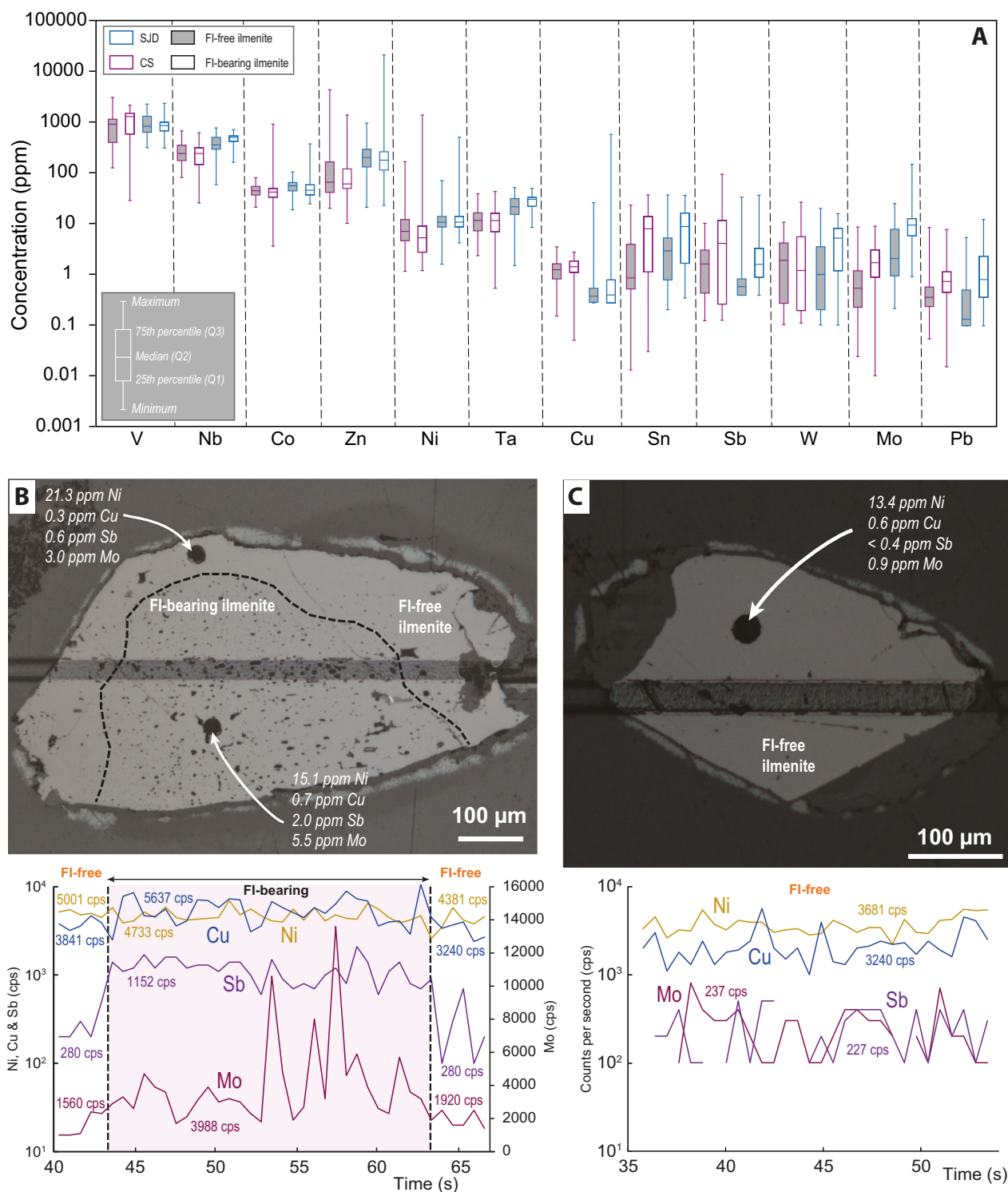


Fig. 4 | Trace element composition of ilmenite. **A** Box plots for trace element contents in FI-bearing and FI-free ilmenite from Saint-Jean-du-Doigt (SJD) and La Codosera syncline (CS) samples. LA ICP-MS traverses of **(B)** ilmenite from the

central part of SJD intrusion with FI-free and FI-bearing domains and **(C)** FI-free ilmenite from the lower part of the SJD intrusion. Spot analyses data for SJD are from Pochon et al.³⁶.

we note, however, that MI have not been identified in any ilmenite from either setting, which does not necessarily infer that they were not trapped but may instead reflect the challenges of identifying them. Of note however is that if MI were exposed at the ilmenite surface, it would be difficult to distinguish if these originated as silicate embayments or crystal intergrowths versus crystallized MI^{40,52,53}. As an example of the latter, we noted the presence of the silicate-rich inclusion in Fig. 1H.

Although there is petrological evidence for a hydrous component in the melt, as indicated by the presence of amphibole and biotite, only cryptic evidence for the former presence of an aqueous fluid phase is generally preserved in plutonic rocks²¹, especially because of the inherently slow post-solidus modification that affects plutons compared to their petrogenetically equivalent chilled volcanic rocks. However, the presence of posited primary FI in ilmenite makes this mineral an ideal candidate to trap and preserve the

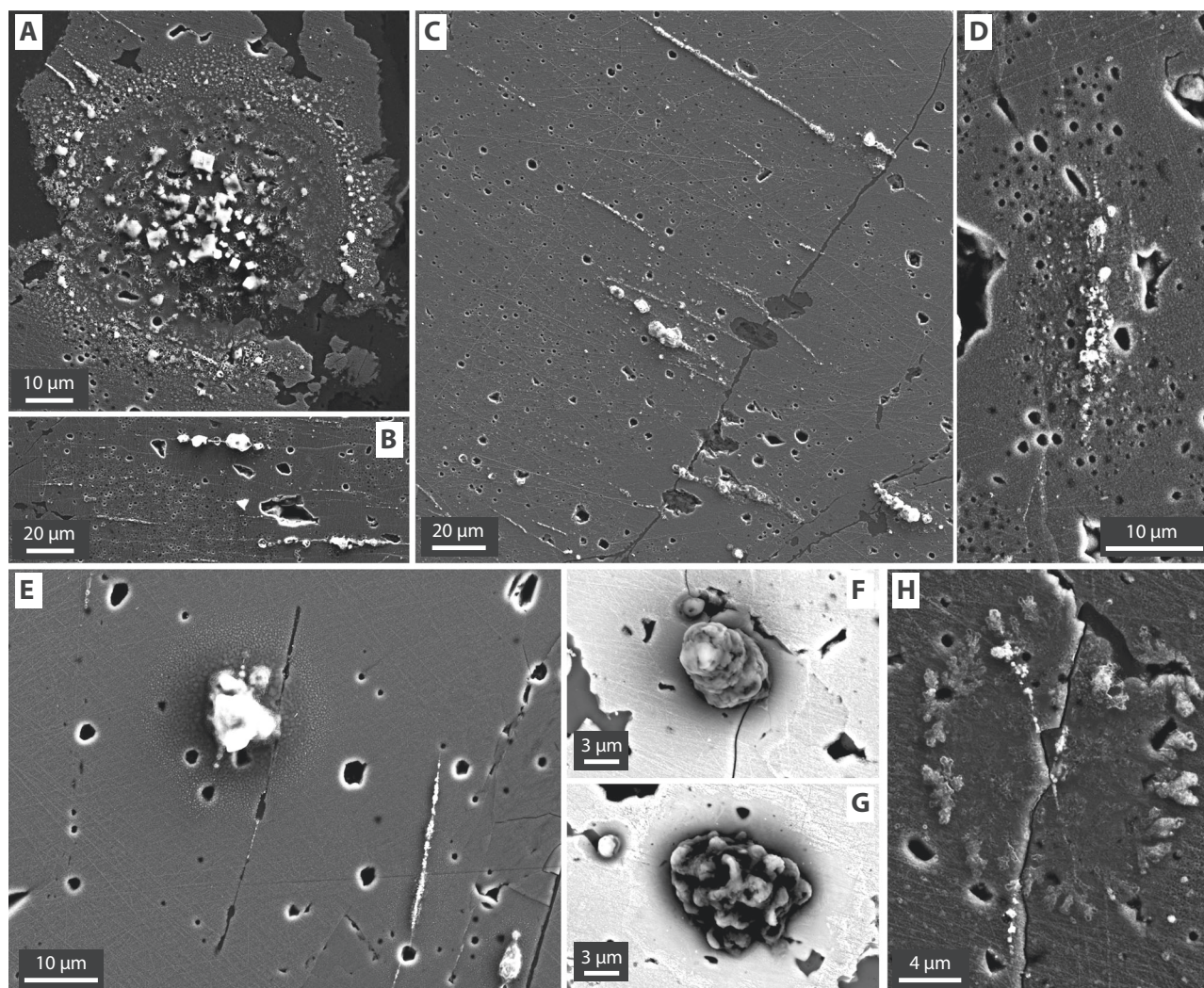


Fig. 5 | Examples of Na-Ca-rich decrepitite mounds from Saint-Jean-du-Doigt (SJD) and La Codosera syncline (CS). A Secondary electron (SE) image of a composite circular evaporate mound from CS; note the cubic habit of the material in the central part and annular array of debris. B–E SE images of decrepitite mounds that form trails and clusters that reflect the presence of FI-rich areas in the sub-

surface of ilmenite from SJD (C, E) and CS (B, D) settings. The trails are the result the fluid migrating up along fractures which were preexisting or generated by the decrepitation. F, G Close-up back-scattered electron (BSE) images of singular evaporate mounds from CS samples. H SE image of circular and partly dendritic mound from CS sample.

MVP as primary FI in basic plutonic rocks. This can offer new perspectives where conventional convincing indicators for the generation of MVP commonly observed in more intermediate-to-felsic magmas, such as comb-layered quartz, miarolitic cavities, or pegmatites, are lacking or not preserved^{54,55}. Thus, where such FI are present their chemistry (e.g., analysis of evaporate mounds) provides the means to access the metal abundances in magmatic fluids exsolved during the last crystallization stages of basic magmas. The solute composition (i.e., Na-Ca-Cl-S-Fe) and presence of metals and metalloids are indeed consistent with those noted to be enriched in arc-related volcanic gases from basic magmas^{56,57} (i.e., Cu, Sn, Mo, Sb, W, and Pb). Although we were unable to measure the aqueous and non-aqueous volatile component (or gas), we infer the MVP to be H₂O-dominated as magmatic amphibole is present and ilmenite is a late-magmatic phase. Indeed, experimentally-based solubility models and studies of volatile contents in MI show that the exsolved volatile phase coexisting with basic magmas is CO₂-rich during early crystallization stages, and increasingly H₂O-rich with subsequent crystallization²¹. Both first boiling (due to magma decompression) and second boiling (due to magma crystallization) lead to an increase in H₂O proportion in the exsolved volatile phase. This is mainly due to the fact that H₂O solubility is higher than CO₂ solubility in basic magmas, as it is for all silicate magmas⁵⁸, at crustal

pressures, and, to a lesser extent, to the different relationships between pressure and solubility, i.e., linear for CO₂ and square root for H₂O⁵⁹.

As evidenced by the presence of primary FI, the late residual melts of these two basic magmas were volatile saturated, but the extreme abundance of trapped fluid (i.e., up to 15 % of the crystal volume noted above) in ilmenite raises questions, especially about processes leading to fluid entrapment. Three mechanisms might account for the generation of FI are considered below, although we do not consider the first two applicable to the present study for reasons discussed. The first is that the FI may have originated from exsolution of dissolved water hosted in the ilmenite crystal lattice. This implies the FI were released directly from the host after it formed, thus analogous to that suggested for origin of FI in some metamorphic host phases such as quartz⁶⁰, kyanite⁶¹ or omphacite in UHP eclogite⁶². Implicit therefore is that ilmenite incorporated some amount of a hydrous species, as suggested for some nominally anhydrous minerals such as pyroxenes or rutile⁶³. Several factors argue against this however. The lack of any data supporting incorporation of some amount of hydrous species into the ilmenite structure. Furthermore, even if this occurred the likely trace amount of water would be insufficient to generate the abundance of the FI observed which we estimated at up to 15% of the ilmenite volume. Lastly, such FI would likely not contain the Na, Cl or S documented in this study as

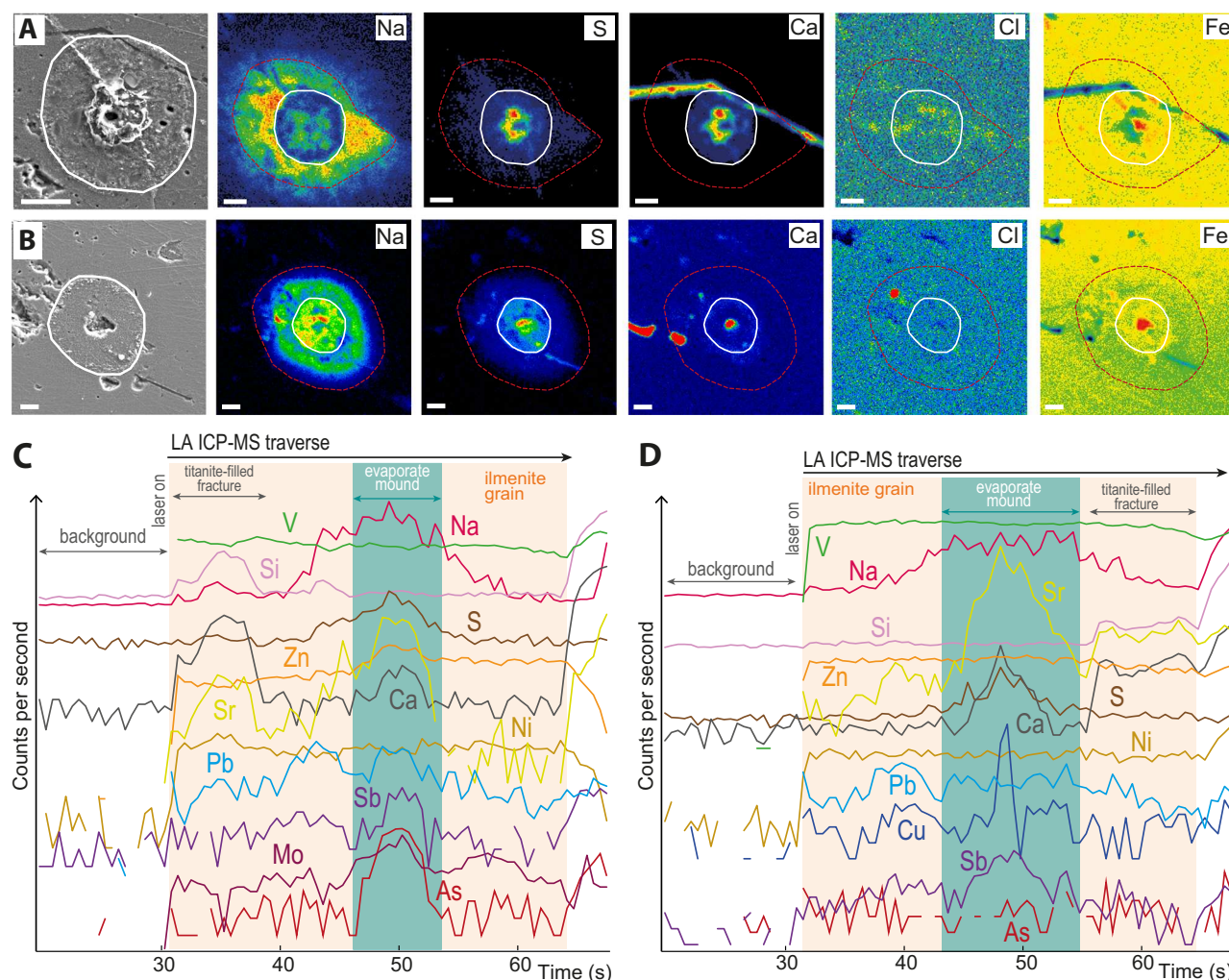


Fig. 6 | Representative chemical maps and time-resolved LA ICP-MS signals of circular evaporate mounds from Saint-Jean-du-Doigt. A, B Chemical maps for representative circular evaporate mounds obtained via electron probe micro-analysis (EPMA). White line circumscribes the mound, while the red-dashed line

circumscribes the halo around the mound. White bar in images is 10 μm . C, D Time-resolved traverses of LA ICP-MS analysis of decrepitated mounds from the same ilmenite grains in (A) and (B), respectively. The curves have been offset vertically for clarity and truncated curves represent zero counts.

these elements would also have to be in the ilmenite crystal lattice and also be exsolved synchronously with the hydrous species. The second mechanism is that ilmenite directly crystallized from the MVP, thus be considered as a hydrothermal phase. However, this is unlikely as the rare cases where ilmenite is interpreted as hydrothermal is reported to be Mn- and/or Zn-rich^{64,65}, which is clearly not the case noted in this study.

We thus propose a third mechanism which might account for the generation of the noted FI hosted by ilmenite. As we have interpreted the FI to represent sampling of an exsolved H_2O -dominated MVP related to second boiling, it implies that residual melt will become H_2O -saturated at the very end of crystallization (i.e., 95 % crystallization⁵¹). From this stage, the documented abundant entrapment of FI by ilmenite could result from the transient trapping of exsolved bubbles in the crystal mush followed by the near-simultaneous nucleation of both ilmenite and bubbles. Thus at the time of ilmenite crystallization a component of the exsolved MVP must have been present as bubbles, at least transiently, in the residual melt of the mush, otherwise a connectivity of the MVP would have formed fluid-like channels which would have caused outgassing of the volatiles^{66,67}. Therefore, it is possible the ilmenite may have acted as a preferential site of bubble nucleation, as is generally observed for Fe-Ti oxides^{68–70}. However, both natural analogues⁷¹ and experimental evidence⁷² of bubble nucleation show that Fe-Ti oxides are generally smaller than coexisting bubbles which are in fact sometimes trapped inside them, which is contrary to our observations.

Ilmenite larger than the trapped bubbles could be explained if we consider a crystallization rate fast enough to prevent bubble coalescence and growth. A CO_2 -bearing melt may be also envisaged, as low- CO_2 diffusivity delays bubble growth and thus promotes almost continuous bubble nucleation which would result in a high density of small bubbles⁷³. However, if the exsolved MVP is instead related to second boiling then the $\text{H}_2\text{O}/\text{CO}_2$ ratio of the residual melt would necessarily be high and would promote coalescence versus nucleation⁷³. The exsolution of MVP could also be triggered by the incipient crystallization of ilmenite in the late residual melt with related progressive exsolution of the MVP at the developing crystal-melt interface with entrapment of FI.

Conclusions

We document here the presence of inferred primary FI in ilmenite which are suggested to represent the trapping of the MVP generated in the latter stages of magma crystallization in two different basic igneous settings. Although the evidence for volatile saturation and magmatic FI in basic magmas is previously reported in other similar settings, the occurrence of primary FI in ilmenite is here recognized and studied for the first time to the best of our knowledge. This study thus highlights that ilmenite might be a suitable host for the MVP, especially where it has not experienced important sub-solidus modification which, as noted herein, can easily be recognized due to the presence of secondary reaction products (e.g., titanite $\pm$ rutile).

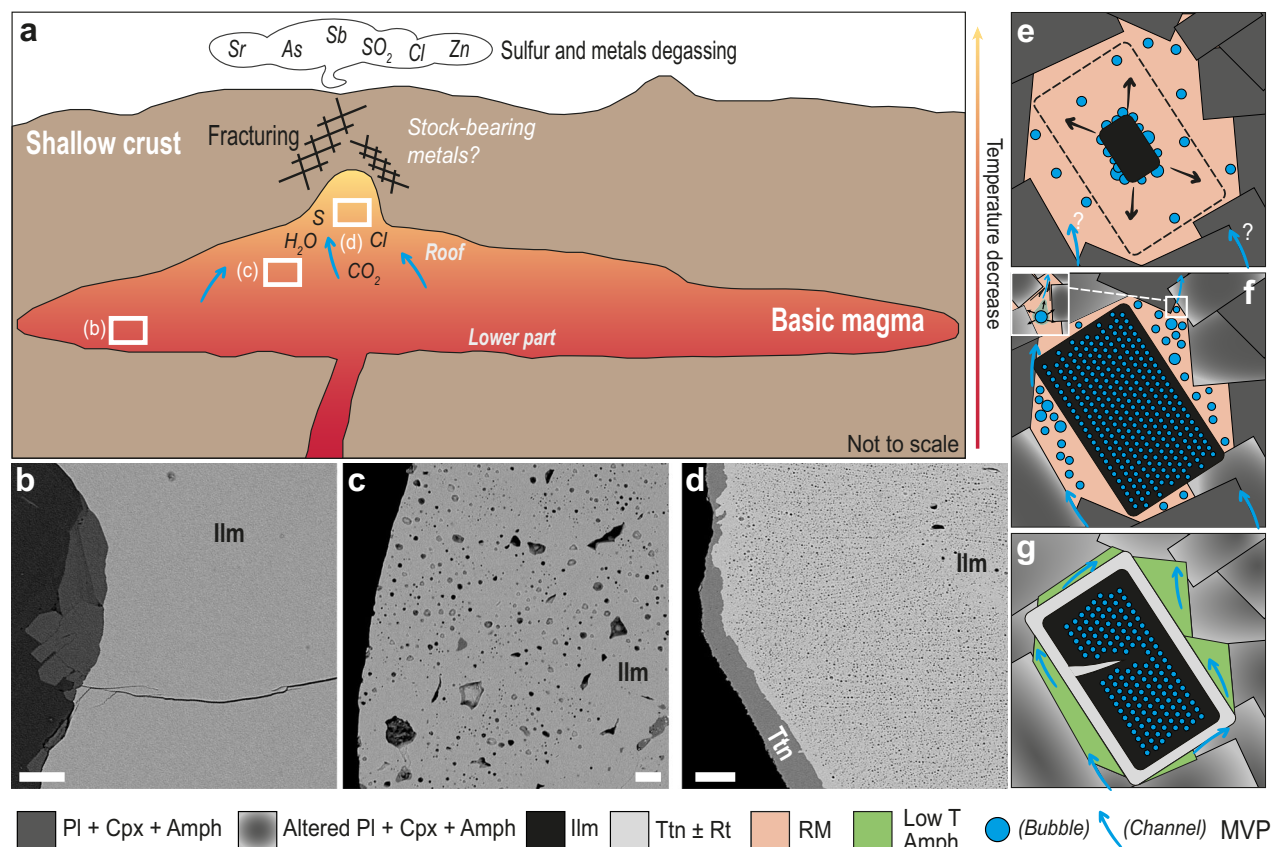


Fig. 7 | Schematic diagram illustrating the conceptual model of entrapment of magmatic volatile phases within ilmenite. a General geometry (not to scale) of a gabbroic intrusion with the location of insets (b), (c) and (d). **b–d** Back-scattered electron (BSE) images of ilmenite (Ilm) texture from the lower (b), central (c) and upper (d) parts of the basic intrusion that records magma degassing from the base to the top. White scale bar represents 20 μm . **e** Onset of volatile exsolution in the residual melt (RM) of the mush and release of a magmatic volatile phase (MVP) via second boiling. Ilmenite may act as a preferential site for nucleation of bubbles during its growth or incipient ilmenite crystallization may act as the trigger of progressive exsolution of bubbles at the developing crystal-melt interface. **f** Ilmenite

grain crystallizes more or less quickly and may easily traps abundant MVP as fluid inclusions (FI) during its progressive crystallization and magma cooling. **g** Following ilmenite formation, trapped FI likely undergo re-equilibration via necking, whereas the untrapped MVP likely escapes via capillary fracturing or others processes and probably coalesce towards the surface. The latter MVP interacts with and modifies earlier crystallized silicate phases. Interaction of ilmenite with fluids saturated in Si and Ca (due to alteration of calcic plagioclase (Pl) and mafic minerals) causes ilmenite breakdown. This fracture-controlled subsolidus alteration is responsible for the formation of FI-free ilmenite and the development of secondary titanite (Ttn) $\pm$ rutile (Rt). Cpx - clinopyroxene, Amph - amphibole, Low T - low temperature.

As the noted FI reported record the late-stage volatile saturation in basic magmas, it offers the rare opportunity to study the chemistry and metal enrichment of such magmatic fluids produced in highly crystallized basic magmas. Although qualitative at this time, our results showed that the FI chemistry (i.e., Na-Ca-Cl-S-Fe for solute composition and Cu, Sn, Mo, Sb, W, and Pb for metal and metalloids) is consistent with what is known and expected for magmatic fluids associated with basic magmas. Additional studies are, however, needed to further quantify the composition (especially solvent species such as H_2O or CO_2 for instance) and enhance the understanding of volatile saturation in basic magmas, as it was not the focus of this study. In this regard, future work might involve the use of high-resolution nano-computed tomography (nanoCT) to quantify the 3D distribution of FI⁷⁴, whereas focused ion beam-scanning electron microscope (FIB-SEM)^{75,76} and/or time-of-flight secondary ion mass spectrometry (TOF-SIMS)⁷⁷ could help to quantify the presence of daughter minerals (without contamination due to polishing), volatile species such as H_2O , CO_2 , sulfur species, and chlorine-bearing compounds, as well as metals.

Finally, this study should encourage others to apply similar methods to look for FI in ilmenite and other opaque phases for those interested in better documenting the presence and nature of the MVP during the latter stages of magma crystallization, which is otherwise challenging to do. This consideration is particularly relevant for contentious settings, where the presence and origin of the fluid phase are still debated. Hence, the implication

might be far reaching for both igneous petrology and relevant ore-forming environments in basic-to-mafic systems.

Methods

For this study, we investigated six representative rock samples from the lower, central, and upper parts of the SJD intrusion and two samples from the roof zone of the CS basic sills (Supplementary Fig. 1 & Supplementary Table 1). A comprehensive suite of analytical techniques was used to study the materials and document the presence, distribution, nature and qualitative chemistry of the FI in ilmenite. Ilmenite was studied on thin and thick sections, as well as polished epoxy mounts in which ilmenite was previously separated and handpicked. About 400 ilmenite grains were characterized using reflected light (RL) microscopy and scanning electron microscopy (SEM) coupled to an energy dispersive spectrometer (EDS). Some ilmenite grains were further analyzed with electron backscatter diffraction (EBSD) and electron micro-probe analyzer (EPMA), the latter providing high-resolution elemental maps. Thick sections of the material were heated to induce decrepitation of FI and formation of evaporate (i.e., salt) mounds which were subsequently analyzed using SEM-EDS to quantify their chemistry with a few selected for elemental mapping with the EPMA. Laser ablation inductively coupled mass spectrometry (LA ICP-MS) was used to qualitatively characterize the chemistry of ilmenite and also to determine the minor- and trace-element chemistry of evaporate mounds. Note that we

prepared double polished thick sections for infrared micro-thermometric FI studies analyses, but the opaqueness of ilmenite and small size of FI precluded observing any FI. We also tried to quantify the 3D distribution of FI by using a Nanotom 180 NF Phoenix X-Ray micro-computed tomography, but the resolution (i.e., 1.2 μm) was not high enough for imaging FI, as most of them being lower than 2 μm .

Quantitative chemical analyses by EPMA

Quantitative analyses of ilmenite from CS were acquired using a Cameca SX-Five EPMA at the common laboratory of the Earth Sciences Institute of Orléans (ISTO) and the French Geological Survey (BRGM) laboratory (Orléans, France). Analyses were performed at an accelerating voltage of 15 kV, a beam current of 10 nA, and with a focused beam, using the following mineral standards: albite (SiK α), hematite (FeK α), MgO (MgK α), and pyrophanite (TiK α , MnK α). Analyzed elements, detailed lists, and detection limits can be found in Supplementary Table 2. Mineral formula stoichiometric charge balanced mineral recalculations were used to determine the amount of Fe³⁺ present in ilmenite⁷⁸. X-ray elemental maps of ilmenite crystals were acquired with the IHP 200 F JEOL EPMA of the ISTO laboratory, using the following operating conditions: 20 kV, 40 nA, 100 ms dwell time and 0.26 μm step.

Electron backscatter diffraction

Scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) analyses were performed on thick and thin sections, both polished at ISTO-BRGM (Orléans, France) using diamond pastes with decreasing granulometries from 3 to 0.25 μm followed by chemico-mechanical polishing using colloidal silica. Each sample was carbon coated (i.e., around 3 nm) to prevent electron charging during EBSD acquisition. The backscattered electron (BSE) images were acquired using a Gemini I field Emission Gun from Zeiss and a TESCANx MIRA 3 XMU equipped with an EDAX Pegasus system available at the ISTO-BRGM. The latter was also used to acquire the EBSD data. While SEM observations were acquired at an accelerating voltage of 15 kV and a beam current of 2–3 nA, EBSD acquisition were performed at 30 kV and 5–6 nA at a working distance of 15 mm. EBSD acquisitions were performed on thin sections tilted at 70°. Data acquisition and post-analyzing cleaning were performed using the TSL-OIM software (OIM data collection and OIM analysis version 7.1; <https://www.edax.com/products/ebstd/oim-analysis>) and a map cleaning procedure⁷⁹. A step size of 1 μm was used for each map. The data were subsequently treated and plotted using the open-source MTEX toolbox (version 5.10; <https://mtext-toolbox.github.io>) for MATLAB. The minimum angles of lattice misorientation to define grain and intragranular boundaries were respectively set to 10° and 2°, each grain containing a minimum of five consecutive pixels on several rows. While continuous low-angle boundaries are referred to as sub-grain boundaries, the discontinuous ones are referred to as inner boundaries. For indexing, we used a trigonal symmetry (point group $\bar{3}$) to avoid artefacts related to twinning in ilmenite.

Laser ablation inductively coupled plasma mass spectrometry

Trace element concentrations of ilmenite were determined in situ by LA ICP-MS at ISTO. The system consists of a RESOLUTION-SE (ASI) 193 nm excimer laser with an S155 ablation cell (Laurin Technic) coupled to an Agilent 8900 triple inductively coupled plasma quadrupole mass spectrometer (QQQ-ICP-MS). Ablation was carried out using a He carrier gas which was mixed with Ar as a cell and nebulizer gas. Calibration was performed before each analytical session on NIST SRM 612 reference glass minimizing U/Th fractionation ($\sim 0.998\%$), and the production of oxides (ThO⁺/Th⁺ $\sim 0.128\%$) and doubly-charged ions (Ca²⁺/Ca⁺ ~ 0.289). A laser beam size of 20 μm , a repetition rate of 10 Hz and a fluence of 3 J/cm² were used. Single analysis consists of 30 s of background collection followed by 40 s of ablation and 15 s of wash-out delay. For each analytical session, about 2–5 reference materials were analyzed before and after each set of 12–15 sample analyses, following classical bracketing procedure. The Ti content of the ilmenite, as determined from electron probe microanalysis,

was used as the internal standard to quantify trace element concentrations. GSE-2g was the primary reference material, and NIST610 and BCR-2g glasses used as quality control materials. Data reduction was carried out using the commercial data reduction software GLITTER⁸⁰. Traverse profiles of ilmenite were acquired with a laser beam of 30 μm , a repetition rate of 7 Hz, a fluence of 3 J/cm² and a scanning speed of 20 $\mu\text{m/s}$.

Evaporate mound coupled with SEM-EDS, EPMA and LA ICP-MS analyses

The solute chemistry of FI was determined using the evaporate mound method^{42,81,82} in order to define the qualitative composition of trapped FI in ilmenite from five samples from SJD and four from CS. The thick sections were heated at a rate of 50 °C / min to about 600 °C to induce decrepitation of the contained FI and subsequently carbon-coated for SEM-EDS analysis and X-ray elemental maps. The maps were acquired with a Cameca SX-Five EPMA at the ISTO-BRGM laboratory, using the following operating conditions: 22 kV, 100 nA, 100 ms dwell time and 0.5 μm step.

LA ICP-MS traverses, using the aforementioned ISTO instrument, were performed on decrepitate mounds coating the surfaces of ilmenite for estimating some of the trace elements and thus the solute chemistry of the FI. The laser was operated at a repetition rate of 10 Hz and fluence of 3 J/cm² on the sample surface. Traverse profiles were acquired with a laser beam of 10 μm and a scanning speed of 5 $\mu\text{m/s}$. The raw data were processed by Iolite 2.5 software⁸³ using the trace element data reduction scheme⁸⁴. The latter results were converted into time-slice data whereby each complete sweep of the mass spectrometer (e.g., about 0.5 s) is considered equivalent to a conventional point analysis⁸⁵. No internal standard was used, and consequently the data are qualitative.

Data availability

The LA ICP-MS data used for the Fig. 4 in this manuscript are published on figshare (<https://doi.org/10.6084/m9.figshare.27045316.v2>). All remaining data used in this paper are included in the main article and its supplementary information file.

Received: 17 May 2024; Accepted: 14 October 2024;

Published online: 25 October 2024

References

1. Sorby, H. C. On the microscopical structure of crystals indicating the origin of rocks and minerals. *Quart. J. Geol. Soc. Lond.* **14**, 453–500 (1858).
2. Blamey, N. J. F. & Brand, U. Atmospheric gas in modern and ancient halite fluid inclusions: A screening protocol. *Gondwana Res.* **69**, 163–176 (2019).
3. Lowenstein, T. K., Timofeeff, M. N., Brennan, S. T., Hardie, L. A. & Demicco, R. V. Oscillations in phanerozoic seawater chemistry: evidence from fluid inclusions. *Science* **294**, 1086–1088 (2001).
4. Goldstein, R. H. Fluid inclusions in sedimentary and diagenetic systems. *Lithos* **55**, 159–193 (2001).
5. Bodnar, R. J., Lecumberri-Sanchez, P., Moncada, D. & Steele-MacInnis, M. Fluid inclusions in hydrothermal ore deposits, in *Treatise on Geochemistry* (second edition), **Vol. 13: Geochemistry of Mineral Deposits**: Oxford, UK (ed. Scott, S. D.) 119–142 (Elsevier, 2014).
6. Touret, J. L. R. & Huizenga, J. M. Fluid-assisted granulite metamorphism: A continental journey. *Gondwana Res.* **21**, 224–235 (2012).
7. Carvalho, B. B. et al. Primary CO₂-bearing fluid inclusions in granulitic garnet usually do not survive. *Earth Planet Sc. Lett.* **536**, 116170 (2020).
8. Andersen, T. & Neumann, E. R. Fluid inclusions in mantle xenoliths. *Lithos* **55**, 301–320 (2001).
9. Campbell, A. R., Hackbarth, C. J., Plumlee, G. S. & Petersen, U. Internal features of ore minerals seen with the infrared microscope. *Econ. Geol.* **79**, 1387–1392 (1984).

10. Lüders, V. Contribution of infrared microscopy to studies of fluid inclusions hosted in some opaque ore minerals: possibilities, limitations, and perspectives. *Miner. Depos.* **52**, 663–673 (2017).
11. Cashman, K. V. Volatile controls on magma ascent and eruption. *Geophys. Monogr. Ser.* **150**, 109–124 (2004).
12. Audétat, A., Pettke, T., Heinrich, C. A. & Bodnar, R. J. The composition of magmatic hydrothermal fluids in barren versus mineralized intrusions. *Econ. Geol.* **103**, 877–908 (2008).
13. Blundy, J., Mavrogenes, J., Tattitch, B., Sparks, S. & Gilmer, A. Generation of porphyry copper deposits by gas–brine reaction in volcanic arcs. *Nat. Geosci.* **8**, 235–240 (2015).
14. Barnes, S. J. et al. Role of volatiles in intrusion emplacement and sulfide deposition in the supergiant Norilsk-Talnakh Ni-Cu-PGE ore deposits. *Geology* **51**, 1027–1032 (2023).
15. Hedenquist, J. W. & Lowenstern, J. B. The role of magmas in the formation of hydrothermal ore deposits. *Nature* **370**, 519–527 (1994).
16. Mungall, J. & Naldrett, A. N. Ore deposits of the Platinum-group elements. *Elements* **4**, 253–258 (2008).
17. Iacono-Marziano, G. et al. 2022, The critical role of magma degassing in sulphide melt mobility and metal enrichment. *Nat. Commun.* **13**, 1–10 (2022).
18. Wallace, P. J. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *J. Volcanol. Geotherm. Res.* **140**, 217–240 (2005).
19. Kent, A. J. R. Melt inclusions in basaltic and related volcanic rocks. *Rev. Mineral. Geochem.* **69**, 273–331 (2008).
20. Métrich, N. & Wallace, P. J. Volatile abundances in basaltic magmas and their degassing paths tracked by melt inclusions. *Rev. Mineral. Geochem.* **69**, 363–402 (2008).
21. Edmonds, M. & Woods, A. W. Exsolved volatiles in magma reservoirs. *J. Volcanol. Geotherm. Res.* **368**, 13–30 (2018).
22. Kelley, D. S., Gillis, K. M. & Thompson, G. Fluid evolution in submarine magma-hydrothermal systems at the Mid-Atlantic Ridge. *J. Geophys. Res. Solid Earth* **98**, 19579–19596 (1993).
23. Kelley, D. S. & Malpas, J. Melt-fluid evolution in gabbroic rocks from Hess Deep. *Proc. Integr. Ocean Drill. Program, Sci. Results* **147**, 213–226 (1996).
24. Kelley, D. S. & Früh-Green, G. L. Volatile lines of descent in submarine plutonic environments: insights from stable isotope and fluid inclusion analyses. *Geochim. Cosmochim. Acta* **65**, 3325–3346 (2001).
25. Hennings, S. K., Wagner, T., Ulmer, P. & Heinrich, C. A. Fluid evolution of the monte mattoni mafic complex, adamello batholith, Northern Italy: insights from fluid inclusion analysis and thermodynamic modeling. *J. Petrol.* **58**, 1645–1670 (2017).
26. Dixon, J. E. & Stolper, E. M. An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. *J. Petrol.* **36**, 1633–1646 (1995).
27. Kelley, D. S., Robinson, P. T. & Malpas, J. G. Processes of brine generation and circulation in the oceanic crust: Fluid inclusion evidence from the Troodos Ophiolite, Cyprus. *J. Geophys. Res. Solid Earth* **97**, 9307–9322 (1992).
28. Bodnar, R. J., Burnham, C. W. & Sterner, S. M. Synthetic fluid inclusions in natural quartz. III. Determination of phase equilibrium properties in the system H₂O–NaCl to 1000 °C and 1500 bars. *Geochim. Cosmochim. Acta* **49**, 1861–1873 (1985).
29. Fournier, R. O. Conceptual models of brine evolution in magmatic-hydrothermal systems. *USG S Prof. Pap.* **1350**, 1487–1505 (1987).
30. Kelley, D. S. & Delaney, J. R. Two-phase separation and fracturing in mid-ocean ridge gabbros at temperatures greater than 700 °C. *Earth Planet. Sc. Lett.* **83**, 53–66 (1987).
31. Castelain, T., McCaig, A. M. & Cliff, R. A. Fluid evolution in an Oceanic Core Complex: A fluid inclusion study from IODP hole U1309 D—Atlantis Massif, 30°N, Mid-Atlantic Ridge. *Geochim. Geophys. Geosyst.* **15**, 1193–1214 (2014).
32. Cline, J. S. & Bodnar, R. J. Can economic porphyry copper mineralization be generated by a typical calc-alkaline melt? *J. Geophys. Res. Solid Earth* **96**, 8113–8126 (1991).
33. Bodnar, R. J. Synthetic fluid inclusions: XII. The system H₂O–NaCl. Experimental determination of the halite liquidus and isochores for a 40 wt% NaCl solution. *Geochim. Cosmochim. Acta* **58**, 1053–1063 (1994).
34. Barboni, M. et al. Timing of incremental pluton construction and magmatic activity in a back-arc setting revealed by ID-TIMS U/Pb and Hf isotopes on complex zircon grains. *Chem. Geol.* **342**, 76–93 (2013).
35. Caroff, M. et al. The mafic-silicic layered intrusions of Saint-Jean-du-Doigt (France) and North-Guernsey (Channel Islands), Armorican Massif: Gabbro-diorite layering and mafic cumulate pegmatoid association. *Lithos* **125**, 675–692 (2011).
36. Pochon, A., Iacono-Marziano, G., Gloaguen, E., Tuduri, J. & Erdmann, S. High-temperature alteration during cooling of mafic intrusions: Insights from the Saint-Jean-du-Doigt intrusive complex (Armorican Massif, France). *Lithos* **436–437**, 106977 (2023).
37. Campos Rodríguez, et al. Mafic magmatism in the Central Iberian Zone: Towards a better understanding of Sb mineralization? In 17th SGA Biennial Meeting, Zürich, Extended Abstracts, 8–11 (2023).
38. López-Moro, F. J., Murciego, A. & López-Plaza, M. Silurian/Ordovician asymmetrical sill-like bodies from La Codosera syncline, W Spain: A case of tholeiitic partial melts emplaced in a single magma pulse and derived from a metasomatized mantle source. *Lithos* **96**, 567–590 (2007).
39. López-Moro, F. J., Murciego, A., López-Plaza, M., Romer, R. L. & de Rafélis, M. 2020, Sequential crystal overproduction triggering Mg–Cr–Ti–V–P–MREE- enrichment in a single-pulse tholeiitic mafic sill in the Central Iberian Zone, Spain. *Lithos* **362–363**, 105464 (2020).
40. Roedder, E. Fluid Inclusions. in *Reviews in Mineralogy* **12** (Mineralogical Society of America, 1984).
41. Bodnar, R. J. Re-equilibration of fluid inclusions. in *Fluid Inclusions: Analysis and Interpretation*, Short Course **32** (eds. Samson, I., Anderson, A. & Marshall, D.) (Mineralogical Association of Canada, 2003).
42. Kontak, D. J. Analysis of evaporate mounds as a complement to fluid inclusion thermometric data: Case studies from granitic environments in Nova Scotia and Peru. *Canad. Mineral.* **42**, 1315–1329 (2004).
43. Klemme, S., Günther, D., Hametner, K., Prowatke, S. & Zack, T. The partitioning of trace elements between ilmenite, ulvöspinel, armalcolite and silicate melts with implications for the early differentiation of the moon. *Chem. Geol.* **234**, 251–263 (2006).
44. Shepherd, K., Namur, O., Toplis, M. J., Devidal, J. L. & Charlier, B. Trace element partitioning between clinopyroxene, magnetite, ilmenite and ferrobasaltic to dacitic magmas: an experimental study on the role of oxygen fugacity and melt composition. *Contrib. Mineral. Petrol.* **177**, 1–21 (2022).
45. Candela, P. A. & Bouton, S. L. The influence of oxygen fugacity on tungsten and molybdenum partitioning between silicate melts and ilmenite. *Econ. Geol.* **85**, 633–640 (1990).
46. Wei, C., Xiong, X., Wang, J., Huang, F. & Gao, M. Partitioning of tin between mafic minerals, Fe–Ti oxides and silicate melts: Implications for tin enrichment in magmatic processes. *Geochim. Cosmochim. Acta* **372**, 81–100 (2024).
47. Putnis, A. Mineral Replacement Reactions. *Rev. Mineral. Geochem.* **70**, 87–124 (2009).
48. Angiboust, S. & Harlov, D. Ilmenite breakdown and rutile-titanite stability in metagranitoids: Natural observations and experimental results. *Am. Mineral.* **102**, 1696–1708 (2017).
49. Pochon, A. et al. Metal mobility during hydrothermal breakdown of Fe–Ti oxides: Insights from Sb–Au mineralizing event (Variscan Armorican Massif, France). *Ore Geol. Rev.* **91**, 66–99 (2017).
50. Putnis, A. Fluid–mineral interactions: controlling coupled mechanisms of reaction, mass transfer and deformation. *J. Petrol.* **62**, egab092 (2021).

51. Burnham, C. W. Magmas and hydrothermal fluids. *Geochem. Hydrothermal Ore Depos.* **71**, 136 (1979). ed. Barnes, H. L.
52. Bodnar, R. J. & Student, J. J. Melt inclusions in plutonic rocks: Petrography and microthermometry. in *Melt Inclusions in Plutonic Rocks*, Short Course **36** (ed. Webster, J. D.) 1–26 (Mineralogical Association of Canada, 2006).
53. Veksler, I. V. Crystallized melt inclusions in gabbroic rocks. in *Melt Inclusions in Plutonic Rocks*, Short Course **36**, (ed. Webster, J. D.) 1–26 (Mineralogical Association of Canada, 2006).
54. Candela, P. A. A review of shallow, ore-related granites: Textures, volatiles, and ore metals. *J. Petrol.* **38**, 1619–1633 (1997).
55. London, D. Pegmatites. (Mineralogical Association of Canada, 2008).
56. Zajacz, Z., Candela, P. A., Piccoli, P. M. & Sanchez-Valle, C. The partitioning of sulfur and chlorine between andesite melts and magmatic volatiles and the exchange coefficients of major cations. *Geochim. Cosmochim. Acta* **89**, 81–101 (2012).
57. Edmonds, M., Mason, E. & Hogg, O. Volcanic outgassing of volatile trace metals. *Ann. Rev. Earth Planet. Sci.* **50**, 79–98 (2022).
58. Behrens, H. & Gaillard, F. Geochemical aspects of melts: volatiles and redox behavior. *Elements* **2**, 275–280 (2006).
59. Iacono-Marziano, G., Morizet, Y., Le Trong, E. & Gaillard, F. New experimental data and semi-empirical parameterization of H₂O–CO₂ solubility in mafic melts. *Geochim. Cosmochim. Acta* **97**, 1–23 (2012).
60. Spear, F. S. & Selverstone, J. Water exsolution from quartz: Implications for the generation of retrograde metamorphic fluids. *Geology* **11**, 82–85 (1983).
61. Philippot, P., Chevallier, P., Chopin, C. & Dubessy, J. Fluid composition and evolution in coesite-bearing rocks (Dora-Maira massif, Western Alps): implications for element recycling during subduction. *Contrib. Mineral. Petrol.* **121**, 29–44 (1995).
62. Zhang, Z., Shen, K., Liou, J. G. & Zhao, X. Fluid inclusions associated with exsolved quartz needles in omphacite of UHP eclogites, chinese continental scientific drilling main drill hole. *Int. Geol. Rev.* **49**, 479–486 (2007).
63. Johnson, E. A. Water in Nominally Anhydrous Crustal Minerals: Speciation, Concentration, and Geologic Significance. *Rev. Mineral. Geochem.* **62**, 117–154 (2006).
64. Jiang, S.-Y. & Palmer, M. R. Mn-rich ilmenite from the Sullivan Pb–Zn–Ag deposit. *Br. Columbia Canad. Mineral.* **34**, 29–36 (1996).
65. Essaifi, A., Ballèvre, M., Marignac, C. & Capdevila, R. Découverte et signification d’une paragenèse à ilménite zincifère dans les métapélites des Jebilet centrales (Maroc). *C. R. Acad. Sci.* **333**, 381–388 (2001).
66. Parmigiani, A., Degruyter, W., Leclaire, S., Huber, C. & Bachmann, O. The mechanics of shallow magma reservoir outgassing. *Geochim. Geophys. Geosyst.* **18**, 2887–2905 (2017).
67. Trosh, J., Huber, C. & Bachmann, O. The physical and chemical evolution of magmatic fluids in near-solidus silicic magma reservoirs: Implications for the formation of pegmatites. *Am. Mineral.* **107**, 190–205 (2022).
68. Hurwitz, S. & Navon, O. Bubble nucleation in rhyolitic melts: experiments at high pressure, temperature and water content. *Earth Planet. Sci. Lett.* **122**, 267–280 (1994).
69. Edmonds, M., Brett, A., Herd, R. A., Humphreys, M. C. S. & Woods, A. Magnetite-bubble aggregates at mixing interfaces in andesite magma bodies. *Geol. Soc. Spec. Publ.* **410**, 95–121 (2015).
70. Gardner, J. E. et al. Bubble formation in magma. *Ann. Rev. Earth Planet. Sci.* **51**, 131–154 (2023).
71. Navon, O. & Lyakhovsky, V. Vesiculation processes in silicic magmas. *Geol. Soc. Spec. Publ.* **145**, 27–50 (1998).
72. Cáceres, F. et al. Can nanolites enhance eruption explosivity? *Geology* **48**, 997–1001 (2020).
73. Buono, G. et al. Dynamics of degassing in evolved alkaline magmas: Petrological, experimental and theoretical insights. *Earth-Sci. Rev.* **211**, 103402 (2020).
74. Richard, A. et al. Advances in 3D imaging and volumetric reconstruction of fluid and melt inclusions by high resolution X-ray computed tomography. *Chem. Geol.* **508**, 3–14 (2019).
75. Anderson, A. & McCarron, T. Three-dimensional textural and chemical characterization of polyphase inclusions in spodumene using a dual focused ion beam – scanning electron microscope (FIB–SEM). *Canad. Mineral.* **49**, 541–553 (2011).
76. Berkesi, M. et al. The role of CO₂-rich fluids in trace element transport and metasomatism in the lithospheric mantle beneath the Central Pannonian Basin, Hungary, based on fluid inclusions in mantle xenoliths. *Earth Planet. Sci. Lett.* **331–332**, 8–20 (2012).
77. Nakamura, T. et al. Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples. *Science* **379**, eabn8671 (2023).
78. Droop, G. T. R. A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineral. Mag.* **51**, 431–435 (1987).
79. Précigout, J., Prigent, C., Palasse, L. & Pochon, A. Water pumping in mantle shear zones. *Nat. Commun.* **8**, 1–10 (2017).
80. Griffin, W. L. GLITTER: data reduction software for laser ablation ICP–MS. *Laser Ablation ICP–MS in the Earth Sciences: Current practices and outstanding issues*, 308–311 (2008).
81. Haynes, F. M. & Kesler, S. E. Chemical evolution of brines during Mississippi Valley-type mineralization: evidence from East Tennessee and Pine Point. *Econ. Geol.* **82**, 53–71 (1987).
82. Haynes, F. M., Sterner, S. M. & Bodnar, R. J. Synthetic fluid inclusions in natural quartz. IV. Chemical analyses of fluid inclusions by SEM/EDA: evaluation of method. *Geochim. Cosmochim. Acta* **52**, 969–977 (1988).
83. Paton, C., Hellstrom, J., Paul, B., Woodhead, J. & Hergt, J. Lolite: Freeware for the visualisation and processing of mass spectrometric data. *J. Anal. Spectrom.* **26**, 2508–2518 (2011).
84. Woodhead, J. D., Hellstrom, J., Hergt, J. M., Greig, A. & Maas, R. 2007, Isotopic and elemental imaging of geological materials by laser ablation inductively coupled plasma-mass spectrometry. *Geostand. Geoanal. Res.* **31**, 331–343 (2007).
85. Gourcerol, B., Kontak, D. J., Thurston, P. C. & Petrus, J. A. Application of LA–ICP–MS sulfide analysis and methodology for deciphering elemental paragenesis and associations in addition to multi-stage processes in metamorphic gold settings. *Canad. Mineral.* **56**, 39–64 (2018).
86. Buddington, A. F. & Lindsley, D. H. Iron–titanium oxide minerals and synthetic equivalents. *J. Petrol.* **5**, 310–357 (1964).

Acknowledgements

This article is dedicated to the memory and scientific legacy of Dr. Eric Gloaguen, who passed away prematurely. This work was carried out in the framework of the ERA-MIN2 Aureole project (i.e., tArgeting eU cRitical mEtals (Sb, W) and predictability of Sb–As–Hg enviroNmental issuEs) with funding from the ANR (grant ANR-19-MIN2-0002) for the French partners. The LabEx VOLTAIRE (ANR-10-LABX-100-01) and EquipEx PLANEX (ANR-11-EQPX-0036) are also acknowledged to have provided support for the electron microprobe and LA–ICP–MS laboratories. All the samples used in this study did not require permissions, except sample coming from the quarry belonging to Villar del Rey Natural Stones S.L., where we had permissions from company. The authors thank Ida Di Carlo, Guillaume Wille and Saskia Erdmann for their help with the EPMA, EBSD and LA ICP–MS analyses, respectively. This project has benefited from the expertise and the facilities of the Platform MACLE – CVL which was co-funded by the European Union and Centre-Val de Loire Region (FEDER). D. Kontak acknowledges financial support from ANR – Carnot (N° 19-CARN-003-01, convention N° 16-CARN-003-01) which facilitated this research. The authors sincerely acknowledge the insightful reviews provided by R. J. Bodnar, D. Moncada, and Z. Zajacz which resulted in a much improved manuscript and clarification of several important points.

Author contributions

A.P., E.G. & G.I-M. have designed the research and A.P. & D.J.K wrote the original draft. A.P., D.J.K., G.I-M., E.G., J.T. & H.C.R. carried out field investigations and sampling. A.P., G.I-M. and T.C. performed SEM-EDS, EPMA and LA ICP-MS analyses. J.P. provided support for EBSD analysis and interpretation. D.J.K., G.I-M., E.G., J.T., T.C., J.P., V.M., B.G. and L.M. contributed to discussions, editing, and revisions.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s43247-024-01788-8>.

Correspondence and requests for materials should be addressed to Anthony Pochon.

Peer review information *Communications Earth & Environment* thanks Daniel Moncada, Zoltan Zajacz and Robert J Bodnar for their contribution to the peer review of this work. Primary Handling Editor: Carolina Ortiz Guerrero. A peer review file is available

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2024

Héctor Ricardo CAMPOS RODRÍGUEZ

Magmatisme mafique et métasédiments dans la Zone-Centro-Ibérique, Espagne : Vers une meilleure compréhension des sources et des mécanismes de minéralisation à Sb?

Afin d'améliorer le ciblage des gisements à Sb, cette thèse apporte des nouvelles perspectives sur leurs sources potentielles dans la Zone-Centro-Ibérique (CIZ), en Espagne. Deux sources et mécanismes potentiels principaux pourraient être liés à la formation de gisements à Sb dans la CIZ, y compris (i) le dégazage magmatique d'intrusions mafiques et (ii) la dévolatilisation de séquences métasédimentaires riches en Sb. (i) Les gisements à Sb dans la CIZ sont spatialement associés à des roches mafiques, lesquelles sont synchrones avec des intrusions mafiques et des gisements à Sb dans le Massif Armoricain en France. La présence d'inclusions fluides primaires dans des ilménites, comportant du Sb, du Cu, du Sn, du Mo, du W et du Pb, suggérerait l'existence d'une phase fluide enrichie en métaux et en métalloïdes dans le magma mafique lors de la cristallisation de l'ilménite. (ii) D'autre part, les données géochimiques révèlent un enrichissement en Sb dans des roches métasédimentaires, ce qui suggère que le Sb aurait pu être mobilisé dans les auréoles de contact à proximité des sills mafiques, au moment de la dévolatilisation thermique.

Des études complémentaires devront être menées afin de quantifier la contribution de ces deux sources à la formation des gisements à Sb dans la CIZ.

Mots clés : Antimoine, sources, magmatisme mafique, métasédiments, Chaîne Varisque.

Mafic magmatism and metasediments in the Central Iberian Zone, Spain: Towards a better understanding of the sources and mechanisms of Sb mineralization?

This thesis aims to enhance the targeting of Sb deposits by offering novel insights into their potential sources in the Central Iberian Zone (CIZ), Spain. Two main potential sources and mechanisms may be associated with the formation of Sb deposits in the CIZ, including (i) magmatic degassing of mafic intrusions and (ii) devolatilization of Sb-rich metasedimentary sequences. (i) Sb deposits in the CIZ exhibit a spatial association with mafic rocks, which are synchronous with mafic intrusions and Sb deposits in the Armorican Massif in France. The presence of primary fluid inclusions in ilmenites, containing Sb, Cu, Sn, Mo, W and Pb, would suggest the existence of a metal- and metalloid-enriched fluid phase in the mafic magma during ilmenite crystallization. (ii) Alternatively, whole rock geochemical data revealed Sb enrichment in metasedimentary rocks, suggesting that Sb may have been mobilized in the contact aureoles adjacent to the mafic sills during thermal devolatilization.

Further studies are required to quantify the contribution of these two sources to the formation of Sb deposits in the CIZ.

Keywords : Antimony, sources, mafic magmatism, metasediments, Variscan belt.



**Institut des Sciences de la Terre
d'Orléans
1A rue due la Férollerie
45100 ORLEANS**

