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An experimental study of sulfur distribution between apatite and silicate melts: application to volcanic degassing

Etude expérimentale de la distribution du soufre entre l'apatite et les liquides silicatés :
application au dégazage volcanique

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Chapter 1

Introduction

Introduction

Les éléments volatils ont été largement étudiés lors des émissions volcaniques, car ils peuvent influencer de manière significative l'atmosphère et le climat de la Terre.

Le soufre, un élément volatil, fait partie des chalcogènes et ses valences sont -2 et +6, +2 et +4, en plus de son état natif (0). Il représente le sixième élément le plus abondant sur Terre et se trouve partout dans l'univers, y compris dans des matériaux plus anciens que notre système solaire (Mandeville, 2010).

Le soufre est un élément mineur dans les magmas (Luhr, 2008 ; Métrich et Mandeville, 2010) et les magmas produits dans différents contextes géodynamiques ont des concentrations variables de soufre (Oppenheimer et al., 2014 et références citées). L'étude du soufre dans les magmas est rendue compliquée par le fait que dans les systèmes volcaniques plusieurs espèces de soufre sont présentes dans les gaz (S_2 , H_2S , SO_2 , SO_3) et le soufre est incorporé dans des phases solides telles que la pyrrhotite, l'anhydrite ou l'apatite, ainsi que dans le liquide silicaté (Oppenheimer et al., 2011b). Les principaux paramètres contrôlant la solubilité du soufre dans les magmas sont la composition du liquide silicaté, la fugacité de l'oxygène, la pression et la température (Carroll et Rutherford, 1985 ; Luhr, 1990 ; Scaillet et al., 1998 ; Jugo et al., 2005). En particulier, de nombreuses études ont démontré que, pour la même composition et les mêmes conditions P-T, la solubilité du soufre augmente de manière significative à haute fO_2 (Boulliung et Wood, 2023 ; Carroll et Rutherford, 1988 ; Hughes et al., 2023 ; Jugo, 2004 ; Luhr, 1990 ; Moretti et Ottonello, 2005 ; Moune et al., 2009 ; O'Neill, 2021 ; Scaillet et al., 1998). Comprendre la quantité de soufre dans les magmas est essentiel pour estimer le budget de soufre impliqué dans le dégazage lors des éruptions.

L'apatite est un minéral présent dans presque tous les types de roches et divers contextes géologiques. Ce minéral a la capacité d'incorporer divers éléments, ce qui en fait une sonde potentielle pour de nombreux processus géochimiques (Watson et Green, 1981 ; Zhu et Sverjensky, 1991 ; Pan et Fleet, 2002 ; Liu et al., 2023 ; Spear et Pyle, 2002 ; Chew et Spikings, 2015 ; Mao et al., 2016 ; Andersson et al., 2019 ; La Cruz et al., 2019 ; Belousova et al., 2002 ; La Cruz et al., 2020 ; Zhou et al., 2022 ; Konecke et al., 2019 ; Tailby et al., 2023). Peng et al. (1997) et Parat et Holtz (2004-2005) sont les principaux auteurs ayant étudié la corrélation entre la quantité de S dans l'apatite et dans le liquide silicaté coexistant. Ainsi, à partir des expériences de Luhr (1990), Peng et al. (1997) montrent que la teneur en

soufre de l'apatite est contrôlée par la concentration de soufre dans le verre, la pression et la température. De plus, il semble que sous des conditions plus oxydantes, l'apatite est enrichie en soufre. Cependant, il a été noté que ces tendances ne sont pas forcément observables dans les échantillons naturels. Les études de Parat et Holtz (2004–2005) ont révélé que dans certaines expériences la teneur en SO_3 dans l'apatite et le verre augmente avec la température. Cependant, dans les expériences saturées en anhydrite, ils ont observé une tendance inverse. Ils ont également étudié si la composition du verre pouvait affecter l'incorporation du soufre dans l'apatite. Malheureusement, ils n'ont pas pu trouver un facteur universel qui puisse expliquer et/ou valider cette hypothèse.

La pyrrhotite, quant à elle, est un minéral appartenant au groupe des sulfures. Elle cristallise dans le système monoclinique et possède une formule non stœchiométrique. Toulmin et Barton (1964) ont été parmi les premiers à utiliser la composition de la pyrrhotite pour calculer la $f\text{S}_2$ dans le système. Au travers d'expériences, ils ont déterminé la fugacité du soufre en équilibre entre la pyrite et une pyrrhotite de composition connue. Sur la base de cette étude, Froese et Gunter (1976) ont pu adapter les équations au système pyrrhotite-vapeur, en utilisant uniquement la composition molaire de ce minéral. Cependant, par la suite, il a été remarqué qu'il est difficile de mesurer avec précision la composition de la pyrrhotite dans des échantillons naturels, en particulier avec la microsonde électronique (Whitney, 1984). L'analyse à la microsonde de ce minéral est en effet difficile en raison de sa petite taille, souvent inférieure à 10 μm . L'incertitude de la composition obtenue à la sonde peut entraîner une erreur dans le calcul de la fugacité du soufre allant jusqu'à un ordre de grandeur en terme de fugacité de S_2 . En raison de ces problèmes, mais aussi de l'absence de pyrrhotite dans certains magmas, certains auteurs préfèrent calculer la $f\text{S}_2$ à partir des modèles de solubilité du soufre dans le verre.

Dans ce contexte, cette thèse expérimentale est divisée en deux sections principales. Dans la première section de la thèse, une étude détaillée est réalisée sur la solubilité du soufre dans les magmas basiques hydratés, avec un accent particulier sur l'éruption de La Palma en 2021. Les magmas mafiques alcalins n'ont pas été très étudiés du point de vue du comportement du soufre, et c'est pourquoi notre choix s'est porté sur ce type de magma: une raison supplémentaire est celle des observations remarquables dont a bénéficié cette éruption, observations qui fournissent un cadre conceptuel très contraint pour l'interprétation des

émissions de soufre. La deuxième section décrit l'étude de la relation entre la teneur en soufre dans l'apatite et le verre et leurs relations avec la fugacité des espèces de soufre. En outre, au cours de cette thèse, un protocole analytique spécifique a été développé avec la microsonde électronique pour obtenir la composition de pyrrhotite la plus fiable possible, à partir de laquelle la fS_2 des systèmes volcaniques étudiés (si saturés en pyrrhotite) peut être dérivée. Dans la dernière partie de ce travail, les résultats obtenus sont utilisés pour caractériser des échantillons naturels provenant d'éruptions bien étudiées, dans le but de mieux contraindre le comportement du S dans les systèmes magmatiques.

1. Introduction

Magmatic degassing is a universal process that shapes our atmosphere as well as those of other planets. Quantification of this process remains, however, an harduous task because there is, by definition, very few direct traces of degassing left over in magmatic rocks. Among the minerals capable of recording the activity of volatile elements in magmas, apatite is certainly one of the most promising: although scarce, this mineral is ubiquitous in magmatic rocks. It incorporates in its structure most of the volatile elements produced by volcanic activity, in particular water, halogens and sulphur. Trying to study the relationship of the amount of sulphur in apatite and melt could lead to a better understanding of this process.

1.1 Volatite elements

Volatile elements have been widely studied during volcanic emissions as they can significantly influence, and have influenced, the Earth's atmosphere and climate on both local and global scales, and over timescales ranging from a few years to millions of years. The main volatile components in magmas, in decreasing order of abundance, are water, carbon dioxide, hydrogen sulfide, sulphur dioxide, hydrogen chloride, hydrogen fluoride, and hydrogen.

Volatile elements participate to most of the geochemical cycles shaping our planet (Oppenheimer et al., 2014). Since the mantle, owing to its size, is a reservoir rich in volatile elements, the process of magmagenesis is fundamental for studying the mechanisms of volatile transfer through magmas and their evolution (Oppenheimer et al., 2014).

One of the key factors that can influence the distribution of volatile elements is the viscosity of the melt, which is strongly controlled by pressure, temperature, and melt composition. Viscosity variations are indeed strongly related to changes in the volatile content of the melt, in particular water. Additionally, the volatile content and its variations profoundly influence the nucleation and growth of bubbles within magmas (e.g., Oppenheimer et al., 2014).

Different quantities and/or sizes of bubbles ultimately control the fragmentation of magma and consequently the eruption style. Therefore, an in-depth study of the behavior of volatile elements from the magmagenesis process to degassing is crucial for understanding a volcano's evolutionary history and potential future eruptions, which in turn helps mitigating volcanic risk.

It is therefore evident that the study of volatiles is imperative for comprehending the interconnections between volcanic degassing, crystallization, magma dynamics, eruption style, mineral deposits, and atmospheric and climate change.

1.2 Sulphur: magma solubility and degassing

Sulphur belongs to Group VI of the periodic table and is part of the chalcogens. Its most common valences are -2 and +6, but it can also exist in intermediate states of +2 and +4, as well as in its native state (0). Sulphur represents the sixth most abundant element on Earth and is found throughout the universe in material older than our solar system (Mandeville, 2010). According to Truran (1973) and Clark (1979), sulphur originated in space through nucleosynthesis during the oxygen-burning explosion phase of a supernova.

As stated by Mandeville (2010), in minerals present in the mantle, sulphur occurs as sulfide and as sulfide and sulfate in crust's minerals. Furthermore, native sulphur is primarily found near volcanoes.

Sulphur is a minor element in magmas, yet sulphur-rich magmas are frequently linked to ore deposits (Luhr, 2008; Metrich and Mandeville, 2010). Different geodynamic settings have been observed to result in the production of varying sulphur concentrations (Oppenheimer et al 2014. and ref. therein). In mid-ocean ridge basalts (MORB), the pre-eruptive sulphur content of glasses is about 800–1500 ppm. In ocean island basalts (OIB), it reaches up to 3000 ppm (Hawaiian basalts are slightly depleted, ranging from 200 to 1900 ppm). In back-arc basin basalts (BABB), the typical range is 200–400 ppm, never exceeding 1000 ppm. Dacites and rhyolites are usually sulphur-poorer with contents below 200 ppm, but they are often saturated in anhydrite and pyrrhotite.

This element is released into the atmosphere mainly in the form of SO_2 and H_2S , which form aerosol particles that can impact climate, as seen in historical eruptions such as Tambora (1815), Laki (1783–1784), and Pinatubo (1991). These volcanic emissions lead to chemical changes in the atmosphere (Rampino and Self, 1992; Thordarson et al., 2001; Robock, 2003; Wallace, 2005; Moune et al., 2009; Oppenheimer et al., 2014).

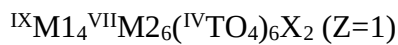
Sulphur solubility in magma is complicated by the fact that volcanic systems contain both volatile phases (S_2 , H_2S , SO_2 , SO_3) and non-volatile solid phases such as pyrrhotite and anhydrite, as well as a liquid/melt phase (Oppenheimer et al., 2011b). Several studies have shown that sulphur dissolves as sulphide and sulfate (Fincham and Richardson, 1954;

Métrich and Mandeville, 2010). The main parameters controlling sulphur solubility in magma are, in addition to melt composition, oxygen fugacity, pressure, and temperature, all of which also influence magma differentiation (Carroll and Rutherford, 1985; Luhr, 1990; Scaillet et al., 1998; Jugo et al., 2005).

Redox conditions play a fundamental role in determining sulphur speciation in magma (Carroll and Rutherford, 1987; Clemente, 2004; Oppenheimer et al., 2014). In particular, numerous studies have demonstrated that, for the same composition and P-T conditions, sulphur solubility increases significantly at high fO_2 (Boulliung and Wood, 2023; Carroll and Rutherford, 1988; Hughes et al., 2023; Jugo, 2004; Luhr, 1990; Moretti and Ottonello, 2005; Moune et al., 2009; O'Neill, 2021; Scaillet et al., 1998). Carroll & Rutherford (1985, 1987) have shown that in hydrated magmas, pressure and temperature have a positive effect on sulphur solubility in melts with FeO > 5 wt.%, both under reducing and oxidizing conditions. Overall, understanding the amount of sulphur in magmas is essential for estimating the sulphur budget involved in degassing during eruptions. However, constraining sulphur behaviour in magmas is challenging due to its highly volatile behavior.

1.3 Apatite and sulphur

Apatite is the common name used to identify a large group of minerals present in almost all types of rocks and various geological settings, sharing the same atomic structure:



In the typical chemical structure of this mineral, calcium (Ca) predominantly occupies the M sites, but it can be substituted by other cations such as Na, Pb, Ba, Sr, Mn, Ce, La, Y, and Bi.

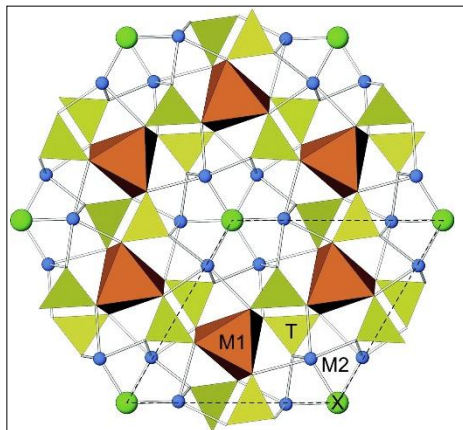


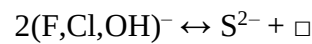
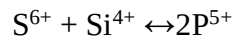
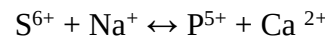
Fig. 1 The crystal structure of apatite is seen along the c-axis. The unit cell is delineated by dashed lines. Image from Pasero et al., (2010)

Potassium is located in the T sites, which can also accommodate As, V, Si, and B. The X site primarily contains fluorine (F), chlorine (Cl), and the hydroxyl (OH) group (Fig. 1). This brief, non-exhaustive summary of the apatite structure highlights its significance as a highly interesting mineral to study. In fact, its ability to incorporate various elements makes it a potential probe for many geochemical processes. Additionally, apatite is highly resistant to weathering and alteration (Elliott et al., 1973).

The chemical structure of apatite and the incorporation of specific elements in various sites depend on several factors: pressure, temperature, oxygen fugacity, melt / fluid chemistry, and metamorphic conditions. Many authors have demonstrated that the chemistry of igneous apatites potentially informs the magmatic system's history (Watson and Green, 1981; Zhu and Sverjensky, 1991; Pan and Fleet, 2002). For instance, Liu et al. (2023) showed that Rare Earth Elements (REEs) in apatite could be used to trace back the melt source. Spear and Pyle (2002) and Chew and Spikings (2015) have shown that the U-Pb and Lu-Hf systems can be used to quantify the timing of apatite crystallization. Key factors influencing mineral ore exploration include the concentration of Sr, Mn, and Y, REE patterns of apatite normalized to chondrites with Eu anomalies, and halogen fractionation (Br/Cl and I/Cl ratios), as these characteristics in apatite appear to be distinctive for different rock types (Mao et al., 2016; Andersson et al., 2019; La Cruz et al., 2019; Belousova et al., 2002; La Cruz et al., 2020; Zhou et al., 2022). More recently, it has been possible to determine the oxygen fugacity of

the magmatic system and the timing of apatite crystallization through the calibration of its $S^{6+}/\sum S$ ratio with fO_2 (Konecke et al., 2019; Tailby et al., 2023).

Sulphur can enter into the crystalline structure of apatite through various substitution mechanisms. Kim et al. (2017) highlighted that different sulphur valences could be incorporated into two distinct sites: S^{2-} is compatible with the M site, while S^{6+} and S^{4+} are accommodated in the T site. Several authors (Rouse and Dunn, 1982; Liu and Comodi, 1993; Tepper and Kuehner, 1999; Parat et al., 2011; Kim et al., 2017) have proposed different substitution mechanisms, identifying relationships between sulphur and other major elements:



Experimental studies have been conducted to establish correlations between the sulphur content in the melt with its incorporation in apatite. The main studies on this topic can be traced back to Peng et al., (1997) and Parat and Holtz (2005, 2004). Peng et al. (1997) compared the experimental results of Luhr (1990) with natural samples. At the experimental level, the sulphur content in apatite is controlled by the sulphur concentration in the melt, pressure, and temperature. At a given P – fO_2 , the sulphur content in apatite decreases with increasing temperature, while at a given T – fO_2 , sulphur content correlates positively with pressure. Additionally, it appears that under more oxidizing conditions, apatite becomes enriched in sulphur. Nevertheless, it was emphasised that these trends are not observable in natural samples.

The studies by Parat & Holtz (2004–2005) focused on experiments conducted on silicic melts at temperatures between 900–1100°C, pressures around 200 MPa, and two oxygen fugacities: $NNO+3.7$ and $NNO+2.3$. Most of their experiments were performed using a haplogranitic starting material and a smaller subset involving andesitic compositions. In anhydrite-undersaturated experiments, they observed that the SO_3 content in both apatite and melt increases with temperature, a trend opposite to the findings of Peng et al. (1997). Yet anhydrite-saturated runs exhibit a reverse trend (Fig. 2a)

To better understand whether melt composition affects sulphur incorporation in apatite, the calcium content in the melt from various experiments is shown on Fig. 2. A slight negative correlation is observed between sulphur in apatite and increasing Ca content in the melt (Fig. 2b). However, this correlation alone is insufficient to fully explain sulphur distribution in apatite between different experiments, as the lowest CaO content in the melt does not correspond to the highest sulphur content recorded in apatite (Parat and Holtz, 2005).

Analyzing the partition coefficient for sulphur between apatite and melt ($K_{dS}^{ap/melt}$) reveals a negative correlation between K_d and the sulphur content in the melt (Fig. 2 c). However, since the melt sulphur content is itself influenced by temperature, this correlation is based on experiments conducted at different temperatures and cannot be directly used to determine K_d . On the other hand, when comparing K_d and sulphur content in apatite and melt from experiments using andesitic compositions, no significant differences were observed compared to previously identified trends.

Nevertheless, Parat & Holtz (2005) emphasized that further studies are necessary to better

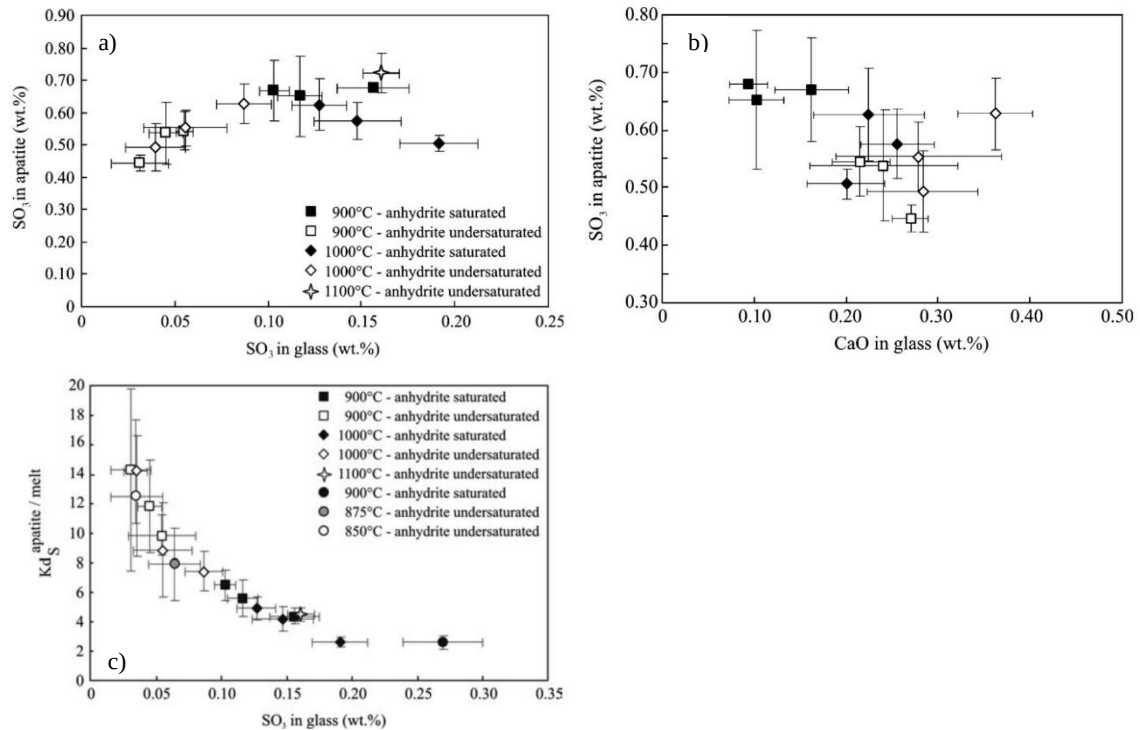


Fig. 2 All the images are from Parat and Holtz (2005). Panel a) shows the relationship between the amount of sulphur in apatite and melt; panel b) illustrates a broad negative correlation between SO_3 wt. in apatite and CaO wt. in glass; panel c) shows the negative trend between partition coefficient of sulphur between apatite and melt and the amount of sulphur in the glass.

understand the influence of melt composition on sulphur content in the melt and the $K_{dS}^{ap/melt}$.

1.4 Pyrrhotite and fS_2

Pyrrhotite is a mineral belonging to the sulfide group, where sulphur, in a negative valence

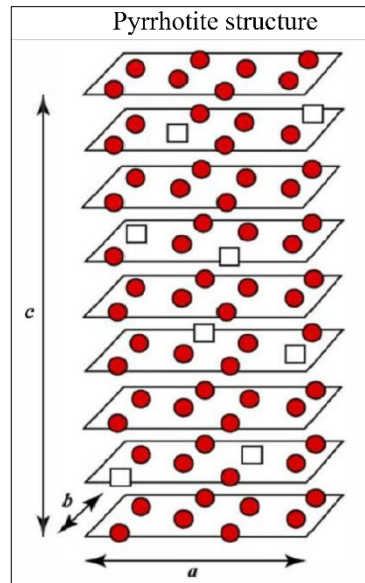


Fig. 3 Pyrrhotite structure of the monoclinic specie. Only the Fe atom layers are shown with their vacancies represented by square. Image from Vaughan and Corkhill (2017).

state, is combined with a metals or semimetals. It crystallizes in the monoclinic system (Fig. 3) and has a non-stoichiometric formula, expressed as:



where $0 < x < 0.125$.

Pyrrhotite is an accessory mineral found in many rocks and is often associated with ore deposits. Additionally, it is well known that this mineral exhibits a wide compositional range due to its solid solution with pyrite. In volcanic samples, pyrrhotite typically appears with a circular morphology, mainly as inclusions in phenocrysts, but it can also occur as phenocrysts within the groundmass.

In pyrrhotite-bearing magmas, fS_2 ranges between 10 and 10^{-4} bars, with a negative correlation with increasing temperature and oxygen fugacity (Whitney, 1984). Meanwhile, fSO_2 behaves similarly concerning temperature and fO_2 , but its values range between 10^3 and 10^{-3} bars (Whitney, 1984). In contrast, fH_2S varies between 10 and 100 bars being strongly dependent on the assumed water fugacity (Whitney, 1984).

Toulmin and Barton (1964) were among the first to use the composition of pyrrhotite to calculate the f_{S_2} in the system. In fact, they measured the fugacity in equilibrium between pyrite and a pyrrhotite of known composition. This allowed them to calculate the activity of FeS in pyrrhotite by integrating the Gibbs-Duhem equation. To apply this type of equation to the pyrrhotite-vapor phase system, one must assume a solution with $\log f_{S_2}$ tending to infinity and the mole fraction of FeS tending to 1 (Froese and Gunter, 1976). These conditions can be applied for pyrrhotites, even natural ones, as they show no defects in the sulphur lattice (Froese and Gunter, 1976).

Based on these prerequisites, Froese and Gunter (1976) succeeded in creating a model for calculating the sulphur fugacity in an FeS-S system from the molar composition of pyrrhotite in a simple way. However, it has been noticed over the years that in natural samples accurately measuring the composition of pyrrhotite is difficult. Among the major difficulties are size, spontaneous exsolution during quenching, oxidation during cooling and vitrification. Microprobe analysis of this mineral is difficult owing to its small size, often less than 10 μm . The uncertainty of the composition obtained at the probe could lead to an error in the calculation of the sulphur fugacity of up to an order of magnitude.

For this reason, Whitney (1984) developed an Fe-S₂-O₂-SiO₂ system, based on the position of the pyrrhotite-magnetite boundary. Comparing his method with that of Toulmin and Burton (1964), Whitney (1984) states that the error associated with his calculations is equal to or less than the analytical error associated with measuring the composition of pyrrhotite at the microprobe. But the pyrrhotite-magnetite boundary model allows the calculation of the fugacities of sulphur species in samples where the mineral has exsolved or oxidised.

Due to the assumptions of the models explained above, but also to the lack of pyrrhotite in some magmas, it is also possible to calculate f_{S_2} from sulphur solubility in melt models (e.g., Clemente et al., 2004). Indeed, as described in section 1.2, the solubility of sulphur in melt is strongly related to its fugacity. Thus, a common approach has been to use the sulphur content of the pre-eruptive magma to derive the f_{S_2} . Over the years, various solubility models have been developed, both either composition-specific or generic (O'Neill and Mavrogenes, 2002; Clemente et al., 2004; Lesne et al., 2015; Li and Zhang, 2022; O'Neill, 2021; Boulliung and Wood, 2023). Nonetheless, even with these models, errors can arise when assessing the

actual sulphur content in the pre-sulphur system, which can lead to inaccurate estimation of S fugacity.

1.5 Geological setting of studied eruptions

In this section where briefly explained the geological setting of eruptions, which products are used as starting materials.

1.5.1 La Palma

La Palma Island is part of the oceanic island basalt system of the Canary Islands, which is fed by a hotspot of presumed mantle origin, which is probably influenced by the rotation of the African plate. (e.g., Day et al., 2022 and references therein).

La Palma is composed of two volcanic centres. The oldest of these is the Taburiente centre, located in the northern part of the island, and the currently active Cumbre Vieja centre, situated in the southern region (Carracedo et al., 2001 and references therein). The volcanic activity of the Cumbre Vieja area commenced approximately 123,000 years ago, with its complex extending from north to south. The main mode of volcanic activity of this area is that of single lived individual eruptive centres, which are distributed along fissures. The eruptive products are classified as members of the alkaline series, and include the following: alkaline basalts, basanites, trachybasalts, tephrites and phonolites. (e.g., Carracedo et al., 2001). In the period preceding the 2021 event, a number of eruptions have been documented over the last five centuries (approximately eight in total). These eruptions were characterized by the occurrence of explosive events on the summit and effusive lava flows along the flanks. (Carracedo et al., 2001).

The 2021 Cumbre Vieja eruption on the island of La Palma resulted in the production of approximately 0.23 km³ of alkali basalt emitted over a period of three months, causing considerable destruction to both the built environment and farming activities (González et al., 2019; Bonadonna et al., 2022; Dayton et al., 2024; Del Fresno et al., 2023; Ubide et al., 2023). This eruption was marked by vigorous degassing of CO₂ and S gas species, which were measured intermittently using a variety of sensors (e.g., Burton et al., 2023). Estimates of the quantity of the total SO₂ emitted range from 1 to over 4 Tg (Albertos et al., 2023; Hayer et al., 2022; Burton et al., 2023; Dayton et al., 2024). Melt inclusion analyses reveal an average pre-eruptive S content of ~ 3000 ppm (Burton et al., 2023; Castro and Feisel,

2022; Dayton et al., 2024). Syneruptive degassing of this sulphur could be expected to yield over 3 Tg of SO₂. This is within the estimated range of emissions (e.g., Dayton et al., 2024)). However, estimates of initial CO₂ contents lie in the range 3–5 wt% (Burton et al., 2023), which is more than sufficient to saturate a basanite magma (e.g. Jiménez-Mejías et al., (2021); Lo Forte et al., (2024)) at crustal pressures (<1 GPa).

1.5.2 Fasnía

Fasnía eruption took place on the island of Tenerife in the Canary Islands archipelago in January 1705. The island of Tenerife is formed by the combination of two volcanic complexes. The island's terrain is predominantly composed of a shield volcano, with a basaltic-phonolitic complex having developed on its summit (Martí et al., 1994; Carracedo et al., 2001; Albert et al., 2015). The volcanic history of Tenerife is characterized by monogenic volcanism distributed along two rift systems: to the North-West branch is the Santiago Rift Zone and to the North-East one the Dorsal Rift Zone. To the south of these two systems lies a monogenic field known as the Southern Volcanic Zone. The Fasnía eruption is a fissural eruption which emitted basanitic magmas along the Dorsal Rift Zone (Albert et al., 2015). The Fasnía eruption has been associated with a succession of at least three magmas mixing and mingling events involving increasingly primitive magma arrivals (Albert et al., 2015). Albert et al (2015) analyzing the historical evidence and making a detailed study of the petrology hypothesized that it was a series of processes that began at least a year before the eruption.

1.5.3 Santorini

The eruptive history of Santorini has ancient origins, with the earliest evidence dating back to around 650 kyr. The island of Santorini is characterized by two main eruptive cycles: the first (360-172 ka) produced five Plinian eruptions, while during the second cycle (172-3.6 ka) seven Plinian eruptions occurred (Druitt et al., 1999; Cadoux et al., 2014). The end of the second cycle is marked by the catastrophic Minoan eruption, selected in this thesis, which occurred about 3.6 ky ago. The Minoan eruption unleashed a first Plinian phase characterised by rhyodacitic composition and two minor andesitic components called cauliflower andesitic enclave and micropheno crystal-rich andesitic pumice. The second phase is phreatomagmatic, and it was followed by a third phase of low-temperature pyroclastic flow.

Finally, the Minoan eruption ended with a phase of hot pyroclastic flow associated to caldera collapse. Cadoux et al. (2015) performed experiments and calculations to reconstruct the total budget of volatiles emitted during this eruption. These authors pointed out that the melt associated with the Santorini eruption had extremely low sulphur (≤ 100 ppm) and fluorine (500-800 ppm) contents, but was rich in water (5-6 w.t.%) and chlorine (2500-3500 ppm). Druitt et al. (1999) report a phase assemblage consisting mainly of orthopyroxene, clinopyroxene, oxides, apatite and pyrrhotite minerals.

1.6 Aim and structure of the manuscript

This experimental thesis is divided into two main sections. In the first section of the thesis, a detailed study is made of the solubility of sulphur in hydrous basaltic magmas and its effects on the corresponding phase relationships, a system little studied experimentally, with a focus on the eruption of La Palma 2021.

The second section describes the study of the relationship between the sulphur content in apatite and melt and their relationships to the fugacity of sulphur species. In addition, during this thesis, a specific analytical protocol was developed with the electron microprobe to obtain the most reliable pyrrhotite composition possible, from which the f_{S_2} of the volcanic systems studied can be derived.

In the final part of this work, the obtained results are used to characterize natural samples coming from well-studied eruptions, in an effort to shed light on the behaviour of S in magmatic systems.

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Chapter 2

Material and methods

Matériel et méthodes

Trois éruptions différentes ont été choisies pour fabriquer les matériaux de départ (verres silicatés anhydres) : les basanites de Fasnja (1705) et de La Palma (2021), ainsi que la rhyodacite de l'éruption minoenne de Santorin. Deux matériaux de départ différents ont été préparés à partir de la basanite de La Palma, l'un dopé avec 2 % d'apatite de Durango (*lpm+ap*) et l'autre sans apatite (*lpm+s*). Les matériaux de départ de Fasnja (*fas+s*) et de Santorin (*san+s*), ont déjà été dopés avec de l'apatite, lors de la thèse de doctorat de Morgane Rondet (2020). Toutes les expériences ont été réalisées avec des autoclaves à chauffage interne à l'Institut de science de la Terre d'Orléans.

Deux types d'expériences différentes ont été réalisées. La première série expérimentale a été conçue pour étudier la solubilité du soufre dans la basanite de La Palma. La deuxième série d'expériences visait à étudier la relation entre le soufre dans l'apatite et le liquide, ainsi que sa fugacité. Toutes les séries expérimentales ont été réalisées à 200 MPa, 1000-1040°C et sur une large gamme de fO_2 .

Tous les échantillons ont été analysés à l'aide du microscope électronique à balayage (MEB), de la microsonde Cameca SX FIVE (CNRS-Université d'Orléans-BRGM) et de la microsonde JEOL IHP-200F (plateforme MACLE-CVL) à l'Institut de Science de la Terre d'Orléans. Afin d'assurer des analyses les plus précises possibles, quatre calibrations distinctes ont été utilisées : un programme silicaté, deux programmes pour l'apatite, et un programme pour la pyrrhotite. Un protocole spécial a été créé pour la pyrrhotite afin de permettre une analyse précise.

La proportion de chaque phase a été calculée par bilan de masse à l'aide d'un modèle des moindres carrés contraints avec propagation des erreurs analytiques des phases expérimentales (Albarède, 1996; Scaillet et Evans, 1999). La proportion de verre a également été calculée en traitant les images SEM à un grossissement de 100x à l'aide du logiciel ImageJ, sur une base sans vésicules pour la série expérimentale *lpm+s*.

La quantité de soufre dans la phase fluide coexistant a été estimée par bilan de masse, c'est-à-dire en soustrayant les masses de S dans les phases contenant du soufre (verre, sulfure, sulfate) de la masse initiale de soufre, en tenant compte des pourcentages de phases calculés

ci-dessus. Enfin, des calculs thermodynamiques ont été effectués pour estimer $f_{\text{H}_2\text{S}}$ et f_{SO_2} dans les expériences avec pyrrhotite et principalement f_{SO_2} dans les charges sans pyrrhotite à $\text{NNO} > 2$.

2. Material and methods

During this thesis, different experimental approaches and analytical procedures were used. Most of the analytical time was spent on the microprobe, where well-calibrated analytical programs were developed for the obtained experimental products

2.1 Experimental methods

	<i>Rondet PhD Thesis 2020</i>			
	<i>lpm+s</i>	<i>lpm+ap</i>	<i>fas+s</i>	<i>san+s</i>
SiO ₂	44.11 (0.26)	42.09 (0.27)	44.11 (0.35)	67.28 (0.86)
TiO ₂	3.83 (0.10)	3.63 (0.16)	3.6 (0.12)	0.39 (0.04)
Al ₂ O ₃	14.42 (0.13)	13.64 (0.23)	14.53 (0.110)	13.55 (0.14)
FeO	12.22 (0.26)	11.81 (0.23)	11.96 (0.37)	2.86 (0.25)
MnO	0.18 (0.05)	0.18 (0.08)	0.19 (0.04)	0.09 (0.06)
MgO	7.49 (0.05)	6.94 90.11)	7.58 (0.13)	0.64 (0.05)
CaO	10.92 (0.11)	12.92 (0.14)	11.16 (0.11)	5.36 (0.36)
Na ₂ O	4.05 (0.08)	4.01 (0.05)	3.63 (0.08)	4.43 (0.11)
K ₂ O	1.73 (0.1)	1.66 (0.07)	1.51 (0.05)	3 (0.09)
P ₂ O ₅	0.97 (0.07)	3.01 (0.16)	1.73 (0.18)	2.35 (0.40)
Cl	0.01 (0.01)	0.01 (0.01)	0	0.06 (0.02)
SO ₂	0.01 (0.01)	0.02 (0.01)	0	0
Cr ₂ O ₃	0.03 (0.03)	0.02 (0.02)	0	0
NiO	0.03 (0.05)	0.04 (0.05)	0	0
Total	97.75 (0.48)*	97.92 (0.35)*	100	100

Table 1 Starting material composition. In the parentheses the standard deviation is reported. *=original total

Three different eruptions were chosen to create the starting materials: the basanites of Fasnja (1705) and La Palma (2021) and the rhyodacite from the Minoan eruption of Santorini. Two different starting materials were prepared from the basanite of La Palma, one doped with 2% of Durango apatite (*lpm+ap*) and one left apatite free (*lpm+s*). The starting materials of Fasnja (*fas+s*) and Santorini (*san+s*), already doped with apatite, prepared during the PhD thesis of Morgane Rondet (2020), have been reused. All the starting materials, after being finely grounded in agate mortar and, in some cases, mixed with apatite, were subjected to a

double fusion at 1400°C at 1 atm in a platinum crucible to obtain a homogeneous, anhydrous glass. A portion of the glass obtained was analysed by electron microprobe analyzer (EMPA) to check their homogeneity (Table 1), the rest of the material being ground to a fine, homogeneous powder.

All Experiments were carried out with internally heated pressure vessels (IHPV) at the Institut de science de la terra d'Orléans. The IHPV allows experiments to be performed between 50 and 400 MPa and at high temperatures, up to 1400 °C. The capsules are placed in a ceramic sample holder that is suspended with a rhenium or platinum wire depending on fO_2 conditions (Fig.4). Care must be taken that the sample holder is positioned between the two S-type thermocouples (Pt/Pt₉₀Rh₁₀), which guarantees a temperature uncertainty of $\pm 5^\circ\text{C}$. During the experiments, the gradient between the lower and upper thermocouples was kept below 10°C. Molybdenum furnaces were used for all experiments. By introducing different gas mixtures into the autoclave, pure Ar for oxidising conditions or a mixture of Ar and H₂ for more reduced conditions, it was also possible to vary the redox conditions. The final oxygen fugacity value was obtained from the solid sensor consisting of NiPd for medium and high oxygen fugacity conditions and CoPd for low oxygen fugacity conditions

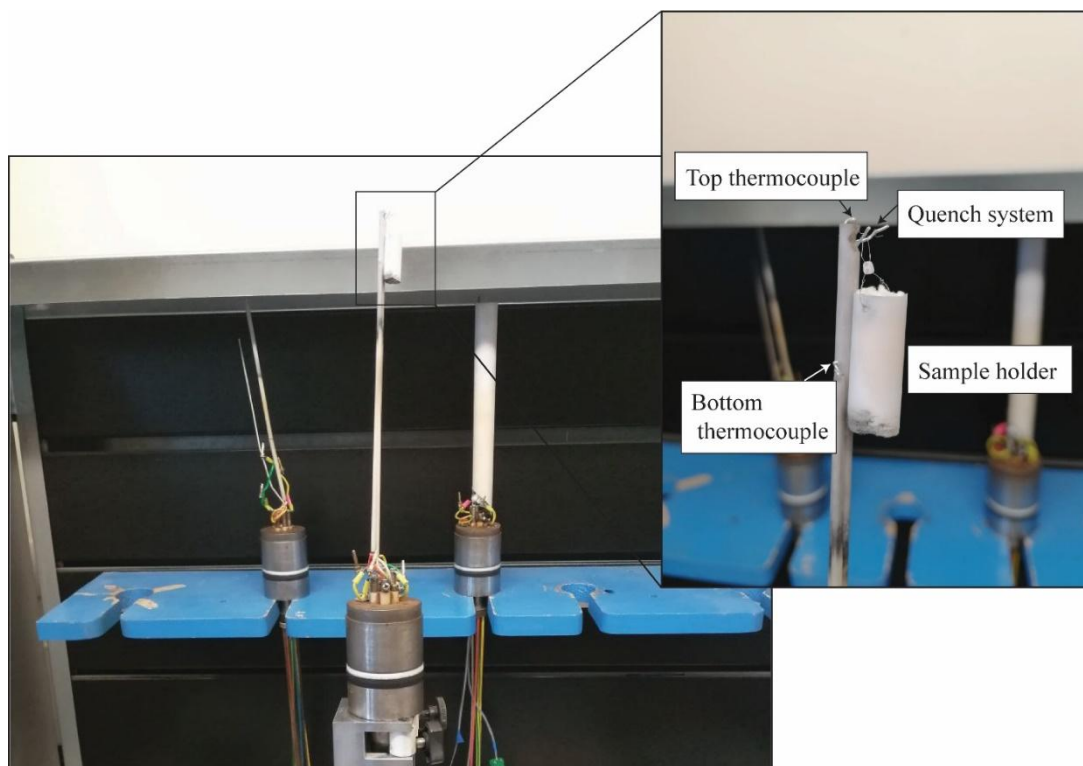


Fig. 4. The images presented here illustrate the quench system and type-S thermocouples.

(Taylor et al., 1992). Almost all the experiments ended with a rapid drop quench with cooling rates of order 100°C/s (Di Carlo et al., 2006).

For each experiment, five to seven Au capsules were prepared (inner and outer diameter of 2.5–2.9 mm, height of 1.5 cm). Gold was employed in order to reduce the loss of sulphur and iron.

Two different types of experiments were conducted. The first experimental series was designed to investigate the solubility of sulphur in La Palma basanite. The second series of experiments aimed to investigate the relationship of sulphur between apatite and melt, as well as with sulphur fugacity. For the solubility sulphur experimental series, the starting material *lpm+s* was used, from which three batches were obtained: one doped with 2 wt% native sulphur, one with approximately 1.1 wt% sulphur in the form of FeS and one sulphur-free. Capsules were loaded first with 3 mg of deionized water, to reach H₂O saturation, then with 30 mg of silicate powder prepared by mixing S- or FeS-doped powder with S-free glass in various proportions to obtain different bulk concentrations of sulphur. In the following sections, the two series will be referred to as S-doped or FeS-doped charges. The weight of the capsules was measured three times: after welding, after a test in an oven at 125 °C for at least 1 h, and finally after the experiment to check for volatile leaks. Only charges with a difference of less than 0.0003 g were considered successful.

The second experimental series were carried out to investigate the relationship between the amount of sulphur in apatite and melt and its relationship to sulphur fugacity. In this case, starting materials doped in apatite were used (*lpm+ap*, *fas+s*, *san+s*). The capsules were filled using the same methodology for the S-solubility experiments with minor differences. In the case of La Palma (*lpm+ap*) and Fasnja (*fas+s*), only native sulphur was added in order to reach approximately 2 wt%, 1 wt% and 0.5 wt%.

Furthermore, two experiments were conducted with the starting material *lpm+ap* to determine whether the addition of chlorine influenced the sulphur content. The preparation of capsules was done following the previously described methodology, replacing demineralised water by an aqueous solution comprising 15% HCl (*lpm+ap cIs*). Subsequently, experiments were conducted with varying concentrations of HCl (15%, 10%, 5%, and 0%) while maintaining a constant S concentration of 2% (*lpm+ap sCl*).

For the Santorini (*san+s*) runs, capsules were prepared, again at H₂O saturation, with about 60 mg total product and S was added in the form of FeS with the same percentages of *lpm+ap*. To better understand what the relationship between apatite and pyrrhotite might be, an experiment was also carried out consisting of 2 capsules, both of which were filled with 15 mg ground pyrrhotite, 15 mg Durango apatite powder, and 30 mg *lpm+s* with two different amounts of water: 4-5%.

We also synthesised sulphur-bearing glass standards at high fO_2 , with 1000-3000-5000 ppm S and approximately 2% H₂O. Capsules were prepared with the starting material *lpm+s* and native sulphur and the experiment was run at 1200°C-200 MPa for ca 2 hours and drop quenched. Although some Fe-oxides occur in run product glasses, the analyses of these glasses reveal a content practically identical to that expected (Fig. 5). This shows that both the Cameca and Jeol microprobes, with the calibration described below (Sect.2.2), satisfactorily reproduce S concentrations without the need for an external reference material. All experimental conditions are given in Table 2.

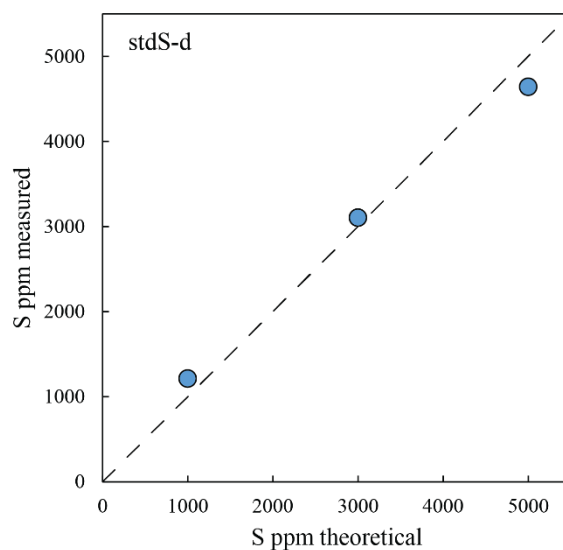


Fig. 5 Sulphur content theoretical vs measured in stdS-d

<i>Serie id</i>	<i>P(Mpa)</i>	<i>T(°C)</i>	<i>NNO</i>	<i>duration</i>
<i>lpm+s 1-6</i>	200	1040	1.34	6h
<i>lpm+s 17-12</i>	200	1040	2.38	6h
<i>lpm+s 13-18</i>	200	1040	3.3	6h
<i>lpm+s 19-25</i>	200	1040	4.1	6h
<i>lpm+s 26-32</i>	200	1040	-0.48	6h
<i>lpm+s 33-34</i>	200	1040	1.45	6h
<i>fas+s 1-3</i>	200	1040	3.51	6h
<i>lpm+ap 1-4</i>	200	1040	4.17	6h
<i>lpm+ap 9-12</i>	200	1040	-0.49	6h
<i>lpm+ap 13-16</i>	200	1040	0.66	6h
<i>lpm+ap 20-22</i>	200	1040	-0.58	6h
<i>lpm+ap 23-26</i>	200	1040	0.45	6h
<i>lpm+ap clS 1-4</i>	200	1040	-0.59	6h
<i>lpm+ap sCl 1-4</i>	200	1040	-0.82	6h
<i>san+s 1-4</i>	200	1000	2.78	4 days
<i>san+s 6-9</i>	200	1000	0.58	5 days
<i>san+s 10-13</i>	200	1000	-0.47	5 days
<i>FeS+ap 4-5</i>	200	1000	0.47	3 days
<i>sdtS-d</i>	200	1200		2h

Table 2 Shows all experimental runs done in this work

2.2 Analytical techniques and data treatment

All samples were prepared for analysis by the scanning electron microscope (SEM), the Cameca SX FIVE microprobe (CNRS-Université d'Orléans-BRGM) and the JEOL IHP-200F microprobe (MACLE-CVL platform) at the Institute de Science de la Terre d'Orléans. To ensure the most precise analyses, three distinct calibrations were used: a silicate program, two apatite programs, and a pyrrhotite program. A special protocol was created for pyrrhotite in order to allow for precise analysis, which will be described in more detail later (sect. 2.2.3)

2.2.1 Silicate and anhydrite analysis

Silicate minerals, oxides and glass were analysed on both Cameca and Jeol probes. The two instruments were set with the following counting time on peak: the major elements were measured for 10" and the S for 60". Table 3 reports in details the two calibrations.

	<i>sp1</i>	<i>sp2</i>	<i>sp3</i>	<i>sp4</i>	<i>sp5</i>
<i>Cameca EMPA</i>	<i>PET</i>	<i>TAP</i>	<i>LIF</i>	<i>LTAP</i>	<i>LPET</i>
	K (orthoclase)	Si (albite)	Fe (Fe ₂ O ₃)	Na (albite)	Ca (andradite)
	Ti (MnTiO ₃)	Al (Al ₂ O ₃)	Mn (MnTiO ₃)	Mg (MgO)	P (apatite)
			Ni (NiO)		Cr (Cr ₂ O ₅)
					S (baryte)
					Cl (Vanadinite)
<i>Jeol EMPA</i>	PETJ	LPET	LLIF	LTAP	TAP
	Ti (TiO ₂)	Cr (Cr ₂ O ₅)	Fe (Fe ₂ O ₃)	Na (NaCl)	Si (orthoclase)
	Ca (andradite)	P (apatite)	Mn (MnO)	Mg (andradite)	Al (Al ₂ O ₃)
	Cl (NaCl)	S (baryte)	Ni (NiO)		
	K(orthoclase)				

Table 3 Calibration for silicate programs at Cameca and Jeol EMPA. The standards employed for the calibration of the two microprobes are specified in parentheses.

Analyses were performed at 15kv and 20nA using a focused beam for minerals and defocalised 5 µm, 10 µm, 20 µm for glass, depending on the size of glass pools and crystals. For anhydrite, a program that included only S and Ca at 10" was employed. This was due to the thinness and brittleness of anhydrite. Indeed, had the silicate program been used as usual, significant beam damage would have been likely to have occurred. The H₂O concentration

in the run products was estimated following Devine et al. (1996), analysing at the beginning and end of each analytical session basanitic and rhyodacitic standards with a known water contents. For the experiments with La Palma and Fasnía, the F1c, F05, F3c2 and F2b standards were analysed (Jiménez-Mejías et al., 2022), while for Santorini, the KFT rhyolitic standards of Scaillet and Evans, (1999) were used.

2.2.2 Apatite analysis

In order to create a well-calibrated apatite program, spectra at 15kV and 50nA were carried out to assess possible interference, which was not found. In an analytical test session, two programs were created: one where Ca and P were calibrated on chloroapatite (CLAP program) and one on fluoroapatite (FLAP program). After a series of analysis per program on the same experimental run and on a piece of Durango apatite, it was decided to continue with the CLAP program. The analysis carried out with the FLAP program shows a problem on the analysis of the F. In fact, analysing apatite of a known composition, it was not possible to reproduce the correct amount of F using FLAP program. The CLAP program is built up as follows: on spectrometer sp1 (PC1) F was analyzed for 30"; on sp2 (TAP) P for 10", Si for 30" and Al for 10"; on sp3 (PET) Ca for 10"; on sp4 (LPET) S for 60" and on sp5(LPET) Cl for 30" (Table 4). P and Ca were calibrated on a chloroapatite standard, F on topaz, Al on its corresponding oxide (Al_2O_3), Si on andradite, S (6+) on barite and Cl on vanadite. The background settings were adjusted to -500+600 for P, ± 650 for Ca, ± 500 for Cl, -1350+2250 for F and -400+350 for S.

In addition, a second program was used for some experiments to evaluate the influence of trace elements of sulphur distribution (Table 4). Trace elements were calibrated on the following standards: Y on YPO_4 , As on AsGa, Fe on Fe_2O_3 , Mn on Manganite, Nd on NdPO_4 , Sr on SrSO_4 , Ce on CePO_4 , La on LaPO_4 and Th on ThO_2 . This second program was extremely long, each analysis lasting 5 minutes.

Al_2O_3 is used as a sensor to monitor any contamination from glass or surrounding minerals. Si was also analysed since several studies have shown that Si can be incorporated into apatite (Konecke et al., 2017 and references herein).

	<i>sp1</i> <i>PC1</i>	<i>sp2</i> <i>TAP</i>	<i>sp3</i> <i>PET</i>	<i>sp4</i> <i>LPET</i>	<i>sp5</i> <i>LPET</i>
<i>Program standard</i>	F (30")	P (10") Si (30") Al (10")	Ca (10")	S (60")	Cl (30")
<i>Program trace elements</i>	F (10")	P (10") Y (30") Si (10") As (30")	Fe (30") Mn (30") Nd (60")	S (30") Sr (30")	Ce (30") La (30") Ca (10") Th (30") Cl (10")

Table 4 . Calibration of apatite program.

The analyses were conducted at 15kV and 10 nA, for the standard program, and 15 kV and 20 nA, for the trace elements program, using a focalized or defocalized beam depending on the size of the minerals. For most experimental apatites, the use of a defocused beam was not feasible due to the dimensions of crystals. Furthermore, in some instances, the analysis of apatite was not possible without contamination. For this reason, a post-analysis correction was made. For the analyses that had Al₂O₃ greater than 0 wt% and SiO₂ greater than 1 wt%, Al₂O₃ was set at 0 wt% and SiO₂ at 4wt%, which on average is the amount of silica that can be found in natural apatites. Subsequently, the composition was recalculated to 100. To minimize S overestimation errors, this correction was applied to only those analyses that had a total greater than 98 wt% and both Al₂O₃ and SiO₂ summing up to less than 10 wt% (values taken arbitrarily).

2.2.3 Pyrrhotine analysis

A considerable effort was invested in the development of an EMPA calibration program, with the objective of enabling precise analysis of pyrrhotite. It was imperative that the chemical composition of this mineral be accurately determined, in order to calculate the fS_2 .

2.2.3.1 SEM and micro fluorescence analysis

Experimental pyrrhotites, Po5 and Po7, synthesized by Clemente et al. (2004), whose composition is known by X-ray (Table 5), and unknown sulphides were first analyzed using the ZEISS scanning electron microscope (FEG) equipped by EDS and XRF Bruker from the

ISTO laboratory. On doing the EDS spectrum, it was immediately noticed that the quantification with this method was not precise enough to allow a precise determination of the composition of the experimental sulphides.

	Po5	Po7
<i>d(102)</i>	2.082	2.050
<i>NFeS</i>	0.975	0.920
<i>% at Fe</i>	48.770	45.970

Table 5 X-ray value of Po5 and Po7 from (Clemente et al., 2004)

We also checked for the presence of any impurities, using micro fluorescence analyses which were carried out on Po5, Po7 and the pyrrhotite standard (Po-std) used on the Cameca SX FIVE microprobe (CNRS-Université d'Orléans- BRGM) at the Institut des Science de la Terre d' Orléans (ISTO).

The analytical conditions at which the spectra were carried out are 50 kV, 60 mA, 30 W for 60 seconds on a spot of approximately 40 μm . The main impurities found are Ni, Cu, Ti, Ag, Ca and Mo, whose average contents, in ppm, are reproduced in Table 6. These impurities, although clearly visible in micro-XRF analyses, are present at sufficiently low concentrations to be safely ignored in the following treatments.

	Po5	Po7	Po-std
<i>Ni</i>	523	727	338
<i>Cu</i>	910	1117	597
<i>Ti</i>	155	66	-
<i>Ca</i>	249	112	802
<i>Mo</i>	81	97	32
<i>Cr</i>	596	1035	3287

Table 6 List of impurities found out in Po5, Po7 and Po-std by the micro fluorescence analysis (ppm).

2.2.3.2 Electron microprobe analyzer and protocol

Considering the uncertainty in the identification of unknow sulphides with EDS-SEM and in order to determine their precise composition, two analytical programs were tested with the Cameca EMPA: one calibrated on a synthetic pyrrhotite (Po-std) and the other on natural pyrite (Py-std) made available by the Bureau de Recherches Géologiques et Minières

d'Orléans (BRGM). As a first step, the presence of interferences was checked on the two standards by making a WDS spectrum at 30nA, 20kV and dwell time of 200 ms. This methodology also permitted the precise determination of the position of the S and Fe peaks of the standards. Furthermore, under the same conditions, a peak search was also carried out on Po5 and Po7, which were taken as reference materials. The values and peak positions of the two standards and reference materials are shown in Table 7.

The peak position is the same in all the materials analysed, however, the count per seconds (cps) values of S of the K α 1 on the PET and LPET crystal and K α 2 on the TAP crystal are markedly different between Py-std and Po-std, Po5 and Po7 (Fig. 6).

	<i>Sp1 (PET)</i>		<i>Sp2 (TAP)</i>		<i>Sp3 (LIF)</i>		<i>Sp4 (LPET)</i>		<i>Sp5 (LLIF)</i>	
	<i>SKα1</i>		<i>SKα2</i>		<i>FeKα1</i>		<i>SKα1</i>		<i>FeKα1</i>	
	Sin θ	cps	Sin θ	Cps	Sin θ	Cps	Sin θ	Cps	Sin θ	cps
<i>Py-std</i>	61476	8143.1	41760	1073.8	48063	10080	61369	22662	48113	25000
<i>Po-std</i>	61476	5114.9	41760	581.1	48063	13468	61369	14497	48113	33389
<i>Po5</i>	61476	5399.5	41760	756.9	48063	33629	61369	14563	48113	13878
<i>Po7</i>	61476	5882	41760	822.2	48063	31697	61369	15660	48113	12468

Table 7 The positions and values of the S and Fe peaks for Sp 1,2,3,4,5 on the Po-std, Py- std and on the reference materials Po5 Po7 are shown. With regard to the S peaks, a difference is evident between the cps values of pyrite std and pyrrhotite std, Po5 Po7.,

The peak search for S and Fe in Po-std revealed that the pre-defined peak positions of the Cameca microprobe (61408 and 48084, respectively) do not correspond to those of the pyrrhotite mineral. Therefore, it is advisable to redo the peak search at each analytical session and enter the position manually during calibration. This ensures that the position is set and fixed, preventing it from being searched for during each analysis.

Subsequently, two programs were created with the same structure. S is analysed for 10" on Sp1(PET) and 20" on Sp4(LPET), Fe 10" on Sp3(LIF) and Sp4(LLIF), Si 10" Sp2(TAP), Ni 10" Sp3(LIF) and Cu 10" Sp5(LLIF) (Table 8).

<i>Sp1</i>	<i>Sp2</i>	<i>Sp3</i>	<i>Sp4</i>	<i>Sp5</i>
<i>PET</i>	<i>TAP</i>	<i>LIF</i>	<i>LPET</i>	<i>LLIF</i>
S (10")	Si (10")	Fe (10")	S (20")	Fe (10")
		Ni (10")		Cu (10")

Table 8 Calibration of pyrrhotite program.

The S values recorded by the two spectrometers are summed. It was preferred to use the PET crystal and, where possible, LPET, to analyse the S to maximize the count statistics. The TAP crystal could have been used to analyse SK α 2 emissions, as the peak positions remain stable and the concentration is sufficiently high. However, the counts are so low for the TAP crystal that choosing it would have led to a larger error in the measurement. Si is considered as a sensor to monitor possible contamination of the glass or other mineral phases. pyrrhotite. Si is calibrated on andradite, Ni and Cu on their respective metals. An element loss test, performed on Po5 for 1 minute on PET, LPET and LIF spectrometers,

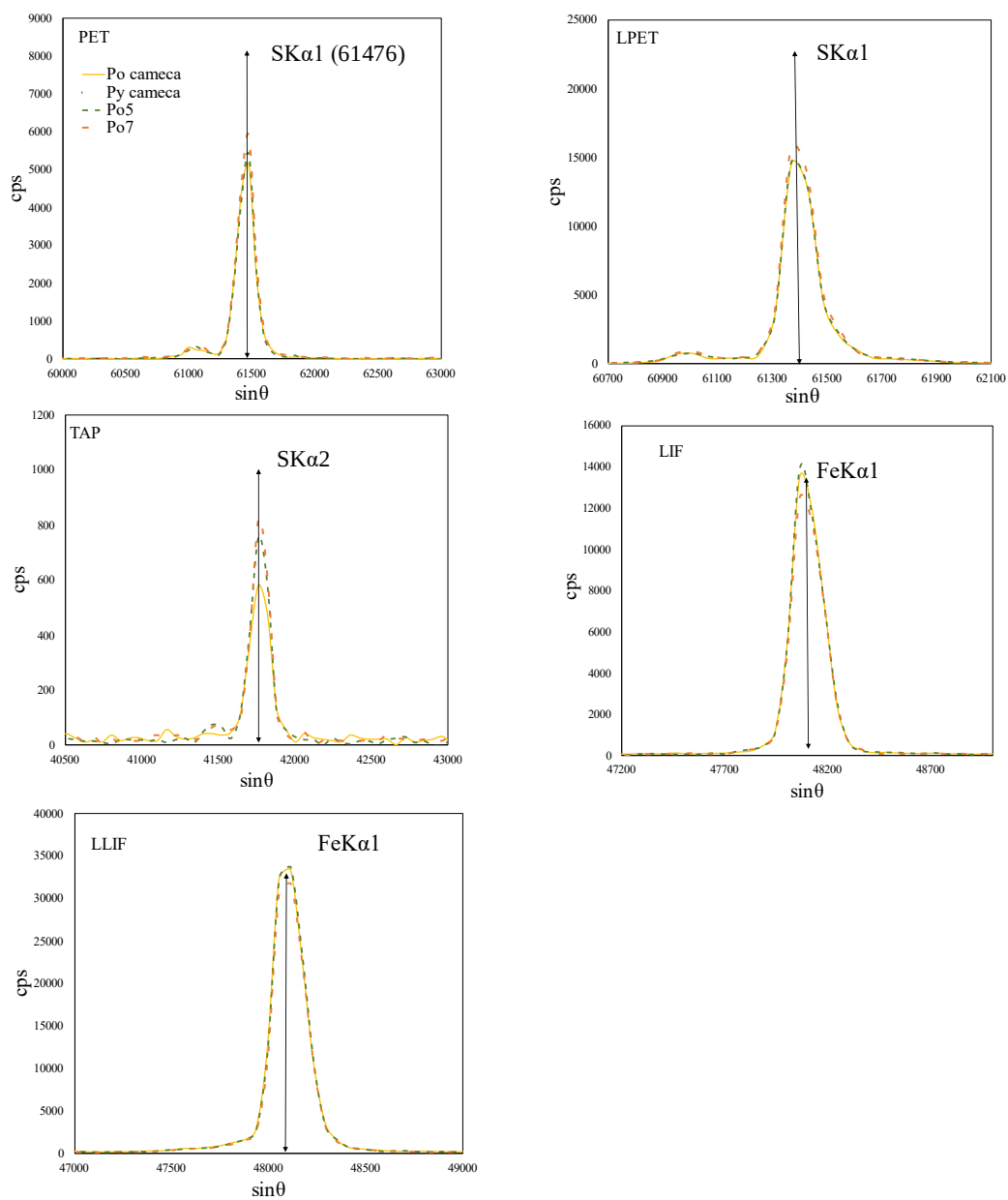


Fig. 6. Position of the S and Fe peaks on the different spectrometers for py-std, po-std, Po5 and Po7.

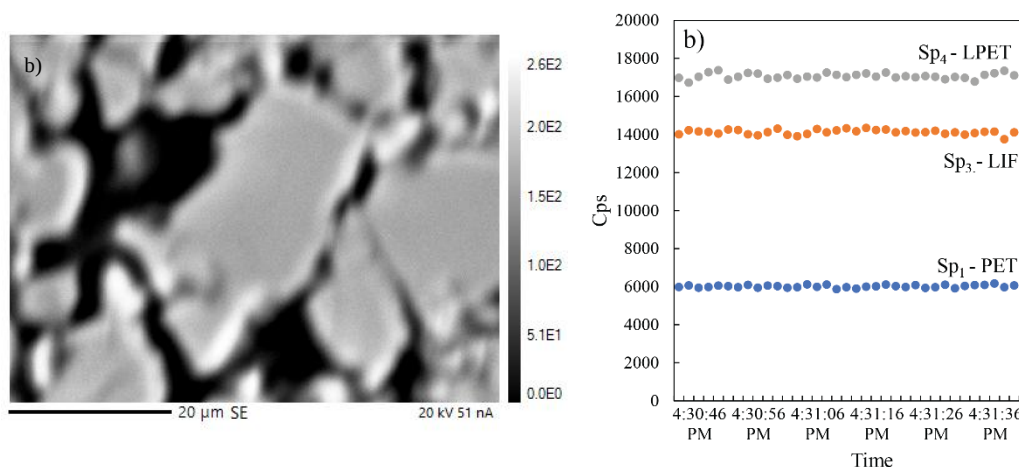


Fig. 7 a) BSE image on Po5 after 1 minute of element loss test at microprobe; b) Element loss graphic showing no variation during test.

The difference between the two programs is that S and Fe are calibrated either on pyrite or pyrrhotite. To demonstrated the absence of S and/or Fe loss (Fig. 7b) and beam damage (Fig. 7a). The same procedure was done to check stability at the fixed background positions. The analyses were conducted at 20 kV and 50 nA with a focused beam. Although the peak positions of Fe and S are the same in the two minerals, pyrite and pyrrhotite, their values are markedly different (Fig.6 and Table 7), which is due to the chemical formula of the two minerals (FeS_2 for pyrite and Fe_{1-x}S for pyrrhotite). This means that when analysing pyrrhotite with the pyrite program, the mineral's crystallo-chemical formula is incorrect.

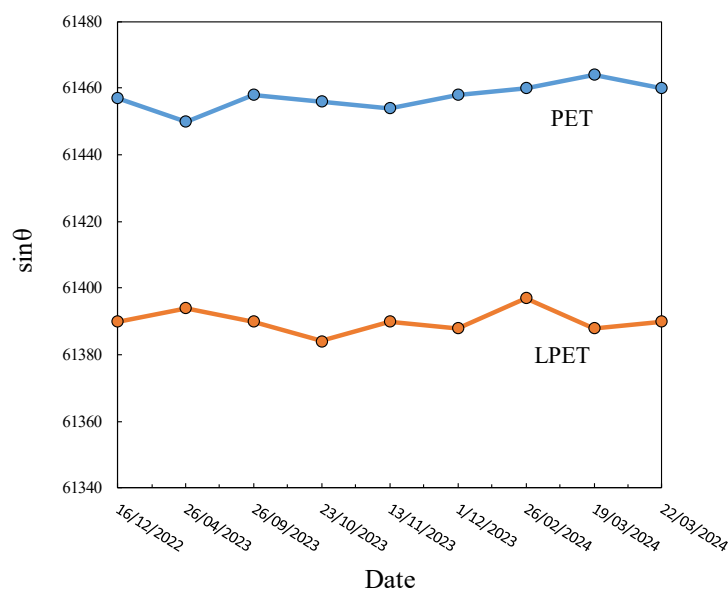


Fig. 8 Peak position imposed on the S on the LPET and PET spectrometer during the various analytical sessions.

By comparing the positions imposed of the S K α peak on Sp1 (PET) and Sp2 (LPET), during several analytical sessions, we verified its veracity. In fact, as illustrated in Fig. 8, the peaks remained relatively stable between the different sessions.

In Fig. 9 the atomic percent (at%) of Fe values of Po5 and Po7 during various analytical

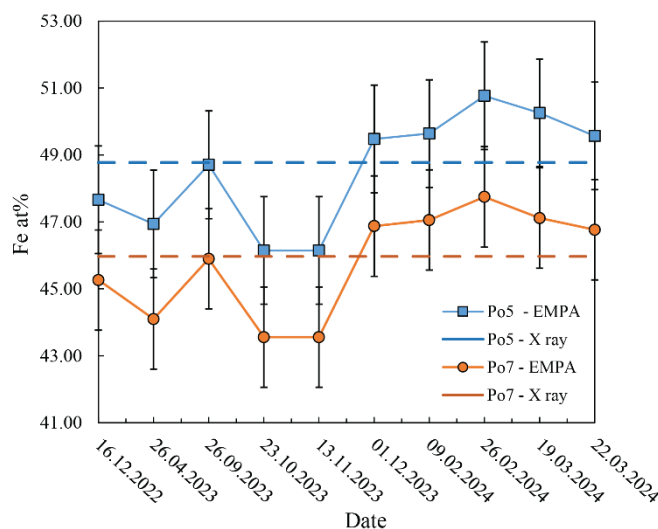


Fig. 9. Comparison of at% Fe values between microprobe and x-ray analysis during the various analytical sessions.

sessions are compared with their respective X-ray calculated values. This highlights the need for the use of reference material as a basis for post-analysis calibration.

In order to obtain an accurate microprobe composition of pyrrhotite, it is also of fundamental importance to analyse the two reference materials both at the beginning and end of the

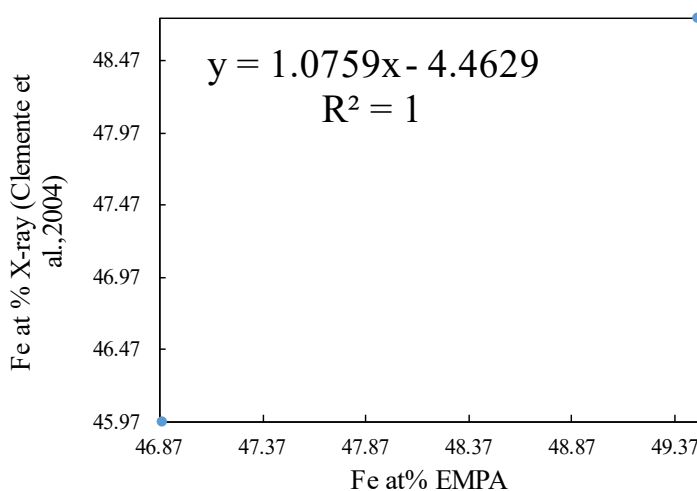


Fig. 10. Example of at%Fe calibration curve.

session. This is essential for ensuring that the calibration remains stable and for recalculating the composition of the unknown sample by reconstructing a calibration curve.

The most important analytical limitation of this technique is the size of experimental pyrrhotite crystals. Indeed, analysis of pyrrhotites measuring less than 2-3 μm or exhibiting low thickness, shows the presence of significant contamination by glass or other surrounding mineral phases. The calibration curve was constructed by calculating the Fe at% from the microprobe analysis of the reference materials and comparing it with the X-ray value obtained by Clemente et al. (2004), as shown in Fig. 10. Thanks to the trend line obtained, it is possible to calculate at% of Fe corrected. This calibration permits the calculation of S fugacity according to Froese and Gunter, (1976) equation. After analyzing the experimental pyrrhotite in several analytical sessions and calculating fS_2 for each run, the average of them was used as the fS_2 of the sample. Fig. 11 shows the difference of some $\log fS_2$ calculated before and after the Fe at% correction. It can be seen that the calculated fugacity of S without

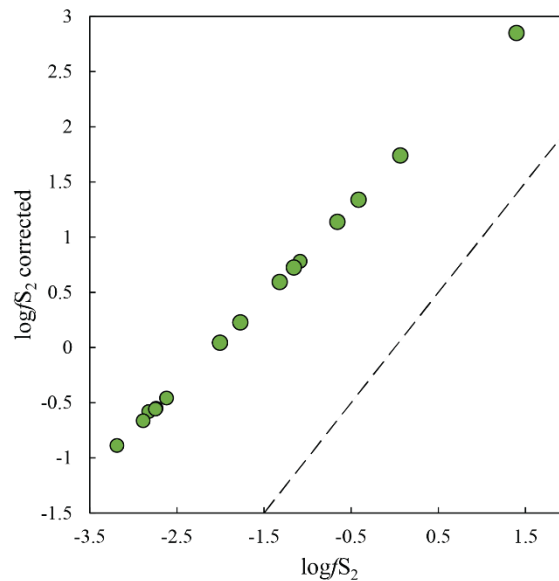


Fig. 11 Comparison between the $\log fS_2$ calculated with Fe at% not corrected and the $\log fS_2$ with the correction.

the correction is lower than the one obtained with the calibration.

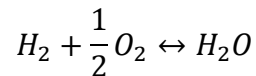
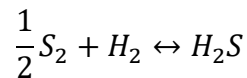
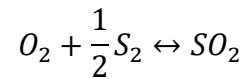
2.2.4 Mass balance

The proportion of each phase was calculated by mass balance using a constrained least-squares model with the propagation of analytical errors of the experimental phases (Albarède, 1996; Scaillet and Evans, 1999). The proportion of glass was also calculated by processing SEM images at 100 μm magnification using ImageJ software, on a vesicle-free basis for the experimental series of *lpm+s*.

The amount of sulphur in the coexisting fluid phase was estimated by mass balance, i.e., by subtracting the masses of S in sulphur-bearing phases (glass, sulphide, sulphate) from the initial mass of sulphur, taking into account the phase percentages as calculated above. The S wt% was then calculated by determining the amount of H_2O in the fluid using the same method. For runs containing Cl, the amount of chlorine in the fluid was implemented in the calculation.

2.2.5 $f\text{H}_2\text{S}$ and $f\text{SO}_2$ calculation

In the experiments where pyrrhotite was present, to calculate the $f\text{H}_2\text{S}$ and $f\text{SO}_2$, a system made of H_2O , S_2 , H_2S and SO_2 species was assumed. So, the reactions at equilibrium are:



From here, it is possible to derive the equilibrium constant as a function of fugacities:

$$K = \frac{f\text{SO}_2}{(f\text{S}_2)^{\frac{1}{2}} * f\text{O}_2}$$

$$K = \frac{f\text{H}_2\text{S}}{(f\text{S}_2)^{\frac{1}{2}} * f\text{H}_2}$$

$$K = \frac{f\text{H}_2\text{O}}{(f\text{O}_2)^{\frac{1}{2}} * f\text{H}_2}$$

The equilibrium constants are calculated as $\log(K) = -\Delta_r G_T^0 / (RT * 2.303)$, while f_{H_2O} is calculated from the model of Jiménez-Mejías et al., (2022) for the basanitic runs and Burgisser and Scaillet (2007) for the rhyodacitic experiments. At this point, knowing f_{S_2} , f_{O_2} it is possible to calculate f_{SO_2} , f_{H_2} and f_{H_2S} .

In charges lacking pyrrhotite at $NNO > 2$, it is assumed a model where $P_{tot} = P_{H_2O} + P_{SO_2}$. Knowing that $f_i = X_i \gamma_i P_{tot}$ and calculating the f_{H_2O} from the solubility models, it is then possible to calculate X_{H_2O} as $X_{H_2O} = f_{H_2O} / (\gamma_{H_2O} * P_{tot})$. Assuming that the system is only composed by H_2O and SO_2 , implies $X_{SO_2} = 1 - X_{H_2O}$. Using this procedure, it is possible to estimate $f_{SO_2} = X_{SO_2} \gamma_{SO_2} P_{tot}$.

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Chapter 3

*Sulphur solubility in
the la Palma 2021
basanite*

Solubilité du soufre dans la basanite de La Palma 2021

Ce chapitre présente les résultats de la série expérimentale sur solubilité du S réalisée avec le matériau de départ $lpm+s$. Les résultats obtenus ont été publiés pendant les derniers mois du processus de rédaction de la thèse (Frascerri et al., 2024). La première partie de cette section est centrée sur la description et la discussion des résultats expérimentaux, tandis que la seconde partie se concentrera sur une approche thermodynamique pour reconstruire les conditions pré-éruptives de La Palma et le processus de dégazage.

D'après l'étude du diagramme de phases et du Mg# des minéraux Mg-Fe, il apparaît que le soufre n'affecte pas de manière significative la composition des phases solides cristallines. En revanche, la fugacité de l'oxygène est le principal paramètre contrôlant la concentration en soufre des verres silicatés. Ces données montrent également qu'il n'y a pas d'effet systématique du soufre sur les proportions de phases dans les différentes expériences, à l'exception des cas évidents de sulfure ou d'anhydrite. Là encore, la fugacité de l'oxygène semble exercer l'influence la plus forte.

La comparaison des éléments majeurs du verre résiduel des charges expérimentales avec des données de la littérature montre des tendances similaires. Ces tendances reflètent la nature des cristaux observés dans les expériences et sont régies de manière importante par la fO_2 et non par la teneur en soufre. Comme pour les tendances des éléments majeurs, la concentration de soufre dans les verres est influencée par la fO_2 . Ainsi, les verres trempés des charges produites à faible fO_2 sont considérablement moins riches en soufre que ceux produits à haute fO_2 . Les changements de composition du verre semblent ne pas affecter l'effet globalement positif de la fO_2 sur la teneur en soufre.

Les teneurs en S mesurées dans les verres saturés en pyrrhotite peuvent être comparées à celles calculées à l'aide des modèles de solubilité du S de Lesne et al. (2015) et de Boullion et Wood (2023), montrant une bonne concordance.

Ces données expérimentales ont ensuite été appliquées au cas de l'éruption de La Palma en 2021. La fugacité d'oxygène pré-éruptive (fO_2) de la basanite de Cumbre Vieja de 2021 a été estimée de NNO à NNO+1 (Day et al., 2022 ; Erdmann et al. 2024). Les données expérimentales dans cette gamme de fO_2 indiquent que la teneur en soufre du magma était d'environ 2500–5000 ppm, une proportion importante étant dissoute dans le verre. Ainsi, la plus haute teneur en S mesurée dans les inclusions de verre (4800 ppm, Burton et al., 2023)

suggère une fO_2 à l'extrémité supérieure de la gamme de fO_2 déduite à partir des concentrations en V de l'olivine, ou peut-être des températures plus élevées. Les résultats expérimentaux rapportés dans ce travail indiquent que, pour reproduire la teneur en soufre moyenne d'environ 3000 ppm dans les inclusions de verre de la basanite de La Palma 2021, étant donné la plage de fugacité d'oxygène pré-éruptive (fO_2) de NNO+0,6 à NNO+1,6 (Day et al., 2022), la fugacité du soufre (fS_2) devrait être autour de 0,1–1 MPa. Cela est en accord avec la composition de la pyrrhotite dans nos produits expérimentaux.

Les calculs suivants ont été effectués afin de modéliser la composition de la phase fluide, en tenant compte des contraintes existantes sur le système profond, pour trois scénarios différents : I) Le calcul de la composition du fluide à l'équilibre avec le magma basanite, qui est supposé être initialement situé à environ 300 MPa dans le réservoir crustal, a été effectué comme première étape. (D'Auria et al., 2022 ; Pérez, 2022 ; Del Fresno et al., 2023 ; Ubide et al., 2023 ; Dayton et al., 2024 ; Andujar et al., soumis). II) La deuxième étape a consisté à calculer le dégazage du magma pendant son ascension, à partir d'un réservoir à 300 MPa et pour différentes quantités de fluide exsolvé dans le réservoir crustal. III) Enfin, le processus de dégazage a été simulé pour des pressions plus élevées (c'est-à-dire des niveaux plus profonds correspondant au manteau supérieur source des magmas) et des températures plus élevées (environ 1125 °C), conformément aux contenus élevés en CO_2 dissout (jusqu'à 1,2 % en poids) mesurés dans les inclusions vitreuses des olivines (par exemple, Dayton et al., 2024 ; Zanon et al., 2023) et aux données sismiques (par exemple, D'Auria et al., 2022 ; Del Fresno et al., 2023) qui indiquent une source mantellique à 400-800 MPa.

Dans l'étape I), le calcul détermine la pression de saturation pour les espèces fluides suivantes : H_2O , CO_2 , SO_2 et H_2S . L'hypothèse fondamentale est qu'il y a un équilibre entre les fugacités des volatils dans le fluide et celles dans le liquide silicaté et fournit la composition des fluides arrivant à la surface, après avoir quitté le réservoir crustal en étant découplé du magma source, et traversant la section crustale dans un état non modifié. Ce premier scénario fournit un cadre conceptuel pour l'interprétation de la surveillance des gaz pendant les périodes de repos.

La deuxième étape II) considère le processus de dégazage pendant l'ascension du magma. En particulier, on a pris en compte les espèces de soufre, d'eau et de carbone, car elles peuvent s'exsolver à différentes profondeurs (Oppenheimer et al., 2014). Le calcul complet prend

également en compte l'impact potentiel du fluide en excès (bulles) dans le réservoir crustal. La quantité totale de S libérée a été calculée pour 0,2 km³ de magma émis ainsi que le rapport X_{CO_2}/X_{SO_2} du gaz en sortie de conduit (magma + fluide), et ce en fonction de la fugacité de l'oxygène. Les résultats de ces calculs indiquent la présence d'une quantité significative de fluide libre (en excès) dans le système de plomberie crustal, comme le suggèrent des études précédentes (par exemple, Burton et al., 2023 ; Sandoval-Velasquez et al., 2023 ; Zanon et al., 2023).

La dernière étape III) étudie la partie plus profonde du système de plomberie. Par conséquent, des calculs ont été effectués en utilisant des teneurs de CO₂ dissout plus élevées, allant de 5000 à 10000 ppm (correspondant à des pressions entre 400-800 MPa).

Concernant le rapport X_{CO_2}/X_{SO_2} , une pression croissante implique une f_{S_2} élevée (1 MPa) ce qui est moins probable qu'une valeur plus faible (0,1 MPa), car l'ensemble des courbes pour $f_{S_2}=1$ MPa ne reproduit pas le rapport X_{CO_2}/X_{SO_2} mesuré dans les gaz émis. En termes de quantité de SO₂ libérée, un magma avec une $f_{S_2}= 1$ MPa nécessiterait une f_{O_2} légèrement au-dessus de NNO, tandis qu'un magma avec une $f_{S_2}= 0,1$ MPa nécessiterait des conditions légèrement plus oxidantes. Les calculs ci-dessus montrent que pour reproduire les observations de l'éruption de La Palma, en particulier la teneur en S des inclusions de verre, la composition des gaz et la quantité de S libérée, cela nécessite un équilibre délicat entre la f_{O_2} , la f_{S_2} et la quantité de fluide initial dans le magma (en plus de la température et de la pression).

3. Sulphur solubility in the la Palma 2021 basanite

This chapter will show the results of the experimental solubility series carried out with the starting material *lpm+s*, at experimental conditions listed in Table 9. The results obtained were the subject of an article that was published in the final months of the thesis writing process (Frascer et al., 2024). The first part of this section is focused on the description and discussion of the experimental results, meanwhile the second part will focus on a thermodynamic approach to reconstruct the pre-eruptive conditions of La Palma and the outgassing process.

3.1 Mineral phase

Fig. 12 shows the equilibrium phase diagrams of S- and FeS-series, depending on fO_2 and the amount of sulphur added. In the S-doped series, depending on fO_2 , anhydrite and pyrrhotite crystallizes. In detail, anhydrite is found only in charges with 2 wt.% added S at NNO+4.1, while pyrrhotite is present with 1 wt.% and 2 wt.% S added at NNO+1.34 and NNO-0.48. Olivine occurs in almost every charge, except for S-poor runs at high fO_2 . Apart from three charges with 2 wt.% S added at NNO+2.38, 3.3 and 4.1, pyroxene is present in all experimental charges. Amphibole did not crystallise in charges with 2 wt.% and 1 wt.% S at NNO+2.38, in any experiments at NNO+3.3, in the charge at 2 wt.% S under the most oxidising conditions and in the S-free charge at NNO-0.48 (Fig.12a). The phase diagram of

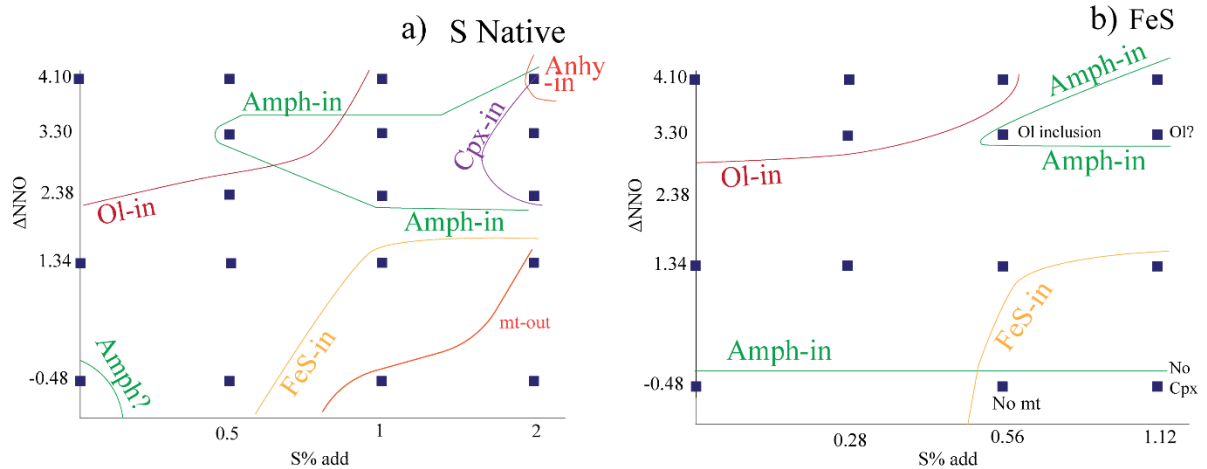


Fig. 12 Equilibrium phase diagram at 1040°C and 200 MPa for both S-doped (a) and FeS-doped (b) charges. Phases lie inside their stability field. Ol=olivine; Cpx= clinopyroxene; Amph = amphibole; Anhy = anhydrite; mt=magnetite

the FeS-doped series is broadly similar. The olivine has a stability range almost identical, but it was also observed in the 0.56 wt.% S charge at NNO+4.10.

Run	P (MPa)	T (°C)	Time (min)	Δ NNO	log fO ₂	log fS ₂ (bar)	H ₂ O&	S% and type loaded	S wt% Glass	S wt% Fluid	Mineral assemblage
lpm 1	200	1040	960	1.34	8.40	0.28	4.1	2%-native	0.22 (0.02)	9.2	Ol-Amph-Px- FeS
lpm 2						-0.24	1.8	1%-native	0.11 (0.01)	5.2	Ol-Amph-Px - Mt-FeS
lpm 33						-	4.0	0.5%-native	0.18 (0.01)	5.4	Ol -Amph - Px - Mt
lpm 4						-0.24	3.1	1.12%-FeS	0.23 (0.01)	5.1	Ol-Amph-Px- Mt-FeS
lpm 5						-	4.1	0.56%-FeS	0.21 (0.03)	6.3	Ol - Amph-Px -Mt
lpm 6						-	5.9	0.28%-FeS	0.10 (0.02)	3.5	Ol-Amph-Px- Mt
lpm 34						-	4.5	0%S	-	-	Ol-Amph-Px- Mt
lpm 7	200	1040	960	2.38	7.37	-	3.8	2%-native	0.73 (0.04)	16.6	Ol-Mt-Ilm
lpm 8						-	4.7	1%-native	0.86 (0.06)	3.6	Ol-Px-Mt
lpm 9						-	3.9	0.5%-native	0.57 (0.03)	2.5	Ol-Amph-Px- Mt
lpm 13	200	1040	360	3.30	6.44	-	5.4	2%-native	0.75 (0.04)	21.1	Ol-Mt-Ilm
lpm 14						-	6.3	1%-native	0.75 (0.04)	13.3	Ol-Px-Mt
lpm 15						-	6.8	0.5%-native	0.65 (0.09)	--	Px-Mt
lpm 16						-	2.0	1.12%-FeS	0.79 (0.03)	6.9	Px-Mt-Ilm
lpm 17						-	6.1	0.56%-FeS	0.65 (0.09)	0.3	Ol-Px-Mt
lpm 18						-	6.5	0.28%-FeS	0.33 (0.03)	1.7	Amph-Px-Mt
lpm 19	200	1040	360	4.10	5.65	-	4.8	2%-native	0.68 (0.05)	-	Ol-Px-Mt- Ilm-Anhy
lpm 20						-	5.6	1%-native	0.64 (0.01)	9.3	Ol-Amph-Px- Mt-Ilm
lpm 21						-	4.5	0.5%-native	0.58 (0.05)	3.1	Amph-Px-Mt
lpm 22						-	5.2	1.12%-FeS	0.71 (0.04)	9.0	Ol-Px-Mt
lpm 23						-	5.8	0.56%-FeS	0.65 (0.03)	3.1	Amph-Px-Mt
lpm 24						-	6.4	0.28%-FeS	0.38 (0.03)	1.4	Amph-Px-Mt- Ap
lpm 25						-	4.6	0%S	-	-	Amph-Px-Mt
lpm 26	200	1040	360	-0.48	1023	-0.63	3.5	2%-native	0.12 (0.01)	3.7	Ol-Amph-Px- FeS
lpm 27						-1.59	2.4	1%-native	0.10 (0.01)	1.2	Ol-Amph-Px- FeS
lpm 28						-	3.1	0.5%-native	0.13 (0.01)	5.5	Ol-Amph-Px- Mt
lpm 29						-1.02	3.6	1.12%-FeS	0.19 (0.03)	6.7	Ol-FeS-Mt
lpm 30						-0.75	3.1	0.56%-FeS	0.19 (0.03)	3.7	Ol-Px-FeS
lpm 32						-	4.7	0%S	-	-	Ol-Amph?- Px-Mt

Table 9 Experimental conditions, water and sulphur contents of quenched glasses. H₂O is calculated with the method of Devine et al., (1995). The fS₂ is calculated using the method of Froese and Gunter, (1976). Amph? = quench phase

In the sulphur-rich experiment at NNO+3.3, this mineral was not found but owing to its low abundance in other charges, it may have been overlooked. In the charge *lpm-17*, olivine is present as inclusions in the clinopyroxene. Except for *lpm-29*, clinopyroxene is ever-present in all charges. FeS has a similar stability field to that identified by the S-doped series, however it is absent at 0.56 wt.% S and NNO+1.34. The amphibole field is also similar in S-doped case, except that it is not found at NNO-0.48 (Fig. 12b).

The Mg# of mg-Fe minerals has not been appreciably affected by the amount of S added at fixed fO_2 . Though at NNO < 1.5, charges with higher bulk S contents tend to crystallise phases with higher Mg# (in particular for charges with 2 wt.% added S). At high fO_2 the reverse is observed. The Mg# of olivine and glass increases slightly with the fO_2 , as shown

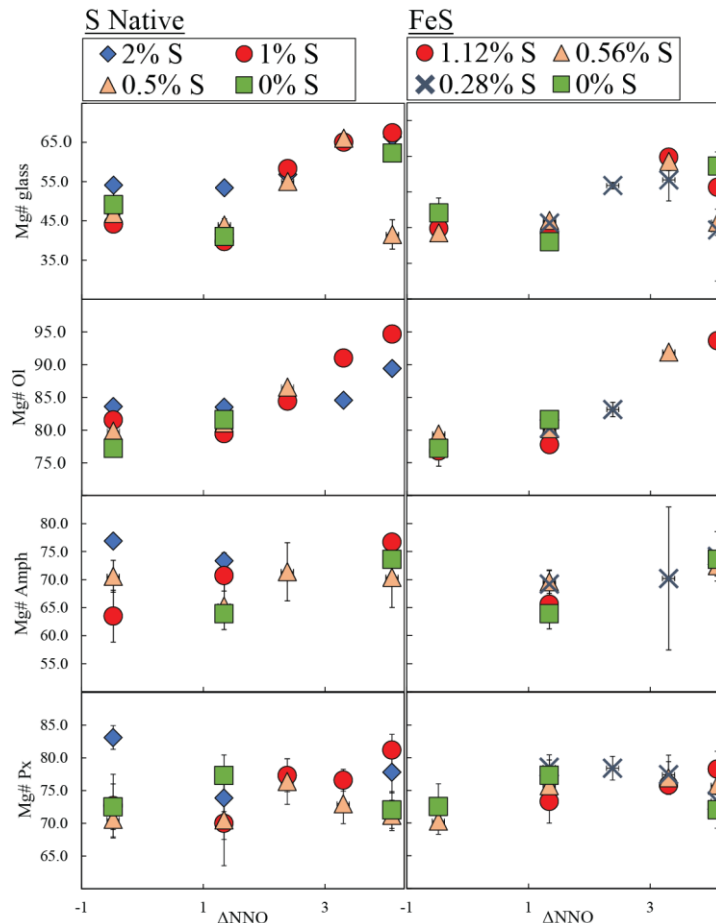


Fig. 13 Relationship between the Mg# of glass, olivine, amphibole, pyroxene and the ΔNNO . When not shown, the error bars are smaller than the symbol size.

in Fig. 13. No clear trends with S appear for either amphibole or pyroxene compositions (Fig. 13). These results emphasize the control of fO_2 on the S-carrying capacity of silicate melts,

as shown in many previous studies (e.g., Carroll and Rutherford, 1985; Luhr, 1990; Scaillet et al., 1998; Jugo et al., 2005). Depending on the fO_2 , the effects of sulphur on phase relations are characterised by subtlety and complexity. For example, amphibole is unstable in sulphur rich charges at NNO between +2.38 and +4.10, while sulphide precipitates only below NNO+1.5. The higher amount of iron in FeS-doped series may explain the minor difference with S-doped experiments. Sulphur does not appear to exert a significant effect on the composition of individual phases. In fact, no significant trends can be observed relating to the quantity of sulphur added, though there is a tendency for FeMg silicate phases to become more Mg-rich with sulphur increasing. In contrast, oxygen fugacity is the main controller for the phase compositions, in particular olivine and glass: their Mg# increases with the oxygen fugacity in both experimental series.

3.2 Mass balance

For most experiments, with no distinction between S-doped and FeS-doped series, the volumetric percentage of glass obtained by mass balance is similar to that calculated using ImageJ (Table 10). The mass balance results indicate that the highest amphibole content is 40 wt.%, while clinopyroxene abundance is generally below 10 wt% and not higher than 19 wt%(Table 10). Similarly, olivine magnetite and ilmenite phases do not exceed 10 wt.%.

Knowing that the P_2O_5 abundance in the melt is mainly controlled by the amount of apatite in the runs, the calculated wt.% of glass correlates well with P_2O_5 abundance (Fig. 14). In Fig. 14, the dashed line indicates a perfectly incompatible behaviour of P_2O_5 . Any deviation, which happens after 20-30 wt.% of crystallization, from this suggests the formation of apatite.

Except in the clear cases of sulphide or anhydrite, sulphur does not affect the phase distribution. In fact, once again, the oxygen fugacity is the main parameter that influences the phase distribution. Obviously, the amounts of oxides, both titanomagnetite and ilmenite, increase from reducing to oxidising conditions (Table 10). Further confirmation that it is the fO_2 of the system that influences the abundance of phases, not the amount of sulfur, is the distribution of the amphibole. This mineral increases more in oxidised runs than in reduced ones.

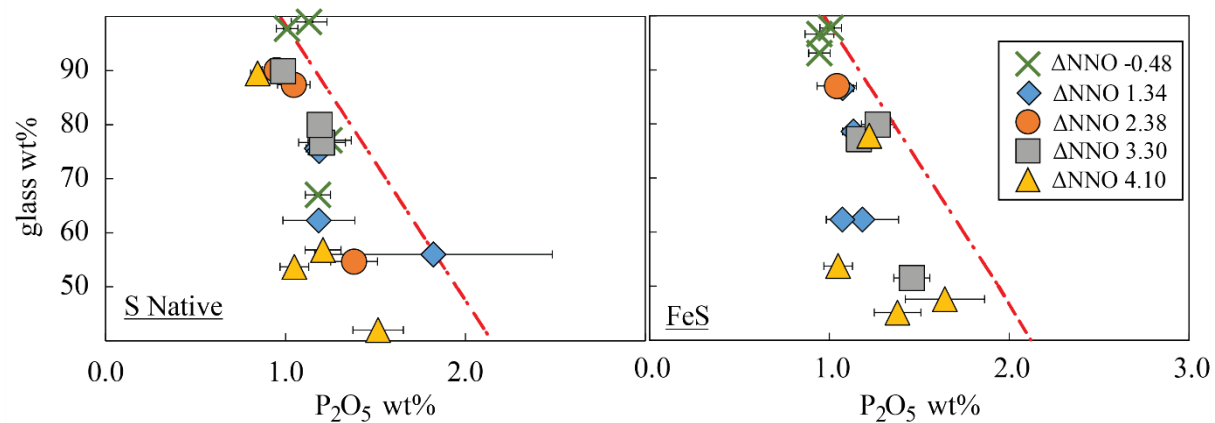


Fig. 14 P₂O₅ w.t.% glass content versus the w.t.% of glass calculated with ImageJ. The dashed line shows the 1:1 correlation.

	Mass balance											ImageJ estimation
	Gl wt%	Ol wt%	Amph wt%	Cpx wt%	Fes wt%	Anhy wt%	Mt wt%	Ilm wt%	Ap wt%	Gl vol%	Sr	Gl %
lpm 1	75.6 (0.02)	<1 (0.01)	18.5 (0.03)	4.6 (0.01)	2.8 (0.002)	-	-	-	-	79.4	0.22	86.5
lpm 2	56.0 (0.01)	<1 (0.03)	33.4 (0.03)	8.2 (0.01)	1.1 (0.01)	-	1.7 (0.01)	-	-	61.0	0.18	55.1
lpm 33	75.1 (0.03)	3.6 (0.01)	15.9 (0.04)	3.0 (0.01)	-	-	2.4 (0.003)	-	-	79.1	0.41	72.2
lpm 4	78.6 (0.03)	3.6 (0.01)	10.0 (0.04)	4.4 (0.02)	1.3 (0.005)	-	1.9 (0.01)	-	-	82.6	0.02	84.3
lpm 5	86.6 (0.03)	2.5 (0.01)	7.8 (0.03)	0.2 (0.03)	-	-	2.9 (0.003)	-	-	89.5	0.53	72.2
lpm 6	77.7 (0.02)	4.8 (0.01)	15.8 (0.03)	<1 (0.01)	-	-	2.5 (0.003)	-	-	81.4	1.22	77.4
lpm 34	62.3 (0.02)	2.5 (0.004)	17.0 (0.03)	14.0 (0.01)	-	-	4.3 (0.003)	-	-	68.0	0.16	57.0
lpm 7	90.1 (0.01)	3.3 (0.002)	-	-	-	-	5.5 (0.003)	1.1 (0.002)	-	93.7	7.22	95.2
lpm 8	87.4 (0.01)	1.5 (0.003)	-	5.1 (0.009)	-	-	6.0 (0.002)	-	-	92.4	1.20	99.3
lpm 9	54.7 (0.03)	<1 (0.01)	26.1 (0.05)	11.8 (0.02)	-	-	8.5 (0.003)	-	-	77.9	0.08	68.2
lpm 13	89.9 (0.01)	1.8 (0.003)	-	-	-	-	12.2 (0.004)	<1 (0.003)	-	95.3	9.99	91.8
lpm 14	76.7 (0.01)	2.1 (0.003)	-	12.7 (0.01)	-	-	8.5 (0.002)	-	-	84.6	6.15	78.7
lpm 15	80.0 (0.01)	-	-	11.6 (0.01)	-	-	8.3 (0.002)	-	-	85.8	1.59	70.6
lpm 16	77.2 (0.01)	-	-	9.8 (0.01)	-	-	13.4 (0.003)	<1 (0.003)	-	84.5	0.80	84.5
lpm 17	79.9 (0.01)	2.1 (0.003)	-	4.3 (0.01)	-	-	7.0 (0.003)	-	-	86.8	1.54	84.6
lpm 18	51.5 (0.01)	-	37.1 (0.03)	1.6 (0.02)	-	-	9.8 (0.003)	-	-	60.8	3.10	72.3
lpm 19	89.5 (0.01)	7.4 (0.01)	-	<1 (0.02)	-	5.7 (0.004)	11.4 (0.003)	0.4 (0.003)	-	94.0	0.40	93.4
lpm 20	56.8 (0.02)	<1 (0.01)	33.3 (0.04)	3.6 (0.01)	-	-	12.1 (0.004)	<1 (0.003)	-	63.4	1.07	68.5
lpm 21	43.0 (0.01)	-	39.7 (0.02)	9.0 (0.01)	-	-	8.4 (0.002)	-	-	48.57	0.96	59.8
lpm 22	77.8 (0.01)	6.1 (0.003)	-	2.5 (0.01)	-	-	13.6 (0.002)	-	-	86.6	4.48	84.7
lpm 23	47.6 (0.01)	-	27.9 (0.01)	13.8 (0.01)	-	-	10.7 (0.002)	-	-	57.5	2.51	62.8
lpm 24	45.1 (0.01)	-	31.1 (0.03)	12.0 (0.04)	-	-	10.3 (0.002)	-	1.6 (0.004)	51.7	0.97	55.6
lpm 25	57.3 (0.01)	-	14.4 (0.01)	18.8 (0.01)	-	-	9.5 (0.002)	-	-	67.2	1.27	66.4
lpm 26	77.1 (0.0)	0.8 (0.01)	8.4 (0.04)	9.6 (0.01)	4.1 (0.002)	-	-	-	-	81.5	0.26	72.3
lpm 27	67.0 (0.02)	3.2 (0.004)	18.8* (0.04)	<1 (0.02)	2.1 (0.002)	-	-	-	-	71.7	1.22	82.5
lpm 28	99.0 (0.13)	<1 (0.01)	<1 (0.14)	-	-	-	<1 (0.003)	-	-	99.0	1.19	94.8
lpm 29	93.1 (0.01)	4.8 (0.003)	-	<1 (0.01)	1 (0.003)	-	-	-	-	95.0	0.20	89.5
lpm 30	96.6 (0.03)	6.6 (0.003)	-	<1 (0.01)	0.2 (0.003)	-	0.5 (0.01)	-	-	97.5	0.53	86.5
lpm 32	80.0 (0.12)	9.3 (0.005)	17.5* (0.13)	<1 (0.01)	-	-	1.7 (0.01)	-	-	83.1	2.96	97.8

Table 10 Phase proportions calculated by mass balance and image analyses (glass, using ImageJ software).

3.3 Major element glass and sulphur solubility

The major elements trends of glasses of both the S and FeS doped series (Table 11) show similar patterns (Fig. 15). SiO_2 content rises with increasing $f\text{O}_2$, from approximately 44 wt.% to 56 wt.%. Similarly, Al_2O_3 content increases to up to 20 wt.%, indicating the lack of

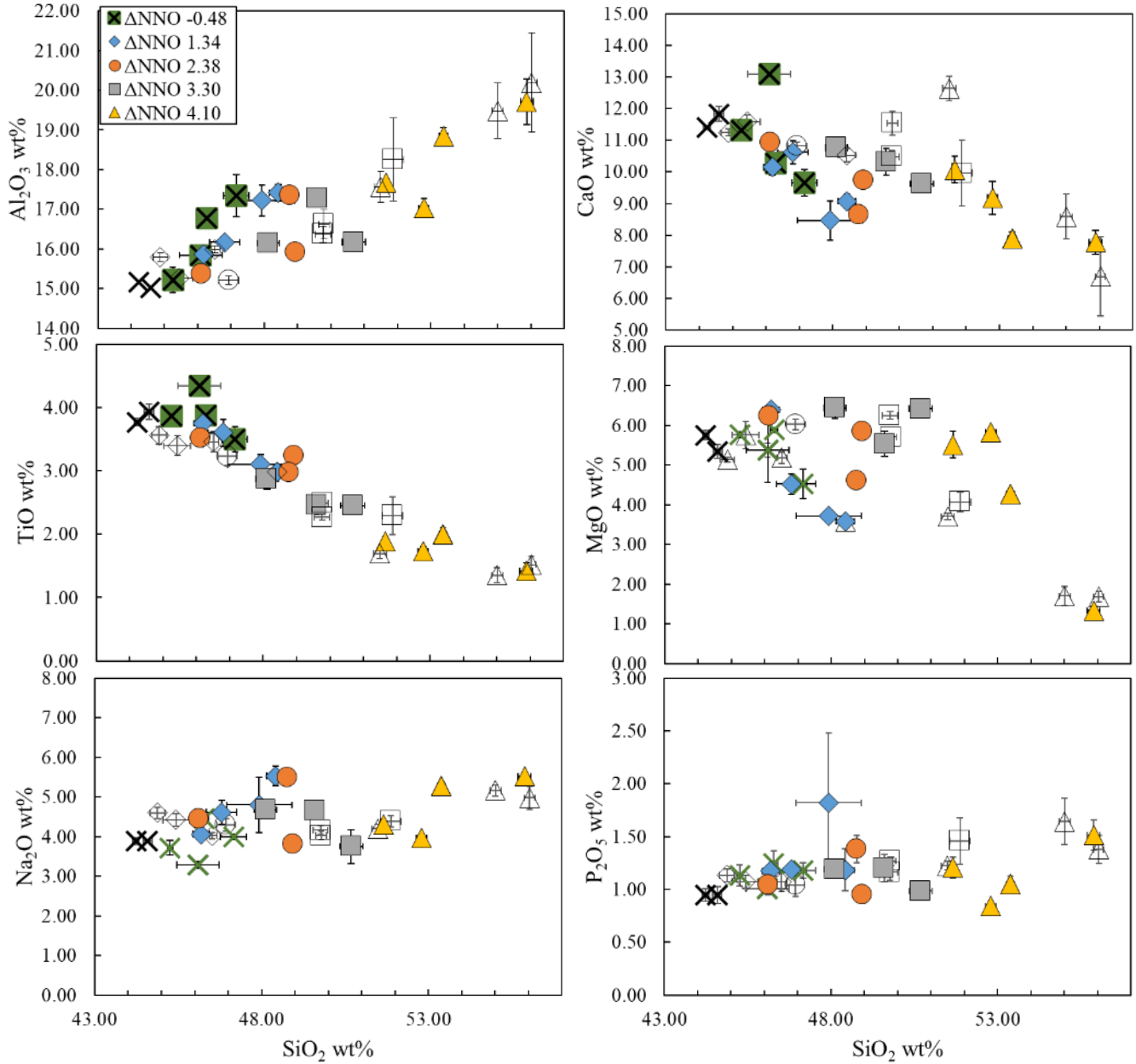


Fig. 15 Variation of oxides with SiO_2 of experimental glasses in S doped (coloured symbols) and FeS doped (open symbols) charges. When not shown, the error bars are smaller than the symbol size.

plagioclase crystallization under the investigated conditions and a corresponding increase in

overall crystallization. CaO shows an opposite trend: it decreases with the increasing SiO_2 and $f\text{O}_2$. This behavior reflects the clinopyroxene crystallization.

The alkalis show no clear trends, exception for Na_2O which increased slightly with SiO_2 . FeO and TiO_2 have the same behaviour of CaO, which perhaps best illustrate the changes in melt composition. In particular from NNO-0.48 to NNO+4.10 both of these two elements decrease in the glass by 75%, reflecting substantial crystallisation of magnetite and ilmenite. The fractionation trends reported reflect the effect of the main crystallising phases, but above all the increasing abundance of magnetite crystallisation as $f\text{O}_2$ increases and in the main time the lack of plagioclase crystallization.

The major elements results were compared with hydrous and sulphur solubility experiments performed at comparable P-T- H_2O conditions on basaltic-andesitic magmas erupted in contrasting geodynamic contexts (Fig.16 and Fig.17): the Hekla volcano in 2000, which is taken to here represent mid-ocean ridge volcanism, though interaction with plume material is possible (Moune et al., 2009) and the trachyandesite magma erupted at El Chichón

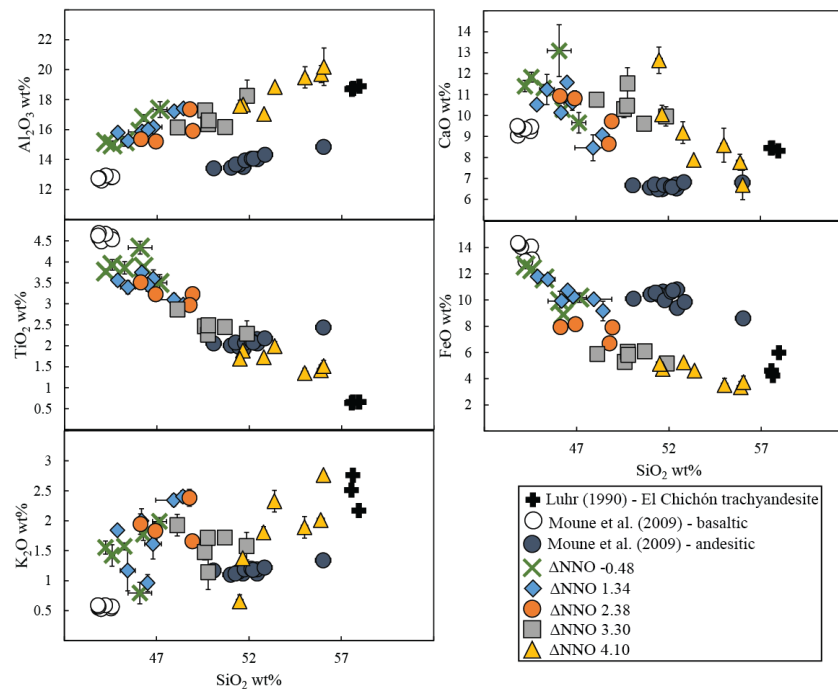


Fig. 16 Concentration of major element versus SiO_2 wt.%. The experiments are compared to the water-saturated, 1050°C and 200-300 MPa experiments of Moune et al. (2009) and the composition A (trachyandesite) performed at 1000°C , 200 MPa from Luhr (1990).

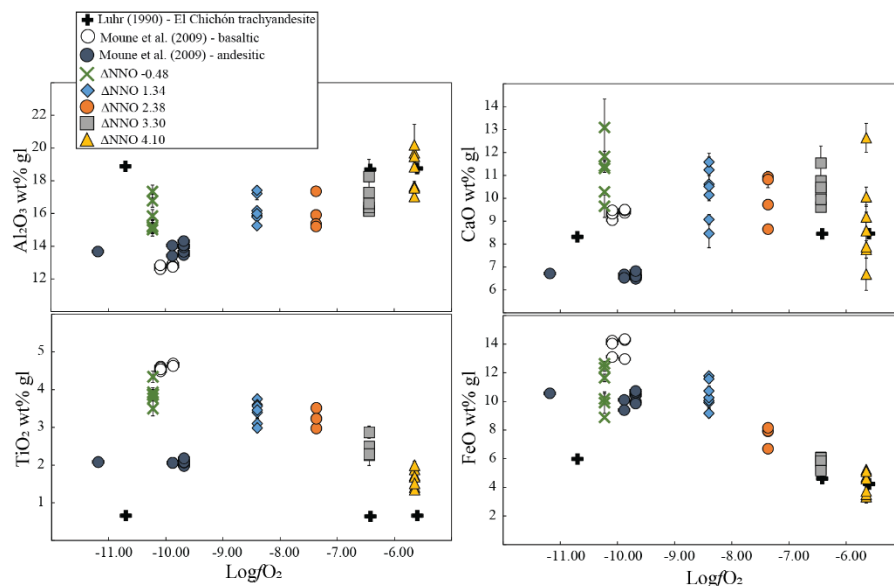


Fig. 17 Concentration of major element versus LogfO₂. The experiments are compared to the water-saturated, 1050°C and 200–300 MPa experiments of Moune et al. (2009) and the composition A (trachyandesite, at 1000°C, 200 MPa) from Luhr (1990).

volcano in 1982, which belongs to an arc setting (Luhr, 1990) though some rift related processes are likely (Arce et al., 2014). Since it is known that water content, redox conditions, temperature and pressure are the main controller on the phase crystallization and melt composition only same experiments reported in Moune et al. (2009) and Luhr (1990) are compared with this thesis data: the water-saturated, 1050°C and 200–300 MPa experiments of Moune et al., (2009), and the composition A (trachyandesite) performed at 1000°C, 200 MPa from Luhr (1990), (Fig. 16). While the trends were generally similar to ours, differences in some oxide contents (e.g. CaO, Al₂O₃) are evident for any given SiO₂. These can be attributed to bulk compositional effects (Fig. 16) and to slightly different experimental conditions which impart different degrees of crystallization. The broad correspondences remain when oxygen fugacity is considered (Fig. 17). The TiO₂ content of the andesitic charges of Moune et al (2009) and Luhr (1990) are lower than ours, reflecting the lower Ti content of the corresponding starting materials. This is particularly evident in the Luhr (1990) experiments, in which the concentration of TiO₂ in the starting composition is so low that no difference exists between reduced and oxidised conditions. Irrespective of geodynamic context, the factor that most influences melt composition is oxygen fugacity.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Total *
lpm- 1	46.19 (0.25)	3.75 (0.10)	15.68 (0.14)	9.93 (0.36)	0.20 (0.08)	6.39 (0.10)	10.14 (0.25)	4.07 (0.05)	2.00 (0.20)	1.17 (0.06)	0.22 (0.02)	93.75
lpm- 2	47.93 (0.98)	3.10 (0.15)	17.22 (0.39)	10.06 (0.19)	0.31 (0.07)	3.72 (0.15)	8.46 (0.62)	4.81 (0.62)	2.34 (0.700)	1.82 (0.66)	0.11 (0.01)	96.23
lpm- 33	46.81 (0.45)	3.60 (0.21)	16.17 (0.07)	10.27 (0.34)	0.20 (0.07)	4.52 (0.25)	10.62 (0.37)	4.61 (0.25)	1.61 (0.25)	1.19 (0.06)	0.18 (0.01)	92.59
lpm- 4	44.88 (0.22)	3.56 (0.14)	15.79 (0.11)	11.79 (0.12)	0.25 (0.05)	5.14 (0.10)	10.52 (0.15)	4.60 (0.15)	1.84 (0.06)	1.13 (0.06)	0.23 (0.01)	94.81
lpm- 5	45.43 (0.40)	3.40 (0.16)	15.25 (0.21)	11.58 (0.28)	0.20 (0.09)	5.76 (0.57)	11.24 (0.72)	4.42 (0.16)	1.17 (0.34)	1.07 (0.06)	0.21 (0.03)	93.74
lpm- 6	46.52 (0.15)	3.46 (0.16)	16.00 (0.09)	10.73 (0.34)	0.22 (0.08)	5.19 (0.27)	11.58 (0.16)	4.03 (0.08)	0.96 (0.14)	1.07 (0.09)	0.10 (0.02)	91.88
lpm- 34	48.42 (0.27)	2.98 (0.11)	17.42 (0.21)	9.17 (0.30)	0.19 (0.05)	3.58 (0.09)	9.08 (0.22)	5.54 (0.25)	2.40 (0.10)	1.18 (0.02)	0.00 (0.01)	92.60
lpm- 7	48.93 (0.23)	3.24 (0.06)	15.92 (0.12)	7.92 (0.09)	0.15 (0.03)	5.85 (0.06)	9.73 (0.13)	3.81 (0.06)	1.66 (0.09)	0.95 (0.08)	0.73 (0.04)	93.55
lpm- 8	46.13 (0.28)	3.52 (0.14)	15.36 (0.10)	7.95 (0.26)	0.21 (0.02)	6.24 (0.17)	10.93 (0.23)	4.44 (0.09)	1.94 (0.17)	1.05 (0.09)	0.86 (0.06)	93.00
lpm- 9	48.78 (0.15)	2.97 (0.10)	17.36 (0.21)	6.71 (0.21)	0.20 (0.07)	4.61 (0.18)	8.66 (0.22)	5.50 (0.07)	2.38 (0.14)	1.38 (0.13)	0.57 (0.03)	94.81
lpm- 13	50.68 (0.35)	2.45 (0.11)	16.17 (0.22)	6.10 (0.30)	0.20 (0.08)	6.42 (0.09)	9.62 (0.14)	3.75 (0.42)	1.72 (0.06)	0.99 (0.05)	0.75 (0.04)	92.63
lpm- 14	49.60 (0.21)	2.47 (0.16)	17.28 (0.22)	5.29 (0.19)	0.24 (0.09)	5.53 (0.32)	10.32 (0.42)	4.65 (0.12)	1.48 (0.13)	1.20 (0.12)	0.75 (0.04)	91.99
lpm- 15	48.12 (0.33)	2.87 (0.16)	16.15 (0.10)	5.89 (0.20)	0.19 (0.07)	6.44 (0.26)	10.76 (0.14)	4.68 (0.07)	1.93 (0.18)	1.19 (0.06)	0.69 (0.05)	92.01
lpm- 16	49.77 (0.23)	2.27 (0.04)	16.37 (0.21)	6.07 (0.23)	0.12 (0.04)	6.25 (0.05)	10.48 (0.08)	4.17 (0.06)	1.72 (0.11)	1.16 (0.00)	0.79 (0.03)	91.16
lpm- 17	49.79 (0.169)	2.49 (0.12)	16.62 (0.37)	5.83 (0.23)	0.20 (0.11)	5.17 (0.58)	11.54 (0.75)	4.03 (0.33)	1.14 (0.29)	1.27 (0.09)	0.65 (0.09)	89.92
lpm- 18	51.87 (0.31)	2.29 (0.30)	18.26 (1.05)	5.17 (0.52)	0.26 (0.07)	4.07 (0.90)	9.96 (0.46)	4.39 (0.45)	1.58 (0.23)	1.46 (0.10)	0.33 (0.03)	89.41
lpm- 19	52.79 (0.15)	1.73 (0.08)	17.04 (0.23)	5.24 (0.09)	0.17 (0.07)	5.83 (0.06)	9.19 (0.52)	3.97 (0.03)	1.80 (0.24)	0.85 (0.04)	0.68 (0.05)	91.44
lpm- 20	51.66 (0.09)	1.89 (0.07)	17.67 (0.10)	4.74 (0.07)	0.22 (0.04)	5.52 (0.34)	10.07 (0.42)	4.32 (0.05)	1.37 (0.12)	1.21 (0.10)	0.64 (0.01)	90.53
lpm- 21	55.88 (0.19)	1.42 (0.13)	19.71 (0.58)	3.35 (0.44)	0.23 (0.05)	1.33 (0.11)	7.77 (0.38)	5.52 (0.10)	2.01 (0.17)	1.51 (0.14)	0.58 (0.05)	91.59
lpm- 22	51.50 (0.19)	1.69 (0.08)	17.57 (0.39)	5.13 (0.19)	0.25 (0.07)	3.71 (0.53)	12.64 (0.63)	4.20 (0.11)	0.65 (0.08)	1.22 (0.04)	0.71 (0.04)	90.99
lpm- 23	55.01 (0.17)	1.35 (0.11)	19.49 (0.71)	3.51 (0.52)	0.26 (0.10)	1.71 (0.95)	8.59 (0.81)	5.17 (0.14)	1.89 (0.24)	1.64 (0.22)	0.65 (0.03)	90.14
lpm- 24	56.03 (0.45)	1.52 (0.13)	20.19 (1.25)	3.74 (0.47)	0.20 (0.09)	1.68 (0.64)	6.69 (0.70)	4.98 (0.29)	2.76 (0.13)	1.38 (0.13)	0.38 (0.03)	89.50
lpm- 25	53.38 (0.12)	2.00 (0.11)	18.85 (0.21)	4.62 (0.22)	0.27 (0.11)	4.28 (0.05)	7.89 (0.07)	5.28 (0.11)	2.33 (0.10)	1.05 (0.08)	0.01 (0.01)	91.49
lpm- 26	46.28 (0.12)	3.88 (0.06)	16.78 (0.22)	8.89 (0.11)	0.22 (0.09)	5.88 (0.06)	10.28 (0.06)	4.45 (0.05)	1.77 (0.10)	1.24 (0.12)	0.12 (0.01)	92.87
lpm- 27	47.16 (0.38)	3.50 (0.20)	17.35 (0.52)	10.19 (0.36)	0.24 (0.14)	4.53 (0.37)	9.66 (0.49)	4.00 (0.77)	1.99 (0.06)	1.18 (0.07)	0.10 (0.01)	94.19
lpm- 28	45.26 (0.07)	3.86 (0.15)	15.22 (0.32)	11.65 (0.26)	0.21 (0.05)	5.77 (0.07)	11.31 (0.17)	3.72 (0.19)	1.57 (0.06)	1.13 (0.10)	0.13 (0.01)	93.35
lpm- 29	44.24 (0.10)	3.77 (0.06)	15.16 (0.06)	12.64 (0.18)	0.21 (0.04)	5.75 (0.23)	11.40 (0.27)	3.89 (0.09)	1.55 (0.25)	0.94 (0.06)	0.19 (0.03)	92.82
lpm- 30	44.59 (0.14)	3.93 (0.12)	15.02 (0.23)	12.36 (0.26)	0.20 (0.05)	5.34 (0.14)	11.83 (0.23)	3.89 (0.09)	1.42 (0.11)	0.95 (0.08)	0.19 (0.03)	93.35
lpm- 32	46.09 (0.64)	4.34 (0.15)	15.85 (0.14)	9.92 (0.75)	0.14 (0.05)	5.38 (0.81)	13.09 (1.24)	3.29 (0.17)	0.79 (0.18)	1.01 (0.06)	0.01 (0.01)	92.35

Table 11 Major elements compositions, normalized to 100% anhydrous, and S contents of quenched glasses; *Original total.

As seen for the major elements trends, the concentration of sulphur in the glasses does not differ between the S- or FeS-doped experiments (Fig. 18). The charges produced at low fO_2 are significantly poorer in sulphur than those at high fO_2 , the former having S concentration in the range 1000–2300 ppm, while the later have S contents ranging between 3300–8800 ppm. Changes in melt compositions seems to do not affect the overall positive effect of the fO_2 on sulphur content.

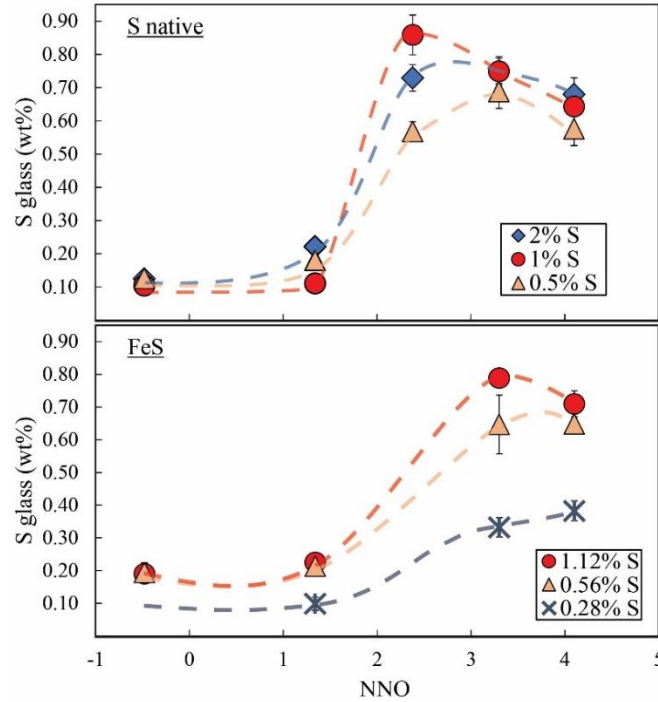


Fig. 18 Variation of S content of the glass with fO_2 as a function of wt.% of sulphur added to the capsules. When not shown, the error bars are smaller than the symbol size.

The measured S contents in glasses saturated with pyrrhotite can be compared to those calculated using the S-solubility model of Lesne et al. (2015), which was developed for hydrous alkali-rich basalts, using the fS_2 determined by pyrrhotite (Table 9). Additionally, S contents were calculated using the model of Boulliang and Wood (2023). The results, shown in Fig. 19, demonstrate a generally good correspondence between the calculated S contents from both models and the measured values, although the Boulliang and Wood (2023) model tends to underestimate S contents.

Discrepancies likely arise from analytical uncertainties in the pyrrhotite composition as determined by EPMA, which translates into an uncertainty in the calculated fS_2 of approximately ± 1 log unit (e.g., Whitney, 1984). For example, increasing the log fS_2 of

charge lpm 29 from -1.02 to -0.5 (Table 9) would raise the calculated S content from 0.14 wt% to 0.19 wt%, matching the measured amount (Fig. 19).

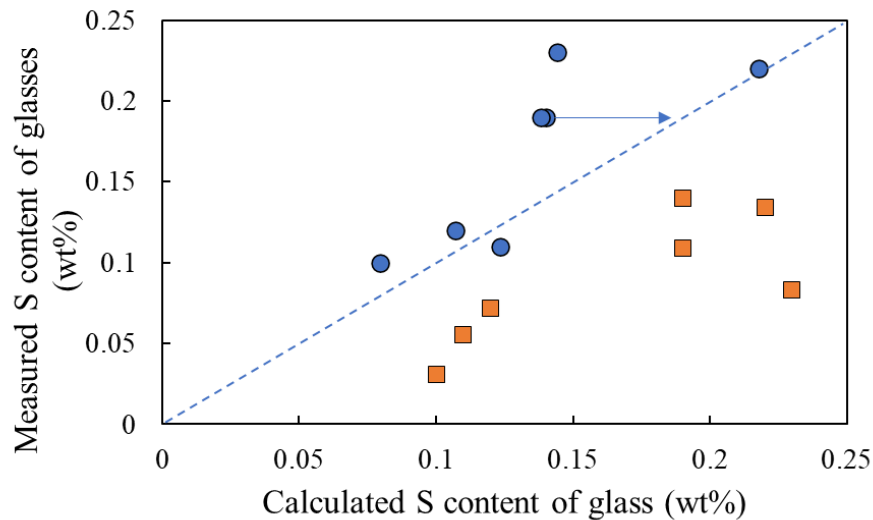


Fig. 19 Comparison between the measured S content of experimental glasses saturated in pyrrhotite with that calculated using the model of Lesne et al. (2015) and Boulliong and Wood (2023). The arrow shows the effect of increasing fS_2 by 0.5 log unit on the calculated S content of melt. Lesne et al., (2015) is in blue rounded symbols, while Boulliong and Wood, (2023) is in square orange symbols.

As in many previous studies, the amount of S in the glass is principally controlled by fO_2 (Fig. 20 and Fig. 21). At low fO_2 , the sulphur concentrations in the glasses measured by Moune et al., (2009) and Luhr (1990) are comparable to those found in our experiments, most falling in the interval 1000–2500 ppm. Furthermore, as noted by Moune et al. (2009), at fO_2 between FMQ-0.3 and FMQ+0.3, sulphur abundance in the glass increases with the added sulphur, until bulk S exceeds 0.5 wt.% (Fig. 20) and levels off at 2000 ± 100 ppm. A similar pattern is observed with a positive trend up to about 1 wt.% sulphur added, at which point the dissolved S levels off at 0.7 wt%, for $NNO > +2.38$.

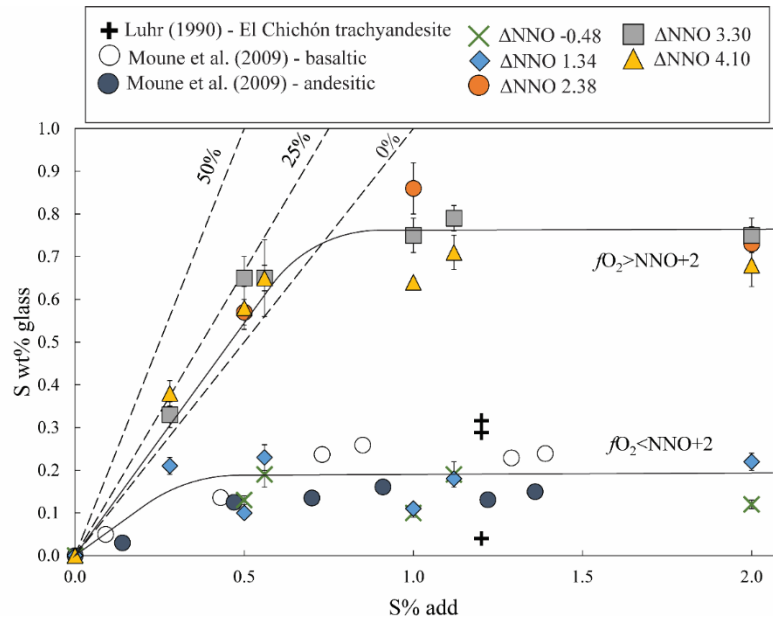


Fig. 20 Sulphur concentration in the melt versus the amount of sulphur added in the runs. The experiments are compared to the water-saturated, 1050°C and 200-300 MPa experiments of Moune et al. (2009) and the composition A (trachyandesite) performed at 1000°C,

The experiments of Luhr (1990) under oxidised conditions resulted in lower S concentrations in the glass than we obtained for the same amount of sulphur added. Anhydrite crystallization in the Luhr (1990) runs, which did not occur in our experiments under the same conditions, likely explains this. The levelling off of both trends at high bulk S contents likely results from the buffering effect of other S-bearing phases. Under reducing conditions, this would be sulphide, while under oxidising conditions, in the absence of anhydrite, the buffering phase is likely to be the coexisting fluid. Oxidised charges with less than 0.5 wt.% added S fall on, or close to, the 1-to-1 correlation line, which shows that under these conditions a significant proportion of S resides in the melt phase (those data that fall above the 1/1 line reflect the amount of crystallisation of charges). (Fig.20)

3.4 Natural applications : La Palma eruption

The pre-eruptive oxygen fugacity (fO_2) of the 2021 Cumbre Vieja basanite has been estimated using vanadium (V) systematics in olivine, falling between NNO+0.6 and NNO+1.3 (Day et al., 2022). However, Erdmann et al.(2024) suggested that current methods for determining fO_2 using V may overestimate the values by up to 0.7 log units in hydrous basalts. This adjustment would place the redox state of the La Palma magma in the range of NNO to NNO+1.

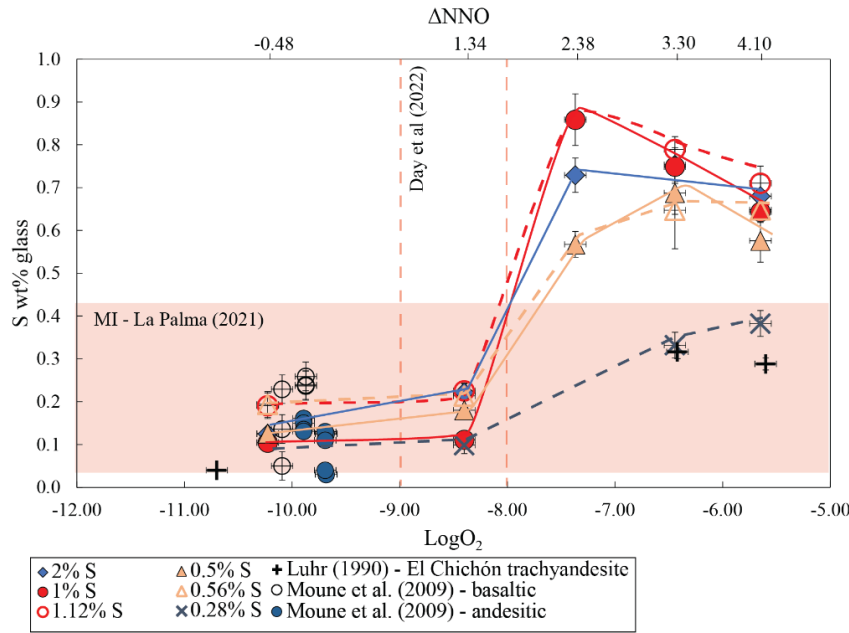


Fig. 21 Sulphur concentration in the melt versus $\log fO_2$. The experiments are compared to the water-saturated, 1050°C and 200-300 MPa experiments of Moune et al., 2009 and the composition A (Trachyandesite) performed at 1000°C, 200 MPa from Luhr, 1990; MI-La Palma (2021) = S wt% in the basanite melt inclusions.

Considering this revised range (NNO to NNO+1.3), the experimental data indicate that the bulk sulphur (S) content of the magma was approximately 2500–5000 ppm, with a significant portion dissolved in the melt (Fig. 21). This is generally consistent with analyses of melt inclusions (e.g, Burton et al., 2023; Castro and Feisel, 2022; Dayton et al., 2024). Notably, the highest measured S content in melt inclusions (4800 ppm, Burton et al., 2023) suggests an fO_2 at the upper end of the range inferred from V in olivine, or possibly higher temperatures

The occasional presence of sulfide inclusions in phenocrysts within the erupted products (Andujar et al., 2025) aligns with our experimental findings at NNO+1.34. However, the

absence of sulfide in the matrix glass indicates that the erupting magma was not sulfide-saturated.

Experimental results reported in this work indicate that to match the observed sulphur content of approximately 3000 ppm in melt inclusions of the 2021 La Palma basanite, given the inferred pre-eruptive oxygen fugacity (f_{O_2}) range of NNO+0.6 to NNO+1.6 (Day et al., 2022), the sulphur fugacity (f_{S_2}) should be around 0.1–1 MPa. This is supported by the composition of pyrrhotite in our experimental products, as detailed in Table 9.

The following calculations have been conducted in order to model the fluid phase composition, taking into account the given constraints, for three different scenarios:

- I. The calculation of the fluid composition at equilibrium with the basanite magma, which is hypothesised to be situated at approximately 300 MPa within the crustal reservoir, was conducted as a preliminary step. (D’Auria et al., 2022; Pérez, 2022; Del Fresno et al., 2023; Ubide et al., 2023; Dayton et al., 2024; Andujar et al., 2025)
- II. The subsequent stage of the research will involve the calculation of magma degassing during ascent, starting at 300 MPa with a variable amount of exsolved fluid.
- III. Finally, the degassing process was simulated from higher pressures (i.e. deeper levels) and higher temperatures (approximately 1125°C), in accordance with the elevated CO₂ dissolved contents (up to 1.2 wt%) retrieved from olivine inclusions (e.g., Dayton et al., 2024; Zanon et al., 2023) and seismic data (e.g., D’Auria et al., 2022; Del Fresno et al., 2023) which point to a mantle source at 400-800 MPa.

For step I., the following constraints were employed: an initial dissolved CO_2 content ranging from 3,000 to 5,000 ppm, and a dissolved $\text{H}_2\text{O}_{\text{melt}}$ of 1–3 wt%, as determined by melt inclusion analyses (e.g., Burton et al., 2023; Dayton et al., 2023). The calculations are conducted at 1080°C , which broadly aligns with the estimated temperature for basaltic magma in equilibrium with amphibole (González-García et al., 2023; Sandoval-Velasquez et al., 2023; Andujar et al., 2025). The calculations are done using an MRK equation of state for fluid, along with the S solubility model of Lesne et al. (2015), which is calibrated for alkali-rich basalt melts, and the CO_2 - H_2O solubility model of Jiménez-Mejías et al., (2021). The calculation produces the saturation pressure for the following fluid species: H_2O , CO_2 , SO_2 and H_2S . The fundamental supposition is that there is an equilibrium between the fugacities of volatiles in the fluid and those in the melt (e.g. Lesne et al., 2015). In light of the inevitable uncertainty surrounding the redox state of the magma, as well as its possible

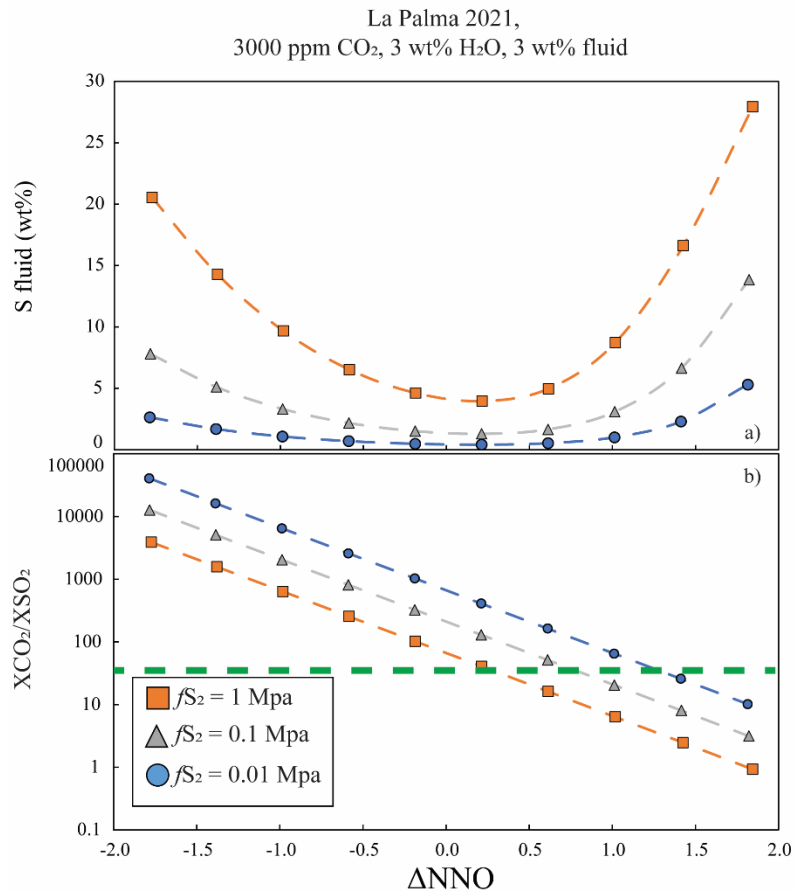


Fig. 22 (a) Evolution of the S content of the excess fluid in the reservoir at 300 MPa with f_{O_2} . (b) Evolution of the ratio $X_{\text{CO}_2}/X_{\text{SO}_2}$ of the fluid with ΔNNO . The calculations have been made at three different f_{S_2} ; the thick horizontal green dashed line indicates the measured value of the corresponding parameter.

variations during decompression (e.g., Burgisser and Scaillet, 2007; Moussallam et al., 2016), calculations were conducted for a range of fO_2 spanning from NNO-2 to NNO+2. Fig. 22a illustrates the variation of S content of the fluid in the reservoir at 300 MPa with fO_2 , calculated for three different fS_2 .

This calculation provides the composition of fluids at the surface leaving the crustal reservoir without being coupled with melts, and traverse the crustal section in an unmodified state.

While the applicability of this scenario to the La Palma 2021 eruption is perhaps not direct, it provides a conceptual framework for the interpretation of gas monitoring during repose periods.

Within the range of fO_2 as inferred by Day et al. (2022), the S content of the fluid varies between 1 and 10 wt%, dependent on fS_2 , and is comparable to S contents calculated for more silicic compositions (e.g., Scaillet et al., 2003) and to that calculated by mass balance for the majority of our experiments (Table 9). Fig. 22b shows the inverse correlation between XCO_2/XSO_2 and fO_2 : as fO_2 increases this ratio decreases. In the fO_2 interval NNO+0.7 to NNO+1.3, XCO_2/XSO_2 ranges from ~2 to ~100, which is consistent with the range of measurements of volcanic gas emissions during the 2021 La Palma eruption (Burton et al., 2023). The measured ratios range from 35 for explosive activity to less than 10 for effusive emissions (Burton et al., 2023). The higher end of this range is favored as a characteristic of gas-rich magma, presumably of deeper origin.

The second step II. considers the degassing process during magma ascent. In particular it was taken into account sulphur and water species, since they can exsolve near the surface (Oppenheimer et al., 2014). The complete calculation should also consider the potential impact of excess fluid in the crustal reservoir. For example, the bulk CO_2 content of La Palma magma is estimated at 4 ± 1.5 wt% based on measured S emissions and the average XCO_2/XSO_2 ratio (Burton et al., 2023). Using a conservative fluid content of 3 wt% (with 3 wt% H_2O and 3000 ppm CO_2 dissolved in the melt, corresponding to the volatile content of a fluid-saturated basanite at 300 MPa), the total amount of S released was calculated by the 0.2 km^3 of erupted magma and the XCO_2/XSO_2 ratio of the gas at the vent (melt + fluid) as a function of oxygen fugacity. This calculation accounts for the 400–600 ppm of S remaining in the matrix glass (Fig. 23). With these constraints and assuming an fO_2 of approximately

NNO+1, the pre-eruptive magma must have had an fS_2 in the range of 0.1-1 MPa (Fig. 23a). An fS_2 significantly lower than 0.1 MPa would not reproduce this figure. Regarding the final

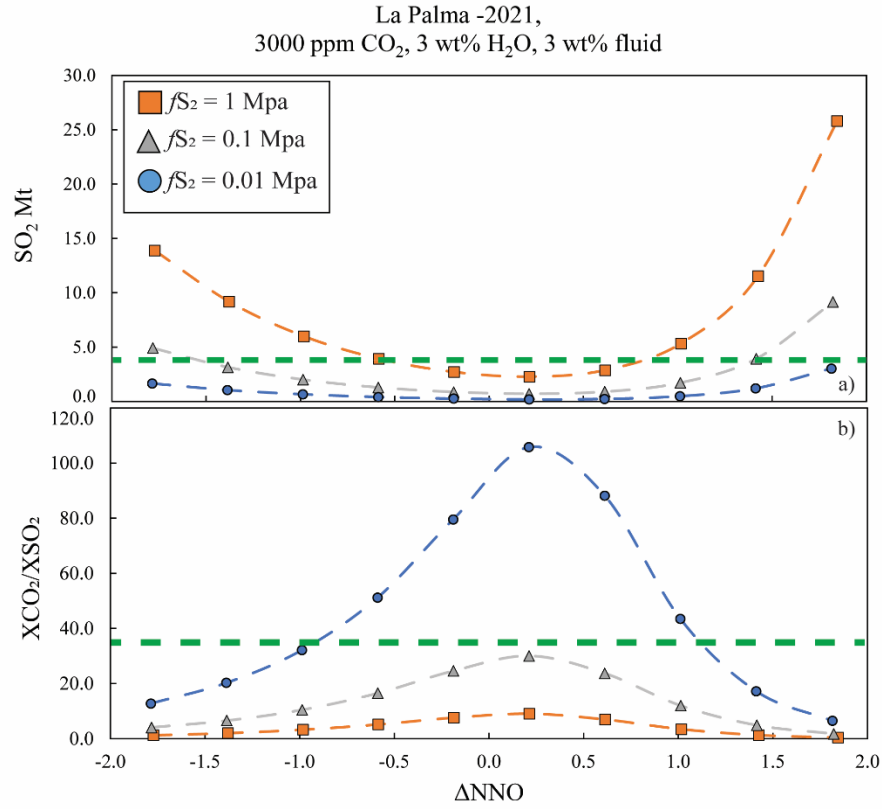


Fig. 23 a) Evolution of total amount of SO₂ degassed by 0.2 km³ of basanite magma with fO_2 expressed as ΔNNO . (b) Evolution of the XCO₂/XSO₂ ratio of the gas emitted at the vent with ΔNNO . The calculations have been performed at 1080°C. In all panels the thick horizontal green dashed line indicates the measured value of the corresponding parameter.

XCO₂/XSO₂ ratio measured at the vent, the same calculations show a bell-shaped pattern with a maximum between NNO and NNO+0.5 (Fig. 23b). For fS_2 values in the range of 0.1-1 MPa, the maximum possible XCO₂/XSO₂ ratio is about 30, slightly above NNO, indicating a more reduced fO_2 than that derived from V systematics.

The variation of XH₂O/XSO₂ ratio, measured during the 2021 La Palma eruption (Burton et al., 2023), with fO_2 , in relation to the amount of excess fluid in the reservoir, is illustrated in Fig. 24b. The XH₂O/XSO₂ is similar to the XCO₂/XSO₂ ratio. The calculations are performed for magma at 300 MPa with 4000 ppm CO₂, 2 wt% H₂O, and an fS_2 of 0.2 MPa at 1080°C. These conditions align with available melt inclusion and phase equilibrium constraints for the upper portion of the plumbing system (González-García et al., 2023; Sandoval-Velasquez et al., 2023; Andujar et al., 2025). Both ratios exhibit a similar bell-shaped trend with fO_2 ,

and they are sensitive to the amount of free fluid. As the free fluid increases, the $\text{XH}_2\text{O}/\text{XSO}_2$ ratio decreases, while the $\text{XCO}_2/\text{XSO}_2$ ratio increases due to the differing H_2O and CO_2 contents in the melt and fluid phases. During the most explosive phase of the La Palma eruption, gas emissions had an $\text{XCO}_2/\text{XSO}_2$ ratio of approximately 35 and an $\text{XH}_2\text{O}/\text{XSO}_2$ ratio of around 22 (Burton et al., 2023). For the conditions shown in Fig. 24, these ratios are

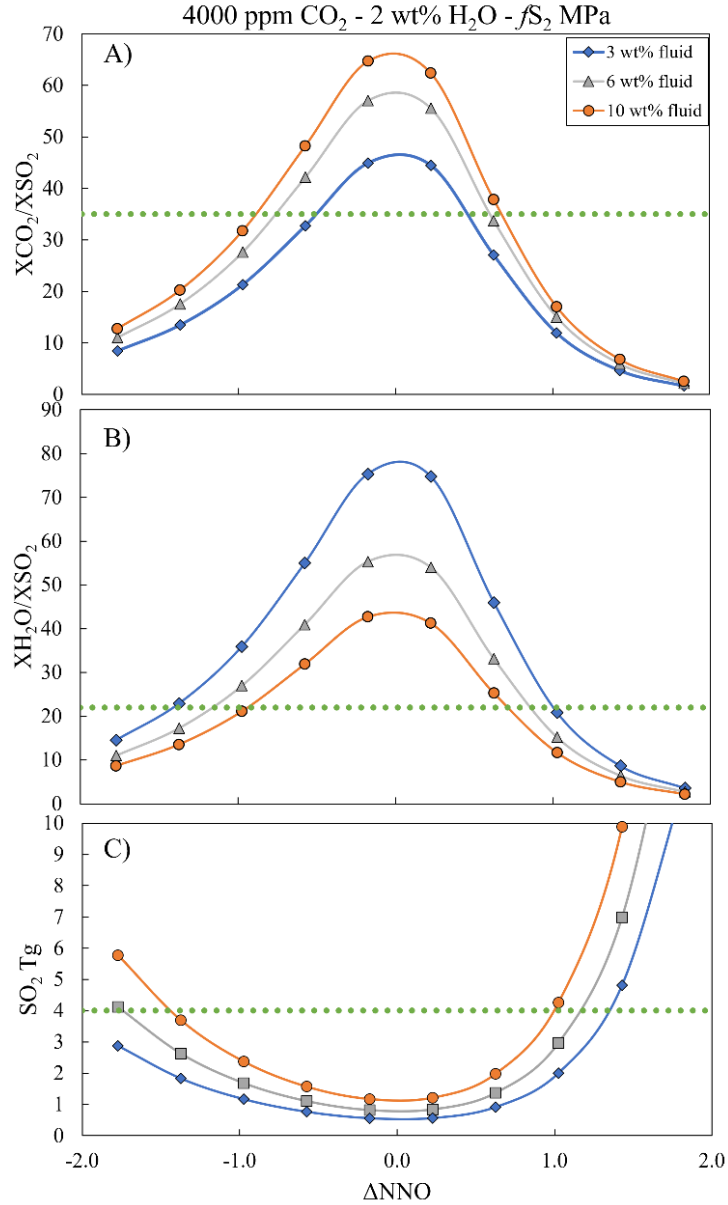


Fig. 24 Evolution of the $\text{XH}_2\text{O}/\text{XSO}_2$ (a) and $\text{XCO}_2/\text{XSO}_2$ (b) ratios of gases vented at 0.1 MPa with $f\text{O}_2$, for different amounts of exsolved fluid in the reservoir at 300 MPa. (c) Evolution of the mass of SO_2 produced for the three different amounts of fluid. In all panels the horizontal green dashed line indicates the measured value of the corresponding parameter.

reproduced at around NNO+0.5 to NNO+1 with 6 wt% excess fluid, which is broadly consistent with previous findings.

The amount of SO₂ released increases with the amount of pre-eruptive fluid in the crustal reservoir (Fig. 24c). Under these conditions, an fO_2 in the range of NNO+1 to NNO+1.5 is required to yield 4 Tg of SO₂. These calculations indicate the presence of a significant amount of free fluid in the plumbing system, as suggested by previous studies (e.g., Burton et al., 2023; Sandoval-Velasquez et al., 2023; Zanon et al., 2023).

The last step (III) studies the deeper part of the plumbing system. As previously noted, melt inclusions within olivine record dissolved CO₂ levels up to 5000 ppm (e.g., Dayton et al., 2024). When accounting for the presence of exsolved fluid in these inclusions, the CO₂

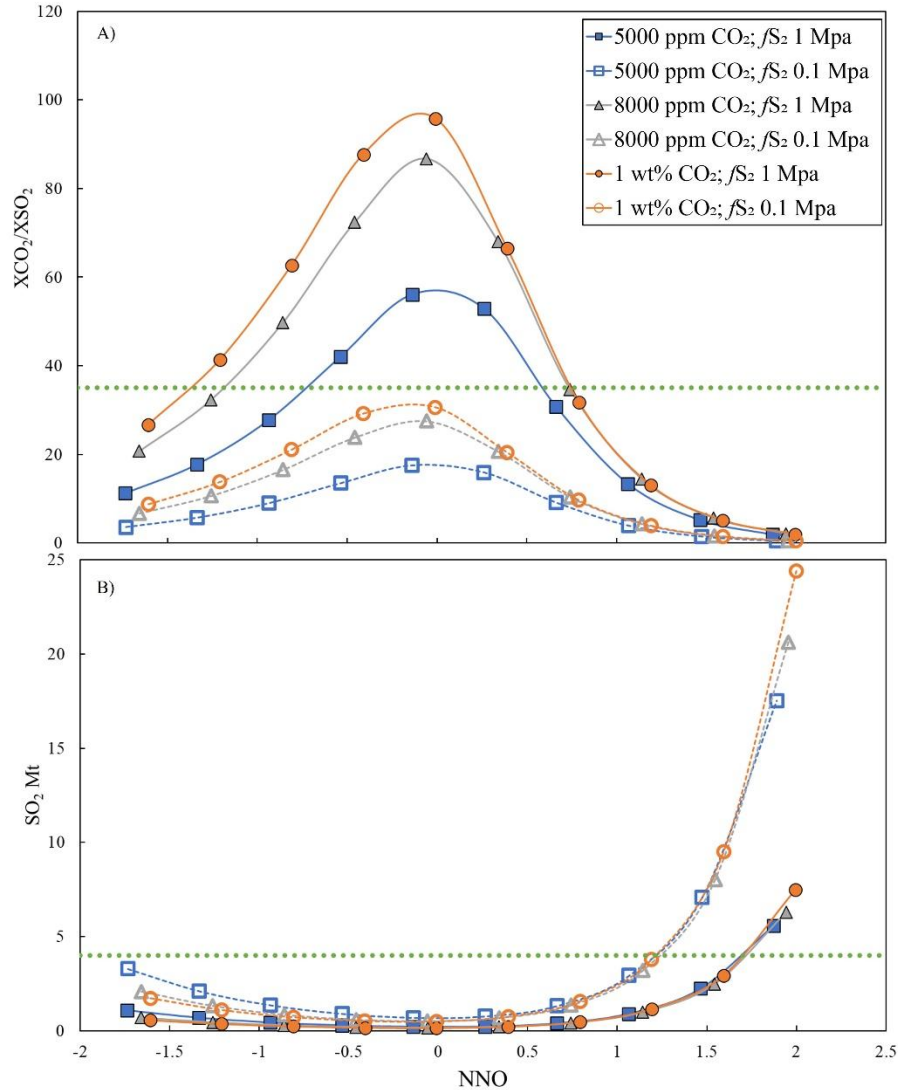


Fig. 25 Evolution of total amount of SO₂ degassed by 0.2 km³ of basanite magma with fO_2 expressed as ΔNNO with increasing CO₂ from 5000 ppm to 10000 ppm. (b) Evolution of the X_{CO_2}/X_{SO_2} ratio of the gas emitted at the vent with ΔNNO with increasing CO₂. In all panels the horizontal green dashed line indicates the measured value of the corresponding parameter.

content increases to 1.2 wt% (Dayton et al., 2024), highlighting the deep mantle origin of some magma erupted during the eruption. Consequently, we have also performed calculations using higher dissolved CO₂ levels, ranging from 5000 to 10000 ppm (corresponding to pressures between 400-800 MPa). We maintained the excess fluid at 3 wt%, consistent with most previous calculations, and kept the dissolved H₂O at 3 wt% (thus, the total volatile content exceeds 6 wt%). The results are presented in Fig. 25.

Regarding the XCO₂/XSO₂ ratio, increasing pressure makes a high f_{S_2} (1 MPa) less likely than a moderate one (0.1 MPa), as the set of curves for f_{S_2} =1 MPa does not reproduce the observed XCO₂/XSO₂ ratio of vented gases. Notably, for an f_{S_2} of 0.1 MPa, the intersection occurs around NNO+1, which is slightly lower than the f_{O_2} inferred by (Day et al., 2022). In terms of the amount of SO₂ released, a magma with an f_{S_2} of 1 MPa would require an f_{O_2} slightly above NNO, while a magma with an f_{S_2} of 0.1 MPa would need slightly more oxidizing conditions. Both f_{S_2} values are consistent with the inferred redox state range of La Palma magma (Dayton et al., 2024). The calculations above demonstrate that reproducing the observations from the La Palma eruption, particularly the S content of melt inclusions, gas composition, and the amount of S released, requires a delicate balance of f_{O_2} , f_{S_2} , and the amount of fluid in the magma (in addition to temperature and pressure). High S contents in the melt indicate f_{O_2} conditions above NNO (Fig.20). The f_{S_2} should be around 0.1 MPa to match the amount of SO₂ released (Fig. 22a and Fig. 24c). An f_{S_2} that is too high would not align with the observed XCO₂/XSO₂ ratio, especially if most of the outgassed sulphur originates from deep mantle-derived magma (Fig. 25).

The amount of fluid in the reservoir is also crucial for ensuring that the final released fluid has an XH₂O/XSO₂ ratio lower than the XCO₂/XSO₂ ratio, as observed. According to our calculations, fluid amounts significantly below 5 wt% (at 300 MPa) cannot meet this requirement (Fig.24). An XH₂O/XSO₂ ratio of 22 and an XCO₂/XSO₂ ratio of 35 necessitate an f_{O_2} of approximately NNO+0.6, which is lower than inferred and would not support high S content in the melt. This highlights the challenge of identifying conditions that satisfy all observations.

Beyond model uncertainties, these discrepancies may also reflect gas fractionation during magma ascent, either near the surface (Burton et al., 2023) or deeper in the plumbing system. Significant uncertainties remain regarding the magma's oxygen fugacity, and further work is

needed to refine the redox state of La Palma, given the importance of this parameter in S behavior. Additionally, the observed gases at La Palma likely represent a mixture of volatiles from magma that had been stagnating in the reservoir, possibly for years before the eruption (e.g., Day et al., 2022; Andujar et al., 2025), as well as from volatile-rich, mantle-derived magmas injected shortly before or during the eruption (Dayton et al., 2024; Zanon et al., 2024). These complex processes, likely occurring, are not fully captured by our current analysis.

3.5 Conclusion

The composition of the residual glass, as well as the phase relationships and their proportions, are primarily influenced by oxygen fugacity, with the amount of sulphur in the system playing a secondary role. Experiments also highlight the significant impact of fO_2 on the solubility of S in silicate melts (fig.16 and Fig.20). Between NNO-0.48 and NNO+1.34, the maximum S concentration in the residual glass is 0.2 ± 0.01 wt%, while at oxygen fugacities above NNO+2.38, the maximum value increases to 0.7–0.8 wt%. These limits are determined by the buffering effect of sulfide/sulfate phases in addition to the fluid.

Modeling the fluid phase composition using an MRK equation of state for fluid and the volatile solubility models of Lesne et al. (2015) and Jiménez-Mejías et al. (2021) indicates that the S content of the fluid ranges between 1 and 10 wt%, depending on fS_2 . Overall, the calculations show that to release 2-4 Mt of SO_2 , the pre-eruptive magma must have had a fS_2 around 0.1 MPa (Fig. 25a) with an fO_2 above NNO. This aligns with the oxidized character inferred for hotspot basalts (Moussallam et al., 2019) and suggests the coexistence of a significant amount of exsolved fluid in the crustal reservoir.

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Chapter 4

*Sulphur correlation
between apatite and
melt and links to
sulphur fugacity*

Corrélation du soufre entre l'apatite - verre et la fugacité du soufre

Ce chapitre présente les résultats des expériences de cristallisation de l'apatite réalisées avec *lpm+ap*, *fas+s* et *san+s*. Un accent particulier est mis sur les relations entre les concentrations de soufre dans le verre et l'apatite et l'influence de la fugacité des espèces de soufre (fS_2 , fH_2S et fSO_2). En comparant la concentration de SO_3 en poids dans l'apatite avec celle du verre résiduel, certaines similitudes peuvent être observées dans toutes les compositions étudiées. Une corrélation positive est observée : à mesure que le SO_3 en poids augmente dans le minéral, le SO_3 en poids analysé dans le verre augmente également.

Les expériences avec la rhyodacite de Santorin montrent des concentrations de SO_3 significativement plus faibles à la fois dans l'apatite et dans le verre par rapport aux compositions moins évoluées. Par ailleurs, les compositions rhyodacitiques et basanitiques ont des teneurs en soufre plus élevées à des valeurs de fO_2 élevées ($NNO > 2$). En revanche, les valeurs les plus faibles sont enregistrées dans les expériences avec une fO_2 inférieure à $NNO-0,50$.

Ces observations confirment que les concentrations de soufre dans le verre et l'apatite sont fortement influencées par le fO_2 . Néanmoins, la fO_2 ne permet pas d'expliquer de manière exhaustive toutes les tendances observées. Les données disponibles suggèrent qu'il existe également un facteur de composition susceptible d'influencer la répartition du soufre entre l'apatite et le verre, c'est pourquoi une étude sur les éléments traces dans l'apatite a été réalisée: elle révèle que des certains éléments en trace de l'apatite semblent être corrélés avec le S dans l'apatite: c'est le cas du Fe en particulier, mais probablement de certains lanthanides aussi (La, Ce). Les expériences de Parat et Holtz (2004-2005), réalisées sans Fe, montrent une corrélation positive entre les quantités de soufre dans le verre résiduel et dans l'apatite. Cependant, toutes les valeurs de SO_3 dans les apatites rapportées par Parat et Holtz sont significativement plus élevées que dans les charges *san+s*, même dans les charges à 900°C de Parat et Holtz (2004, 2005). Considérant qu'il existe une corrélation positive entre la température et l'activité du soufre dans ce minéral (Parat et Holtz, 2004), les expériences à des températures plus élevées devraient afficher des valeurs plus élevées de SO_3 , ce qui n'est pas le cas. Ainsi, en considérant que, pour un même fO_2 , il existe une différence considérable

entre les compositions plus évoluées telles que *san+s* ou les expériences de Parat et Holtz (2004, 2005), et les expériences plus mafiques *lpm+ap*, *fas+s*, on peut conclure que la composition du matériau de départ exerce d'une manière ou d'une autre une influence sur la quantité de S qui peut être intégrée dans l'apatite. Parmi les facteurs supplémentaires à prendre en compte, qui pourraient expliquer une partie des tendances observées, il y a bien évidemment la solubilité du soufre, qui varie considérablement entre les différentes compositions. En effet, les magmas plus mafiques, tels que ceux de La Palma et Fasnja, ont une solubilité en soufre plus élevée, ce qui favorise probablement l'incorporation de plus de soufre dans l'apatite et le verre. En définitive, dans l'ensemble, même en tenant compte des différences de solubilité du soufre, il est évident que le facteur dominant contrôlant le système est fO_2 .

Du point de vue thermodynamique, les fugacités des espèces de soufre (fH_2S , fSO_2 et fS_2) ont été calculées pour la plupart des charges expérimentales afin d'établir d'éventuelles corrélations avec la quantité de soufre dans l'apatite. En considérant la fS_2 des expériences dans lesquelles la pyrrhotite a cristallisé, aucune tendance claire ne peut être observée (avec le S dans l'apatite). En revanche, les valeurs de fH_2S et fSO_2 montrent une légère corrélation positive entre le SO_3 dans les apatites. Il est important de souligner que même en tenant compte de la fugacité du soufre, les expériences avec *san+s* affichent des valeurs plus faibles que celles réalisées avec Fasnja et La Palma.

La somme des trois espèces a également été testée comme paramètre de contrôle global du contenu en soufre de l'apatite : à mesure que la concentration de SO_3 dans l'apatite augmente, la somme de fS_2 , fH_2S et fSO_2 augmente également. Pour un même fO_2 et en additionnant les fugacités des espèces de soufre, on peut constater que les apatites dans les charges *san+s* ont des valeurs de SO_3 significativement plus faibles que les apatites dans *lpm+ap* ou *fas+s*, soulignant le rôle de la composition du système au sens large sur les teneurs en soufre de l'apatite. En ce qui concerne les corrélations avec fO_2 , en tenant compte de la composition équivalente du matériau de départ, le cumul des fugacités des espèces de soufre correspond à des valeurs plus élevées de SO_3 en poids et à des conditions redox plus oxydantes.

Nous avons également calculé les fSO_2 des expériences de Parat et Holtz (2004, 2005) de la même manière que pour les expériences à $NNO > 2,38$. En ajoutant ces valeurs à celles de cette thèse, deux tendances similaires apparaissent, chacune avec une pente légèrement

différente: l'une pour les compositions mafiques, l'autre pour les compositions felsiques. Par exemple, à $\sum fS_2$, fH_2S et fSO_2 entre 80 et 120 MPa, les expériences avec lpm+ap ont des concentrations de SO_3 dans l'apatite entre 1,33 % en poids et 1,50 % en poids, tandis que pour Parat et Holtz (2004, 2005), les valeurs sont de 0,16 % en poids et 0,72 % en poids. Cela souligne à nouveau qu'une propriété compositionnelle, probablement la solubilité du soufre, doit être prise en compte.

Une approche simple de modélisation a ainsi été suivie pour permettre l'estimation de la concentration en soufre dans l'apatite à partir de la somme des fugacités des espèces de soufre et vice versa. Trois modèles ont été créés : le premier modèle est pour des magmas avec un contenu en silice d'environ 45-50 % en poids, le deuxième est pour des magmas plus évolués avec un $SiO_2 > 60$ % en poids et le dernier est une équation générale.

En parallèle, une série de modèles de solubilité du soufre a été appliquée, en utilisant les valeurs de fS_2 calculées dans les expériences avec pyrrhotite pour déterminer la quantité de soufre dans le verre. Cette approche permet de tester la précision du nouveau protocole développé dans cette thèse pour analyser la pyrrhotite. Quatre modèles de solubilité ont été utilisés pour ce test : le modèle de Clemente et al. (2004), le modèle de Lesne et al. (2015), le modèle de Li et Zhang (2022), et le modèle de Boulliung et Wood (2023). Un examen préliminaire montre que tous les modèles reproduisent globalement les valeurs de soufre dans le verre pour la majorité des expériences. Le modèle de Clemente et al. (2004) est le modèle le moins adapté aux expériences de ce travail, car il est calibré essentiellement pour des compositions rhyolitiques ou similaires. Ce modèle sous-estime légèrement la valeur mesurée mais, dans la plupart des cas, reste dans l'erreur analytique. Le modèle développé par Lesne et al. (2015) montre un bon accord avec les valeurs mesurées. Les modèles de Li et Zhang (2022) et de Boulliung et Wood (2023) reproduisent la teneur en soufre avec une précision raisonnable (bien que, dans le détail, le modèle de Boulliung et Wood tende systématiquement à sous-estimer les valeurs mesurées).

Ces résultats montrent également que la valeur de fS_2 dérivée de la composition de la pyrrhotite, lorsque l'on utilise un protocole analytique adapté, est suffisamment précise pour reproduire la teneur en soufre du verre en utilisant divers modèles thermodynamiques.

4. Sulphur correlation between apatite and melt and links to sulphur fugacity

This chapter will show the results of apatite crystallization experiments conducted with *lpm+ap*, *fas+s* and *san+s*. A focus will be made on the relationships between the sulphur concentrations in melt and apatite and the influence of the fugacity of the sulphur species (f_{S_2} , f_{H_2S} and f_{SO_2}). As described in Chapter 2, experiments were carried out with 2 wt%, 1 wt% and 0.5 wt.% S added to the starting material. Then two experimental *lpm+ap* series with 3 wt.%, 4 wt.% and 5 wt.% S added, and another *lpm+ap* series where Cl was added at different percentages were carried out. The *FeS+ap* experimental series (9 wt.% of sulphur added) was a first approach to evaluate the relationship between apatite and pyrrhotite with different NFeS and H₂O contents. Unfortunately, it was not possible to continue in this direction due to time limits. Tables 12-13 provide details of the experimental conditions.

Given the considerable volume of data, it was judged preferable to exclude the values of the experimental S-free runs from the graphs, as they would have been in close proximity to zero. In addition, in some experimental charges such as *lpm+ap cl S 4* and *lpm+ap s Cl 4* the size of the apatites was so small that reliable chemical analyses were not possible and they will not be taken into account anymore. Prior to reaching this conclusion, the data set was subjected to rigorous analytical scrutiny during numerous analytical sessions.

It is important to emphasise that a complete analysis of each capsule required at least two to five analytical sessions of EMPA as each capsule was analysed with two or four different programs: a silicate program and one or two apatite programs. Moreover, in capsules where pyrrhotite crystallised, it was necessary to carry out at least 5 analytical sessions per capsule in order to confirm that the program described in Chapter 2 was reliable. The pyrrhotite program was developed during the course of this thesis through an analysis of experimental pyrrhotites. This development process entailed not only the experimentation with different calibrations, but also an assessment of their stability and veracity. Consequently, it was deemed necessary to analyse each experimental charge at least five times with the calibration explained in Section 2.2

Fig.26 illustrates representative features of the experimental products. The synthesized apatites exhibit a range of morphologies, including euhedral, elongated, and globular forms. Elongated crystals frequently posed challenges during analysis. In contrast, pyrrhotite grains consistently display a rounded morphology, although their sizes vary considerably. All chemical analyses of the apatite, glass and pyrrhotite are reported in Annex.

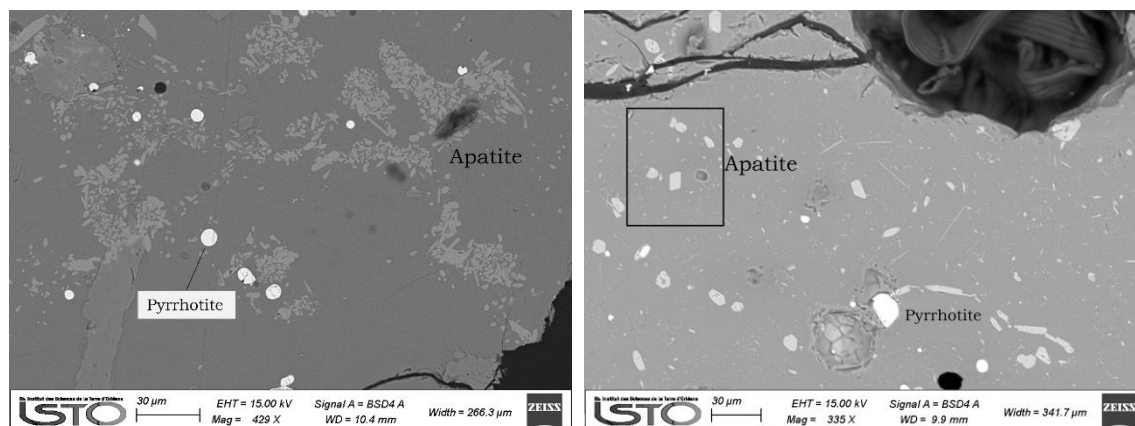


Fig. 26 The SEM images below present two examples illustrating the occurrence of apatite and pyrrhotite in the experimental products obtained during this study. Apatite crystals exhibit variable morphologies, including euhedral, acicular, and globular forms. Pyrrhotite, by contrast, consistently displays a rounded morphology, though grain sizes vary significantly.

4.1 Sulphur distribution between apatite and melt

The same trend as described in Chapter 3 on the correlation between the amount of sulphur added in the system and S concentration in the residual melt was also found in these experiments for all compositions: a progressive increase of S wt.% in the melt until S-bearing minerals buffer the system (sulfide in reduced runs and anhydrite in oxidized runs) with a difference between the oxidized and reduced experiments.

Regarding the SO_3 concentration in apatites, the *lpm+ap* and *fas+s* experiments show no clear trends with the sulphur added in the system, though broad positive correlations emerge under oxidizing conditions in particular. *San+s*, on the other hand, shows a correlation similar to that of S in the residual melt, influenced once again by $f\text{O}_2$ (Fig. 27).

Comparing the concentration of SO_3 wt.% in the apatite with the residual melt, some similarities can be seen in all the compositions studied (Fig.28). Since the chlorine added in the *lpm+ap cl S* and *lpm+ap s Cl* experimental series does not seem to influence the general trends discussed hereafter, these runs will be described together with the Cl-free experiments. However, it must be emphasised that a possible influence of Cl cannot be totally ruled out as these two series cover a limited compositional and experimental conditions range.

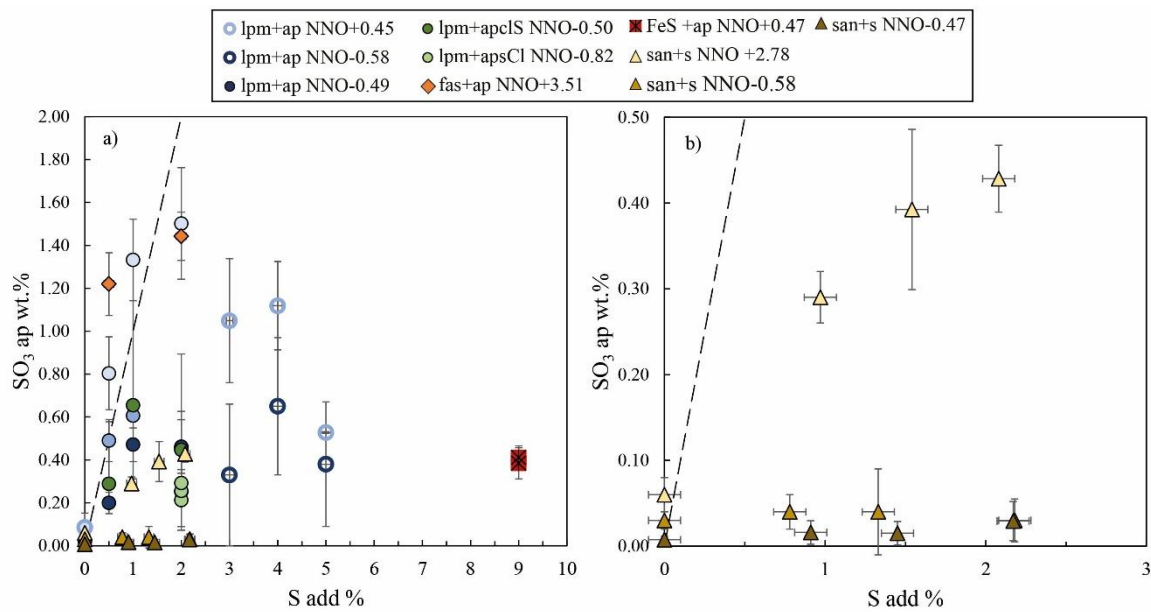


Fig. 27 Sulphur concentration in the apatites versus the percentage added in the system. The only series that have a trend is *san+s* one. Panel a) show all the experiment; panel b) is a focus on the *san+s* series to highlight the positive trend. The dashed line represents the 1:1 correlation.

<i>Run</i>	<i>P</i> (MPa)	<i>T</i> (°C)	<i>Time</i> (h)	<i>ANNO</i>	<i>H₂O</i>	<i>S wt.%</i> <i>loaded</i>	<i>Cl</i> <i>wt.%</i> <i>load</i>	<i>SO₃</i> <i>wt.%</i> <i>glass</i>	<i>SO₃</i> <i>wt.%</i> <i>apatite</i>	<i>Mineral</i> <i>assemblage</i>
<i>lpm+ap1</i>	200	1040	6	4.17	4.59	2	-	2.61 (0.08)	1.50 (0.26)	ap-mt-ilm
<i>lpm+ap2</i>	200	1040	6	4.17	4.61	1	-	2.03 (0.09)	1.33 (0.19)	cpx-ap-mt
<i>lpm+ap3</i>	200	1040	6	4.17	5.01	0.50	-	1.18 (0.03)	0.80 (0.17)	cpx-ap-mt
<i>lpm+ap4</i>	200	1040	6	4.17	6.90	0	-	b.d.	b.d.	cpx-ap-mt
<i>lpm+ap9</i>	200	1040	6	-0.49	4.62	2	-	0.30 (0.09)	0.46 (0.13)	ol-cpx-amph-ap-po
<i>lpm+ap10</i>	200	1040	6	-0.49	3.89	1	-	0.39 (0.06)	0.47 (0.16)	cpx-amph-ap-fes
<i>lpm+ap11</i>	200	1040	6	-0.49	4.02	0.50	-	0.44 (0.04)	0.20 (0.05)	ol-amph-ap
<i>lpm+ap12</i>	200	1040	6	-0.49	4.66	0	-	b.d.	b.d.	ol-amph-ap-mt
<i>lpm+ap13</i>	200	1040	6	0.66	3.39	2	-	0.55 (0.06)	0.46 (0.17)	ol-cpx-amph-ap-po
<i>lpm+ap14</i>	200	1040	6	0.66	3.97	1	-	0.91 (0.06)	0.61 (0.06)	amph-ap-po
<i>lpm+ap15</i>	200	1040	6	0.66	5.28	0.50	-	0.58 (0.03)	0.49 (0.10)	amph-ap
<i>lpm+ap16</i>	200	1040	6	0.66	5.30	0	-	b.d.	b.d.	ol-amph-ap-mt
<i>lpm+ap20</i>	200	1040	6	-0.58	4.32	3	-	0.27 (0.04)	0.33 (0.33)	ol-cpx-ap-po
<i>lpm+ap21</i>	200	1040	6	-0.58	4.14	4	-	0.28 (0.04)	0.65 (0.32)	cpx-ap-po
<i>lpm+ap22</i>	200	1040	6	-0.58	3.69	5	-	0.22 (0.03)	0.38 (0.29)	cpx-ap-po
<i>lpm+ap23</i>	200	1040	6	0.45	3.89	3	-	0.58 (0.07)	1.05 (0.29)	cpx-ap-po
<i>lpm+ap24</i>	200	1040	6	0.45	5.45	4	-	1.44 (0.10)	1.12 (0.21)	cpx-ap-po
<i>lpm+ap25</i>	200	1040	6	0.45	4.02	5	-	0.45 (0.10)	0.53 (0.00)	cpx-ap-po
<i>lpm+ap26</i>	200	1040	6	0.45	5.21	0	-	b.d.	b.d.	ap
<i>lpm+ap cl S 1</i>	200	1040	6	-0.50	4.07	2	15	0.46 (0.26)	0.45 (0.19)	amph-ap-po
<i>lpm+ap cl S 2</i>	200	1040	6	0.50	4.23	1	15	0.35 (0.19)	0.66 (0.12)	amph*-ap-po
<i>lpm+ap cl S 3</i>	200	1040	6	-0.50	4.36	0.50	15	0.24 (0.08)	0.29 (0.20)	ol-amph-ap-po
<i>lpm+ap cl S 4</i>	200	1040	6	-0.50	3.52	0	15	b.d.	b.d.	amph-ap
<i>lpm+ap s Cl 1</i>	200	1040	6	-0.82	3.27	2	15	0.27 (0.02)	0.25 (0.06)	ol-cpx-ap-po
<i>lpm+ap s Cl 2</i>	200	1040	6	-0.82	3.93	2	10	0.39 (0.06)	0.21 (0.14)	amph*-ap-po
<i>lpm+ap s Cl 3</i>	200	1040	6	-0.82	4	2	5	0.35 (0.10)	0.26 (0.17)	ol-ap-po
<i>lpm+ap s Cl 4</i>	200	1040	6	-0.82	3.75	2	0	0.36 (0.04)	-	cpx-amphap-po
<i>fas+s 1</i>	200	1040	6	3.51	7.70	0.50	-	1.84 (0.18)	1.22 (0.15)	cpx-amph-ap-mt
<i>fas+s 3</i>	200	1040	6	3.51	7.34	2	-	1.98 (0.20)	1.44 (0.11)	ol-cpx-amph-ap-mt-anhy
<i>FeS+ap4</i>	200	1000	72	0.47	6.46	9	-	0.11 (0.04)	0.38 (0.07)	ol-cpx-amph-ap-po
<i>FeS+ap5</i>	200	1000	72	0.14	6.06	9	-	0.10 (0.02)	0.41 (0.05)	amph-mt-ap-po

Table 12. Experimental conditions and main characteristics of the capsule preparation and the run product of basanite starting material.

<i>Run</i>	<i>P</i> (MPa)	<i>T</i> (°C)	<i>Time</i> (h)	<i>ΔNNO</i>	<i>H₂O</i>	<i>S% and type loaded</i>	<i>Cl% load</i>	<i>SO₃ wt.% glass</i>	<i>SO₃ wt.% apatite</i>	<i>Mineral assemblage</i>
<i>san+s1</i>	200	1000	96	2.78	5.02	2.08	-	0.22 (0.05)	0.43 (0.04)	mt-ap-anhy
<i>san+s2</i>	200	1000	96	2.78	5.41	1.54	-	0.21 (0.02)	0.39 (0.09)	mt-ap-anhy
<i>san+s3</i>	200	1000	96	2.78	5.07	0.97	-	0.16 (0.03)	0.29 (0.03)	mt-ap-anhy
<i>san+s4</i>	200	1000	96	2.78	5.63	0	-	b.d.	b.d.	mt ^{&} -ap
<i>san+s6</i>	200	1000	120	0.58	6.07	2.18	-	0.07 (0.03)	0.03 (0.03)	ap-po
<i>san+s7</i>	200	1000	120	0.58	4.92	1.33	-	0.02 (0.02)	0.04 (0.05)	ap-po
<i>san+s8</i>	200	1000	120	0.58	5.60	0.78	-	0.03 (0.02)	0.04 (0.02)	ap
<i>san+s9</i>	200	1000	120	0.58	5.86	0	-	b.d.	b.d.	ap
<i>san+s10</i>	200	1000	144	-0.47	6.29	2.17	-	0.05 (0.03)	0.03 (0.02)	ap-po
<i>san+s11</i>	200	1000	144	-0.47	6.86	1.45	-	0.07 (0.02)	0.02 (0.01)	ap-po
<i>san+s12</i>	200	1000	144	-0.47	6.28	0.91	-	0.10 (0.09)	0.02 (0.01)	ap-po
<i>san+s13</i>	200	1000	144	-0.47	6.15	0	-	b.d;	b.d.	ap

Table 13 . Experimental conditions and main characteristics of the capsule preparation and the run product of rhyodacitic starting material.

Fig.28 shows, for all compositions examined, a positive correlation between sulphur concentration in apatite and in residual melt: as SO₃ wt.% increases in the mineral, SO₃ wt.% analysed in the glass increases.

For the experiments with the basanitic composition, both *lpm+ap* and *fas+s*, the maximum values are 2.63 wt.% SO₃ in melt and 1.5 wt.% SO₃ in apatite (*lpm+ap* 1) while the minimum value for apatite is 0.20 wt% SO₃ (*lpm+ap* 11) and for the residual melt is 0.22 wt.% SO₃ (*lpm+ap* 22), as seen in Fig.28b.

The experiments with Santorini rhyodacite have significantly lower SO₃ concentrations in both apatite and melt compared to the less evolved compositions. *San+s 1* has a maximum concentration of 0.23 wt.% SO₃ in melt and 0.43 wt.% SO₃ in apatite (Fig.28a and c). Furthermore, a difference can be seen with oxygen fugacity (*f*O₂) with the two compositions. Indeed, both the rhyodacitic and basanitic compositions have higher sulphur contents at high *f*O₂ (NNO>2). In contrast, the lowest values are recorded in experiments with NNO below -0.50. The entire data set displays an almost 1:1 linear trend for the more reduced conditions, up to about NNO+0.45, the slope of the correlation decreasing slightly at more oxidised conditions.

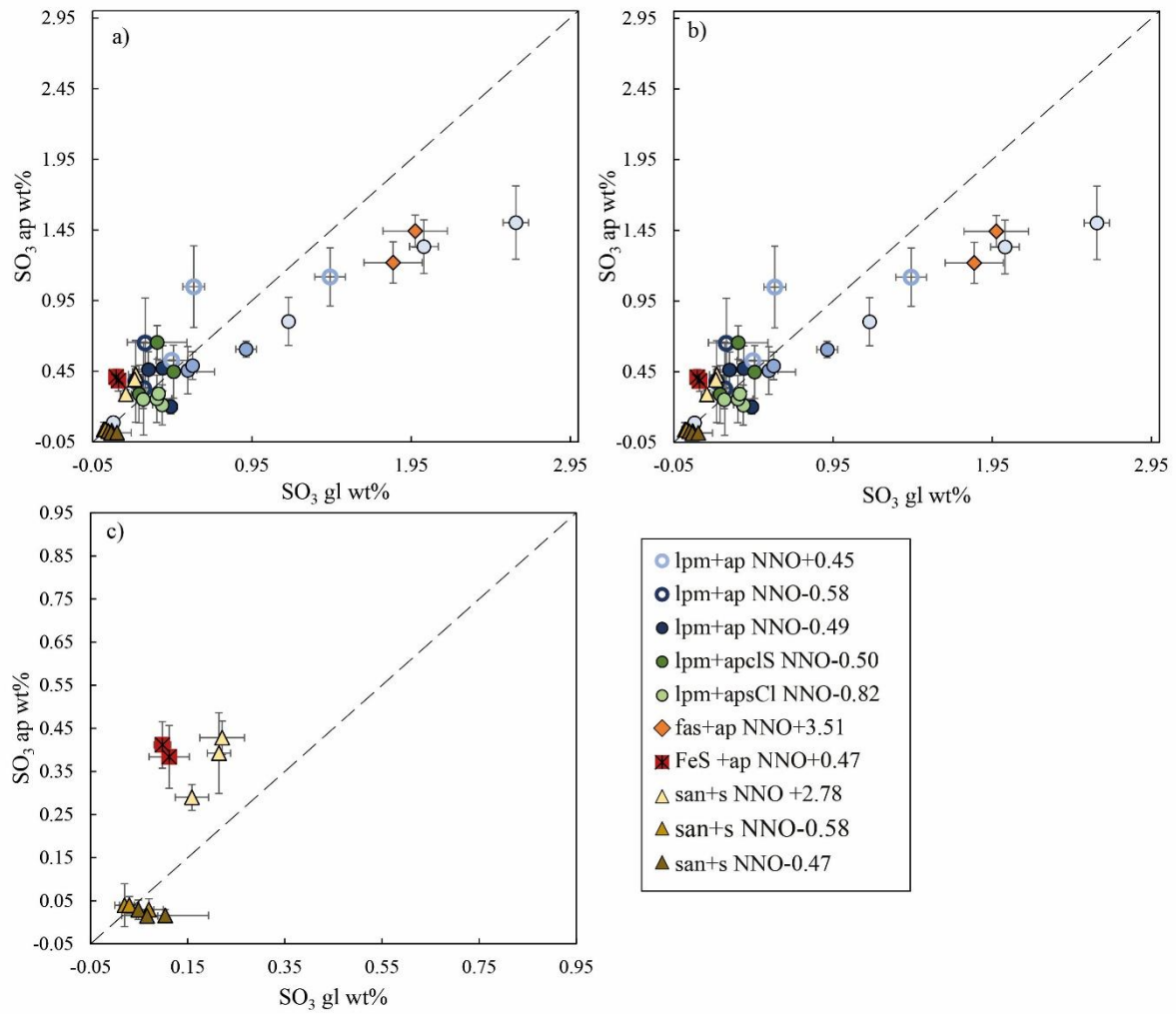


Fig. 28. A positive correlation between the amount of sulphur present in the apatite and the melt composition was observed, with redox conditions and melt composition also influencing this relationship. Panel a) shows the general trend considering all the experiments. Panel b) focuses on the mafic composition in particular on *lpm+ap*, *fas+s*, *FeS=ap*. Panel c) shows a zoom on the evolved compositions (*san+s*). In all panels the dashed line represents the 1:1 correlation.

The present observations confirm that sulphur concentrations in melt and apatite are markedly influenced by fO_2 . Nevertheless, the sole consideration of fO_2 does not provide a comprehensive explanation for the mentioned trends. In fact, at the same fO_2 , the more evolved melt composition exhibits a lower sulphur concentration. Comparison of the major elements in the melt such as CaO, SiO₂, K₂O, and SO₃ shows obvious differences between rhyodacites and basanites at the same fO_2 (Fig. 29). In particular, the calcium concentrations in the melt are significantly higher in the *lpm+ap* and *fas+s* runs than in *san+s*. In both compositions, there is a slight negative trend with increasing sulphur in the apatite and fO_2 (Fig. 29a). In contrast, the melt silica content does not seem to influence the amount of S in

apatites: it is only noted that at high fO_2 apatites are more sulphur-rich (Fig.29b). K_2O exhibits a negative correlation with SO_3 wt.% in apatites with a distinction between evolved and less evolved runs (Fig.29c). In fact, *san+s* runs have higher K_2O contents. Indeed, when considering the data obtained under oxidised conditions ($NNO > 2$), it becomes evident that La Palma and Fasnja exhibit higher sulphur contents compared to Santorini. In all these plots, however, the main controlling factor seems to be fO_2 . It can therefore be concluded that the major elements of the coexisting melt do not exert a direct influence on the concentration of sulphur in the apatites. This brings the question as to whether the trace elements in apatite play a role on these differences between the less evolved and the rhyodacitic compositions.

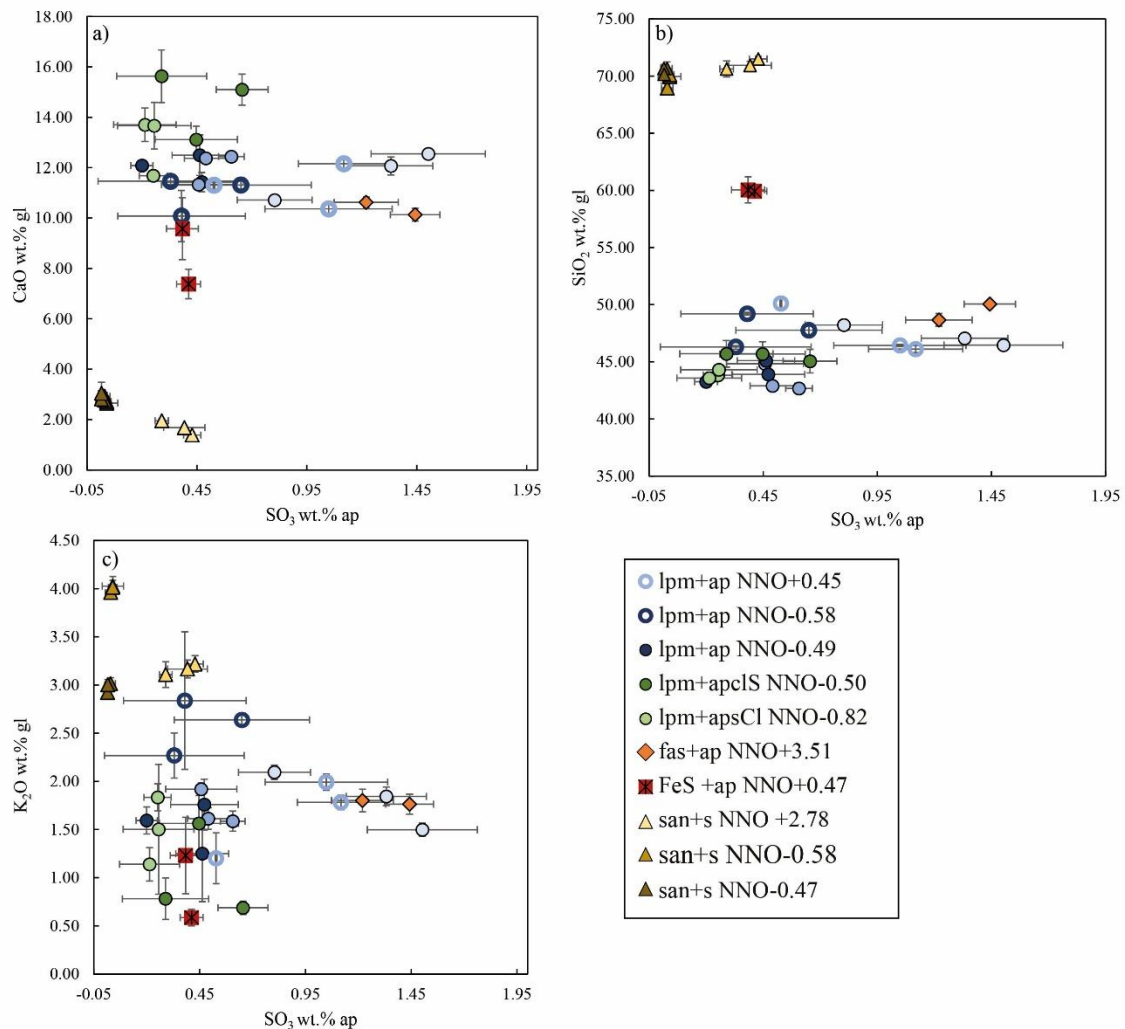


Fig. 29. Comparison of some major elements in melt with SO_3 wt.% in apatites:

The existing literature on this topic is unfortunately relatively scarce. The most significant works are: Peng et al., 1997 re-using Luhr's (1990) runs, Parat and Holtz (2004, 2005), Konecke et al. (2017, 2019). However, it was decided to compare the results of this thesis with only the Parat and Holtz (2004-2005) experiments. This is due to the fact that the apatites described by Peng et al. (1997) show zonations and are therefore most probably not fully at equilibrium with the system. Initially, the results of Konecke et al. (2017, 2019), who performed experiments at 300 MPa and 1000 C, were compared with the values obtained in this thesis (Fig.30a). In their experiments, Konecke et al. used an Antarctic lamproite with a composition significantly different from those considered so far, and in some cases at significantly different fO_2 conditions (Fig. 30a). For these reasons, it was decided not to consider these data in the following discussion. Since, as Parat and Holtz (2004, 2005) reported, temperature influences the behaviour of sulphur in melt and apatite, only experiments at 200 MPa and at temperatures in the range of 900-1100 °C were considered. It must also be emphasised that the experimental conditions of Parat and Holtz (2004, 2005) are highly oxidizing, between NNO+3.7 and NNO+3.6. Their SO₃ wt.% in the melt and in the apatites show a similar trend to the experiments in this thesis: a positive correlation between the amounts of sulphur in the residual melt and in the apatite (Fig. 30). The only exceptions are the experimental charges 58, 59, 60 which show an inverse trend that Parat and Holtz attribute to the presence of anhydrite. However, the *san+s* 1, *san+s* 2 and *san+s* 3 experiments, despite having anhydrite at higher percentages than Parat and Holtz (2004, 2005) (5.1 wt.%, 4.2 wt.% and 4.3 wt.% respectively; calculated with the mass balance model of Scaillet and Evans, 1999), still display a positive trend (Fig. 30). Furthermore, all SO₃ values in the apatites reported by Parat and Holtz are significantly higher than in the *san+s* charges. In fact, the minimum value of SO₃ in apatites reported by Parat and Holtz (2004, 2005) is 0.58 wt.% and the maximum value of the *san+s* experiments is 0.43 wt.%. In this case, fO_2 cannot be blamed, as in both cases the conditions are oxidising (between NNO+2.78 and NNO+3.7). It is of fundamental importance to note that even with the same fO_2 , the experimental charges at 900°C of Parat and Holtz (2004, 2005) have SO₃ values in apatite greater than or equal to those of *san+s*. Considering that there is a positive correlation between temperature and S-activity in this mineral (Parat and Holtz, 2004), experiments at higher temperatures should have higher SO₃, which is not the case (Fig. 30). This again

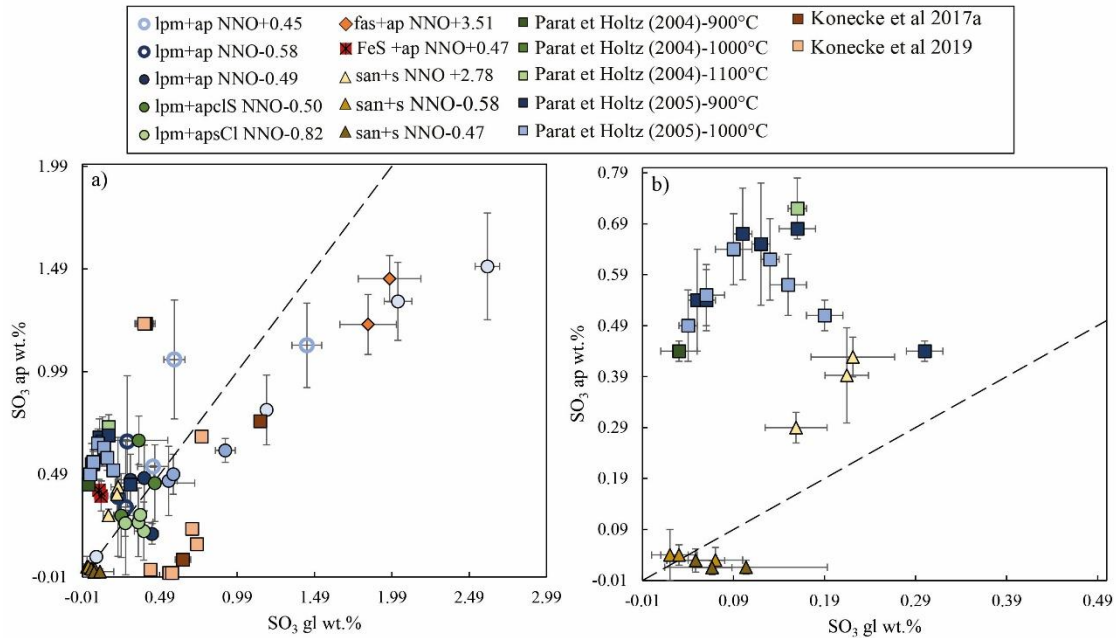


Fig. 30 SO_3 wt.% in apatite versus SO_3 wt.% in the melt compared with literature. The dashed line represents the 1:1 correlation.

suggests that the composition of the starting melt may influence the behaviour of sulphur in apatite in an indirect way. In fact, Parat and Holtz's starting material is a synthetic haplogranitic composition whose major difference from *san+s* is the lack of Fe and Ti. The data shown in Fig. 29 appear to suggest that the major elements of the melt do not directly impact the relationship between SO_3 wt.% apatite and the SO_3 wt.% melt, as mentioned before. In order to gain further insight of the origin of chemical variations in the apatites, analyses of the minerals present in the runs doped with 2% sulphur using the second apatite program were conducted. This program was focused on REE, SrO, FeO, MgO and MnO, with a duration of five minutes per analysis (see Section 2.2.2). Due to reasons that remain unclear but which probably relate to a deterioration of the sample, it was only possible to obtain good analyses for *lpm+ap 1*, *lpm+ap cl S 1*, *lpm+ap s Cl 1*, *san+s 1*, *san+s 6* and *san+s 10*. Among the elements analysed, significant variations were noted in the following oxides: FeO, SrO, Ce_2O_3 and La_2O_3 . A comparison of these elements with the amount of S in the apatites reveals that *lpm+ap 1* has lower FeO, Ce_2O_3 and La_2O_3 concentrations and higher SO_3 wt.% (Fig. 31). Furthermore, a negative correlation between these oxides and the sulphur in the apatites is observed in general. It is important to highlight that rhyodacitic samples have higher concentrations of La_2O_3 and Ce_2O_3 relative to *lpm+ap*. With regard to SrO, no discernible

trend emerges. However, it is apparent that the experimental runs involving san+s exhibit lower strontium concentrations than those with lpm+ap. Thus, considering that, for the same fO₂, there is a considerable difference between the more evolved compositions such as san+s

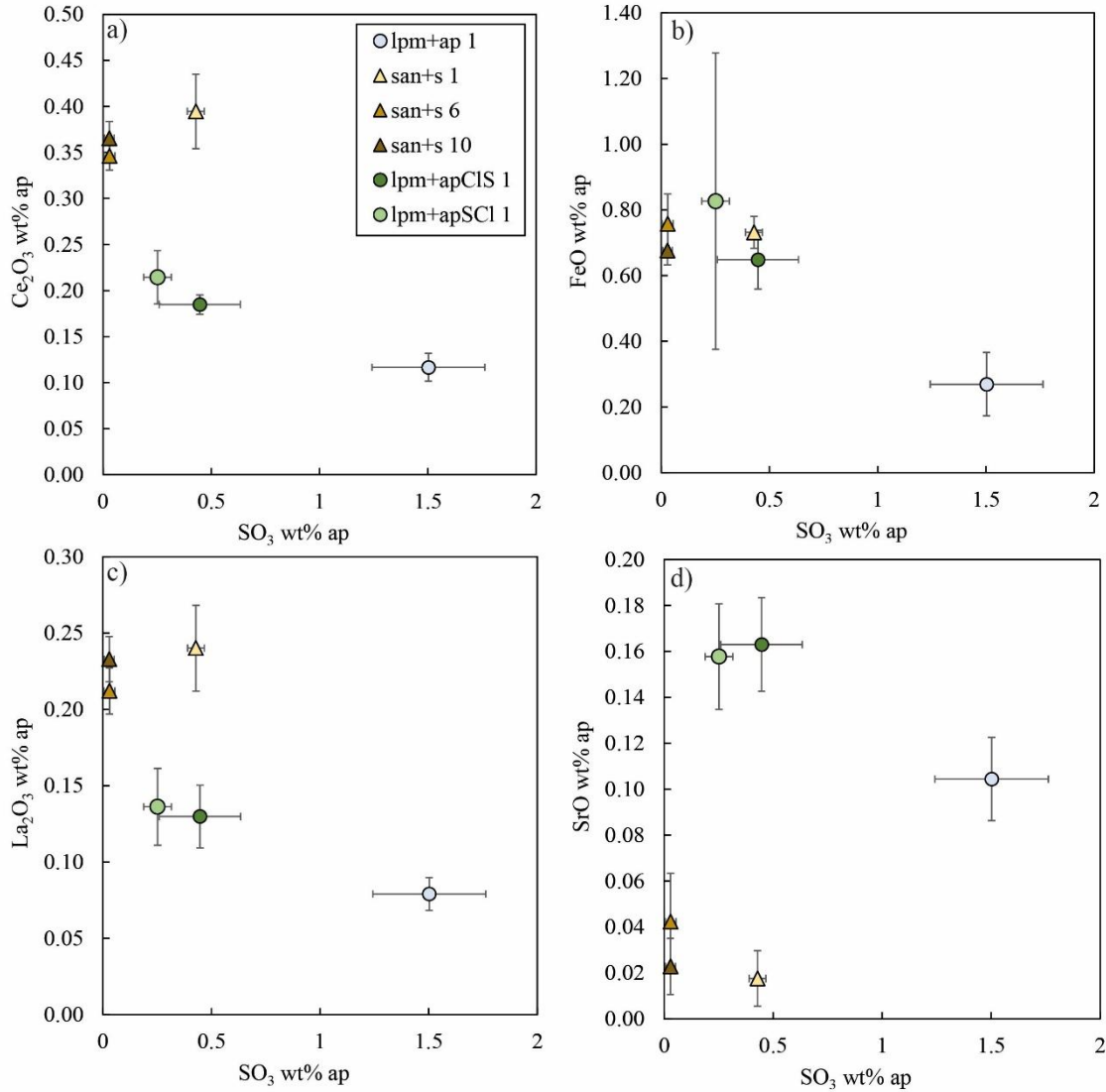


Fig. 31 Correlation of a) FeO, b) Ce₂O₃, c) La₂O₃ d) SrO in apatite with the amount of sulphur analysed

or the Parat and Holtz (2004, 2005) runs, and the more mafic lpm+ap, fas+s experiments, it can be concluded that the composition of the starting material in some way exerts an influence on the amount of S that can be integrated into the apatite. However, it is reiterated that the major elements of the melt do not show clear patterns that could explain the correlation of sulphur concentrations between apatite and melt. In contrast, the trace elements

(Fig. 31) show more promising correlations. The decrease in S content as Fe increase could explain why the apatite of Parat and Holtz (2004, 2005), which is Fe-free, has on average a S content higher than that crystallised from our Fe-bearing rhyodacite. Unfortunately, the few data available do not allow one to explore in greater detail the sulphur behaviour observed so far. More work in this area is clearly needed. One additional factor to be taken into account that could explain part of the observed trends is the sulphur solubility, which changes considerably between the various compositions. In fact, more mafic magmas, such as La Palma and Fasnja, have a higher sulphur solubility, and this likely favours the incorporation of more sulphur into apatite and melt. Overall, however, even taking sulphur solubility differences into account, it is clear that the overarching factor controlling the system is fO_2 .

4.2 The relationships between the fugacities of sulphur species (f_{S_2} , f_{H_2S} , f_{SO_2}) and the S content of apatite

As described in Chapter 2, the fugacities of the sulphur species (f_{H_2S} , f_{SO_2} and f_{S_2}), were calculated for most of the experimental charges in order to establish possible correlations with the amount of sulphur in the apatite. Table 14 provides a detailed listing of all calculated sulfur species fugacities. Considering the f_{S_2} of the experiments in which pyrrhotite crystallised, it can be seen that in general this fugacity is fairly homogeneous in the f_{O_2} range between NNO+0.58 and NNO-0.82. On average, the f_{S_2} values are in the range 0.01 MPa - 0.37 MPa. The only experimental runs outside this range are the *lpm+ap* 23 and *lpm+ap* 25 capsules whose f_{S_2} values are 2.5 MPa and 1.5 MPa, respectively. Altogether, comparing the SO_3 wt.% concentrations in the apatites and the calculated f_{S_2} values, no trend can be seen. The values of f_{H_2S} on the contrary are more diverse and range from a minimum of 0.01 MPa up to a maximum of 37 MPa, with most of the values lying above 10 MPa. There is a slight positive correlation between SO_3 in apatites and f_{H_2S} , therefore suggesting that the amount of S included into the apatite frame is also partly controlled by the fugacity of the sulphur species, as could have been anticipated. The value of f_{SO_2} varies also as a function of f_{O_2} , in fact the experimental runs can be split into 3 subgroups. The first one is represented by the experiments at reduced conditions ($NNO < 0.45$) with a maximum of f_{SO_2} 0.55 MPa (*san+s* 7). The second group is represented by the experiments at NNO+0.66 and NNO+0.45 in which f_{SO_2} is calculated between 4.4 MPa and 5.5 MPa. At these intermediate NNO, f_{SO_2} was only calculated in the capsules in which pyrrhotite was present, since it could not be assumed in the others that the only sulphur species produced was the oxidised one. The last group is the experiments at $NNO \geq +2.78$, which, as anticipated, have higher f_{SO_2} values, between 41.95 MPa and 84.9 MPa. Again, as with f_{H_2S} , there is a slight positive trend with the amount of sulphur measured in the apatites. It is important to emphasise that even when taking into account the fugacity of sulphur, the experiments with *san+s* display lower values than those carried out with Fasnja and La Palma.

Finally, the sum of the three species was also tested as a bulk controlling parameter of S content of apatite. The graph in Fig.32 clearly shows that as the concentration of SO_3 in the apatite increases, so does the sum of f_{S_2} , f_{H_2S} and f_{SO_2} . For the same f_{O_2} and summing up

<i>Id serie</i>	<i>NNO</i>	<i>fS2 Mpa</i>	<i>fH2S Mpa</i>	<i>fSO2 Mpa</i>	<i>ΣfH2S, fSO2, fS2 Mpa</i>
lpm+ap1	4.17			84.92	84.92
lpm+ap2	4.17			83.77	83.77
lpm+ap3	4.17			65.96	65.96
lpm+ap9	-0.49	0.03	14.17	0.10	14.30
lpm+ap10	-0.49	0.02	10.41	0.10	10.53
lpm+ap13	0.66	0.37	11.51	5.52	17.39
lpm+ap14	0.66	0.24	9.28	4.41	13.92
lpm+ap20	-0.58	0.03	14.74	0.10	14.87
lpm+ap 21	-0.58	0.08	22.56	0.15	22.79
lpm+ap22	-0.58	0.29	37.00	0.28	37.58
lpm+ap23	0.45	2.42	33.42	8.79	44.64
lpm+ap25	0.45	1.51	27.52	6.93	35.96
lpm+ap cl S 1	-0.50	0.04	14.75	0.12	14.92
lpm+ap cl S 2	0.50	0.01	5.95	0.05	6.01
lpm+ap cl S 3	-0.50	0.01	5.66	0.05	5.71
lpm+ap s Cl 1	-0.82		5.24	0.01	5.26
lpm+ap s Cl 2	-0.82	0.01	8.48	0.02	8.51
lpm+ap s Cl 3	-0.82		7.47	0.02	7.50
fas+s 1				65.96	65.96
fas+s 3				65.96	65.96
FeS+ap4	0.47	0.01	2.48	0.36	28.43
FeS+ap5	0.14	0.01	2.44	0.35	27.95
san+s1	2.78			60.71	60.71
san+s2	2.78			41.95	41.95
san+s3	2.78			58.28	58.28
san+s6	0.58	0.01	1.18	0.44	1.63
san+s7	0.58	0.01	1.49	0.55	2.05
san+s10	-0.47	0.04	9.25	0.10	9.39
san+s11	-0.47	0.02	6.82	0.07	6.91
san+s12	-0.47	0.03	8.88	0.09	9.00
<i>Parat and Holtz (2004)</i>					
35	3.60			52.16	52.16
27	3.60			63.15	63.15
51	3.60			102.61	102.61
<i>Parat and Holtz (2005)</i>					
56	3.70			72.21	72.21
57	3.70			64.07	64.07
27	3.70			63.15	63.15
58	3.70			97.86	97.86
59	3.70			107.51	107.51
60	3.70			115.21	115.21
35	3.70			52.16	52.16
61	3.70			21.91	21.91
62	3.70			26.42	26.42

Table 14. continued

63	3.70	30.38	30.38
64	3.70	22.92	22.92
60-65	3.70	96.65	96.65

Table 14 The fugacities of the sulfur species are expressed in MPa. The fugacity of S_2 (fS_2) was calculated based on the composition of pyrrhotite, whereas the fugacities of H_2S (fH_2S) and SO_2 (fSO_2) were determined using thermodynamic modeling. The methodologies applied are described in detail in Sections 2.2.3 and 2.2.5.

the fugacities of the sulphur species, it can be seen that apatites in charges *san*+*s* have significantly lower SO_3 values than apatites in *lpm*+*ap* or *fas*+*s*. As for the fO_2 correlations, taking into account for the equivalent starting material composition, the cumulative sulphur fugacity species correspond to higher SO_3 wt.% and more oxidising redox conditions.

We also calculated the fSO_2 from the experiments of Parat and Holtz (2004, 2005) in the same way as the experiments at $NNO > 2.38$. The calculated fugacity values vary between 115 MPa and 22.9 MPa (Fig.32b). The range of values gathered arises from the fact that, although they have the same experimental P-T conditions, each charge has slightly different H_2O content in the residual glass, hence imparting a different XH_2O of the coexisting fluid which thus results in different XSO_2 in each capsule. Combining these fugacities values with the experimental data of this thesis, two similar trend lines are apparent, each with a slightly different slope. For example at $\sum fS_2$, fH_2S and fSO_2 between 80 and 120 MPa the runs with

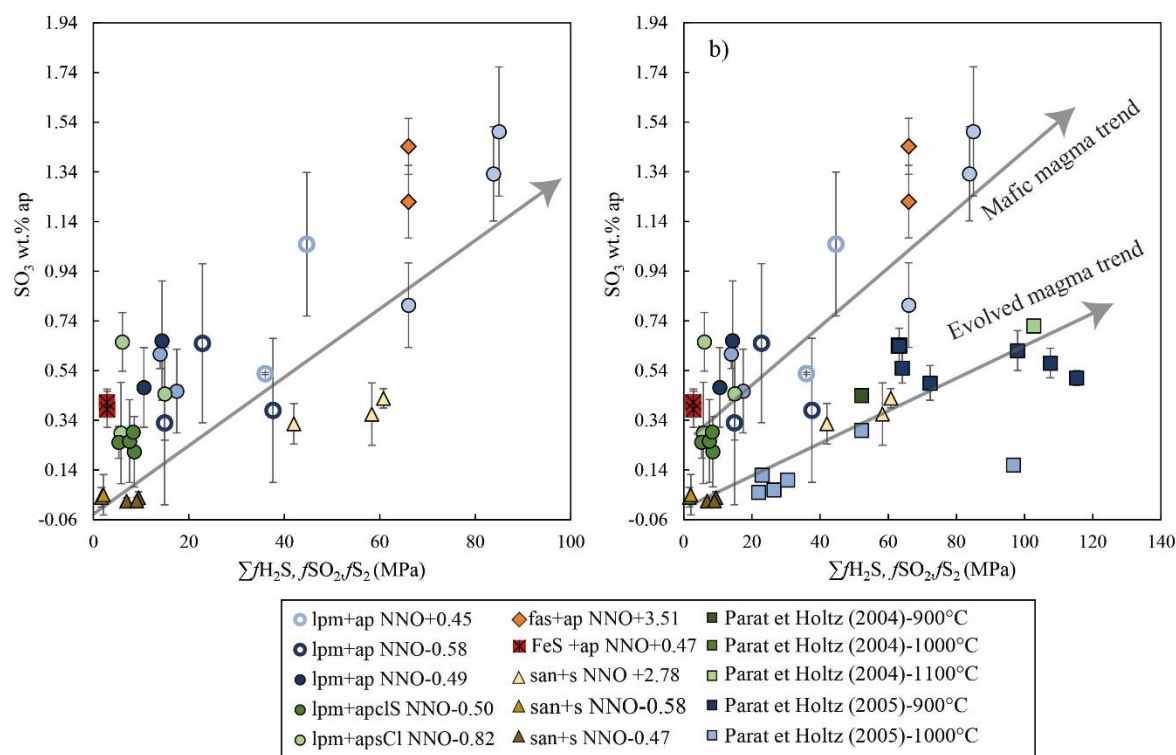


Fig. 32 Positive correlation between the amount of sulphur in apatites and the sum of the fugacity of sulphur species.

lpm+ap have SO₃ concentrations between 1.33 wt.% and 1.50 wt.%, whereas for Parat and Holtz (2004, 2005) the values are 0.16 wt.% and 0.72 wt.%. This once again underlines that a compositional property, probably the solubility of sulphur, must be taken into account. Based on the trends seen in Fig. 31b, a simple modelling approach was followed to allow one to calculate the sulphur concentration in apatite from the sum of the sulphur species fugacities and vice versa. In both models, the intercept was set to 0. The first model is for magmas with a silica content between of about 45-50 wt% (eq. 1.1), while the second is for more evolved magmas with SiO₂ wt% greater than 60 (eq. 1.2).

$$SO_3 \text{ wt. \% apatite} = 0.0182 * (\sum fS_2, fH_2S, fSO_2) \quad R^2 = 0.8635 \quad (1.1)$$

$$SO_3 \text{ wt. \% apatite} = 0.0068 * (\sum fS_2, fH_2S, fSO_2) \quad R^2 = 0.9809 \quad (1.2)$$

The following general equation relating SO₃ in apatite with $\sum fS_2, fH_2S, fSO_2$ and the SiO₂ content of the melt can be then derived:

$$SO_3 \text{ wt. \% apatite} = ((-0.0005 * SiO_2 \text{ wt\%}) + 0.0396) * (\sum fS_2, fH_2S, fSO_2) \quad R^2 = 0.99 \quad (1.3)$$

In the Chapter 5, the application of these models to natural samples will be illustrated.

4.3 S in melt and fS_2 : comparison with different models

In this section, a series of sulphur solubility models will be applied, using the fS_2 values calculated in the pyrrhotite-bearing experiments to determine the amount of sulphur in the melt. This approach enables testing the accuracy of the new protocol developed in this thesis for analyzing pyrrhotite. Accurate analysis of this mineral allows its composition to be precise enough to calculate the sulphur fugacity in the system. Four solubility models were applied for this test: the model of Clemente et al. (2004), the model of Lesne et al. (2015), the model of Li and Zhang, (2022), and the model of Boulliung and Wood, (2023).

Clemente et al. (2004) developed a thermodynamic model for sulphur solubility based on a series of experiments conducted on hydrous rhyolitic melts at temperatures between 800–1000°C. For this reason, this model was applied only to the more evolved experiments, i.e. those performed with the Santorini starting material. Lesne et al. (2015) calibrated their model using data acquired on hydrous basaltic magmas (including the data of Moune et al. 2009), with experiments performed at higher temperatures, in the range 1050-1200°C. This model was applied to the experiments conducted with the La Palma starting material.

Li and Zhang (2022) constructed a thermodynamic model based on the formalism developed by O'Neill and Mavrogenes (2002), taking into account the contribution of water and making it applicable to a broader range of compositions. Similarly, Boulliung and Wood (2023) developed a thermodynamic model for various compositions but based their calculations on anhydrous melts. Indeed, they suggest that the effect of water on the solubility of S^{6+} and S^2 is minimal.

The same solubility calculations explained in Frascerra et al., (2024) are here reported and implemented with other models for comparison with the other experiments. The results of all the models are listed in Table 15.

In Fig.33, the sulphur values in the melt calculated using the different models are compared to the content measured by EMPA. A preliminary examination shows that all the models broadly reproduce the sulphur values in the melt for the majority of the experiments.

Clemente et al., (2004) is the model applied to the fewest experiments, as it is calibrated only for rhyolitic or similarly evolved compositions. In Fig. 34A, it can be observed that this

model slightly underestimates the measured value but, in most cases, remains within the analytical error.

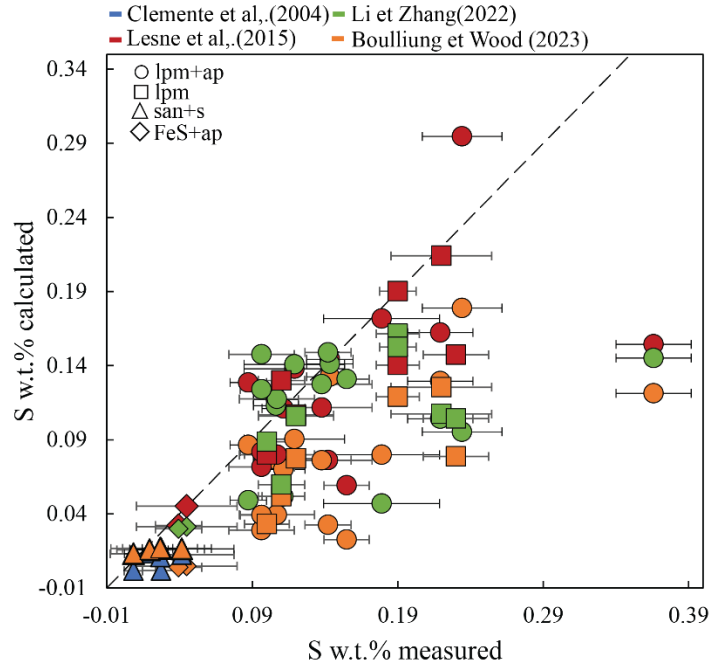


Fig. 33 Comparison between the measured sulphur content in the melt and calculated value. The dashed line represents the 1:1 correlation.

The model developed by Lesne et al. (2015) also shows good accuracy in reproducing the measured value, with only one experiment deviating significantly from the 1:1 correlation. This is experiment *lpm+ap* 14, where the model underestimates the measured value by 0.21 wt.%. Most of the calculated values fall within a range of ± 0.04 wt.%, with only one other experiment exceeding or equalling a deviation of 0.1 wt.% (Fig. 34B).

However, moving to the more general models, the situation changes slightly. It should be noted that both the model by Li and Zhang (2022) and that by Boulliung and Wood (2023) also underestimate experiment *lpm+ap* 14 by more than 0.20 wt.%. The fact that all three models show this divergence, suggests that there is an error in the measurement of sulphur in the melt. An analytical issue related to the EMPA is ruled out, since *lpm+ap* 14 is the only experiment, out of 29 products considered in this subsection, that exhibits such a discrepancy between measured and calculated values. It could be due to a problem with the homogenization of sulphur in the melt, or to analyses performed too close to a sulphur-bearing mineral that slightly altered the composition, or to the presence of microcrystals also containing sulphur, resulting from an imperfect quenching process.

Both general models reproduce the sulphur content with a reasonable accuracy (though the Boulling and Wood model tends to systematically under-estimate measured values), with only six experiments for Li and Zhang (2022) and five for Boulling and Wood (2023) showing a difference from the measured value greater than or equal to 0.1 wt.% (Fig. 34 C-D). These results also demonstrate that the fS_2 value derived from the composition of pyrrhotite is sufficiently accurate to reproduce the sulphur content of the melt using various thermodynamic models

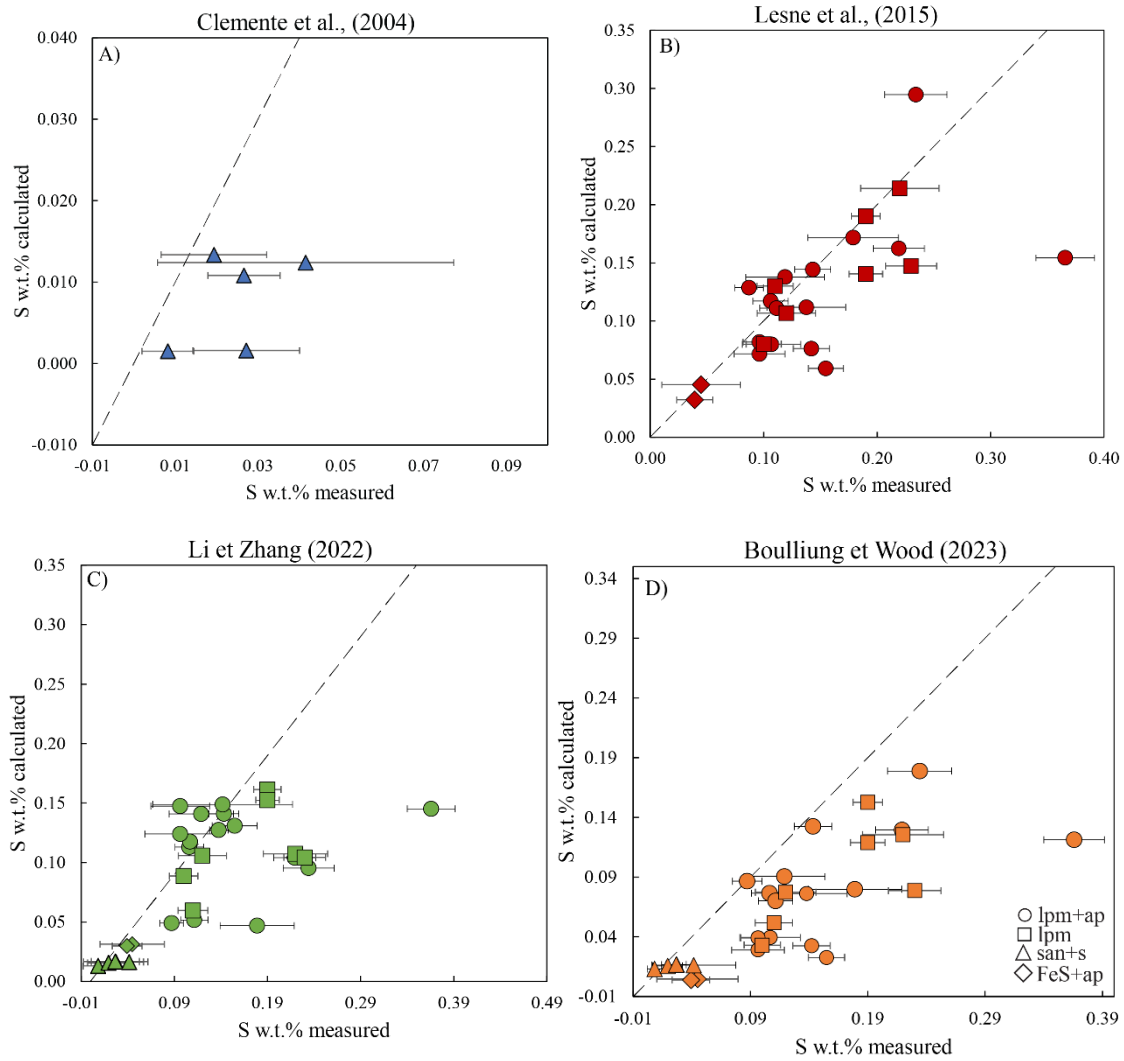


Fig. 34 Comparison between the measured sulphur content in the melt and calculated value. Panel A) show the results of the Clemente et al., (2004) model; Panel B) show the values calculated with Lesne et al., (2015); panel C) reports the results from Li et Zhang (2022); panel D) illustrate the comparison with the Boulling et Wood (2023) value. In all pannels the dashed line represents the 1:1 correlation.

	S wt.% measured	Clemente et al. (2004)	Lesne et al. (2015)	Li et Zhang (2022)	Boulliung et al. (2023)
lpm 1	0.22 (0.02)		0.21	0.11	0.13
lpm 2	0.11 (0.01)		0.13	0.06	0.05
lpm 4	0.23 (0.01)		0.15	0.10	0.08
lpm 26	0.12 (0.01)		0.11	0.11	0.08
lpm 27	0.10 (0.01)		0.08	0.09	0.03
lpm 29	0.19 (0.03)		0.14	0.16	0.12
lpm 30	0.19 (0.01)		0.19	0.15	0.15
lpm+ap 9	0.12 (0.03)		0.14	0.14	0.09
lpm+ap 10	0.14 (0.02)		0.14	0.14	0.13
lpm+ap 13	0.22 (0.02)		0.16	0.10	0.13
lpm+ap 14	0.37 (0.03)		0.15	0.15	0.12
lpm+ap 20	0.11 (0.02)		0.12	0.11	0.08
lpm+ap 21	0.11 (0.01)		0.11	0.05	0.07
lpm+ap 22	0.09 (0.01)		0.13	0.05	0.09
lpm +ap 23	0.23 (0.03)		0.29	0.10	0.18
lpm+ap 25	0.18 (0.04)		0.17	0.05	0.08
lpm+ap cl s 1	0.14 (0.01)		0.11	0.13	0.11
lpm+ap cl S 2	0.14 (0.08)		0.08	0.15	0.08
lpm+ap cl S 3	0.10 (0.03)		0.07	0.15	0.07
lpm+ap s Cl 1	0.011 (0.001)		0.08	0.12	0.08
lpm+ap s Cl 2	0.15 (0.02)		0.06	0.13	0.06
lpm+ap s Cl 3	0.10 (0.04)		0.08	0.12	0.08
FeS+ap 4	0.04 (0.02)		0.05	0.03	0.005
FeS+ap 5	0.04 (0.01)		0.03	0.03	0.004
san+s 6	0.03 (0.01)	0.002		0.02	0.02
san+s 7	0.01 (0.01)	0.002		0.01	0.01
san+s 10	0.02 (0.01)	0.01		0.02	0.02
san+s 11	0.03 (0.01)	0.01		0.02	0.02
san+s 12	0.04 (0.04)	0.01		0.02	0.02

Table 15. Content of sulphur in the melt for all experiment with pyrrhotite, calculated and measured.

4.4 Conclusion

In this chapter, it was shown that the composition of apatite does not appear to be uniquely influenced by the amount of sulphur and/or chlorine added to the system.

A positive correlation between the amount of sulphur in the apatite and the melt appears in Fig.28 and Fig. 30. However, this trend appears to be mainly influenced by two factors: fO_2 and the composition of the melt. Experiments at more oxidising conditions have on average higher SO_3 values in apatite and melt than at reducing conditions. It can also be seen that apatites synthesised from Santorini rhyodacite and haplogranite (Parat and Holtz, 2004, 2005) show lower S values for the same fO_2 . Parat and Holtz (2004, 2005) exclude that the melt composition can influence the S content of apatites. However, their observations, as also reported for natural samples (Li et al., 2024), are focused on the compositions of the major elements such as CaO, SiO_2 and K_2O . This work also shows that there are no clear trends between these elements in the melt and the amount of sulphur in the apatites (Fig. 29). In contrast, the trace elements show some interesting correlations, especially between lanthanum and cerium with the amount of sulphur in the apatites (Fig. 31). This would suggest that the sulphur in apatite is influenced by different compositional factors in the melt, such as REE and trace elements. However, these elements have not been analysed in the melt, either in this thesis or in most previous works.

In addition, a study was made about the correlation between sulphur concentration in the apatite and the fugacities of the sulphur species (fH_2S , fS_2 and fSO_2) (Fig.32). The most important finding lies in the use of sum of the three fugacities, which show two trends, depending on bulk rock compositions. Both have a positive trend: as the sum of fugacities increases, so does the sulphur content of the apatite, with the slope of the less evolved compositions being higher than that of the more evolved composition. Finally, two models were derived for the estimation of sulphur concentrations in apatite, based on the sum of the sulphur fugacities, and vice versa, for a broad range of compositions.

As a final and remarkable point, this chapter has demonstrated that the analytical protocol developed during this thesis for analyzing pyrrhotite is accurate and provides insightful constraints on the fS_2 of the system.

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Chapter 5

Application to natural systems

Application aux systèmes naturels

Ce chapitre présente les applications aux systèmes naturels des relations et des modèles entre la teneur en soufre des apatites, la teneur en soufre dans le verre et les fugacités des espèces de soufre. Les données prises dans la littérature ont été prises en considération et analysées au cours de cette thèse.

Les échantillons naturels confirment l'existence d'une corrélation positive entre la teneur en soufre dans l'apatite et dans le verre. Cependant, aucune corrélation particulière ne peut être observée entre la teneur en silice du verre et la teneur en soufre dans l'apatite. En général, il est possible de constater que les expériences de Santorin reproduisent assez bien le système naturel (données de cette thèse). Les apatites du Pinatubo (Van Hoose et al. 2013), de l'Aso-4 (Keller et al 2023), du El Chichòn (Luhr et al. 1984) et de l'éruption de Fondo Riccio dans les Champs Flegréens (données de cette étude et de Cannetelli et al. 2007) sont également réparties le long de la tendance expérimentale. Dans le détail, les échantillons mafiques naturels des Champs Flegréens présentent des valeurs très similaires aux expériences réduites de La Palma, tandis que les apatites plus oxydées des éruptions du Vésuve montrent une teneur en soufre plus élevée. Cela confirme que la fugacité de l'oxygène est un paramètre qui exerce une influence fondamentale sur la teneur en soufre des apatites.

Les éruptions d'Aso-4 et Pinatubo sont caractérisées par des fO_2 de NNO+1.1 et NNO+1.7, respectivement, mais nos expériences suggèrent que la quantité de SO_3 dans les apatites devrait être plus élevée que celles mesurées dans ces éruptions. Cependant, les conditions de température et de pression de ces événements étaient plus basses que celles des expériences menées, ce qui peut expliquer les différences observées, comme suggéré par des études précédentes (Parat et Holtz, 2004-2005).

Deux approches différentes des modèles expliqués dans le chapitre 4 sont présentées pour illustrer les applications possibles. Dans un premier temps, les modèles sont appliqués selon une approche directe, dans laquelle la teneur en soufre des apatites est dérivée de la somme de toutes les fugacités des espèces de soufre, calculées à partir de fS_2 (pyrrhotite) et de la fO_2 correspondante. En comparant les deux résultats obtenus, l'un avec la contribution de la silice (modèle général) l'autre sans (modèle spécifique), on remarque que le modèle basé sur la composition produit des valeurs plus élevées.

En comparant la teneur en SO_3 en poids dans l'apatite mesurée avec les valeurs calculées, des différences apparaissent tant pour les magmas plus évolués que pour ceux plus mafiques. Les échantillons naturels qui sont le mieux reproduits par les modèles sont ceux des Champs Flégéens, les seuls ayant été entièrement analysés avec les programmes développés au cours de cette thèse.

Cela suggère qu'il est en premier lieu nécessaire d'avoir des données chimiques plus abondantes acquises via des analyses effectuées avec les mêmes programmes. Bien évidemment, ce modèle, aussi prometteur soit-il, doit être amélioré en intégrant d'autres paramètres tels que la pression et la température.

La deuxième étape consiste en l'application inverse des modèles : à partir de la teneur en soufre des apatites, la somme des fugacités des espèces de soufre est calculée. Cette approche est importante, car elle rend plus facile l'estimation des fugacités des espèces de soufre dans les systèmes volcaniques, une estimation qui est rarement faite, le calcul des pressions de saturation en volatils se limitant presque exclusivement aux espèces H_2O et CO_2 . Cependant, cette approche donne des valeurs de fugacité des espèces soufrées parfois trop élevées, allant au-delà de 150 MPa, un chiffre qui semble peu réaliste. Cela met encore en évidence la nécessité d'intégrer la pression et la température dans les modèles et d'avoir des protocoles analytiques adaptés.

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5. Application to natural systems

This chapter shows the applications to the natural system of the relationships and models between the sulphur content of apatites with the sulphur content in melt and the fugacities of sulphur species already explained in Chapter 2. In order to do this, whenever possible, apatites, pyrrhotites and melt inclusions were analyzed during this thesis in a series of natural samples: pumices from the Minoan eruption of Santorini, lapilli and lavas from Montaña Negra 1706, La Palma 2021, a bomb from the eruption of Fasnía (Canary Islands), and lapilli from the Campi Flegrei eruptions of Fiumicello and Fondo Riccio. Moreover, literature data from large eruptions were also integrated. Table 16 lists the values of SO_3 w.t.% in the apatites, SiO_2 w.t.% in the melt inclusions and the pre-eruptive conditions used to calculate the fugacities of the sulphur species.

5.1 Geological setting

Before beginning to show the applications of the models, a brief excursus will be made on the geological setting of each eruption, not yet described in Chapter 1 which will be treated in this chapter indicating also the conditions used for the models. For the eruptions already introduced (Santorini, Fasnía e La Palma), only the pre-eruptive conditions will be introduced.

5.1.1 Campi Flegrei

The Campi Flegrei volcanic district (CFVD) is an area of about 200 km² located in the Gulf of Pozzuoli in southern Italy. This area is characterised by a succession of eruptions that spans more than 80,000 years (Osservatorio Vesuviano - I Campi Flegrei - Inquadramento). The most notable events are the two high intensity eruptions of Campanian Ignimbrite (39 ka) and Neapolitan Yellow Tuff (15 ka) (e.g., Cannatelli, 2012; Cannatelli et al., 2007). However, for this work we preferred to focus on the less evolved products belonging to the Fondo Riccio (FR) and Fiumicello (F) deposits, which are largely believed to feed the plumbing system giving rise to evolved magmas produced during large scale events (trachytes and phonolites). The FR eruption occurred around 9.5 ka next to Gauro volcano located near the centre of the CFVD (D'Antonio et al., 1999). Associated deposits indicate a Strombolian activity consisting mainly of coarse slag and ash. Fiumicello deposits are

characterised by a ring tuff produced about 55 ka on the island of Procida. This event ejected the most mafic rock so far recognized at CFVD. Only half of the crater of this eruptive center remains visible. (De Astis et al., 2004). In this thesis the compositions of apatite and pyrrhotite of these deposits were analysed, while melt inclusions could not be analysed: thus the data collected by Cannatelli et al. (2007) were taken as a reference. To calculate f_{H_2S} and f_{SO_2} , the P and T of the reservoirs from Bardeglinu's doctoral thesis (2020) were taken as reference, along with the f_{S_2} which was calculated from the pyrrhotite composition. The oxygen fugacity was taken from Cannatelli (2012) and the CO₂ content from Mangiacapra et al. (2008). All reference values are shown in Table 16.

5.1.2 Santorini

During this thesis, apatite and melt inclusions from rhyodacitic pumices belonging to the Plinian phase were analysed. However, although its presence was reported (Druitt et al., 2016), no pyrrhotite could be found. For this reason, we used the pyrrhotite composition of the LP2 pumices (Gertisser et al., 2009) to calculate f_{S_2} . This event belongs to the first explosive cycle of Santorini, and the ejected rock compositions and eruptive conditions are broadly similar to the Minoan event. The values for pressure, temperature, oxygen fugacity, H₂O content and CO₂ were taken from (Cadoux et al., 2015) (Table 16)

5.1.3 Vesuvio – Monte Somma

The geological and volcanic history of Vesuvius is very complex and only three eruptions will be considered in this thesis: the eruptions of Pompeii, Pollena and the Avellino which emitted phonolitic to phonotephritic compositions. The Plinian eruption of Pompeii in 79AD has been extensively studied, going back to Pliny the Younger's descriptions (Cioni et al., 1995 and references therein) and is divided into three main stages: an initial phreatomagmatic stage, a second stage of Plinian pumice fallout and a final stage of pyroclastic flows and surge (Cioni et al 1995). The composition of magma erupted during this eruption varies from phonolitic to tephri-phonolite ((Barberi et al., 1981; Cioni et al., 1995; Lirer et al., 1973; Wolff and Storey, 1984).

Pollena is a sub-Plinian eruption dated 472 AD ((Rosi and Santacroce, 1983; Sulpizio et al., 2005). Sulpizio et al. (2005) subdivide this eruption into a first subplinian phase, a second phase of fall and flow forming deposits and a final phreatomagmatic phase. The Avellino

Pumice eruption is dated at 3945 BP (Sevink et al 2011). The first phase is characterised by a pulsating magmatic fragmentation phase followed by a paroxysmal phase with an increase in the eruptive column. The final phase is characterised by strong phreato magmatic component related to the onset of a caldera collapse that marks the beginning of the Plinian phase (Balcone-Boissand et al 2012; Cioni et al 1999b).

The compositions of apatite and pyrrhotite of these three events were taken from Melluso et al.(2022). Both minerals were analysed in the Pompeii and Pollena eruptions, while in the Avellino eruption only apatite was analysed. The pre-eruptive conditions required to calculate the fugacities of sulphur species were taken from (Scaillet et al., 2008). The amount of CO₂ and sulphur in melt inclusions were taken from Cioni (2000) and Scaillet et al. (2008 and 2024).

	P (MPa)	T (°C)	SiO ₂ MI w.t. %	SO ₃ MI w.t. %	SO ₃ ap w.t. %	ΔNNO	fS ₂ (MPa) [§]	fH ₂ S (MPa)	fSO ₂ (MPa)	H ₂ O w.t. %	CO ₂ ppm
<i>Campi Flegrei</i>											
Fondo Riccio	200	950	50	0.22	0.20	-0.47	0.09	16.36	0.15	3	1000
Fiumicello	200	1025	50	-	0.48	-0.48	0.81	32.61	0.83	3	1000
Santorini	200	900	70	0.02	0.01	-0.86	0.01	23.29	0.01	5.7	bdl
<i>Mt Mazama – Crater Lake</i>											
Climatic eruption	200	885	69	0.03	0.06-0.36	1-1.2	0.03	1.89 – 1.50	0.50-0.79	5-6	bdl
Cleetwood	200	950	69	0.04	0.06-0.36	1.2	0.74	13.19	0.08	5-6	bdl
Llao Rocks	100	740	69	0.02	0.06-0.36	1.2	0.01	1.27	0.07	5-6	bdl
El Chichón	200	850	68	0.09	0.34	1	0.05	26.85	0.12	n.d.	-
Krakatau	880-890	100 -150	70	-	-	1.43 – 0.94	0.03-0.04	1.60-4.53	3.10–1.38	4-5	bdl
<i>Vesuvio</i>											
Pompei	192	815	55	0.02	0.99	1	0.87	38.40	3.73	6-6.5	20
Pollena	100	800	56	-	0.74	1	0.06	5.87	0.73	3-4	20
Avellino	190	785	57	0.056	0.94	-	-	-	-	5.5	-
La Palma	300	1080	50	1.19@	-	0.5	0.04	6.23	0.02	3.9	3000
Fasnia	300	1080	44.4	-	-	0.5	0.56	67.40	0.18	3.6	3000
Montaña Negra	300	1060	50	-	0.42	0.5	0.66	53.85	0.38	3.6	3000
<i>Aso Supervolcano</i>											
Early pumice	300	900	66.89	0.15	0.49	1.1	-	-	-	-	-
Late pumice	300	900	63.97	0.32	0.54	1.1	-	-	-	-	-
Late scoria	300	900	64.04	0.23	0.52	1.1	-	-	-	-	-
Pinatubo	220	760	76.89	0.017	0.18#-0.13& 0.11*	1.7	-	-	-	-	-

Table 16 List of pre-eruptive conditions used in thermodynamic models, SO₃ w.t.% in apatite and SiO₂ w.t.% in melt inclusions measured and the fugacities of sulphur calculated.

bdl= below detections limit. § from Pyrrhotite composition

- = data not available.

= SO₃ w.t.% from Van Hoose et al 2013

& = SO₃ w.t.% from Peng et al.1997

* = SO₃ from Imai et al., (1996)

@ = (Burton et al., 2023)

5.1.4 Mt Mazama

Mount Mazama, belonging to the Cascade arc, is mainly known for the caldera forming eruption of Crater Lake that occurred at about 7700 years BP, known as Climatic eruption (Mandeville et al., 2009). The emitted magma compositions range from rhyodacite to andesite. In this thesis a focus was made on the rhyodacitic members of the Climatic eruption, the Llaó Rocks deposit (~200 years before the Climatic eruption), and the Cleetwood event which erupted shortly before the 7700 BP event. Pre-eruptive conditions and the composition of pyrrhotite are from Mandeville et al. (2009). Apatite is present in the Mt Mazama deposits and was analyzed by Peng et al. (1997) and Mandeville and Langstaff (2007). However, (Peng et al., 1997) report an average value that seems to have been obtained from analyses of samples from different deposits without specifying to which eruption apatites belong, which makes difficult to use these data. Mandeville and Langstaff (2007) only published an abstract where they report the maximum and minimum SO₃ w.t.% values present in those three eruptions, respectively 0.06 w.t.% and 0.36 w.t.%.

5.1.5 Pinatubo

Mount Pinatubo is part of the Taiwan-Luzon volcanic arc and is related to the Manila subduction (Prouteau and Scaillet, 2003 and references therein). The entire arc has been active since the late Miocene (Richard et al., 1986). The eruptive history of the Pinatubo is divided into two periods: the ancestral (1 Ma-35 ka) and the modern (35 ka-current) periods. Over the last 35,000 years, the Pinatubo has produced at least 6 major eruptions before the 1991 one with volumes emitted and return times decreasing with time (Newhall and Punongbayan, 1996; Prouteau and Scaillet, 2003). The 1991 eruption, considered for this thesis, began with the production, in about 6 days, of an andesite dome. Subsequently there were a series of several lateral blasts, followed by the main Plinian event. Blasts marked a compositional change: from andesitic to dacitic, more precisely a cummingtonite-bearing dacite, which was emitted during the Plinian phase (Pallister et al., 1996; Prouteau and Scaillet, 2003). Both apatites and sulfide were found in the pyroclastic deposits (Peng et al., 1997; Prouteau and Scaillet, 2003; Scaillet and Evans, 1999; Van Hoose et al., 2013). However, available information on the composition of sulphides indicate mostly a Cu-bearing phase (bornite) though rare pyrrhotites in the dacitic pumices also occur (Hattori et

al., 1996). Sulphur in Pinatubo's apatite were analysed by Imai et al. (1996), Peng et al. (1997) and Van Hoose et al. (2013), with similar values between 0.11 w.t.% and 0.18 w.t.% SO₃. P-T- f_{O_2} are from Van Hoose et al. (2013) and Scaillet et Evans (1999) (Table 16).

5.1.6 El Chichón

El Chichón is a volcano, located along the Chiapanecan Arc in Mexico (Damon and Montesinos, 1978; Luhr et al., 1984), mainly composed by breccias and pyroclastic deposits (Luhr et al., 1984). The 1982 eruption consisted of three major pulses, one in March and two in April, which produced fallout deposits and pyroclastic flows. These three layers of deposits have a trachyandesitic composition (Luhr et al. 1984). Luhr et al. (1984) studied the mineralogy of these deposits in detail, which made it possible to derive compositional data of pyrrhotite and apatite and perform thermodynamic calculations which allowed to derive the fugacities of the sulphur species, though the calculations were done at 400 MPa, which is too high to reproduce the natural system. In a subsequent experimental work in 1990, Luhr calculated the f_{S_2} of the experiment designed to reproduce the natural system in two ways. Where pyrrhotite was present, the model of (Toulmin and Barton, 1964) was applied, although this model is calibrated to slightly lower temperatures than the eruption and does not take into account the pressure contribution. (Luhr, 1990) also constructed a fugacity diagram (f_{S_2} vs f_{O_2}) based on a vapor-saturated simplified O-H-S-Si-Ca-Fe-Ti system. Both approaches are susceptible to errors. For this reason, it was decided to redo all the thermodynamic calculations based on the pyrrhotite composition of Luhr et al. 1984 and the pre-eruptive conditions of Luhr 1990.

5.1.7 Aso

The super volcano Aso, located in southern Japan, is characterized by two main activity styles: caldera forming eruptions, plinian and ultra-plinian, with rhyolitic composition and inter-caldera activity characterised by basaltic and rhyolitic compositions. In the eruptive history there are four caldera forming eruptions from 266 ka to 86.4 ka. The data used in this thesis come from the work of (Keller et al., 2023), who specifically analyzed the Aso-4 eruption (86 ka BP) and divided the products into late-erupted scoria, late-erupted silicic pumice and early erupted silicic pumice. For this eruption, it was only possible to reconstruct the sulphur content in the apatites and the composition of the melt inclusions (Table 16), in

fact there is no evidence for the presence of pyrrhotite reported for this eruption. P-T- fO_2 are from Ushioda et al. (2020).

5.1.8 Krakatau

Krakatau volcano is part of the Sunda arc, generated by the convergent movement between the Eurasian and Indo-Australian plates. This volcano is well known for its catastrophic eruption in 1883 that caused a general cooling of the entire northern hemisphere (Mandeville et al., 1996) and references therein). The explosive activity of this eruption began in May 1883 and lasted until mid-August, opening at least three vents. The paroxysmal moment of the eruption that caused the caldera collapse was between 26-27 August (Mandeville et al. 1996). A total of 12.5 km³ of product was produced, of which 90% was rhyodacitic, 4% mafic dacite and 1% andesitic. Both apatite and pyrrhotite were observed in these samples. The pressure, temperature and fO_2 values of the white rhyodacite, used in this work, were taken from Mandeville et al 1996. The H₂O, CO₂ contents of melt inclusions and the pyrrhotite composition are from (Mandeville et al., 1998). Peng et al. (1997) report apatite composition found within andesite pumices found in the sea just after the 1883 eruption. Given the difference in composition between the rhyodacite component taken into account and also the uncertainty of sample attribution, this sample was omitted.

5.1.9 Canary Island Eruptions

Montaña Negra and Fasnía are two historical eruptions of Tenerife, a volcanic island belonging to the Canary Island archipelago, whose geology was briefly described in Chapter 1. The eruption of Montaña Negra took place between May and June 1706 and led to the destruction of many villages, including Garachico (Solana and Aparicio, 1999). The eruption had an effusive style and caused the opening of several fissural eruptive vents. The lavas emitted are mainly basalts, basanites and phonolitic tephrites, which are compositions typical of this context (Solana et Aparicio, 1999). During this thesis work, it was possible to analyse the composition of apatite and pyrrhotite in lavas and lapilli. Unfortunately, there are no data in the literature describing the pre-eruptive conditions of this eruption. To model the fugacity of the sulphur species, the pre-eruptive conditions were assumed to be close to those of the last eruption of la Palma 2021, in view of the similarity of phase assemblages between the two events (Andujar et al. under review), with the difference that Montaña Negra eruption

was likely slightly cooler (personal communication- J. Andujar). The same procedure was applied to the Fasnía and La Palma 2021 eruption, whose geological context is explained in Chapter 1. In both of these samples, it was possible to analyse the composition of pyrrhotite. In Fasnía sample, apatite was observed, yet it was impossible to analyse due to its small size. In La Palma samples no apatite was found.

5.2 SO₃ w.t.% apatite vs SO₃ w.t.% melt

A comparison is first made between the experimental data produced in this thesis and those of the natural system, both analysed during this thesis and taken from the literature. Comparing the sulphur content in the melt inclusions with that of coexisting apatites, it can be seen that the natural samples follow the experimental trend discussed in Chapter 4: as the amount of sulphur in the melt increases, the sulphur in the apatites increases (Fig.35a). In detail, even in this case, no particular correlation can be seen between the silica content of

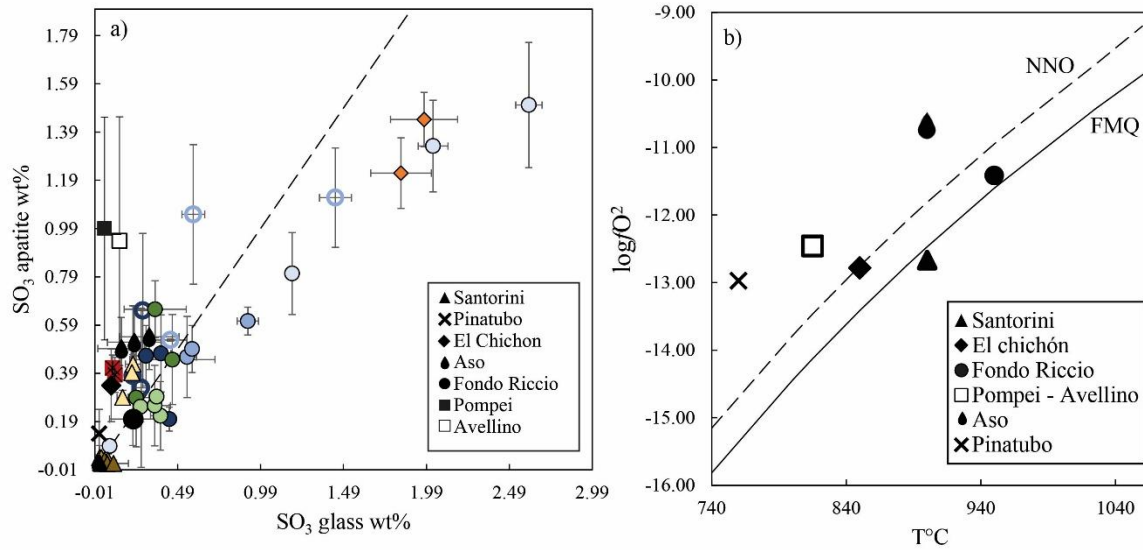


Fig. 35 The natural samples follow the positive correlation between sulphur in apatite and sulphur in melt. Coloured symbols are those from the experiments of this thesis (Panel a; the dashed line represents the 1:1 correlation.). Panel b) shows the comparison between log fO₂ and temperature of natural samples.

the melt and the sulphur content in the apatite. Owing to the lack of data, it was not possible to look for correlations between trace elements (i.e. REE) and S content. In general, it can be seen that the Santorini experiments fairly closely reproduce the natural system (data from this thesis). The apatites from Pinatubo (Van Hoose et al. 2013), Aso-4 (Keller et al 2023), El Chichón (Luhr et al. 1984) and the Fondo Riccio eruption in the Campi Flegrei (data from this study and Cannetelli et al 2007) are consistently distributed along the experimental trend. In Fig.34b the studied eruptions are plotted in a t-log fO₂ diagram. On a closer inspection, the natural mafic samples from the Campi Flegrei exhibit values very similar to the reduced La Palma experiments, while the more oxidised apatite from the Vesuvio eruptions show a higher amount of sulphur. This suggests that the oxygen fugacity is a parameter that exerts a fundamental influence on S content of apatite. The situation is further complicated by the

consideration of the Aso-4 eruption and the 1991 eruptions of Pinatubo. These eruptions are characterized by fO_2 of respectively $NNO + 1.1$ and $NNO + 1.7$ (Ushioda et al., 2020 and Scaillet et Evans, 1999). At these conditions, following our experiments, the SO_3 amount in apatites should be higher. However, it must be taken into account that the P-T conditions are quite different from our experiments. More precisely, these eruptions are cooler than our experimental conditions, around $900^\circ C$ and $760^\circ C$, respectively. Parat et Holtz (2004) suggested that temperature influences positively the amount on sulphur in apatite. This may provide an explanation for the significant differences observed between the natural samples from Aso and Pinatubo and the results of our experiments.

5.3 $\sum fH_2S, fS_2, fSO_2$ vs SO_3 w.t.% apatite

Two different approaches to the models will be shown to illustrate possible applications.

In a first step, the models will be applied in a direct approach, in which the sulphur content of the apatite species is derived from the sum of all fugacities of sulphur species, calculated from fS_2 (pyrrhotite) and the corresponding fO_2 . The results are compared with the SO_3 w.t.% actually measured in the apatites. The second step is the inverse application of the models: from the S content of the apatites, the sum of the fugacities of the sulphur species will be derived. Table X presents the SO_3 wt% values in apatite, as calculated through modeling approaches.

5.3.1 Direct approach: from pyrrhotite composition to SO_3 w.t.% in apatite

In this first part, the models will be tested with volcanic eruptions for which the compositions of pyrrhotite and apatite are known. For each eruption both equations, with and without the contributions of silica content in the melt, have been applied. Fig. 36 shows the calculated amount of SO_3 w.t.% in apatite: the values estimated with the model without the contribution of SiO_2 w.t.% are in green and those with the contribution of silica are in blue. It can be seen that in general, the values obtained from the first model are slightly higher than the general model. However, the largest difference obtained in these calculations is 0.22 w.t.% for the eruptions of Pompeii (Mt Vesuvius) and Cleetwood (Mt Mazama) (Fig.35). This difference can be explained by the fact that both models were calibrated on two specific rhyodacitic and

basanitic compositions and that therefore for some particular cases the addition of SiO_2 in the melt makes a difference. However, in all other cases the difference is below 0.07 wt.%.

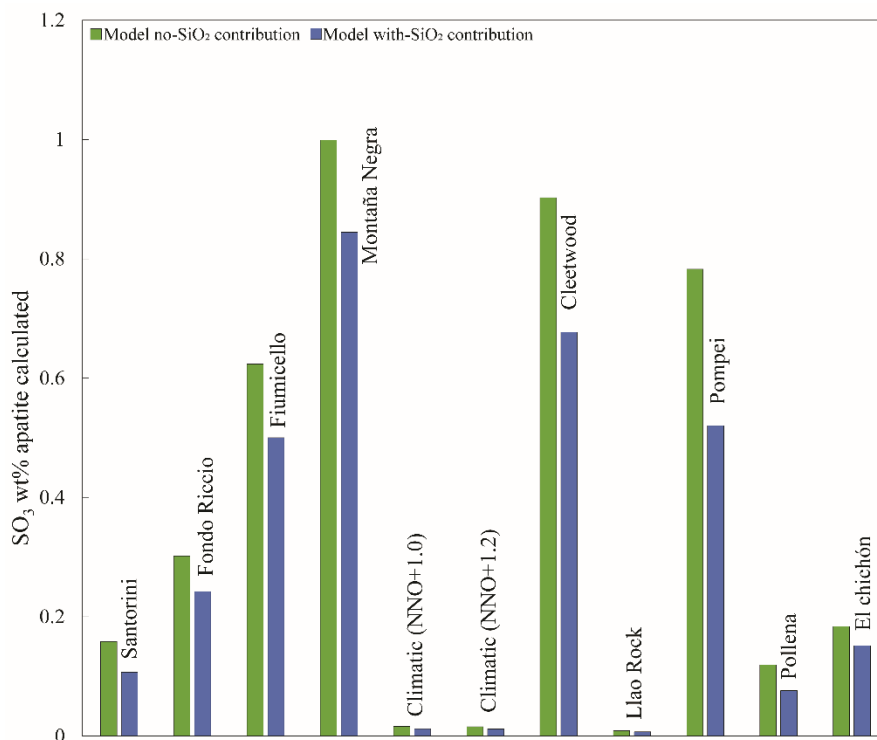


Fig. 36 Comparison of SO₃ wt.% in apatite calculated by the models with and without silica contribution, using the f_{S2} given by the pyrrhotite.

A more in-depth discussion must be undertaken in comparing the calculated values with the measured ones (Fig. 37). We first examine the more evolved magmas and then the less evolved ones. The sulfur content measured in the Santorini apatites is very low, approximately 0.02 wt.%. The values calculated using the two models are also low, yet higher than that measured (0.16–0.11 wt.% without and with the contribution of SiO_2 , respectively). These findings are consistent with a sulfur-poor system, as is believed to characterize the Minoan eruption (Cadoux et al., 2015). Peng et. al (1997) analysed apatites from other Santorini eruptions and the SO₃ w.t.% contents were also very low, at around 0.03 w.t.%, suggesting that Santorini volcano is overall a small sulphur emitter, reflecting probably regional source characteristics. For El Chichón eruption of 1982, the measured value is 0.34 w.t.% (Luhr et al., 1984) whilst the calculated values range from 0.18 w.t.% to 0.15 w.t.%. In this case, taking into account the associated error, it can be observed that our models

replicate the lowest analysed amount. In the case of the Mt Mazama eruptions, the comparisons are more difficult to do, as only maximum and minimum values (0.06 w.t.% and 0.36 w.t.%) have been reported for the three eruptions (Mandeville and Langstaff, 2007). The values calculated for these eruptions are between 0.01 and 0.02 w.t.% for the Climatic and Llao Rock eruptions but rises up to 0.9 w.t.% for Cleetwood eruption (Fig. 37B). At first sight, this discrepancy could be attributed to several factors: the first lies in the uncertainty of the values between the different apatites in the different eruptions, the second in the accuracy of the composition of the pyrrhotites, which is the basis for deriving the the fugacities of the sulphur species needed to calculate the sulphur quantities in the apatite. The uncertainty of the pyrrhotite compositions essentially arises from the calibration used for the microprobe. It is worth pointing out that (Mandeville, 1996) analysed the sulphides using a program calibrated on pyrite. As shown in Chapter 2, this set up could lead to errors of pyrrhotite composition.

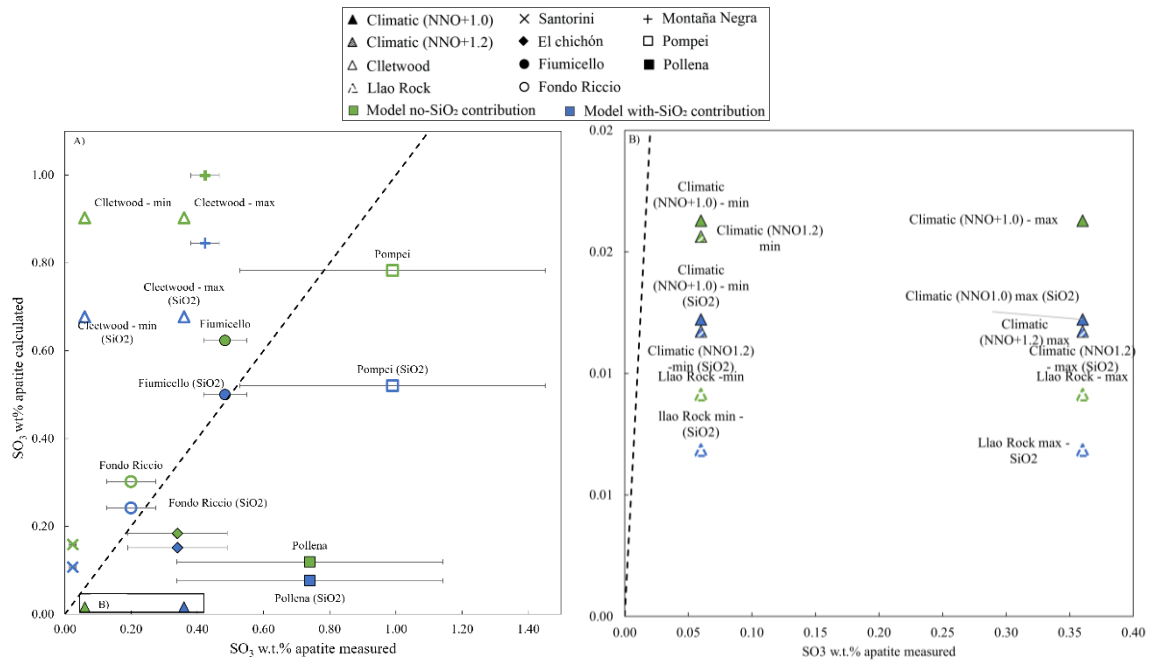


Fig. 37 Comparison between SO_3 w.t.% in apatite calculated by models and measured. In Panel A) are shown SO_3 w.t.% in apatite calculated for all eruption. In Panel B) a focus is made in the Climatic and Llao Rock eruptions. Symbols in green indicate the value obtained by the model without the silica contribution, in blue those with the silica contribution. In all panels the dashed line represents the 1:1 correlation.

We next consider eruptions of less evolved magmas (Fig. 37A). The eruption of Montaña Negra (Tenerife) ejected a magma very similar to the 2021 eruption of La Palma used as the starting material for most of the experiments. The SO_3 content of apatite measured in this eruption is 0.42 wt.% while the values calculated by the models are 1.00 wt.%, without the silica contribution, and 0.82 w.t.% with the silica contribution. It is important to reiterate that the uncertainty of the pre-eruptive conditions could lead to a miscalculation of the fugacity of sulphur. Nevertheless, the difference between measured and calculated values is intriguing, since the models are calibrated on a composition similar to that of Montaña Negra. In contrast, the samples of Campi Flegrei, Fiumicello and Fondo Riccio, both exhibit a high degree of correlation between calculated and measured values. The SO_3 values measured in the Fiumicello apatites are 0.48 w.t.% while those modelled are 0.62 w.t.% (without the silica contribution) or 0.50 w.t.% (with the silica contribution). For Fondo Riccio, the measured value is 0.20 w.t.% while the modelled values are 0.30 w.t.% without the contribution of SiO_2 and 0.24 w.t.% with the contribution of silica. In this case for the Campi Flegrei samples, the model that best reproduces the natural values is the one with the silica contribution.

Comparing the data from the Vesuvius eruptions, it can be noticed that the average of the measured values of SO_3 in the Pompeii apatite is 0.99 w.t.% and the calculated values are 0.78 w.t.% and 0.52 w.t.%, respectively without and with the contribution of silica, altogether hinting at a sulphur-rich system. For the Pollena eruption, the average of the measured values is 0.74 w.t.% and the calculated sulphur is 0.12 and 0.08 SO_3 w.t.%. This considerable difference can be primarily ascribed to the uncertainty on the quality of the analyses performed by Melluso et al. (2023). In fact, the data were collected with an EDS set up and no specific programs were used to analyze apatite and sulphide. Moreover, the S was calibrated on sphalerite, that, as already said, is not the best protocol to have a correct composition of pyrrhotite and moreover is not indicated to quantify the SO_3 w.t.% in apatite. Given the challenges in reproducing specific sulfur contents in apatite, an iterative method was employed to determine the sum of the fugacities of sulfur species that most accurately represent the SO_3 wt% in apatites. Fig. 38 presents the calculated values of the fugacity sum plotted against their theoretical counterparts. Notably, the maximum observed discrepancy

(>100 MPa) between the calculated and theoretical values is associated with the eruptions of Mt. Mazama. This large difference is essential to reproduce the minimum sulfur content in apatites reported by Mandeville and Langstaff (2007) for Cleetwood.

In contrast, the smallest discrepancy between the calculated and theoretical values is 0.6 MPa for the Fondo Riccio eruption when employing the model that includes the silica contribution. However, when utilizing the model without the silica contribution, the discrepancy increases to 4.6 MPa, which remains relatively low. Similarly, for the Fiumicello eruption, the difference calculated using the silica-inclusive model is approximately 2.25 MPa, whereas it

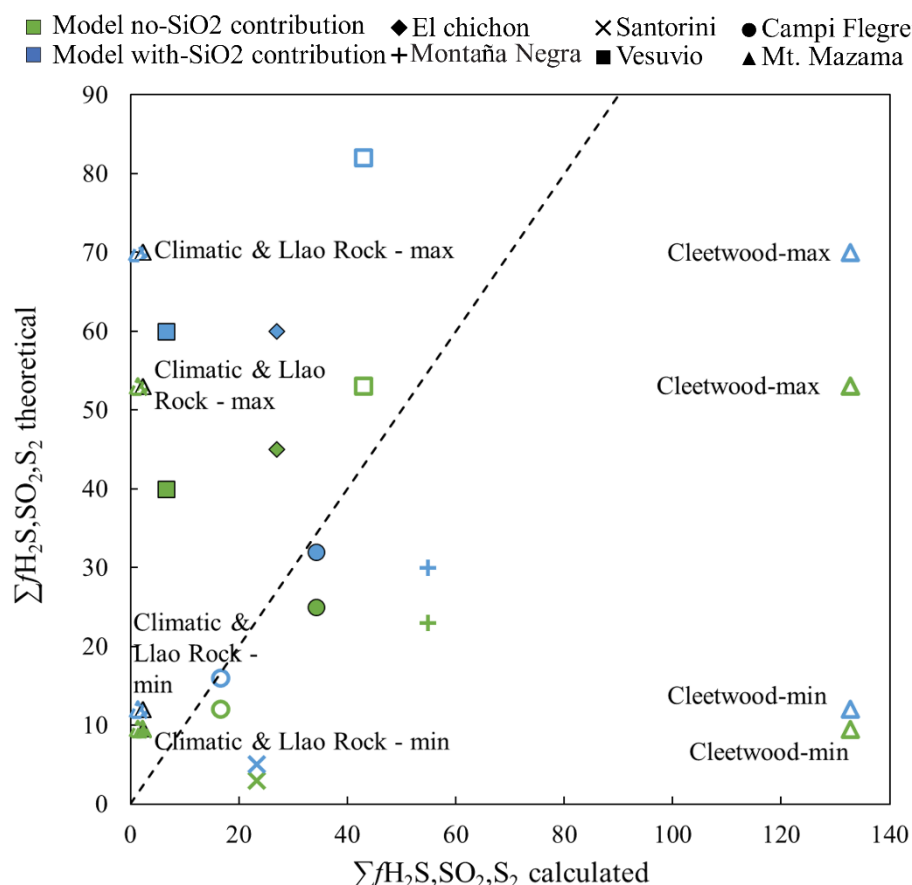


Fig. 38 Sum of the sulphur fugacities derived using available Po compositions plotted against the corresponding theoretical values corresponding to the S content of apatites. The dashed line represents the 1:1 correlation.

risers to about 9 MPa without the contribution of SiO₂.

It is important to outline that these two eruptions are the only cases where direct measurements of apatite and pyrrhotite compositions have been performed, and for which the pre-eruptive conditions are relatively well constrained.

These findings suggest that developing a comprehensive and generalized model requires not only the integration of pressure and temperature contributions but also the analysis of as many natural samples as possible using consistent programs and EMPA protocols. These additional data can then be incorporated to refine and enhance the model

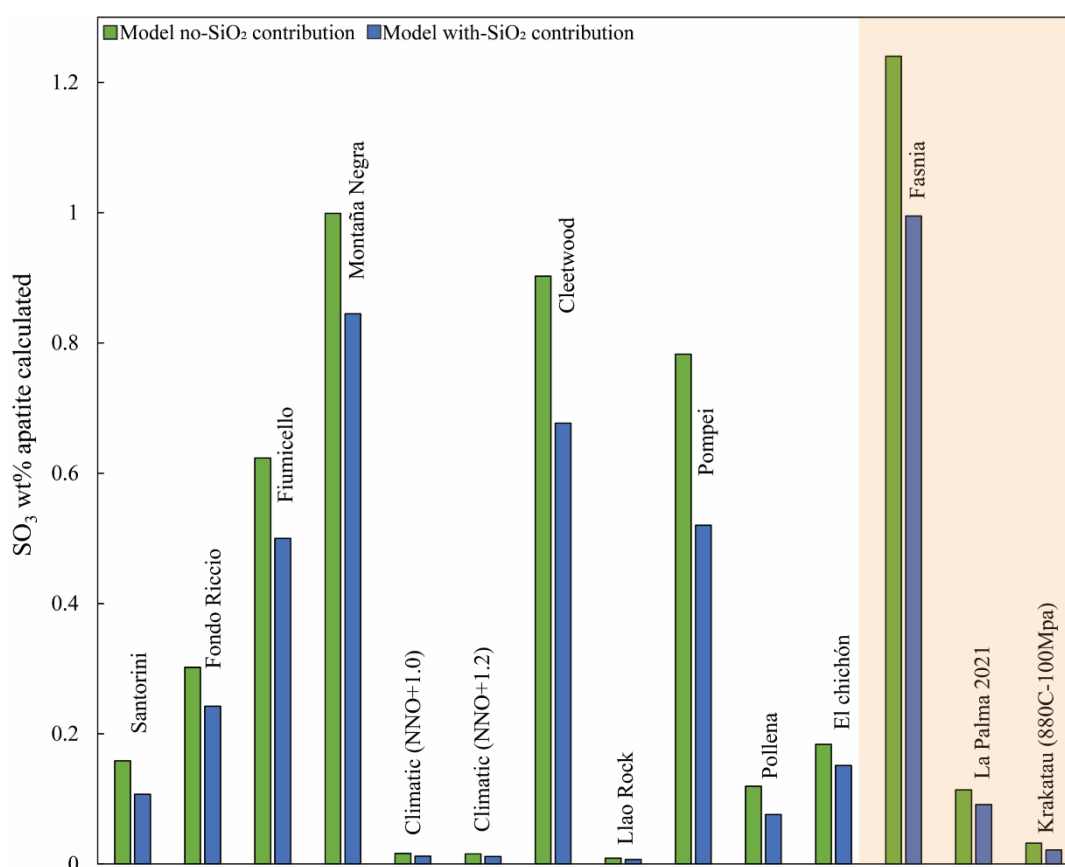


Fig. 39 Comparison between the SO₃ w.t.% in apatite inferred from Po composition and calculated by the model with and without silica contributions. The yellowish rectangular domain indicates the eruptions where apatite was not analysed or not present..

Lastly, where it was feasible to analyse or derive data from the literature on the composition of pyrrhotites, but not those of apatites, an attempt was made to estimate a potential SO₃ w.t.% value in apatites for comparison with those already known in related products (Fig. 39). In particular, pyrrhotites found in a bomb from the Fasnía eruption and in lapilli from the 2021 La Palma eruption were analysed. For the 1882 eruption of Krakatau the composition of the pyrrhotites determined by Mandeville (1996) was used. In the case of Fasnía, it can be seen that the values are very high 1.24 w.t.% without the contribution of silica and 0.99 w.t.% with the contribution of silica. On the other hand, La Palma's values

lead back to a sulphur content in apatite of SO_3 between 0.18 w.t.% and 0.14 w.t.% between the two models. It is intriguing that these two eruptions, which have a similar composition and presumably pre-eruptive compositions, result in such disparate f_{S_2} and a different sum of fugacity and SO_3 in apatite. The Krakatau eruption calculated values of SO_3 in apatite are between 0.05 and 0.03 w.t.% between the two models. The case of Fasnja and the minor inconsistencies observed in the other eruptions indicate that, although the models demonstrate a reasonable degree of accuracy in reproducing the SO_3 content in apatites, there is still room for improvement: obvious factors to be considered in the modelling are temperature and probably pressure, to enhance the precision of the calculations.

5.3.2 Inverse approach: from SO_3 w.t.% apatite to $\sum f_{\text{H}_2\text{S}}, f_{\text{S}_2}, f_{\text{SO}_2}$

In this section, we perform the reverse approach: from the concentration of S in apatites to the sum of the sulphur fugacities in the system. This approach is of fundamental importance since the estimation of sulphur fugacities is not always a straightforward process, as already illustrated. Should it be possible to estimate sulfur fugacity based on the sulfur content in apatite, this could be achieved through analysis of the mineral using an electron microprobe.

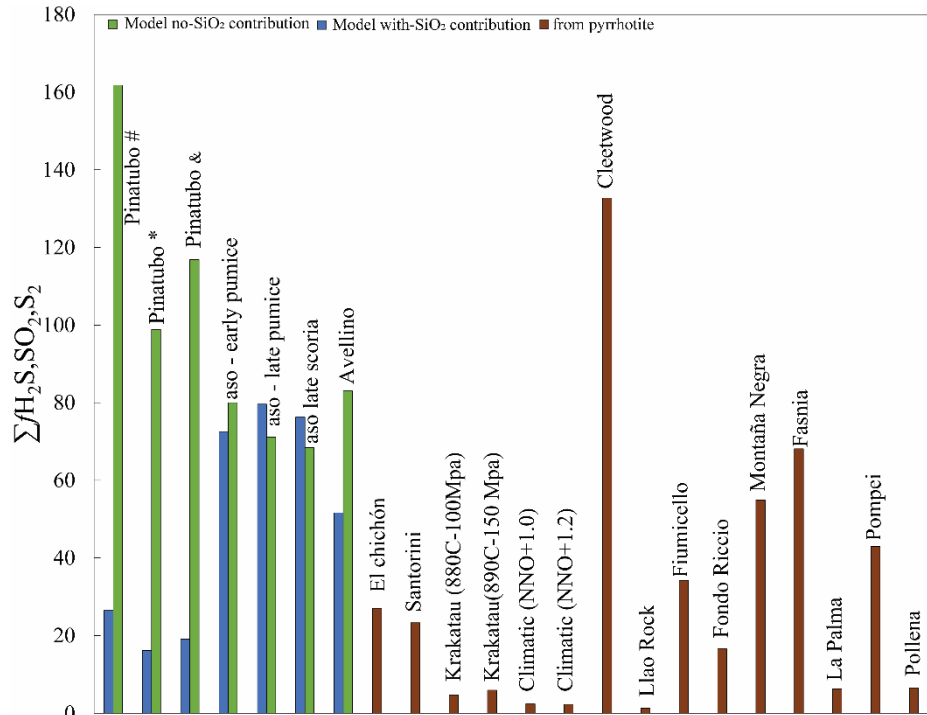


Fig. 40 The green and blue bars show the sum of the fugacities of sulphur species calculated by the two models, respectively without and with silica contribution. The brown bars indicate the sum of fugacities of sulphur species calculated using the pyrrhotite composition. The different Pinatubo value are calculated from the SO_3 w.t.% content in apatite from Van Hoose et al 2013 (#), Imai et al 1996 (*) and Peng et al 1997 (&).

The Pinatubo eruption, the Aso supervolcano and the Avellino eruption were considered in this first part. The maximum and minimum values measured with this model are 19 MPa and 80 MPa without the silica contribution and 46 and 160 MPa with the silica contribution (Fig. 40). The highest value calculated belongs to the Pinatubo eruption using the apatite composition of Van Hoose et al., (2013). In general, it can be seen that the values calculated from the apatite composition are somewhat higher than most of those calculated using the pyrrhotite composition. This again suggests that the model developed, although promising,

is not yet perfectly calibrated and should probably be improved by using other factors such as those mentioned above.

A final important aspect is that the sum of the sulphur fugacities quite often amounts to several x10 MPa. The maximum values actually come from the Pinatubo and Cleetwood data (over 150 MPa), but these values are rather unrealistic and could be due to model uncertainties (Pinatubo case) and/or to the accuracy of the pyrrhotite compositions (Cleetwood case). In all other eruptions the maximum value is around 60 MPa. This highlights that the sulphur may be an important component in the fluid phase and must be taken into account during calculation of degassing processes or when using thermodynamic models to constrain the pressure of fluid saturation which is often taken as the pressure of magma reservoir.

5.4 Conclusion

In this chapter, the data from several natural systems were compared with the experimental results. Natural samples are in accordance with the positive correlation between SO_3 w.t.% in apatite and glass found with the experiment (Fig.35). This pattern is affected by the fugacity of oxygen and also by a compositional factor that is likely more complex than a simple SiO_2 content used as the melt descriptor in this work.

The model correlating the sulphur fugacity with the SO_3 w.t.% was applied to a series of eruptions. Both direct and inverse approaches show a broad correspondence between apatite- and particularly pyrrhotite-based calculations of sulphur fugacities. Another significant factor influencing calculations is the pre-eruptive conditions, as evidenced by the results from the Montaña Negra data. Despite its current shortcomings, the modelling approach proposed in this work looks promising, as illustrated in particular by the results for Campi Flegrei. Clearly, however, further work is required, particularly in regard to investigating the impact of temperature and pressure on the proposed models. We also emphasize the importance of reanalyzing as many natural samples as possible using consistent EMPA protocols. The final section of the chapter will briefly outline the importance of accounting for sulfur species in degassing and thermodynamic calculations related to eruptions

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Chapter 6
*Conclusion
and
perspectives*

Conclusion et perspectives

Trois grands sujets liés au soufre ont été étudiés au cours de cette thèse.

Le premier est la solubilité du soufre dans une basanite, en se concentrant sur l'éruption de La Palma en 2021 ; les expériences ont été menées à température et pression constantes (1040°C, 200 MPa) et à des conditions d'oxidation variant de NNO-0.48 à NNO+4.10. De plus, des modèles thermodynamiques de dégazage ont été utilisés pour reproduire les valeurs de soufre mesurées in situ à partir des émissions gazeuses. Cette étude montre que la composition du verre résiduel, ainsi que les relations de phases et leurs proportions, sont principalement influencées par la fugacité de l'oxygène. La quantité de soufre dans le système a également un impact perceptible sur les relations de phases, bien que dans une moindre mesure.

La modélisation de la composition de la phase fluide indique que la teneur en soufre dans le fluide varie entre 1 et 10 % en poids, en fonction de la fS_2 . Globalement, les calculs suggèrent que, pour libérer 2 à 4 Mt de SO_2 , le magma pré-éruptif devait avoir une fS_2 au niveau de 0,1 MPa avec une fO_2 supérieure à NNO. Cette première partie de la thèse a donné lieu à un article publié en 2024.

Dans les deuxième et troisième grands sujets, la relation entre la teneur en soufre de l'apatite et du verre et l'influence des fugacités des espèces de soufre sur la quantité de soufre dans l'apatite ont été étudiées. À cette fin, un large éventail d'expériences avec différentes compositions et fO_2 a été réalisé. Une corrélation positive entre la teneur en soufre dans le verre et l'apatite est observée pour toutes les compositions. Cette corrélation est principalement dictée par la fugacité de l'oxygène et, de manière secondaire, par la composition du verre. La comparaison avec les données expérimentales de la littérature valide ces hypothèses. Cependant, il n'a pas été possible de trouver un facteur compositionnel unique et d'autres études à ce sujet sont nécessaires.

Parallèlement, la corrélation entre la concentration de soufre dans l'apatite et les fugacités des espèces de soufre a été étudiée. La somme des fugacités montre deux tendances positives, en fonction de la composition du système: à mesure que la somme des fugacités augmente, la teneur en soufre dans l'apatite augmente également, avec des pentes différentes pour les compositions moins évoluées et plus évoluées. Deux modèles empiriques ont ainsi été dérivés, permettant d'estimer les concentrations de soufre dans l'apatite en fonction de la

somme des fugacités du soufre et vice versa, pour des compositions basiques à siliciques courantes. En parallèle, ce travail a montré que le protocole analytique développé pour analyser la pyrrhotite est précis et fournit des contraintes utiles sur la f_{S_2} du système.

Les modèles dérivés ont été appliqués à différents systèmes naturels pour reproduire les valeurs mesurées. De cette application, deux aspects essentiels ont émergé, qui nécessitent chacun davantage d'études. Le premier aspect concerne le type de programme utilisé lors des analyses à la microsonde (tous les travaux précédents n'utilisent pas des programmes adéquats, et il y a des variations d'une étude à l'autre). Le second aspect est la nécessité d'enrichir les modèles développés dans cette thèse avec des paramètres impliquant la pression et surtout la température.

6. Conclusion and perspectives

Three macro topics related to sulphur were studied during this thesis: the sulphur solubility in a basanite composition, focusing on the La Palma 2021 eruption; the relationship between the sulphur content of apatite and melt; and the influence of fugacities of the sulphur species on the amount of S in apatite.

In the first section, the eruption of the island of La Palma in 2021 was studied. Using the erupted basanite, work was carried out on the solubility of sulphur and the phase relations of this composition at constant T and pressure (1040 °C, 200 MPa) and oxidation conditions varying from NNO-0.48 to NNO+4.10. In addition, thermodynamic degassing models were used to reproduce the sulphur values measured in situ from the gaseous emissions. The present study demonstrates that the composition of residual glass, as well as the phase relationships and their proportions, are primarily influenced by oxygen fugacity. However, the amount of sulphur in the system also has a significant impact on phase relationships, even if to a lesser extent.

These experiments highlight once more the critical influence of fO_2 on the solubility of sulphur in silicate melts. The maximum sulphur concentration in the residual glass between NNO-0.48 and NNO+1.34 is found to be 0.2 ± 0.01 wt%; meanwhile at fO_2 above NNO+2.4, the maximum value increases to 0.7–0.8 wt%.

Modeling of the fluid phase composition indicates that the sulphur content in the fluid ranges between 1 and 10 wt%, depending on fS_2 . Overall, the calculations suggest that, in order to release 2–4 Mt of SO_2 , the pre-eruptive magma must have had an fS_2 at the 0.1 MPa level with an fO_2 above NNO. This is consistent with the oxidized nature inferred for hotspot basalts (Moussallam et al., 2019) and implies that the magma coexisted with a significant amount of exsolved fluid in the crustal reservoir. This first part of the thesis produced a paper published in 2024.

Subsequently, a detailed study was made on the relationship between sulphur content in apatite and melt related to the fugacity of sulphur species. For this purpose, a wide range of experiments with different compositions and fO_2 were performed

These experiments reveal how the composition of apatite is not uniquely influenced by the amount of sulphur and/or chlorine added to the system. There is a positive correlation

between the amount of sulphur in apatite and the melt, mainly influenced by two factors: f_{O_2} and the composition of the melt.

Previous studies have concluded that the influence of melt composition on the S content in apatites, is minor, focusing on major elements like CaO, SiO₂, and K₂O, without finding clear correlations. However, this work highlights some promising correlations between trace elements (in apatite), such as lanthanum and cerium, and the amount of sulphur in apatites. This suggests that the sulphur content in apatite is influenced by various compositional factors in the melt, such as rare earth elements (REE) and other trace elements.

In parallel, the correlation between sulphur concentration in apatite and the fugacities of sulphur species (f_{H_2S} , f_{S_2} , and f_{SO_2}) was studied. The sum of the three fugacities shows two positive trends, depending on the bulk rock compositions: as the sum of fugacities increases, so does the sulphur content in apatite, with different slopes for less and more evolved compositions. Two empirical models were derived allowing to estimate sulphur concentrations in apatite based on the sum of sulphur fugacities and vice versa, for common basaltic to silicic compositions.

As a side product, this work has shown that the analytical protocol developed for analyzing pyrrhotite is accurate and provides insightful constraints on the f_{S_2} of the system.

Using the above newly acquired information, systematic work was done to apply the models to the natural systems. The results confirm the positive correlation between the w.t.% of SO₃ in apatite and glass observed in the experiments. This pattern is influenced by the fugacity of oxygen and a compositional factor likely more complex than the simple SiO₂ content.

In detail, the model correlating sulphur fugacity with the SO₃ w.t.% was applied to a series of well known eruptions. Both direct and inverse approaches show a broad correspondence between apatite and, particularly, pyrrhotite-based calculations of sulphur fugacities. This also illustrates that a significant factor influencing calculations is the pre-eruptive conditions, as evidenced by the results from the Montaña Negra data. Despite its current shortcomings, the modeling approach proposed in this work appears promising, as particularly illustrated by the results for Campi Flegrei. The final section of the chapter briefly outlines the importance of accounting for sulphur species in degassing and thermodynamic calculations related to eruptions.

Even if the results on this thesis are promising, however, further work is clearly required, especially regarding the investigation of the impact of temperature and pressure on the proposed models. It is also recommended that further experimentation be conducted in order to ascertain the effects of varying composition across a range of temperatures (T) and pressures (P). Furthermore, it would be advantageous to undertake a more comprehensive analysis of the role of trace elements in relation to sulphur content in apatites. This investigation aims to identify one or more compositional factors that influence sulphur content in apatites. In order to enhance comprehension of the correlations demonstrated in the thesis, it is also imperative to undertake a comprehensive re-analysis of a substantial number of natural samples employing consistent EMPA protocols of all S-bearing phases.

Annex

Annex

I. Experimental Glass Compositions *lpm+ap*, *fas+s*, *san+s*

Glass compositions of the second part of the thesis. All the values are normalized to 100%, but the total reported is the original one.

	Number analysis	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Total
lpm+ap1	8	46.46 (0.27)	2.29 (0.17)	14.70 (0.12)	6.47 (0.12)	0.16 (0.04)	6.94 (0.09)	12.55 (0.16)	3.79 (0.12)	1.50 (0.07)	2.50 (0.15)	2.61 (0.08)		92.86 (0.43)
lpm+ap2	7	47.06 (0.47)	2.39 (0.08)	15.28 (0.12)	5.79 (0.17)	0.21 (0.07)	6.50 (0.17)	12.07 (0.36)	4.48 (0.12)	1.84 (0.10)	2.31 (0.40)	2.03 (0.09)		92.85 (0.44)
lpm+ap3	7	48.23 (0.15)	2.40 (0.10)	16.83 (0.14)	5.22 (0.19)	0.15 (0.05)	6.14 (0.05)	10.72 (0.12)	5.20 (0.07)	2.09 (0.07)	1.74 (0.10)	1.18 (0.03)		92.32 (0.46)
lpm+ap4	8	49.96 (0.30)	2.40 (0.10)	18.21 (0.51)	5.10 (0.29)	0.24 (0.06)	5.72 (0.30)	9.41 (0.46)	5.18 (0.30)	2.02 (0.17)	1.63 (0.37)	-		90.54 (2.50)
lpm+ap9	8	45.09 (0.48)	4.14 (0.11)	15.58 (0.17)	9.04 (0.35)	0.24 (0.04)	5.67 (0.57)	12.50 (0.80)	4.24 (0.30)	1.25 (0.50)	1.93 (0.17)	0.30 (0.07)		93.42 (0.56)
lpm+ap10	6	43.90 (0.46)	3.96 (0.12)	15.28 (0.14)	11.01 (0.30)	0.28 (0.05)	5.64 (0.35)	11.42 (0.38)	4.69 (0.08)	1.76 (0.26)	1.76 (0.10)	0.36 (0.04)		93.84 (0.63)
lpm+ap11	6	43.26 (0.24)	3.79 (0.16)	14.36 (0.15)	12.17 (0.30)	0.17 (0.06)	6.10 (0.11)	12.09 (0.05)	4.11 (0.22)	1.59 (0.14)	1.87 (0.04)	0.44 (0.04)		93.67 (0.55)
lpm+ap12	7	43.60 (1.58)	3.78 (0.11)	14.78 (0.62)	11.25 (0.34)	0.19 (0.08)	5.20 (0.85)	13.39 (1.39)	4.25 (0.27)	1.32 (0.44)	2.57 (1.21)	-		92.76 (0.77)
lpm+ap13	7	44.83 (0.22)	4.17 (0.05)	16.12 (0.23)	8.95 (0.33)	0.21 (0.06)	5.73 (0.10)	11.33 (0.16)	4.31 (0.11)	1.92 (0.06)	1.86 (0.07)	0.55 (0.06)		94.22 (0.42)
lpm+ap14	7	42.66 (0.46)	3.76 (0.10)	13.95 (0.19)	11.22 (0.18)	0.20 (0.06)	6.84 (0.08)	12.44 (0.14)	3.88 (0.20)	1.59 (0.10)	2.48 (0.11)	0.91 (0.06)		93.35 (0.58)
lpm+ap15	7	42.89 (0.13)	3.60 (0.10)	14.04 (0.11)	11.62 (0.14)	0.19 (0.06)	6.84 (0.07)	12.37 (0.10)	3.81 (0.09)	1.61 (0.11)	2.38 (0.09)	0.58 (0.03)		93.36 (0.46)
lpm+ap16	7	43.26 (0.27)	3.80 (0.16)	14.43 (0.15)	11.78 (0.29)	0.20 (0.08)	6.58 (0.11)	12.37 (0.10)	3.67 (0.18)	1.68 (0.08)	2.20 (0.10)	-		93.53 (0.66)
lpm+ap20	7	46.30 (0.11)	4.13 (0.12)	15.91 (0.08)	6.88 (0.20)	0.20 (0.02)	6.62 (0.15)	11.46 (0.22)	4.19 (0.11)	2.27 (0.23)	1.76 (0.04)	0.27 (0.04)		92.20 (0.36)
lpm+ap21	8	47.76 (0.31)	4.15 (0.09)	16.58 (0.10)	4.30 (0.12)	0.20 (0.04)	6.73 (0.08)	11.31 (0.20)	4.34 (0.08)	2.64 (0.07)	1.69 (0.12)	0.28 (0.04)		92.40 (0.37)
lpm+ap22	7	49.20 (0.13)	4.20 (0.13)	17.87 (0.15)	2.69 (0.08)	0.22 (0.03)	6.26 (0.53)	10.08 (1.02)	4.88 (0.16)	2.84 (0.71)	1.51 (0.11)	0.22 (0.03)		92.88 (0.30)
lpm+ap23	7	46.43 (0.10)	4.13 (0.09)	17.10 (0.10)	6.61 (0.09)	0.25 (0.04)	5.85 (0.14)	10.37 (0.23)	4.76 (0.08)	1.99 (0.08)	1.88 (0.06)	0.58 (0.07)		93.56 (0.25)
lpm+ap24	7	46.11 (0.32)	4.12 (0.012)	15.90 (0.16)	4.99 (0.17)	0.20 (0.03)	7.23 (0.11)	12.16 (0.21)	3.98 (0.18)	1.78 (0.08)	2.07 (0.07)	1.44 (0.10)		91.80 (0.50)
lpm+ap25	5	50.11 (0.49)	3.95 (0.20)	18.34 (0.41)	4.06 (0.43)	0.23 (0.05)	4.17 (0.98)	11.31 (0.22)	4.23 (0.17)	1.20 (0.26)	1.92 (0.38)	0.45 (0.10)		92.71 (0.82)
lpm+ap26	7	43.15 (0.25)	3.52 (0.07)	13.85 (0.09)	12.08 (0.14)	0.19 (0.03)	7.22 (0.11)	12.38 (0.21)	3.69 (0.05)	1.41 (0.16)	2.45 (0.16)	-		92.08 (0.27)
lpm+ap cl S 1	5	45.68 (1.07)	3.93 (0.11)	14.96 (0.33)	6.90 (0.77)	0.21 (0.04)	7.08 (0.23)	13.12 (0.54)	2.73 (0.59)	1.56 (0.29)	2.12 (0.08)	0.34 (0.02)	1.34 (0.18)	91.67 (0.72)
lpm+ap cl S 2	7	45.05 (1.03)	3.82 (0.10)	14.62 (0.28)	7.26 (1.40)	0.23 (0.03)	6.11 (0.68)	15.10 (0.62)	3.21 (0.11)	0.69 (0.07)	2.54 (0.11)	0.35 (0.19)	0.96 (0.12)	91.26 (0.61)
lpm+ap cl S 3	3	45.69 (1.17)	3.91 (0.16)	14.85 (0.16)	6.78 (1.97)	0.24 (0.02)	5.20 (0.31)	15.63 (1.05)	3.36 (0.31)	0.78 (0.22)	2.16 (0.09)	0.24 (0.08)	1.12 (0.05)	91.03 (0.25)
lpm+ap cl S 4	8	41.90 (0.12)	3.55 (0.10)	13.71 (0.09)	11.43 (0.13)	0.19 (0.02)	7.16 (0.09)	12.63 (0.14)	3.65 (0.11)	1.79 (0.05)	2.56 (0.04)	-	1.40 (0.05)	91.83 (0.39)
lpm+ap s Cl 1	8	43.83 (0.36)	3.79 (0.11)	15.18 (0.15)	8.80 (0.12)	0.19 (0.03)	6.50 (0.17)	11.68 (0.21)	4.44 (0.47)	1.83 (0.14)	2.21 (0.10)	0.27 (0.02)	1.25 (0.07)	92.26 (0.54)
lpm+ap s Cl 2	7	43.58 (0.19)	3.65 (0.08)	14.23 (0.13)	8.78 (0.31)	0.25 (0.02)	6.84 (0.25)	13.71 (0.66)	3.78 (0.13)	1.14 (0.17)	2.42 (0.09)	0.39 (0.06)	1.20 (0.09)	91.79 (0.26)
lpm+ap s Cl 3	7	44.30 (0.28)	3.80 (0.10)	14.55 (0.19)	8.36 (0.47)	0.21 (0.02)	7.00 (0.63)	13.67 (0.92)	3.59 (0.19)	1.50 (0.67)	2.38 (0.15)	0.35 (0.10)	0.27 (0.04)	91.67 (0.52)
lpm+ap s Cl 4	7	45.03 (0.23)	3.82 (0.09)	15.01 (0.13)	8.46 (0.22)	0.24 (0.02)	5.57 (0.64)	14.00 (0.61)	4.37 (0.12)	0.85 (0.17)	2.22 (0.20)	0.36 (0.04)	-	91.44 (0.25)

fas+s 1	11	48.67 (0.56)	1.98 (0.11)	17.35 (0.15)	5.09 (0.18)	0.19 (0.07)	6.15 (0.17)	10.62 (0.22)	4.38 (0.12)	1.80 (0.12)	1.90 (0.11)	1.84 (0.18)	-	92.32 (0.45)
fas+s 3	15	50.05 (0.37)	1.98 (0.13)	16.68 (0.22)	5.02 (0.23)	0.13 (0.08)	6.44 (0.12)	10.13 (0.25)	4.03 (0.12)	1.76 (0.10)	1.76 (0.16)	1.98 (0.20)	-	92.30 (0.70)
FeS+ap4	5	60.05 (1.14)	0.86 (0.26)	19.57	3.15 (0.70)	0.13 (0.04)	0.14 (0.03)	9.58 (1.23)	3.00 (1.42)	1.71 (0.40)	0.88 (0.42)	0.11 (0.04)	0.20 (0.07)	88.72 (1.55)
FeS+ap5	4	59.93 (0.57)	0.50 (0.16)	20.73 (0.32)	2.11 (0.48)	0.09 (0.04)	0.01 (0.01)	7.38 (0.59)	4.53 (0.24)	2.97 (0.09)	0.81 (0.18)	0.10 (0.02)	0.26 (0.06)	89.41 (0.40)
san+s1	7	71.51 (0.24)	0.35 (0.03)	14.81 (0.10)	2.28 (0.12)	0.06 (0.06)	0.50 (0.02)	1.38 (0.04)	4.36 (0.06)	3.22 (0.09)	1.23 (0.11)	0.22 (0.05)	-	93.16 (0.41)
san+s2	7	70.93 (0.37)	0.36 (0.07)	14.79 (0.23)	2.89 (0.13)	0.04 (0.05)	0.54 (0.06)	1.68 (0.04)	4.35 (0.06)	3.17 (0.09)	0.97 (0.12)	0.21 (0.02)	-	92.71 (0.38)
san+s3	6	70.63 (0.69)	0.39 (0.03)	14.83 (0.15)	3.23 (0.80)	0.05 (0.04)	0.56 (0.03)	1.95 (0.15)	4.48 (0.17)	3.11 (0.13)	0.54 (0.04)	0.16 (0.03)	-	93.62 (0.63)
san+s4	7	68.10 (1.38)	0.35 (0.07)	14.33 (0.31)	2.90 (0.20)	0.07 (0.05)	0.61 (0.02)	4.44 (0.83)	4.20 (0.07)	2.99 (0.08)	1.90 (0.85)	-	-	92.46 (0.40)
san+s6	7	68.96 (0.36)	0.42 (0.08)	14.08 (0.15)	4.67 (0.13)	0.08 (0.02)	0.61 (0.02)	2.93 (0.15)	3.75 (0.14)	3.96 (0.06)	0.42 (0.11)	0.07 (0.03)	-	91.95 (0.64)
san+s7	7	69.97 (0.20)	0.40 (0.04)	14.27 (0.16)	3.42 (0.15)	0.08 (0.03)	0.62 (0.02)	42.65 (0.05)	4.25 (0.10)	4.03 (0.10)	0.25 (0.02)	0.02 (0.02)	-	93.28 (0.79)
san+s8	5	70.13 (0.21)	0.43 (0.04)	14.16 (0.13)	3.47 (0.07)	0.10 (0.04)	0.61 (0.02)	2.72 (0.07)	3.96 (0.09)	4.02 (0.07)	0.30 (0.02)	0.03 (0.02)	-	92.50 (0.35)
san+s9	5	69.85 (0.96)	0.39 (0.05)	14.10 (0.19)	2.73 (0.04)	0.09 (0.03)	0.62 (0.02)	3.53 (0.59)	3.81 (0.11)	3.92 (0.07)	0.92 (0.57)	-	-	92.20 (0.55)
san+s10	6	70.68 (0.56)	0.36 (0.05)	14.40 (0.11)	4.01 (0.14)	0.07 (0.04)	0.63 (0.02)	2.78 (0.13)	3.59 (0.67)	3.02 (0.06)	0.37 (0.07)	0.05 (0.03)	-	91.98 (0.38)
san+s11	7	70.68 (0.33)	0.40 (0.03)	14.51 (0.09)	4.06 (0.10)	0.08 (0.03)	0.65 (0.02)	2.81 (0.08)	3.42 (0.39)	2.92 (0.05)	0.33 (0.02)	0.07 (0.02)	-	91.12 (0.81)
san+s12	7	70.16 (0.77)	0.38 (0.03)	14.30 (0.12)	3.71 (0.16)	0.07 (0.03)	0.63 (0.02)	3.04 (0.44)	3.88 (0.11)	3.00 (0.05)	0.65 (0.43)	0.10 (0.09)	-	91.58 (0.56)
san+s13	7	71.09 (0.91)	0.39 (0.04)	14.51 (0.24)	2.61 (0.06)	0.07 (0.02)	3.14 (0.67)	3.14 (0.67)	3.88 (0.09)	3.01 (0.03)	0.62 (0.55)	-	-	92.12 (0.24)

II. Experimental apatite compositions

The table reports the compositions of the experimental apatite analysed with the “standard” program and, where possible, with the “trace element” program. The total reported is related to the standard program. All the elements are normalized to 100%

	Number analysis	SiO ₂	CaO	P ₂ O ₅	SO ₃	F	Cl	As ₂ O ₃	SrO	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃	ThO ₂	MnO	FeO	Total
lpm+ap1	8	0.97 (0.33)	55.64 (0.31)	41.30 (0.53)	1.50 (0.26)	0.55 (0.10)	0.04 (0.01)	0.01 (0.02)	0.10 (0.02)	bdl	0.08 (0.01)	0.12 (0.02)	0.08 (0.02)	Nd	Bdl	0.27 (0.09)	98.48 (0.51)
lpm+ap2	7	0.71 (0.52)	55.06 (1.59)	369.35 (1.34)	1.27 (0.16)	0.50 (0.06)	0.03 (0.01)	-	-	-	-	-	-	-	-	-	97.81 (2.31)
lpm+ap3	4	0.49 (0.05)	54.49 (1.46)	39.49 (1.18)	0.84 (0.17)	0.49 (0.03)	0.03 (0.01)										97.43 (0.90)
lpm+ap4	4	0.40 (0.001)	52.49 (0.96)	39.56 (1.30)	-	0.43 (0.11)	0.03 (0.001)										95.97 (1.65)
lpm+ap9	3	0.80 (0.48)	56.75 (0.36)	41.39 (0.66)	0.69 (0.22)	0.34 (0.12)	0.02 (0.001)	Bdl (0.02)	0.19 (0.02)	Bdl	0.16 (0.02)	0.18 (0.02)	0.13 (0.03)	0.01 (0.01)	0.04 (0.03)	1.51 (0.39)	96.71 (0.17)
lpm+ap10	4	0.40 (0.001)	54.13 (0.67)	40.77 (0.73)	0.47 (0.16)	0.37 (0.09)	0.02 (0.001)										96.88 (0.70)
lpm+ap11	5	0.40 (0.001)	54.53 (0.96)	40.57 (1.08)	0.20 (0.05)	0.30 (0.05)	0.01 (0.01)										96.34 (0.38)
lpm+ap12	5	3.53 (0.17)	55.40 (0.32)	41.46 (0.82)	-	0.39 (0.08)	0.02 (0.01)										95.03 (1.50)
lpm+ap13	5	0.53 (0.01)	52.19 (1.01)	39.46 (1.24)	0.35 (0.05)	0.26 (0.13)	0.02 (0.01)	Bdl (0.02)	0.15 (0.02)	Bdl	0.14 (0.04)	0.21 (0.04)	0.10 (0.05)	Bdl (0.03)	0.04 (0.02)	1.15 (0.45)	96.47 (1.08)
lpm+ap14	3	0.85 (0.44)	53.75 (1.33)	40.46 (1.82)	0.58 (0.03)	0.30 (0.18)	0.02 (0.001)	Bdl (0.03)	0.14 (0.02)	Bdl	0.09 (0.02)	0.16 (0.02)	0.08 (0.05)	Bdl (0.02)	0.04 (0.02)	0.93 (0.16)	98.01 (2.31)
lpm+ap15	4	0.43 (0.01)	52.68 (1.56)	38.87 (1.22)	0.47 (0.09)	0.14 (0.10)	0.02 (0.01)	Bdl (0.02)	0.16 (0.02)	Bdl	0.12 (0.02)	0.18 (0.02)	0.11 (0.02)	Bdl (0.02)	0.03 (0.02)	1.64 (0.47)	96.32 (1.49)
lpm+ap20	8	0.76 (0.33)	57.19 (1.39)	41.18 (1.07)	0.39 (0.35)	0.46 (0.11)	0.02 (0.001)	Bdl (0.01)	0.18 (0.01)	Bdl	0.12 (0.02)	0.17 (0.05)	0.12 (0.06)	0.01 (0.01)	0.02 (0.02)	0.74 (0.28)	97.13 (2.73)
lpm+ap21	7	0.98 (0.23)	55.93 (0.30)	41.98 (0.47)	0.62 (0.35)	0.47 (0.07)	0.02 (0.01)										100.26 (1.27)
lpm+ap22	7	0.88 (0.17)	55.74 (0.33)	42.41 (0.10)	0.37 (0.27)	0.58 (0.10)	0.02 (0.01)										100.93 (0.57)
lpm+ap23	5	2.93 (2.21)	55.17 (0.79)	40.27 (1.41)	1.05 (0.29)	0.55 (0.04)	0.03 (0.01)	bdl (0.02)	0.15 (0.02)	bdl	0.21 (0.09)	0.30 (0.09)	0.09 (0.02)	0.01 (0.01)	0.05 (0.02)	0.57 (0.07)	99.56 (0.91)
lpm+ap24	6	0.99 (0.37)	56.61 (0.87)	40.80 (0.12)	1.13 (0.22)	0.45 (0.12)	0.02 (0.01)										99.51 (1.51)

lpm+ap25	4	0.50 (0.001)	53.73 (0.37)	40.69 (0.73)	0.53 (0.004)	0.59 (0.09)	0.04 (0.01)										99.86 (0.58)
lpm+ap26	3	0.83 (0.47)	54.35 (1.42)	42.03 (1.24)	-	0.45 (0.10)	0.02 (0.01)										98.66 (0.57)
lpm+ap cl S 1	8	0.69 (0.32)	56.20 (0.62)	40.65 (0.51)	0.45 (0.19)	0.29 (0.07)	1.71 (0.07)	bdl	0.16 (0.02)	bdl	0.13 (0.02)	0.18 (0.01)	0.07 (0.01)	bdl	0.01 (0.02)	0.61 (0.05)	99.61 (1.36)
lpm+ap cl S 2	5	0.69 (0.24)	56.13 (0.46)	40.73 (0.34)	0.66 (0.12)	0.32 (0.08)	1.47 (0.12)										98.31 (2.82)
lpm+ap cl S 3	5	0.71 (0.32)	56.51 (0.70)	40.82 (0.47)	0.31 (0.21)	0.18 (0.11)	1.46 (0.06)										97.74 (1.10)
lpm+ap s Cl 1	6	0.87 (0.36)	55.95 (0.14)	41.11 (0.41)	0.25 (0.06)	0.34 (0.03)	1.49 (0.17)	bdl	0.16 (0.02)	bdl	0.14 (0.03)	0.22 (0.03)	0.12 (0.03)	0.02 (0.02)	0.01 (0.01)	0.86 (0.49)	99.07 (0.90)
lpm+ap s Cl 2	5	0.75 (0.23)	56.31 (0.51)	40.89 (0.20)	0.21 (0.14)	0.30 (0.04)	1.54 (0.03)										98.56 (0.40)
lpm+ap s Cl 3	4	1.77 (1.51)	56.20 (0.86)	40.88 (0.83)	0.23 (0.18)	0.44 (0.03)	0.48 (0.01)										98.47 (0.78)
fas+s 1	7	0.92 (0.40)	56.40 (0.64)	41.21 (0.40)	1.23 (0.14)	0.24 (0.10)	0.02 (0.01)										98.83 (0.96)
fas+s 3	7	0.43 (0.02)	56.46 (0.41)	41.28 (0.43)	1.47 (0.12)	0.33 (0.04)	0.04 (0.001)	bdl	0.12 (0.01)	bdl	0.04 (0.02)	0.08 (0.01)	0.04 (0.02)	bdl	0.07 (0.02)	0.47 (0.08)	98.76 (0.90)
FeS+ap4	9	0.35 (0.04)	55.21 (0.32)	41.35 (0.28)	0.38 (0.07)	2.51 (0.32)	0.19 (0.12)	0.09 (0.04)	0.07 (0.03)	0.02 (0.03)	0.44 (0.07)	0.54 (0.06)	0.11 (0.03)	0.02 (0.03)	0.01 (0.01)	0.31 (0.12)	100.74 (0.32)
FeS+ap5	9	0.38 (0.11)	55.28 (0.17)	41.19 (0.29)	0.41 (0.05)	2.47 (0.26)	0.25 (0.15)										102.25 (0.80)
san+s1	9	0.67 (0.05)	53.05 (0.49)	43.92 (0.44)	0.43 (0.04)	1.61 (0.19)	0.32 (0.01)	bdl	0.02 (0.01)	0.10 (0.02)	0.24 (0.03)	0.39 (0.04)	0.016 (0.02)	bdl	0.20 (0.04)	0.73 (0.05)	98.28 (0.95)
san+s2	12	0.61 (0.07)	53.68 (0.40)	43.32 (0.46)	0.39 (0.09)	1.69 (0.17)	0.30 (0.01)										98.68 (1.34)
san+s3	9	0.66 (0.06)	53.86 (0.86)	42.86 (0.44)	0.42 (0.08)	1.90 (0.60)	0.29 (0.03)										97.42 (1.88)
san+s4	9	0.61 (0.10)	55.35 (0.33)	42.38 (0.38)	bdl	1.38 (0.20)	0.23 (0.05)										84.05 (12.45)
san+s6	8	0.98 (1.18)	55.12 (0.64)	42.11 (0.60)	0.03 (0.03)	1.63 (0.16)	0.12 (0.01)	bdl	0.04 (0.02)	0.04 (0.03)	0.21 (0.02)	0.35 (0.02)	0.11 (0.05)	0.01 (0.01)	0.06 (0.02)	0.76 (0.09)	100.96 (0.69)
san+s7	9	2.99 (1.50)	53.58 (1.84)	40.51 (1.07)	0.05 (0.05)	1.80 (0.19)	0.15 (0.01)										99.56 (1.53)
san+s8	9	1.39 (1.28)	54.88 (1.47)	41.41 (0.89)	0.04 (0.02)	1.80 (0.23)	0.12 (0.02)										100.66 (1.13)
san+s9	9	1.73 (1.52)	55.03 (2.03)	41.26 (1.41)	0.03 (0.01)	1.63 (0.22)	0.14 (0.01)										99.81 (2.38)
san+s10	6	0.75 (0.18)	54.73 (0.62)	42.65 (0.59)	0.03 (0.02)	1.70 (0.10)	0.13 (0.01)	bdl	0.02 (0.1)	0.06 (0.01)	0.23 (0.01)	0.37 (0.02)	0.11 (0.04)	0.01 (0.02)	0.07 (0.03)	0.68 (0.04)	99.64 (3.76)

san+s11	6	0.73 (0.16)	54.62 (0.27)	42.81 (0.34)	0.02 (0.01)	1.67 (0.16)	0.16 (0.01)	98.79 (3.75)
san+s12	6	0.92 (0.20)	54.78 (0.79)	42.39 (0.43)	0.02 (0.01)	1.76 (0.20)	0.13 (0.01)	99.17 (4.55)
san+s13	6	1.47 (1.34)	54.02 (0.48)	42.58 (1.04)	bdl	1.78 (0.07)	0.15 (0.01)	100.50 (4.48)

III. Experimental pyrrhotite compositions

All compositions of the experimental pyrrhotite are reported for each analytical session. Elements are normalized to 100% and the values of totals are the original.

	<i>date</i>	Number analysis	<i>S</i>	<i>Fe</i>	<i>Ni</i>	<i>Cu</i>	<i>Total</i>
<i>lpm+s 1</i>	16.12.2022	8	39.72 (0.23)	59.83 (0.30)	0.20 (0.02)	bdl	99.47 (0.56)
	26.09.2023	7	37.52 (1.05)	60.25 (0.94)	0.25 (0.18)	bdl	92.71 (3.21)
	23.10.2023	5	37.94 (0.43)	61.73 (0.36)	0.15 (0.02)	bdl	98.78 (0.36)
	09.02.2024	5	37.87 (0.49)	60.99 (0.35)	0.18 (0.03)	bdl	97.40 (1.62)
<i>lpm+s 2</i>	16.12.2022	10	39.45 (0.36)	60.13 (0.34)	0.27 (0.02)	bdl	100.07 (0.50)
	26.09.2023	5	38.38 (0.09)	61.33 (0.08)	0.29 (0.02)	bdl	89.88 (8.24)
	23.10.2023	6	36.99 (0.10)	62.43 (0.09)	0.25 (0.02)	bdl	98.55 (0.54)
	09.02.2024	5	37.46 (0.36)	61.16 (0.23)	0.24 (0.03)	bdl	97.59 (1.22)
<i>lpm+s 4</i>	16.12.2022	7	39.63 (0.13)	60.01 (0.13)	0.34 (0.01)	bdl	101.01 (0.36)
	26.09.2023	7	38.08 (0.77)	61.57 (0.77)	0.34 (0.02)	bdl	94.54 (4.84)
	13.11.2023	6	40.68 (0.13)	58.98 (0.15)	0.31 (0.04)	bdl	102.18 (0.31)
	09.02.2024	5	37.98 (0.19)	61.63 (0.20)	0.35 (0.02)	bdl	99.53 (0.92)
<i>lpm+s 26</i>	16.12.2022	5	39.51 (0.19)	59.94 (0.24)	0.16 (0.03)	bdl	99.16 (0.67)
	26.09.2023	7	38.18 (0.48)	61.70 (0.44)	0.12 (0.04)	bdl	92.28 (3.98)
	09.02.2024	4	37.42 (0.61)	61.46 (0.74)	0.17 (0.03)	bdl	95.78 (0.48)
	22.03.2024	3	37.64 (0.41)	61.96 (0.33)	0.18 (0.01)	bdl	98.61 (1.06)
<i>lpm+s 27</i>	16.12.2022	6	38.67 (0.29)	60.89 (0.42)	0.17 (0.03)	bdl	99.29 (0.72)
	26.09.2023	6	37.68 (0.52)	61.73 (0.41)	0.21 (0.07)	bdl	95.48 (1.02)
	09.02.024	4	37.20 (0.17)	62.36 (0.19)	0.14 (0.02)	bdl	96.60 (0.66)
	26.02.2024	5	35.29 (0.31)	64.25 (0.30)	0.26 (0.02)	bdl	100.66 (1.21)
<i>lpm+s 29</i>	16.12.2022	3	39.60 (0.43)	60.08 (0.41)	0.24 (0.03)	bdl	98.21 (1.16)
	26.09.2023	7	37.51 (1.07)	61.95 (1.14)	0.37 (0.04)	bdl	95.98 (2.13)
	09.02.2024	5	37.86 (0.23)	61.79 (0.19)	0.28 (0.05)	bdl	98.49 (0.67)
	19.03.2024	5	37.17 (0.07)	62.44 (0.06)	0.35 (0.03)	0.02 (0.01)	99.91 (0.64)
<i>lpm+s 30</i>	16.12.2022	2	39.07 (0.23)	59.68 (0.08)	0.89 (0.05)	bdl	98.89 (1.81)
	26.09.2023	6	38.12 (0.49)	61.29 (0.43)	0.53 (0.06)	bdl	97.05 (1.75)
	09.02.2024	3	37.72	61.79	0.48	bdl	99.76

			(0.06)	(0.06)	(0.05)		(0.86)
	19.03.2024	5	37.26 (0.14)	62.13 (0.18)	0.57 (0.10)	0.02 (0.02)	101.13 (0.34)
<i>lpm+ap 9</i>	26.04.2023	7	39.93 (0.15)	59.74 (0.17)	0.18 (0.04)	bdl	101.86 (0.37)
	26.09.2023	8	39.86 (0.49)	64.16 (1.04)	0.18 (0.04)	bdl	95.51 (1.70)
	13.11.2023	6	40.72 (0.17)	58.84 (0.11)	0.16 (0.02)	bdl	100.28 (0.40)
	09.02.2024	5	37.44 (0.41)	62.07 (0.27)	0.19 (0.04)	bdl	99.64 (0.56)
<i>lpm+ap 10</i>	26.04.2023	7	39.78 (0.10)	59.85 (0.13)	0.28 (0.03)	bdl	101.81 (0.18)
	26.09.2023	3	38.31 (0.12)	61.54 (0.12)	0.16 (0.03)	bdl	95.4 (2.04)
	13.11.2023	5	40.83 (0.26)	58.64 (0.13)	0.19 (0.03)	0.01 (0.01)	99.70 (0.81)
	09.02.2024	4	37.00 (0.16)	61.79 (0.28)	0.18 (0.06)	bdl	98.09 (0.71)
<i>lpm+ap 13</i>	22.03.2024	5	38.58 (0.67)	61.08 (0.60)	0.14 (0.03)	bdl	99.11 (0.93)
	26.04.2023	7	40.57 (0.40)	59.16 (0.40)	0.17 (0.014)	bdl	101.94 (0.36)
	26.09.2023	5	39.32 (0.52)	59.66 (0.59)	0.12 (0.02)	bdl	94.40 (2.76)
	23.10.2023	5	38.42 (0.79)	61.41 (0.75)	0.13 (0.04)	bdl	98.73 (0.25)
<i>lpm+ap 14</i>	26.04.2023	8	40.54 (0.34)	58.58 (0.33)	0.49 (0.09)	bdl	101.14 (1.15)
	26.09.2023	5	38.55 (0.73)	60.93 (0.71)	0.52 (0.08)	bdl	93.61 (3.21)
	23.10.2023	3	37.64 (0.25)	61.59 (0.19)	0.44 (0.08)	bdl	97.84 (0.55)
	09.02.2024	3	37.79 (0.32)	61.02 (0.80)	0.35 (0.01)	bdl	96.60 (1.74)
<i>lpm+ap 20</i>	23.10.2023	7	37.62 (0.77)	62.20 (0.78)	0.10 (0.02)	bdl	98.93 (0.90)
	13.11.2023	6	40.74 (0.40)	59.08 (0.43)	0.08 (0.03)	bdl	100.20 (0.70)
	01.12.2023	5	37.10 (0.83)	62.73 (0.84)	0.08 (0.04)	bdl	98.02 (2.27)
	26.02.2024	5	36.96 (0.13)	62.91 (0.13)	0.12 (0.02)	bdl	101.94 (0.31)
<i>lpm+ap 21</i>	23.10.2023	7	37.55 (0.53)	62.39 (0.60)	0.01 (0.02)	bdl	98.84 (0.43)
	13.11.2023	7	41.50 (0.16)	58.32 (0.12)	0.01 (0.01)	bdl	100.38 (0.27)
	01.12.2023	6	38.05 (0.11)	61.90 (0.13)	0.03 (0.03)	bdl	100.41 (0.53)
	26.02.2024	5	36.33 (0.04)	63.63 (0.03)	0.03 (0.01)	bdl	102.09 (0.24)
<i>lpm+ap 22</i>	23.10.2023	7	37.91 (0.24)	61.80 (0.23)	0.03 (0.02)	bdl	98.54 (0.29)
	13.11.2023	7	41.90 (0.75)	57.68 (0.37)	0.02 (0.02))	bdl	98.73 (2.82)
	01.12.2023	2	38.21 (0.01)	61.74 (0.1)	bdl	bdl	100.03 (0.53)
	26.02.2024	5	36.75 (0.12)	63.20 (0.13)	0.04 (0.03)	bdl	101.98 (0.31)
<i>lmp+ap 23.</i>	26.09.2023	4	39.48 (0.57)	60.40 (0.55)	0.12 (0.03)	0.01 (0.01)	95.90 (1.94)

	23.10.2023	6	38.74 (0.36)	61.07 (0.37)	0.10 (0.03)	0.01 (0.01)	98.75 (0.35)
	13.11.2023	6	42.63 (0.40)	57.07 (0.37)	0.12 (0.02)	0.04	100.34
	09.02.2024	5	38.51 (0.37)	61.20 (0.38)	0.10 (0.01)	0.03 (0.01)	99.17 (0.32)
<i>lmp+ap 24</i>	26.09.2023	3	39.15 (1.11)	60.54 (1.04)	0.07 (0.02)	bdl	95.20 (1.15)
	23.10.2023	1	39.36	59.23	0.08	0.00	98.82
	13.11.2023	4	42.93 (0.27)	56.98 (0.28)	0.07 (0.01)	bdl	101.22 (0.49)
<i>lmp+ap 25</i>	26.09.2023	6	39.35 (0.75)	60.56 (0.77)	0.08 (0.02)	bdl	93.07 (5.18)
	23.10.2023	2	38.21 (0.16)	61.49 (0.02)	0.06 (0.01)	bdl	98.35 (0.35)
	13.11.2023	6	42.23 (0.44)	57.10 (0.20)	0.07 (0.03)	bdl	99.64 (0.95)
	09.02.2024	5	38.66 (0.45)	61.03 (0.41)	0.09 (0.01)	bdl	98.71 (0.79)
<i>lpm+ap cl S 1.</i>	09.02.2024	5	38.05 (0.18)	61.70 (0.20)	0.23 (0.04)	bdl	100.06 (0.22)
	26.02.2024	5	36.25 (0.06)	63.50 (0.06)	0.20 (0.02)	bdl	101.76 (0.26)
	19.03.2024	5	37.72 (0.14)	61.95 (0.12)	0.22 (0.02)	0.03 (0.01)	100.72 (0.79)
	22.03.2024	5	38.18 (0.15)	61.58 (0.14)	0.21 (0.02)	bdl	100.70 (0.59)
<i>lpm+ap cl S 2.</i>	09.02.2024	5	37.65 (0.20)	62.03 (0.18)	0.28 (0.04)	bdl	99.63 (0.61)
	26.02.2024	5	35.76 (0.08)	63.85 (0.15)	0.26 (0.03)	bdl	100.56 (0.84)
	19.03.2024	4	37.04 (0.15)	62.38 (0.15)	0.31 (0.02)	0.03 (0.01)	99.82 (0.06)
	22.03.2024	5	37.57 (0.12)	61.93 (0.20)	0.28 (0.04)	bdl	99.67 (0.87)
<i>lpm+ap cl S 3.</i>	09.02.2024	4	36.71 (0.35)	61.58 (0.17)	0.33 (0.01)	bdl	96.25 (1.57)
	26.02.2024	3	34.50 (0.51)	62.64 (0.76)	0.30 (0.02)	bdl	95.41 (3.45)
	22.03.2024	2	37.15 (0.06)	61.47 (0.10)	0.31 (0.02)	bdl	97.70 (0.68)
<i>lpm+ap s Cl 1.</i>	09.02.2024	5	37.59 (0.15)	62.25 (0.15)	0.12 (0.01)	bdl	99.54 (0.31)
	26.02.2024	5	35.64 (0.19)	64.22 (0.23)	0.11 (0.03)	bdl	101.30 (1.15)
	19.03.2024	5	37.02 (0.08)	62.79 (0.07)	0.14 (0.01)	0.02 (0.01)	101.29 (0.14)
	22.03.2024	5	37.43 (0.06)	62.42 (0.07)	0.13 (0.02)	bdl	100.80 (0.24)
<i>lpm+ap s Cl 2.</i>	09.02.2024	5	37.63 (0.12)	62.21 (0.12)	0.15 (0.01)	bdl	99.97 (0.53)
	26.02.2024	5	35.90 (0.08)	63.93 (0.08)	0.16 (0.03)	bdl	102.22 (0.17)
	19.03.2024	5	37.23 (0.04)	62.51 (0.04)	0.20 (0.03)	0.02 (0.01)	101.12 (0.18)
	22.03.2024	5	37.75 (0.11)	62.03 (0.12)	0.18 (0.02)	bdl	101.07 (0.32)
<i>lpm+ap s Cl 3.</i>	09.02.2024	5	37.70 (0.14)	62.08 (0.11)	0.18 (0.02)	bdl	99.74 (0.39)
	26.02.2024	5	35.81 (0.22)	63.86 (0.15)	0.12 (0.02)	bdl	101.71 (0.89)

	19.03.2024	5	37.23 (0.09)	62.55 (0.08)	0.17 (0.03)	0.02 (0.01)	100.83 (0.37)
	22.03.2024	5	37.43 (0.07)	62.32 (0.43)	0.14 (0.01)	bdl	9.97 (1.00)
<i>san+s 6</i>	26.09.2023	5	38.89 (0.58)	65.72 (1.87)	0.08 (0.02)	bdl	95.54 (1.25)
	23.10.2023	7	37.38 (0.09)	62.47 (0.15)	0.06 (0.03)	bdl	99.18 (0.57)
	01.12.023	6	37.91 (0.36)	61.96 (0.35)	0.05 (0.01)	bdl	100.09 (0.60)
	22.03.2024	5	37.66 (0.35)	62.16 (0.32)	0.06 (0.01)	Bdl	99.27 (1.12)
<i>san+s 7</i>	26.09.2023	4	37.87 (0.78)	62.07 (0.75)	0.06 (0.04)	bdl	96.34 (1.08)
	23.10.2023	7	37.14 (0.96)	62.71 (0.93)	0.05 (0.03)	bdl	98.14 (1.82)
	01.12.2023	6	37.52 (0.44)	62.39 (0.42)	0.04 (0.02)	bdl	99.79 (0.84)
	22.03.2024	5	37.90 (0.14)	61.96 (0.10)	0.05 (0.02)	Bdl	100.35 (0.32)
<i>san+s 10.</i>	26.09.2023	5	40.27 (0.72)	64.43 (1.97)	0.04 (0.02)	bdl	95.53 (2.35)
	23.10.2023	7	37.36 (0.15)	62.58 (0.15)	0.02 (0.02)	bdl	99.13 (0.45)
	13.11.2023	6	41.34 (0.14)	58.52 (0.16)	0.05 (0.01)	bdl	101.23 (0.55)
	09.02.2024	5	37.76 (0.21)	62.13 (0.20)	0.03 (0.01)	bdl	99.76 (0.68)
<i>san+s 11</i>	26.09.2023	5	37.65 (0.56)	62.33 (0.57)	0.02 (0.02)	bdl	95.44 (1.08)
	23.10.2023	6	37.27 (0.42)	62.60 (0.41)	0.04 (0.022)	bdl	98.60 (0.71)
	13.11.2023	6	41.28 (0.45)	58.36 (0.25)	0.03 (0.02)	bdl	100.13 (0.99)
	09.02.2024	6	37.97 (0.37)	61.84 (0.39)	0.04 (0.02)	bdl	99.02 (0.95)
<i>san+s 12</i>	26.09.2023	5	38.45 (0.30)	61.49 (0.30)	0.06 (0.01)	bdl	95.71 (0.95)
	23.10.2023	6	37.32 (0.25)	62.52 (0.35)	0.02 (0.02)	bdl	99.06 (0.91)
	13.11.2023	6	41.47 (0.40)	58.37 (0.53)	0.05 (0.01)	bdl	100.98 (0.85)
	22.03.2024	5	37.62 (0.44)	62.21 (0.37)	0.04 (0.02)	bdl	99.34 (1.18)
<i>FeS+ap 4</i>	26.09.2023	5	38.31 (0.16)	61.64 (0.16)	0.05 (0.01)	bdl	97.44 (0.54)
	23.10.2023	6	36.77 (0.11)	63.20 (0.08)	0.01 (0.02)	bdl	99.52 (0.26)
	01.12.2023	6	37.37 (0.13)	62.58 (0.12)	0.03 (0.02)	bdl	101.15 (0.58)
	09.02.2024	5	37.57 (0.19)	62.34 (0.20)	0.05 (0.001))	bdl	100.80 (0.60)
<i>FeS+Ap 5.</i>	26.09.2023	9	38.42 (0.29)	61.55 (0.29)	0.03 (0.01)	bdl	98.00 (0.87)
	23.10.2023	7	36.88 (0.10)	63.11 (0.10)	0.01 (0.10)	bdl	99.69 (0.21)
	01.12.2023	7	37.26 (0.58)	62.70 (0.57)	0.03 (0.02)	bdl	100.99 (1.02)
	09.02.2024	5	37.47 (0.23)	62.49 (0.22)	0.03 (0.01)	bdl	101.27 (0.36)

IV. Natural samples compositions

<i>Pyrrhotite</i>						
	Number analysis	S	Fe	Ni	Cu	Total
<i>Fiumicello</i>	3	38.39 (0.19)	61.13 (0.16)	0.08 (0.02)	0.37 (0.02)	100.94 (0.22)
<i>Fondo Riccio</i>	2	38.10 (0.35)	61.63 (0.46)	0.02 (0.46)	0.21 (0.10)	101.20 (0.46)
<i>Fasnia</i>	4	36.53 (0.35)	61.41 (2.56)	2.06 (2.53)	bdl	102.76 (0.16)
<i>La Palma</i>	4	36.18 (0.09)	61.87 (0.47)	1.24 (0.42)	0.67 (0.21)	100.48 (0.80)
<i>Montaña Negra</i>	4	37.29 (0.86)	62.26 (1.01)	0.04 (0.02)	0.29 (0.29)	102.36 (2.23)

Apatite							
	Number analysis	SiO ₂	CaO	P ₂ O ₅	SO ₃	F	Total
Fiumicello	8	1.00	54.74	40.67	0.48	2.38	99.60
		(1.26)	(0.38)	(0.91)	(0.07)	(0.21)	(2.66)
Fondo	5	0.39	55.03	41.02	0.20	2.37	98.53
Riccio		(0.07)	(0.32)	(0.22)	(0.07)	(0.15)	(1.68)
Montaña	3	1.43	54.63	39.90	0.42	3.44	102.08
Negra		(0.98)	(0.33)	(1.08)	(0.04)	(0.38)	(0.69)
Santorini	9	1.12	53.87	41.84	0.01	2.01	102.44
		(0.94)	(0.59)	(0.48)	(0.02)	(0.15)	(1.81)

V. *Model application to natural samples*

	Without SiO ₂ contribution			With SiO ₂ contribution		
	SO ₃ wt% apatite calculated	Calculated $\Sigma fS_2, fH_2S, fSO_2$ Mpa	Theoretical $\Sigma fS_2, fH_2S, fSO_2$ Mpa	SO ₃ wt% apatite calculated	Calculated $\Sigma fS_2, fH_2S, fSO_2$ Mpa	Theoretical $\Sigma fS_2, fH_2S, fSO_2$ Mpa
Santorini	0.16	-	3.00	0.11		5.00
Climatic (NNO+1.0)	0.02		9.50	0.01		12.00
Climatic (NNO+1.2)	0.02		9.50	0.01		12.00
Cleetwood	0.90		9.50	0.68		12.00
Llao Rock	0.01		9.50	0.01		12.00
El chichón	0.18		45.00	0.15		60.00
Fiumicello	0.62		25.00	0.50		32.00
Fondo riccio	0.30		12.00	0.24		16.00
Montaña Negra	1.00		23.00	0.84		30.00
Vesuvio						
Pompei	0.78		53.00	0.52		82.00
Pollena	0.12		40.00	0.08		60.00
Pinatubo#		26.47			161.80	
Pinatubo*		16.18			98.88	
Pinatubo&		19.12			116.85	
Aso - early pumice		72.44			80.01	
Aso - late pumice		79.63			71.10	
Aso late scoria		76.26			68.42	
Avellino		51.65			83.02	

The different Pinatubo value are calculated from the SO₃ w.t.% content in apatite from Van Hoose et al 2013 (#), Imai et al 1996 () and Peng et al 1997 (&).*

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Diletta FRASCERRA

*Etude expérimentale de la distribution du soufre entre l'apatite et les
liquides silicatés : application au dégazage volcanique*

Le dégazage magmatique est un processus universel qui façonne notre atmosphère ainsi que celles des autres planètes, et il provoque également de nombreuses concentrations minérales d'intérêt économique. Le soufre est un élément volatil qui influence de manière fondamentale le dégazage magmatique. Parmi les minéraux capables d'enregistrer l'activité des éléments volatils dans les magmas, l'apatite est certainement l'un des plus prometteurs : bien que rare, ce minéral est omniprésent dans les roches magmatiques.

Cette thèse expérimentale étudie le comportement du soufre sous deux aspects principaux. Le premier est la solubilité du soufre dans les basanites, une composition peu étudiée, avec un focus sur l'éruption de La Palma 2021. Les expériences ont été réalisées à température et pression fixes (1040°C-200MPa) et fugacité d'oxygène entre NNO - 0.47 et NNO+4.10.

Dans la deuxième approche, la distribution du soufre entre l'apatite et le verre silicaté a été étudiée en relation avec la fugacité des espèces du soufre. Une étude a été réalisée sur différentes compositions à 200MPa, température entre 1000 et 1040°C et fugacité d'oxygène entre NNO-0.82 et NNO+4.17.

Les résultats ont montré que la solubilité du soufre dans le verre silicaté est principalement guidée par la fugacité de l'oxygène. Une corrélation positive a été trouvée entre le contenu en S dans le verre silicaté et dans l'apatite, fortement influencée par la fugacité de l'oxygène. Une étude détaillée sur la fugacité des espèces du soufre a permis d'identifier une tendance positive entre le contenu en soufre et la somme des fugacités. À partir de ce modèle, il a été possible de créer des modèles, à la fois pour des compositions générales, pour reconstruire le contenu en soufre dans les apatites à partir des fugacités des espèces du soufre et vice versa.

Mots clés : Soufre, apatite, fugacité du soufre

*An experimental study of sulfur distribution between apatite and silicate
melts: application to volcanic degassing*

Magmatic degassing is a universal process that shapes our atmosphere as well as those of other planets, and also causes many mineral concentrations of economic interest. Sulphur is a volatile element that fundamentally influences magmatic degassing. Among the minerals capable of recording the activity of volatile elements in magmas, apatite is certainly one of the most promising: although scarce, this mineral is ubiquitous in magmatic rocks.

This experimental thesis studies the behaviour of sulphur in two main aspects. The first is the solubility of sulphur in basanites, a composition that has been little studied, with a focus on the La Palma 2021 eruption. The experiments were conducted at fixed temperature and pressure (1040°C-200MPa) and oxygen fugacity between NNO -0.47 and NNO+4.10.

In the second approach, the distribution of sulphur between apatite and silicate melt was studied in relation to the fugacity of sulphur species. A study was carried out on various compositions at 200MPa, with temperatures between 1000 and 1040°C and oxygen fugacity between NNO-0.82 and NNO+4.17.

The results showed that the solubility of sulphur in the silicate melt is primarily driven by oxygen fugacity. A positive correlation was found between the S content in the melt and in apatite, strongly influenced by oxygen fugacity. A detailed study on the fugacity of sulphur species allowed for the identification of a positive trend between the sulphur content and the sum of the fugacities. From this pattern, it was possible to create models, both for general compositions, to reconstruct the sulphur content in apatites from the fugacities of sulphur species and vice versa.

Keywords : Sulphur, apatite, fugacity of sulphur



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