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Tectonics, metamorphism, and fluid circulation in accretionary complexes

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Abstract

Fluids are strongly involved in the majority of subduction zone processes, from influencing seismic activity via the pore fluid pressure variations, to triggering melting of the upper plate mantle through the transfer of water originated from dehydration reactions. Subducted sediments are a major carrier of fluids and volatile species into subduction. While numerous studies have focused on the deep, ductile realm, in comparison, the shallower domain at the brittle-ductile transition and above, has deserved less attention.

We focused on fluid composition and fluid-rock interactions in sedimentary rocks from three accretionary complexes (the Kodiak complex, the Shimanto belt, Japan, and the Western Alps), in the temperature range 220-380°C. Field work has been conducted in Kodiak, to decipher tectonic evolution of the Kodiak complex and its thermal evolution. We were able to discriminate between deformation that occurred along the plate-boundary interface (top-to-the-trench non-coaxial shear) and as intra-wedge deformation (horizontal coaxial shortening). Thermal profile point to small variations in temperatures in the complex (220-380°C), with highest temperatures in central part. The thermal gap is recorded around the unconformity that separates the basally accreted units and the slope sediments (100-140°C), indicating vigorous vertical motion in the complex, with the amplitude of motion up to 10 km.

To evaluate fluid-rock interaction, we applied a wide range of analytical techniques on whole-rock scale, minerals and fluid inclusions (FI). In metapelites from Kodiak and Shimanto, illite-to-chlorite transformation is the main mineral reaction between 250-330°C, in parallel to the salinity increase recorded in FI. Such reaction requires H₂O and the simplest explanation is the consumption of pore fluids, contributing to a decrease of porosity in pelites. Textures, mineral reactions, fluid-mobile elements (FME: Li, B, Rb, Sr, Cs, Ba), and mass-balance calculations point to a local transfer of material as redistribution between minerals without external exchange in Kodiak. In contrast, samples from Shimanto show significant loss of FME from 250 to 330°C, supported by FME loss in chlorite and illite as temperature rises. Finally, $\delta^7\text{Li}$ of FI was analyzed using crush-leach technique. $\delta^7\text{Li}$ of FI covers a very large range, from -1.54 to +17.07‰. In Kodiak, the fluid is relatively heavy (+8.1 to +17.07‰), related to the crystallization of chlorite

characterized by high lithium content. As chlorite preferentially consumes ^6Li , the fluid remains isotopically heavier. Conversely, FI from Shimanto are isotopically lighter (+2.53 to +10.39‰) than from Kodiak, consistent with lithium loss from chlorite as temperature increases. The temperature dependent isotopic fractionation between quartz and fluid is not observed, which may be explained by disequilibrium crystallization of quartz from fluid, or as a result of dissolution-precipitation reactions postdating FI entrapment. Lithium concentrations and $\delta^7\text{Li}$ of FI leachates suggest constant interaction between fluid and sediments, where $\delta^7\text{Li}$ of fluids is shifted towards the signature of the protolith.

While major elements and lithium isotopes do not require any external exchange both in Kodiak and Shimanto, the FME in Shimanto indicate in contrast that significant transfers occurred through the fluid phase. FME appear therefore as the most sensitive geochemical signal to track volatile and elemental transfers at depth. The difference between Kodiak (close) and Shimanto (open system with respect to FME) is interpreted as controlled by the amount of internal strain and the proximity to large-scale fault zones.

Résumé

Les fluides sont fortement impliqués dans la majorité des processus des zones de subduction, depuis l'activité sismique via les variations de pression interstitielle jusqu'à la fusion du manteau de la plaque supérieure par transfert d'eau issue des réactions de déshydratation. Les sédiments subductés sont en particulier un vecteur majeur de fluides et d'espèces volatiles en subduction.

Ce travail de thèse se concentre sur la composition des fluides et les interactions fluide-roche dans les roches sédimentaires de trois complexes d'accrétion (Kodiak, Alaska ; Shimanto, Japon ; les Alpes occidentales), dans la gamme de température 220-380°C. Des travaux de terrain ont été menés à Kodiak, pour décrypter l'évolution tectonique et thermique du complexe de subduction. Nous distinguons la déformation qui s'est produite le long de l'interface plaque-limite (cisaillement non coaxial) de la déformation intra-prisme (raccourcissement coaxial horizontal). Le profil thermique indique des variations de paléotempérature principalement continues dans le complexe (220-380°C), avec des valeurs maximales dans la partie centrale de la formation de Kodiak. La discontinuité thermique principale coïncide avec la discordance qui sépare les unités accrétées à la base et les sédiments de pente (100-140°C), indiquant des mouvements verticaux importants dans le complexe, dont l'amplitude atteint 10 km.

Pour analyser les interactions fluide-roche, nous avons appliqué un large éventail de techniques analytiques sur roche totale, minéraux et inclusions fluides (IF). Dans les métapélites de Kodiak et Shimanto, la transformation de l'illite en chlorite est la principale réaction minérale entre 250 et 330°C, et se produit en parallèle d'une augmentation de la salinité des fluides piégés dans les IF. Une telle réaction nécessite de l'H₂O et a donc consommé de l'eau porale encore présente entre les grains minéraux. Les textures, les réactions minérales, les éléments fluides mobiles (FME ; Li, B, Rb, Sr, Cs, Ba) et les calculs de bilan de masse indiquent à Kodiak un transfert local de matière sous forme de redistribution entre les minéraux, sans échange externe. En revanche, les échantillons de Shimanto montrent une perte significative de FME de 250 à 330°C, en accord avec la baisse de la concentration des FME dans le chlorite et l'illite à mesure que la température augmente.

Enfin, nous avons analysé le $\delta^7\text{Li}$ des IF par la technique de broyage-lixiviation. Le $\delta^7\text{Li}$ des IF varie sur une très large gamme, de -1,54 à +17,07‰. A Kodiak, le fluide est relativement lourd (+8,1 à +17,07‰), lié à la cristallisation de chlorite caractérisée par une forte teneur en lithium. Comme la chlorite consomme préférentiellement du ^6Li , le fluide restant est isotopiquement plus lourd. À l'inverse, les IF de Shimanto sont isotopiquement plus légères (+2,53 à +10,39‰) que celles de Kodiak, ce qui correspond à la perte de lithium issue de la chlorite lorsque la température augmente.

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Résumé étendu

1. Introduction

Depuis l'avènement de la théorie de la tectonique des plaques, la compréhension de la dynamique des zones de subduction représente un enjeu majeur pour les géoscientifiques. Elles représentent la force motrice principale des mouvements des plaques. Le plongement d'une plaque sous une autre provoque généralement une extension provoquant aux limites l'ouverture et la propagation de dorsales médio-océaniques. Les interfaces de plaques localisent les séismes les plus destructeurs sur Terre, tandis que la déshydratation des lithologies enfouies en profondeur est responsable du volcanisme d'arrière-arc. De plus, les fluides sont fortement impliqués dans tous les processus de zone de subduction mentionnés : la présence de fluides interstitiels a un impact important sur le comportement rhéologique des lithologies subductées (par exemple, Fagereng et al., 2018 ; Hacker et al., 2003) ; sur l'activité sismique via les variations de pression interstitielle du fluide (Audet & Schwartz, 2013 ; Davis et al., 1983 ; Saffer & Tobin, 2011) ; les réactions de déshydratation dans les lithologies profondément subductées sont responsables de la génération de magmas d'arc via la fusion des espèces volatiles du manteau (Bebout, 1991 ; Elliott, 2003 ; Hacker, 2008 ; Stern, 2011).

Comme les fluides sont des réactifs ou des produits de réactions métamorphiques, leur abondance, leur nature et leur chimie changent avec l'enfouissement. Au-delà de la limite de portée des forages des programmes ODP/IODP (<5 km), notre connaissance de la composition des fluides s'appuie principalement sur des études d'inclusions fluides et de transformations minérales dans les roches des complexes fossiles subductés puis exhumés (e.g., Agard et al., 2000 ; Herviou et al., 2021 ; Raimbourg et al., 2018 ; Scambelluri et al., 2015). Malgré de nombreuses études concernant les réactions minérales dans les sédiments subductés, on ne sait encore que peu de choses sur leur influence sur l'évolution chimique des fluides interstitiels et sur le budget global des fluides à travers le chemin métamorphique prograde.

Dans les veines qui ont piégé des fluides profonds sous forme d'inclusions fluides, la propriété la plus couramment analysée est la salinité, convertie en équivalent NaCl en supposant que NaCl est le sel dominant (Agard et al., 2000 ; Brantley & Fisher, 1997 ; Herviou et al., 2021 ; Kondo et al., 2005 ; Nishiyama et al., 2021 ; Raimbourg, 2015 ; Raimbourg et al., 2018 ; Rossetti et al., 2006 ; Rowe et al., 2009 ; Sadofsky & Bebout, 2004). Seules quelques études ont réellement analysé la chimie du fluide occlus (par exemple, Scambelluri et al., 2004, 2015 ; Yoshida et al., 2015).

Dans cette étude, nous proposons plusieurs réactions minérales dans les métapélites couvrant les profondeurs sismogènes, et évaluons leur influence sur le bilan hydrique, les concentrations en éléments traces et le $\delta^7\text{Li}$ des fluides dans deux complexes d'accrétion (le complexe d'accrétion de Kodiak, USA, et la ceinture de Shimanto, Japon). L'étude concernant $\delta^7\text{Li}$ est également étendue à deux unités des Alpes occidentales.

2. Méthodologie

Au cours de cette thèse, un large éventail de techniques analytiques et numériques ont été appliquées. Ici, nous décrivons brièvement les objectifs et la méthodologie appliquée dans chaque chapitre.

Dans le chapitre II, la cinématique de déformation à travers le complexe d'accrétion de Kodiak est décrite selon la procédure suivante : l'ensemble des micro- et méso-structures a été mesuré sur le terrain et utilisé pour reconstruire l'évolution tectonique du prisme d'accrétion. Les structures comprennent des indicateurs cinématiques (failles striées métriques, bandes de cisaillement, fractures), des indicateurs de déformation finie (schistosités, crénulation, axes de plis) ainsi que des orientations de contraintes (dykes ou fractures d'extension minéralisées ouverts en mode 1). Les données mesurées ont été traitées suivant Delvaux & Sperner (2003) et Sperner & Zweigel (2010), ce qui inclut la recherche de relations chronologiques sur le terrain, l'attribution d'un niveau de confiance catégoriel à chaque donnée (certaine, probable, supposée, inconnue), et la séparation non automatisée des données en sous-ensembles mécaniquement compatibles. Les données structurales ont été triées manuellement en fonction d'abord de leurs relations transversales, puis en fonction de leur cinématique et de leur orientation.

Dans le chapitre III, l'histoire thermique du complexe d'accrétion de Kodiak (chapitre III) a été quantifiée par méthode de spectroscopie Raman sur matière carbonée (RSCM). Nous avons appliqué cette méthode à l'aide d'un micro-spectromètre Raman Renishaw InVia Reflex à l'ISTO-BRGM et d'un micro-spectromètre Renishaw InVia Qontor au CEMHTI CNRS, Orléans. Trois méthodes de déconvolution différentes ont ensuite été appliquées, en fonction de la forme des spectres Raman. Dans les unités subductées puis accrétées à la base du prisme, les spectres Raman « haute température » du matériau carboné conviennent à la méthode de Lahfid et al. (2010) et

Beyssac et al. (2002), alors que les sédiments « basse température » déposés sur le talus continental sont traités selon la méthode de Schito et al. (2017).

Enfin, une large gamme de méthodes analytiques a été appliquée dans des échantillons de métasédiments et des veines adjacentes du complexe d'accrétion de Kodiak, de la ceinture de Shimanto au Japon et des Alpes occidentales (chapitres IV, V et VI), afin de (i) caractériser les minéraux métamorphiques, déterminer leurs abondances, et identifier des réactions minérales (ICPMS, SEM-BSE, XRD, EPMA), (ii) tester l'existence d'équilibre thermodynamique et calculer les conditions de pression-température (résultats EPMA combinés aux modèles de Dubacq et al., 2010 ; Vidal et al., 2006), (iii) expliquer les variations de la salinité des inclusions fluides (microthermométrie, spectroscopie Raman de la bande OH, méthode de décrépitation), (iv) décrire le bilan fluide-éléments mobiles (ICPMS, LA-ICPMS), et enfin (v) étudier le comportement du lithium et les isotopes du lithium dans les inclusions fluides au cours du métamorphisme prograde en appliquant la technique de lixiviation par broyage (MC-ICPMS).

3. Structures de déformation et histoire thermique du complexe d'accrétion de Kodiak (Chapitres II et III)

La cinématique de déformation des structures observées à travers le complexe d'accrétion de Kodiak correspond principalement à une déformation planaire dans la direction NW-SE, du Crétacé inférieur à aujourd'hui (Fig. 1). Un cisaillement simple est observé dans les mélanges tectoniques et dans la Formation de Kodiak à proximité du chevauchement d'Uganik et interprété comme formé lors de la subduction de ces unités (cad sous le décollement). En revanche, contrairement au cisaillement non coaxial proposé dans la littérature à propos des unités cohérentes, notre étude révèle que le cisaillement pur est dominant et contrôle le raccourcissement horizontal, au sein du prisme d'accrétion (cad au-dessus du décollement), dans les unités de Kodiak Seaward Belt et la formation de Ghost Rocks. Les structures de déformation supplémentaires comprennent des failles décrochantes qui sont postérieures à l'événement magmatique principal à 58-59 Ma, et peut-être un raccourcissement vertical dans la ceinture centrale de Kodiak dont l'intensité n'a pu être déterminée.

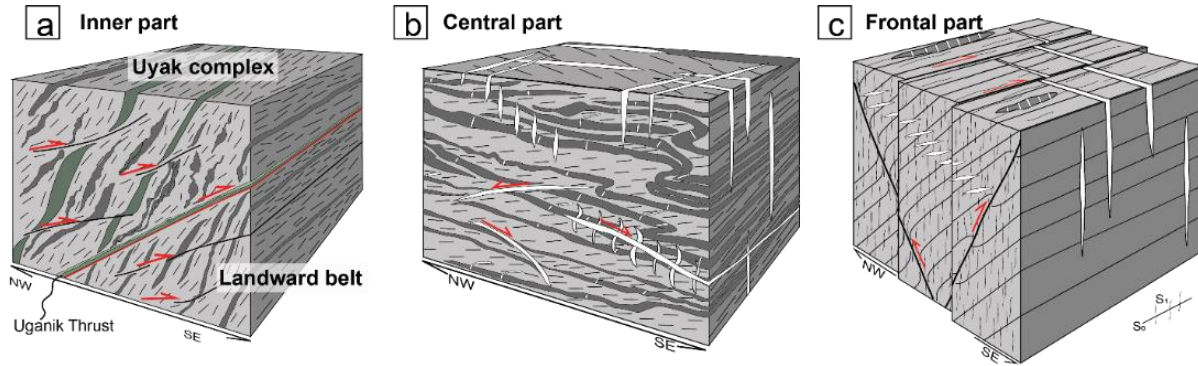


Figure 1. Modèle 3D montrant les variations des structures de déformation observées à travers les unités accrétées, du cisaillement non coaxial du sommet à la tranchée dans le complexe d'Uyak et la ceinture terrestre de Kodiak, sur (b) le raccourcissement vertical dans la ceinture centrale de Kodiak, à (c) un raccourcissement horizontal dans la ceinture de Kodiak Seaward et la formation de Ghost Rocks.

Notre étude RSCM régionale à travers le complexe d'accrétion de Kodiak indique une augmentation des températures entre 220 et 400°C, sans discontinuités à travers les failles délimitant l'unité. Les températures les plus élevées sont mesurées dans les formations de Kodiak Central et Seaward Belt, qui constituent la partie centrale du complexe.

Un saut dans les températures maximales métamorphiques entre les unités accrétées et les sédiments de pente suggère un mouvement vertical significatif local entre le Paléogène et le Miocène (Fig. 2). La période d'exhumation des unités sédimentaires du Crétacé-Paléogène est liée au sous-placage de matériel plus jeune, et l'absence de caractéristiques d'extension significatives indique que l'exhumation s'est produite à la suite d'un raccourcissement horizontal et d'une érosion importante en surface. Plus tard, un épisode de subsidence au Miocène est vraisemblablement lié à une période d'érosion basale. Le soulèvement final de la Formation de Narrow Cape est interprété comme le résultat de l'action des failles actives de la marge. Les taux estimés (0,2-1,3 mm/an) pour le mouvement vertical sont comparables aux estimations d'autres prismes paléo-accrétionnaires.

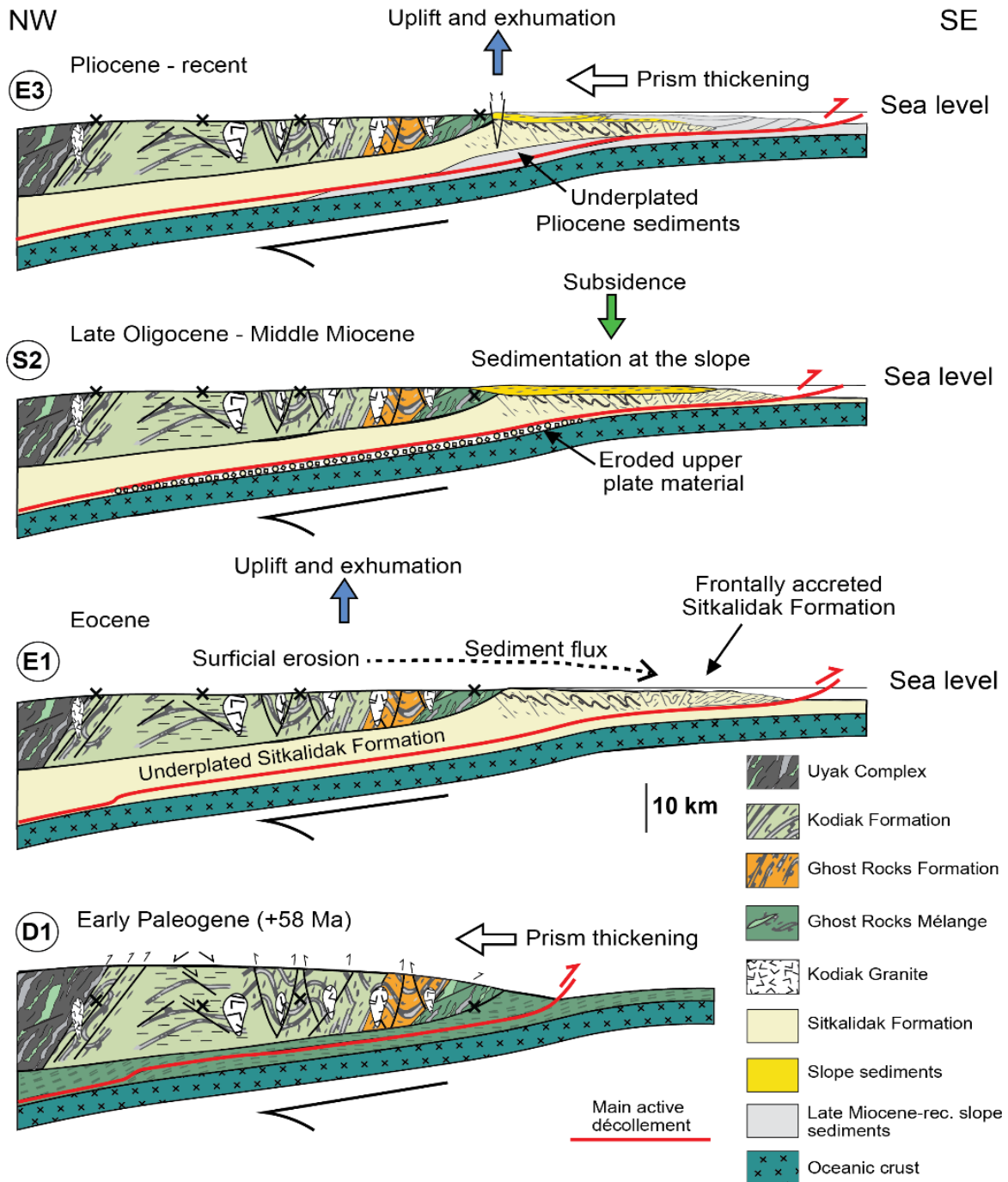


Figure 2. Coupe transversale de l'évolution du complexe d'accrétion de Kodiak avec trois étapes différentes du mouvement vertical : (D1) Une période d'accrétion basale au cours du Crétacé supérieur-Paléogène inférieur, et les structures de déformation associées. (E1) L'exhumation des unités accrétées par sous-placage des strates épaisses de l'Éocène (Moore & Allwardt, 1980). Le soulèvement est contemporain de l'érosion superficielle et de l'exposition des unités profondément accrétées à leur position presque actuelle. (S2) Affaissement enregistré dans les sédiments de pente dans la partie frontale du prisme, très probablement dû à l'érosion basale. (E3) L'exhumation de la partie frontale du complexe. Un profil récent est créé sur la base de profils sismiques (Fisher & Holmes, 1980 ; von Huene et al., 2012) ainsi que d'observations à terre (Carver et al., 2013).

4. Réaction métamorphique et son influence sur le bilan hydrique le long de la zone sismogène (Chapitre IV)

Afin de déterminer les réactions fluide-minéraux et le bilan de fluide dans les zones de subduction, nous avons réalisé une étude pétrologique sur les roches à travers la zone sismogène dans deux complexes d'accrétion, le complexe de Kodiak (Alaska) et la ceinture de Shimanto au Japon. Les températures maximales d'enfouissement dérivées par RSCM vont de 230 à 350°C dans les deux exemples. De plus, nous avons testé l'équilibre thermodynamique entre les phases des échantillons métamorphiques de plus haut grade, en appliquant le modèle multi-équilibre illite-chlorite. Les températures calculées sont en accord avec les résultats du RSCM, alors que les pressions calculées sont d'environ 3 et 4 kbar pour les complexes japonais et d'Alaska, respectivement (Fig. 3).

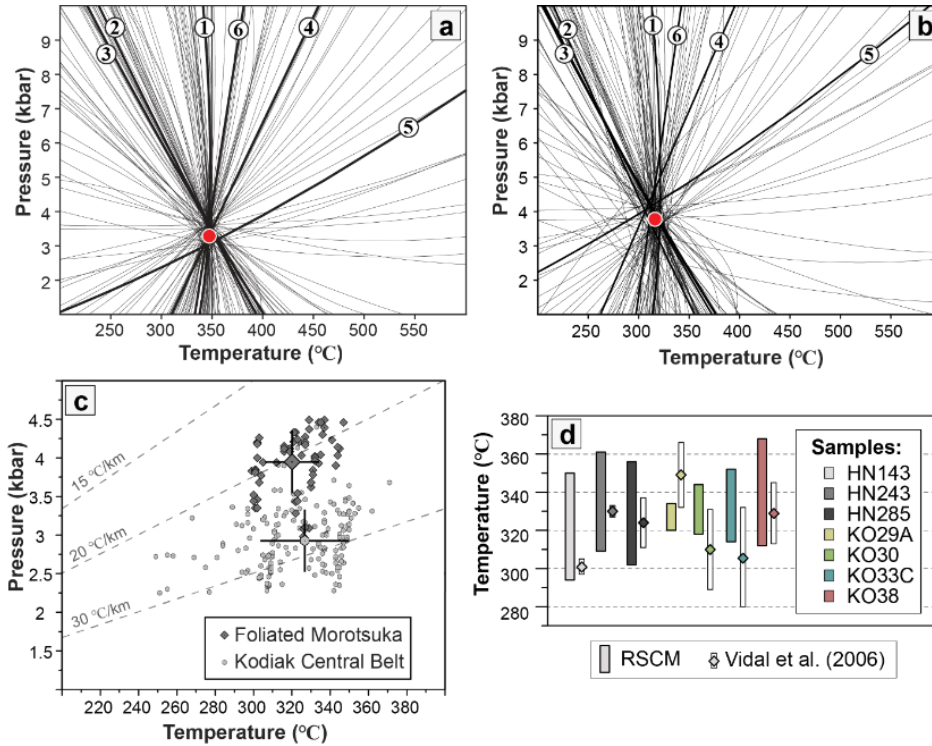
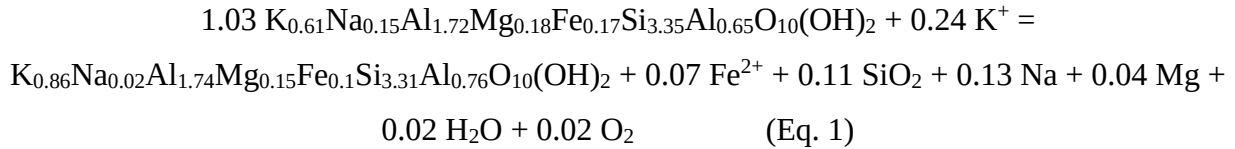
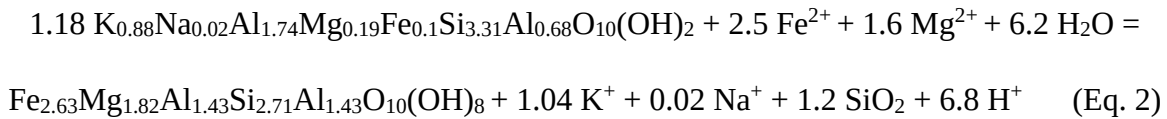


Figure 3. Exemples de calculs d'équilibre illite-chlorite dans des échantillons de (a) la ceinture centrale de Kodiak (KO38, Kodiak) et (b) le Foliated Morotsuka (HN285, Shimanto). Les lignes en gras représentent des réactions indépendantes : (1) $(PrI)_{Phg} = (PrI)_{Phg} + H_2O$; (2) $4 Qtz - (Mg-Am)_{Chl} = 2 (PrI)_{Phg} + 2 (Sud)_{Chl}$; (3) $- 2 (Mg-Cel)_{Phg} + 15 Qtz + 2 (Ms)_{Phg} = 4 (PrI)_{Phg} + (Sud)_{Chl}$; (4) $- 5 (Mg-Cel)_{Phg} + (Clin)_{Chl} = (Fe-Am)_{Chl} + 4 (Fe-Cel)_{Phg} + (Ms)_{Phg}$; (5) $- 4 (Mg-Cel)_{Phg} + 4 (Daph)_{Chl} = 5 (Fe-Am)_{Chl} + (Mg-Am)_{Chl} + 4 (Ms)_{Phg}$; (6) $4 (Mg-Cel)_{Phg} + (Daph)_{Chl} = 5 (Fe-Cel)_{Phg} - (Mg-Am)_{Chl} + (Ms)_{Phg}$. (c) Résultats pression-température de chacune des paires illite-chlorite équilibrées. (d) Comparaison des températures de pic métamorphique déduites de RSCM et de la thermométrie du chlorite en utilisant la méthode de Vidal et al. (2006).

Par ailleurs, avec l'augmentation de la température, les interstratifiés smectite-illite se transforment en illite-muscovite au cours du métamorphisme prograde ; l'occupation de la position interfoliaire est plus élevée avec l'augmentation de la pression-température et donc du potassium supplémentaire est nécessaire (Eq. 1). Nous proposons donc la réaction suivante :



À 230-260°C, la présence de chlorite est interprétée comme un coproduit de la transformation de la smectite en illite. La teneur en chlorite augmente à mesure que la température monte jusqu'à 330-350°C, à la suite de la transformation de l'illite en chlorite (Fig. 4a) :



D'autres réactions comprennent l'oxydation de la pyrite et la dissolution de la titanite et la précipitation de l'anatase. La chimie de la roche totale indique l'absence de changements systématiques entre les échantillons soumis à des températures différentes. Cependant, dans des zones restreintes, la dissolution du quartz et de l'albite a provoqué l'appauvrissement en SiO_2 et en Na_2O de la matrice, contrebalancé par la re-précipitation du quartz et de l'albite dans les veines. L'analyse qualitative de la chimie des inclusions fluides à l'aide de la méthode de décrépitation montre que la composition du fluide piégée dans les pores est significativement différente de l'eau de mer. De plus, la salinité des inclusions fluides dans les veines de quartz à 230-260°C, analysée à l'aide du spectre Raman de l'eau, est inférieure à l'eau de mer (~2 wt. % NaCl eq.) et est donc interprétée comme une dilution de l'eau de mer d'origine par l'eau douce libérée par transformation smectite-illite. En revanche, les veines formées à 330-350°C contiennent des inclusions fluides avec une salinité de l'ordre ou plus élevée que l'eau de mer. L'augmentation de la salinité pour des températures de 250-350°C reflète les réactions d'hydratation, principalement contrôlées par la cristallisation de chlorite (Fig. 4b). Contrairement à la tendance générale des réactions de déshydratation se produisant le long de l'enfouissement rocheux dans les zones de subduction, cette étude montre que la base de la zone sismogène est plutôt dominée par une absorption de fluide interstitiel par des réactions minérales.

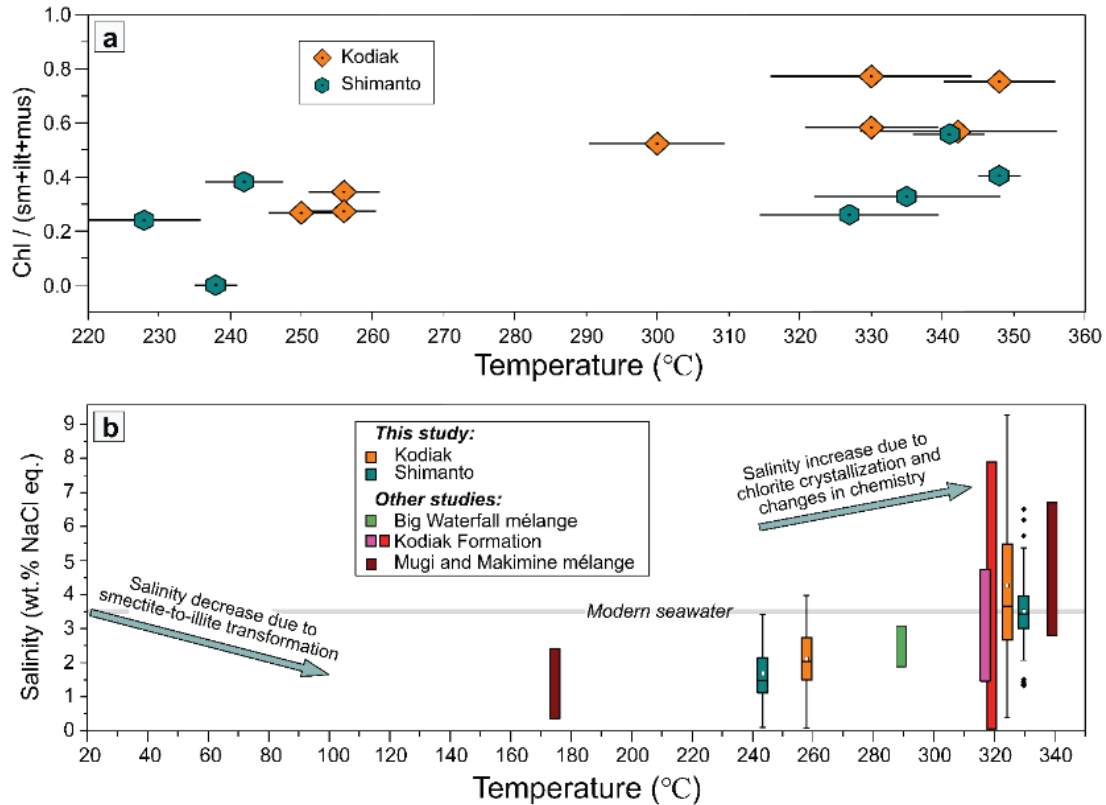


Figure 4. (a) Les ratios chlorite / (smectite + illite + muscovite) basés sur les résultats XRD. A noter que pour les deux localités il y a une augmentation de la proportion de chlorite en fonction de la température. (b) Boîtes à moustaches des salinités d'inclusion fluide dans les veines de quartz de cette étude ainsi que d'études antérieures concernant la salinité dans le complexe d'accrétion de Kodiak et la ceinture de Shimanto au Japon. Compilation de la littérature : Big Waterfall mélange, Kodiak (Rowe et al., 2009) ; Formation Kodiak, Alaska : rose – transect Afognak, rouge – transect Kodiak (Brantley & Fisher, 1997) ; Mugi mélange (Sakaguchi, 1999); Makimine mélange (Nishiyama et al., 2021).

5. Comportement des éléments fluides-mobiles dans les sédiments subductés : étude de cas de roches métapélitiques à P/T faible à modérée (Chapitre V)

Les fluides sont reconnus comme jouant un rôle important dans les processus des zones de subduction. Cependant, l'évolution chimique du fluide interstitiel dans les sédiments subductés n'est pas bien contrainte. Cette étude rapporte le bilan des éléments fluides-mobiles (FME : B, Li, Rb, Sr, Cs et Ba) et évalue les interactions fluide-roche dans les roches métapélitiques à P/T faible à modéré (~230-350°C) de la ceinture de Shimanto au Japon et du complexe d'accrétion de Kodiak en Alaska. Afin d'évaluer l'impact des fluides, la composition de la roche totale, des minéraux et

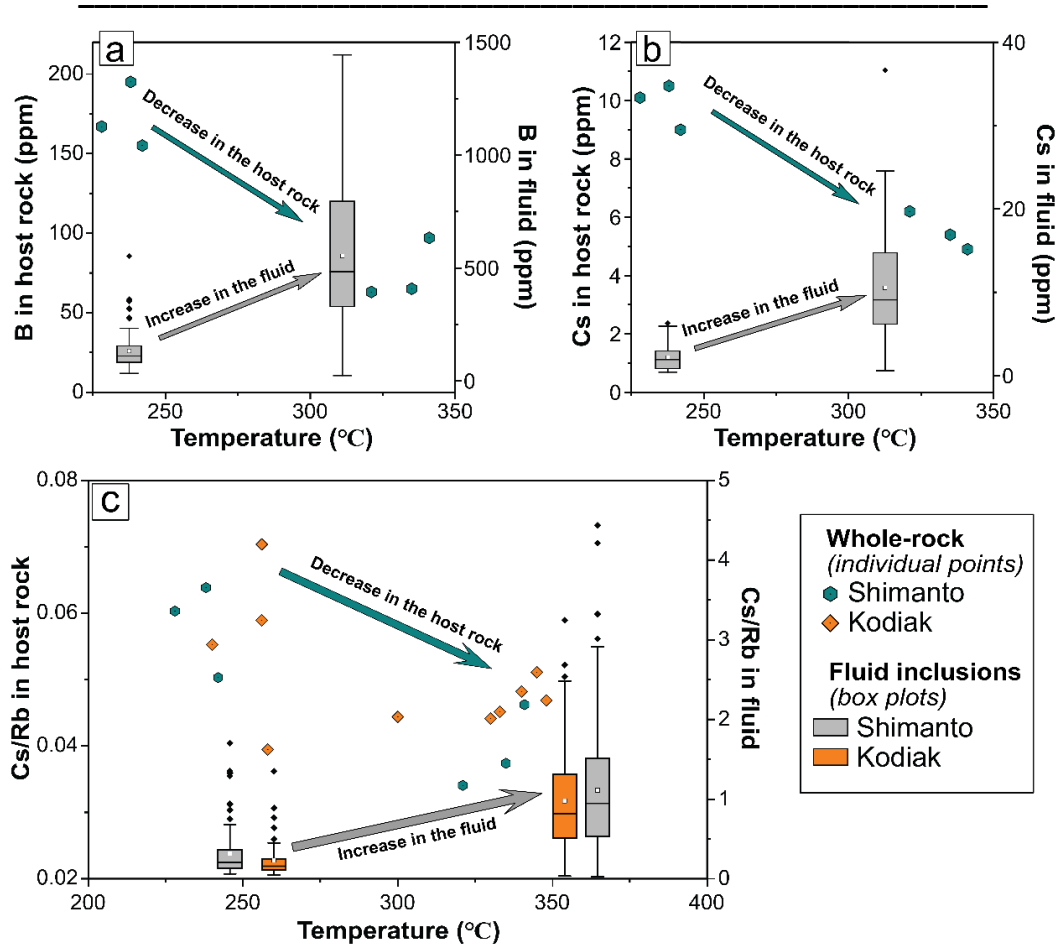


Figure 5. Interactions fluide-roche justifiées par les concentrations de FME de la roche hôte et du fluide déduites des inclusions fluides. (a) Les concentrations de bore et (b) de césium diminuent à l'échelle de la roche entière en fonction de la température dans la ceinture de Shimanto, alors que le fluide montre un enrichissement. Les mêmes observations sont faites pour (c) le rapport molaire Cs/Rb, où une diminution est observée dans la roche hôte et une augmentation des inclusions fluides aux deux localités, Kodiak et Shimanto. Les points individuels représentent les concentrations dans la roche entière et les diagrammes en boîte adjacents représentent les concentrations/rapports molaux dans le fluide.

des inclusions fluides dans les veines de quartz syn-métamorphiques a été déterminée par ICP-MS et LA-ICP-MS. Les roches de grade métamorphique inférieur (c'est-à-dire correspondant à ~230-260°C) conservent une signature FME de roche entière similaire aux exemples turbiditiques du GLOSS-II. En revanche, à des températures plus élevées (jusqu'à ~350°C), les FME (à l'exception de Rb et Sr) sont lessivés des roches de la ceinture de Shimanto, alors qu'aucune perte, à l'exception de Cs, n'est observée dans le complexe de Kodiak. Le bilan de FME est contrôlé au premier ordre par la concentration de FME en chlorite (pour B) et en illite (Li, Rb, Cs, Ba) et leur évolution avec l'augmentation de la température. De plus, les concentrations de FME mesurées dans l'illite et la chlorite du complexe de Kodiak montrent une rétention voire un enrichissement en FME, tandis

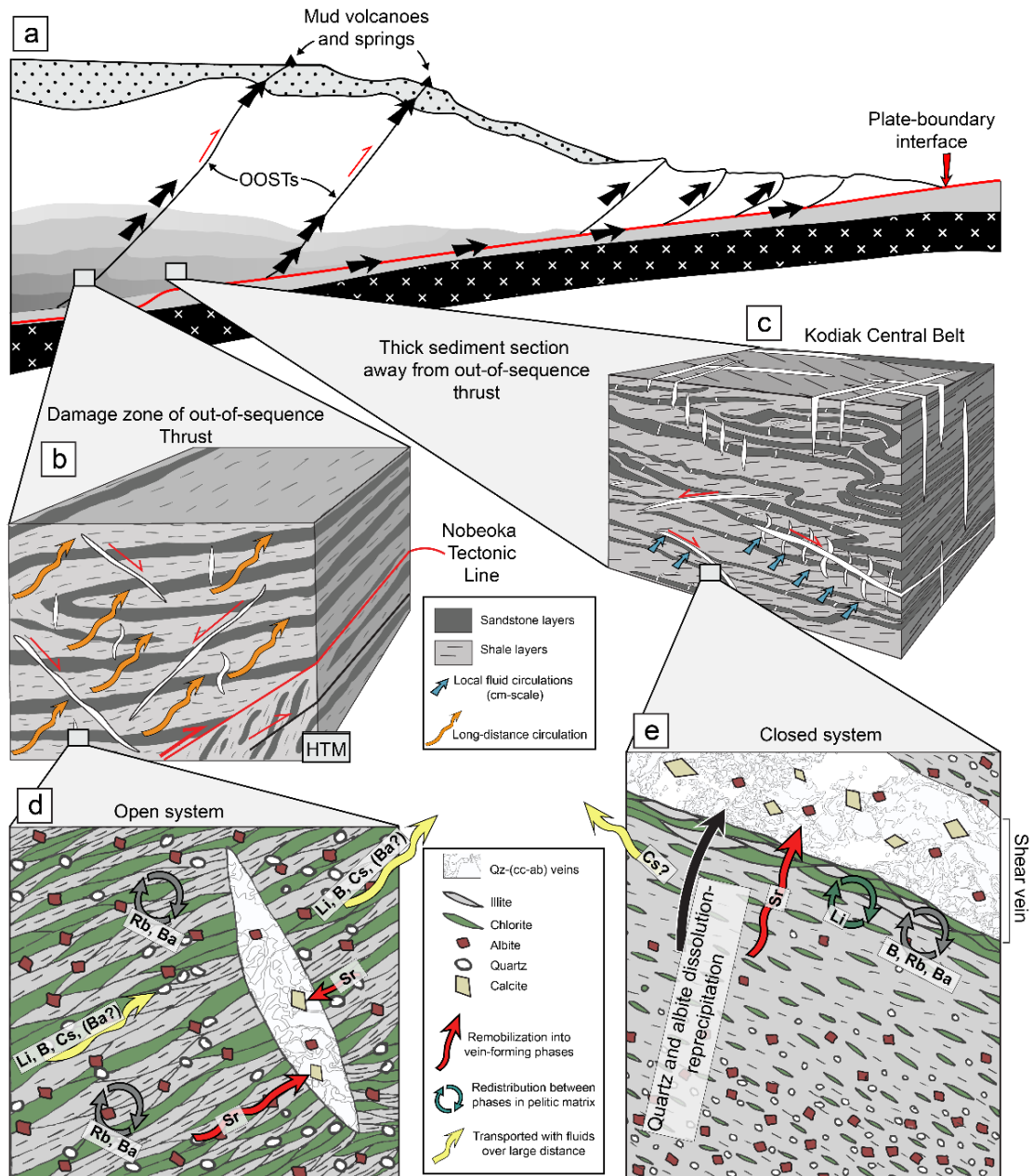


Figure 6. Le scénario schématique de l'évolution du budget FME sur les sites étudiés, de l'échelle du prisme d'accrétion jusqu'à la lame mince : (a) coupe d'un prisme d'accrétion redessiné d'après Kastner et al. (2014) avec les emplacements relatifs des unités étudiées, la Foliated Morotsuka et la Kodiak Central Belt. Le Foliated Morotsuka est situé dans le toit du chevauchement hors séquence (ligne tectonique de Nobeoka), tandis que la ceinture centrale de Kodiak était sous-plaquée au milieu d'une épaisse séquence turbiditique loin de toute faille à grande échelle. Un croquis 3D de (b) le Foliated Morotsuka et (c) la ceinture centrale de Kodiak avec les structures de déformation présentées et les scénarios possibles pour l'écoulement des fluides. (d) et (e) montrent les détails de la minéralogie des métapélites des deux localités et leur influence sur le budget FME. Dans la Morotsuka foliée (d), le lithium, le bore, le césium et le baryum sont lessivés de la roche hôte, seul le strontium étant stocké dans la calcite formant des veines. À l'inverse, (e) dans la ceinture centrale de Kodiak, le lithium, le bore, le rubidium et le baryum, se réorganisent entre illite, chlorite et albite. Seul le césium est potentiellement perdu sur de plus grandes distances.

que l'illite et la chlorite de la ceinture de Shimanto présentent une perte de FME. Les éléments perdus de la roche hôte, tels que le bore et le césium, sont enrichis dans les inclusions fluides. Les rapports molaires des éléments des fluides montrent des tendances d'évolution similaires en fonction de l'augmentation de la température entre les deux études de cas géologiques (par exemple, K/Na diminue, Cs/Rb augmente ; Fig. 5), liées à la réaction minérale dans la matrice, telle qu'une augmentation de sodium due à la dissolution d'albite dans la matrice.

Les roches du complexe d'accrétion de Kodiak se sont donc comportées comme un système fermé, dans lequel la circulation des fluides est limitée aux transferts à l'échelle centimétrique à métrique, de la matrice aux veines métamorphiques adjacentes. En revanche, les unités de la ceinture de Shimanto suggèrent plutôt un système ouvert percolé par de grandes quantités de fluide, comme en témoignent les calculs de bilan massique pour le bore, le césium et le baryum montrant des rapports eau/roche élevés (0,2-1,8). Nous en déduisons que le comportement du système fermé par rapport au système ouvert est contrôlé par la quantité de déformation interne dans les différentes unités et la proximité des zones de failles à grande échelle (Fig. 6). Enfin, les rapports d'éléments dans le fluide diffèrent considérablement des fluides interstitiels d'eau de mer ou de sédiments, mais ont une signature FME similaire à celle des volcans de boue. Cette découverte est cohérente avec les réactions métamorphiques de bas grade influençant la chimie des fluides et contribuant aux fluides expulsés à l'aplomb de l'avant-arc de subduction.

6. Analyse isotopique Li des inclusions fluides dans le quartz des veines syn-subduction

Le lithium et ses isotopes sont reconnus comme des traceurs de fluides importants dans les processus de zone de subduction. Dans cette étude, nous avons examiné les compositions chimiques et isotopiques $\delta^7\text{Li}$ des inclusions fluides et du quartz hôte en appliquant la technique de lixiviation par broyage dans 21 veines dominées par le quartz syn-subduction de trois complexes paléo-accrétionnaires (le complexe de Kodiak en Alaska, la ceinture de Shimanto au Japon, et Alpes occidentales). $\delta^7\text{Li}$ des lixiviats FI de trois localités montre une signature distincte, globalement comprise entre -1,54 et +17,07‰. Les différences entre les sites peuvent être expliquées en examinant les concentrations de lithium dans les minéraux de la roche hôte. Le chlorite est le principal hôte du lithium et il incorpore préférentiellement du ^6Li , laissant le fluide enrichi en ^7Li . Dans le complexe de Kodiak, la chlorite nouvellement formée est caractérisée par

de fortes concentrations de lithium et, par conséquent, le fluide coexistant est isotopiquement, relativement lourd (+8,1 à +17,07 ‰), au contraire de l'importante perte en lithium des chlorites dans la ceinture de Shimanto qui a mené à la formation d'un fluide isotopiquement plus léger (+2,53 à +10,39‰). $\delta^7\text{Li}$ du fluide montre une indépendance par rapport aux autres paramètres utilisés pour tracer les fluides, tels que la salinité, la température ou la composition du fluide en FME.

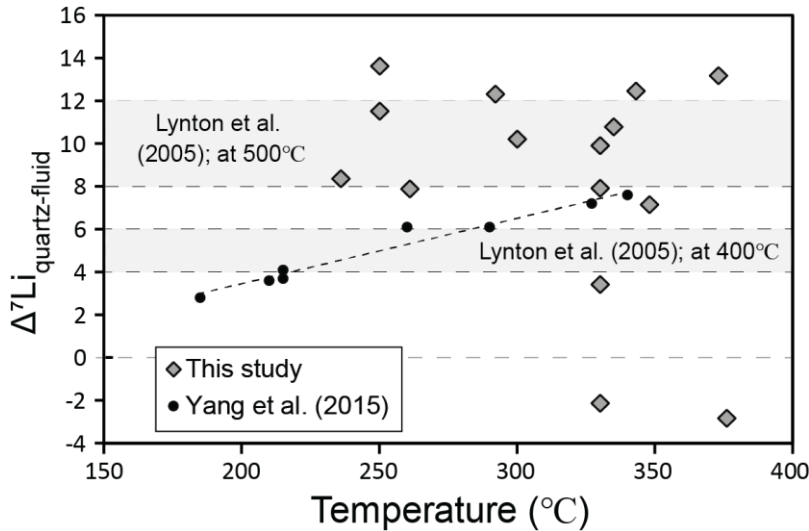


Figure 7. $\Delta^7\text{Li}_{\text{quartz-fluide}}$ de cette étude ainsi que de Yang et al. (2015) en fonction de la température. Les champs gris clair représentent les valeurs dérivées expérimentalement de Lynton et al. (2005), avec $\Delta^7\text{Li}_{\text{quartz-fluide}}$ de +4 à +6‰ à 400°C et de +8 à +12‰ à 500°C.

Le Li du quartz est en général isotopiquement plus lourd que celui des inclusions fluides que le quartz piège, avec $\delta^7\text{Li}$ compris entre +10,93 et +22,61‰. Le fractionnement isotopique entre le quartz et le fluide dans les veines examinées ne montre aucune dépendance à la température. Cependant, $\Delta^7\text{Li}_{\text{quartz-fluide}}$ varie de +7,15‰ à +13,63‰, en accord avec les valeurs dérivées expérimentalement (Fig. 7). L'absence de dépendance à la température du fractionnement des isotopes de lithium entre le quartz et le fluide peut être le résultat (i) d'une cristallisation hors-équilibre du quartz à partir du fluide, ou de (ii) des réactions de dissolution-précipitation entre les inclusions fluides et le quartz postérieures au piégeage des inclusions fluides.

Dans l'ensemble, des concentrations élevées de lithium dans les lixivats FI et un $\delta^7\text{Li}$ relativement faible suggèrent que le lithium est progressivement lessivé des sédiments, où le $\delta^7\text{Li}$ des fluides est déplacé vers la signature d'un protolithe sédimentaire potentiel (Fig. 8). Les similitudes dans les concentrations de lithium et $\delta^7\text{Li}$ entre les lixivats des inclusions fluides et les fluides expulsés

par les sources chaudes et froides de la plaque supérieure confirment l'idée que ces fluides proviennent de sédiments déshydratés.

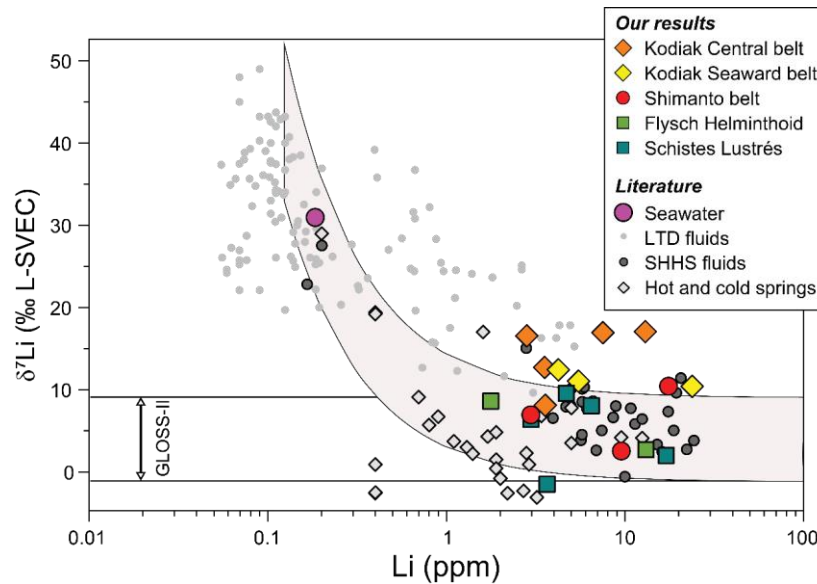


Figure 8 Le $\delta^7\text{Li}$ par rapport aux concentrations de lithium des lixiviats d'inclusions fluides ainsi que les valeurs de l'eau de mer, des fluides interstitiels et de la gamme des sédiments subduits mondiaux (GLOSS-II ; Plank, 2014), adapté d'après (Scholz et al., 2010). La zone grise représente un modèle de mélange binaire entre les fluides interstitiels et GLOSS-II. La majorité des résultats tombent dans le domaine du mélange, indiquant la lixiviation du lithium du matériau solide et le déplacement de la valeur $\delta^7\text{Li}$ des fluides vers le protolithe. Données de référence : eau de mer (Millot et al., 2004) ; Fluides LTD : fluides diagénétiques à basse température (Scholz et al., 2010) ; Fluides SHHS : systèmes hydrothermaux dans les sédiments (Chan et al., 1994 ; James et al., 1999) ; Sources chaudes et froides (Barnes et al., 2019b).

7. Discussion et conclusions

Première partie

Dans le complexe d'accrétion de Kodiak, l'analyse structurale a permis de discriminer la nature des déformations actives lors du sous-charriage (D1) puis ultérieurement après l'incorporation dans le prisme d'accrétion (D2). Simultanément, nous avons pu caractériser la nature des veines associées, témoins de la circulation des fluides. À partir de là, nous nous sommes concentrés sur les veines D1 liées à la subduction et avons ignoré les veines D2 ultérieures.

Les résultats de température obtenus par RSCM indiquent une structure en forme de dôme dans les unités d'accrétion à la base du complexe d'accrétion de Kodiak. Le résultat principal est l'écart de température entre les unités accrétées à la base des prismes et les sédiments plus superficiels du

talus continental. A partir de ces températures, nous avons pu estimer la nature des mouvements verticaux dans la partie frontale du complexe entre le Paléogène et le Miocène. La période d'exhumation des unités sédimentaires du Crétacé-Paléogène est liée au sous-placage de matériel plus jeune, et l'absence d'extension significative dans le prisme lui-même implique que l'exhumation s'est produite à la suite d'un raccourcissement horizontal accompagné d'une érosion superficielle. Plus tard, une étape d'affaissement au Miocène et d'exhumation finale vers une position actuelle pourrait être le résultat du jeu sur une faille de la croûte supérieure et/ou d'un échange entre l'accrétion basale et l'érosion par subduction. Les taux estimés pour ce mouvement vertical sont comparables aux estimations d'autres prismes d'accrétion.

Deuxième partie

Notre étude montre que lors du métamorphisme prograde des métapélites subductées, dans la gamme de 230-260°C à 300-350°C, le changement majeur est une augmentation du rapport chlorite/illite suite à la transformation illite-chlorite. La salinité des inclusions fluides dans les veines de quartz formées à 230-260°C, est constamment inférieure à celle de l'eau de mer du fait de l'héritage de la transformation de la smectite en illite qui a lieu à relativement basse température. À des températures plus élevées, la salinité des inclusions fluides est proche ou plus élevée que celle de l'eau de mer. La cristallisation de la chlorite est une explication possible d'une telle augmentation de la salinité, car ce minéral incorpore de l'eau dans son réseau cristallin. La réaction d'hydratation observée affecte ainsi le bilan hydrique dans les sédiments subductés le long de la zone sismogène.

Les concentrations de FME dans la roche entière, dans les minéraux, et les inclusions fluides dans les veines de syn-subduction indiquent deux comportements contrastés entre le complexe d'accrétion de Kodiak et la ceinture de Shimanto. Dans le complexe de Kodiak, les FME montrent une rétention par redistribution des FME entre phases minérales majeures dans la matrice, ce qui pointe vers un système plutôt fermé, en accord avec les éléments majeurs. Dans la ceinture de Shimanto, des pertes importantes sont signalées pour tous les FME jusqu'à des températures de ~350°C, avec une remobilisation limitée du rubidium et du baryum, un transfert de strontium vers la calcite dans les veines et une lixiviation du lithium, du bore, du césium et partiellement du baryum dans le fluide. Par conséquent, dans la ceinture de Shimanto, les FME suggèrent un

comportement opposé aux éléments majeurs, probablement en raison du fait que les FME sont plus sensibles aux fluides. Les calculs du bilan massique du bore, du baryum et du césium dans la roche hôte et le fluide de la ceinture de Shimanto ont abouti à un rapport massique W/R élevé, indiquant un système plutôt ouvert. Ces valeurs peuvent être expliquées par des circulations de fluides qui se concentrent dans l'unité de Morotsuka Foliée, en raison de sa proximité avec un système de failles à grande échelle (Nobeoka Tectonic Line) et de la déformation interne associée favorisant l'ouverture de perméabilité. De plus, des similitudes chimiques avec les volcans de boue ou les sources dans les avant-arcs de la zone de subduction suggèrent que ceux-ci sont alimentés en partie par des fluides issus des unités sédimentaires subduites le long de la zone sismogène.

Les isotopes du lithium fournissent une information supplémentaire des interactions fluide-roche dans les métapélites. Des concentrations élevées de lithium dans les lixiviats de FI indiquent une interaction fluide-roche importante et un lessivage du lithium de la roche hôte. Les lixiviats des inclusions fluides enregistrent une large gamme de $\delta^7\text{Li}$ (-1,54 à +17,07‰) dans les sédiments subductés. De telles variations sont probablement le résultat de différentes réactions minérales se produisant le long du chemin prograde sur trois sites différents, ainsi que de la perte ou de la rétention de lithium qui en résulte. Les valeurs de $\Delta^7\text{Li}_{\text{quartz-fluide}}$ ne sont pas corrélées avec les températures métamorphiques maximales. L'absence de dépendance à la température du fractionnement suggère que le quartz n'a pas cristallisé à l'équilibre avec le fluide, ou que la cristallisation à l'équilibre est masquée par le rééquilibrage postérieur, par pression dissolution, entre les inclusions fluides et le quartz hôte. Cette étude confirme que le lithium et les isotopes du lithium des fluides piégés dans les inclusions des veines, peuvent être utilisés comme traceurs des fluides et comme outil pour évaluer les interactions fluide-roche dans les zones de subduction.

CHAPTER I – Introduction

I.1. Fluids in subduction zones

Fluids play an important role in majority of subduction zone processes. Fluids and associated fluid flow are primary agent of volatile and solute mass fluxes in the forearc (Fagereng et al., 2018; Hacker, 2008; Kastner et al., 1991; Kastner et al., 2014). Dehydration reactions in deeply subducted lithologies trigger magma generations due to the melting action of volatile species of the mantle (Bebout, 1991; Elliott, 2003; Hacker, 2008; Stern, 2011), simultaneously affecting the chemical and isotopic evolution of the mantle (Bebout, 1995, 2014; Brenan et al., 1998; Deschamps et al., 2013; Hacker, 2008; Hacker et al., 2003; van Keken et al., 2011; Magna, Wiechert, Grove, et al., 2006; Marschall, Pogge von Strandmann, et al., 2007; Peacock, 1993; Rupke, 2004; Scholl & von Huene, 2010). Also, fluid pressure controls the architecture of accretionary wedges and the distribution of fault zones (Dahlen, 1990; Mourgues & Cobbold, 2006). Moreover, overpressured pore fluids have profound effects on the seismic activity as they control effective normal stress, influencing sliding stability on the fault planes (Audet & Schwartz, 2013; Davis et al., 1983; Saffer & Tobin, 2011). Earthquake nucleation and coseismic slip occur at seismogenic zone, explained as a portion of the subduction interface where accumulation of elastic strain in the interseismic periods is sufficient to trigger the failure and generate earthquakes (Di Toro et al., 2011; Faulkner et al., 2010; Harris, 2003; Rice, 2006). The seismogenic zone is limited by the updip (upper aseismic-seismic transition) and the downdip limit (lower seismic-aseismic transition; Heuret et al., 2011; Hyndman et al., 1997; Oleskevich et al., 1999; Wallace et al., 2009). Generally speaking, these transitions are related to a presence of pore fluid and interplay between pore fluid pressure and effective normal stress. The updip limit occurs at 100-150°C, and is hypothetically related to the smectite-to-illite transformation and consequent transition from the stable sliding to the unstable slip (Saffer et al., 2012). Seismogenic zone is then characterized by moderate fluid overpressure, with period of building overpressure, followed by coseismic slip and consequent drop in fluid pressure (Raimbourg et al., 2022; Sibson et al., 1975, 1994). In the seismic-aseismic transition around the downdip limit, slow slip events (SSE) are recognized in several subduction zones, such as Cascadia subduction zone (e.g., Li & Liu, 2016; Schmidt & Gao, 2010; Szeliga et al., 2008). Such phenomena is correlated with high V_p/V_s ratio, explained as a consequence of very high pore fluid pressures in overpressured sediments (Behr et al., 2021; Mochizuki et al., 2021; Wallace et al., 2009). Hence, to understand all mention processes, it is

I.2. Fluid budget and main fluid carriers in subduction

crucial to understand the changes of the fluid and to evaluate the fluid budget along the prograde metamorphic path in subducted lithologies.

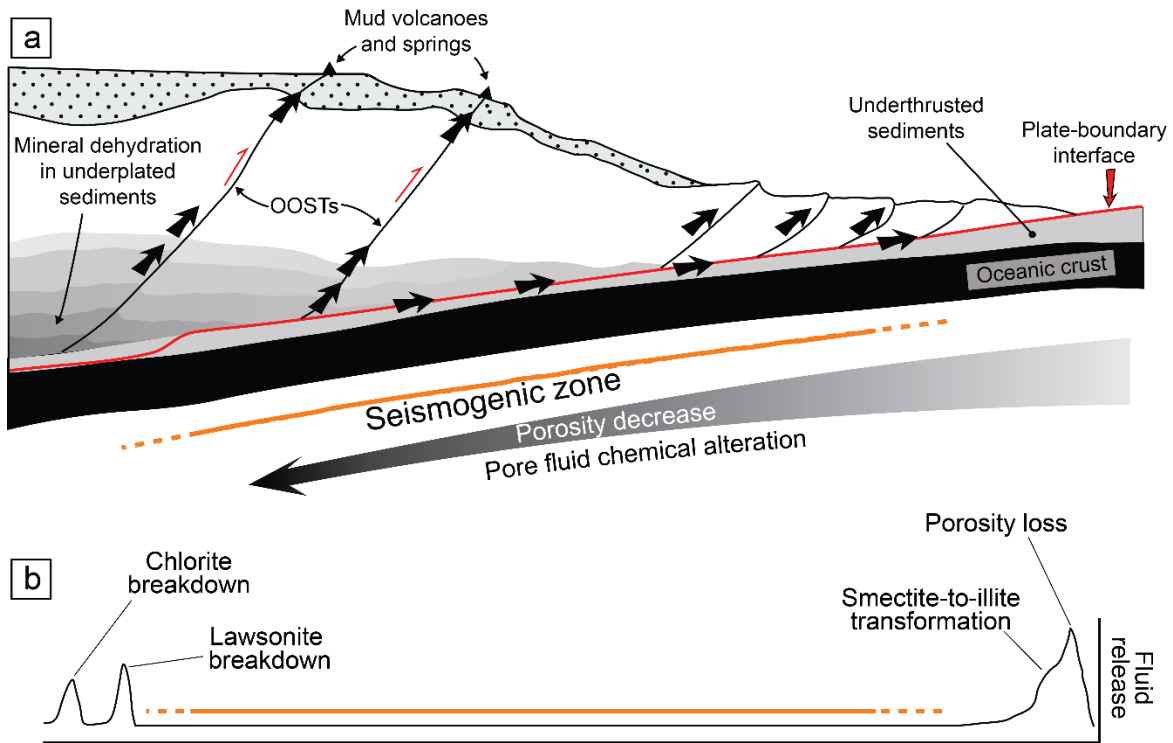


Figure I.1. (a) A schematic cross-section of subduction zone with the orange line corresponding to approximate depths of the seismogenic zone (Kastner et al., 2014). (b) A schematic fluid release as a function of temperature. Note that below temperatures of the estimated depths of the updip limit, majority of pore fluids are expelled from sediments as well as H_2O lost due to smectite-to-illite transformation, whereas along the seismogenic zone no dehydration reaction is proposed, before the breakdown of lawsonite and chlorite (Fagereng et al., 2018).

I.2. Fluid budget and main fluid carriers in subduction

Beside altered oceanic crust and serpentinites, sediments are the main carrier of volatile species in the subduction, both as interstitial pore fluids and mineral-bound water. The amount of pore fluids in the ocean-floor and trench sediments can be up to 60 vol. %, but the majority of these fluids are expelled during diagenesis and early metamorphism (Dasgupta & Mukherjee, 2020; Saffer, 2003; Velde, 1996). The expulsion of pore fluids operates in parallel with cementation and compaction, leaving only few vol.% of pore fluids in sediments at depths >5 km (Fig. I.1b; Kastner et al., 2014; Moore & Vrolijk, 1992; Saffer & Tobin, 2011). Early expelled fluids expelled back to the ocean as large-scale channelized fluid flow along the high permeability horizons, such as the decollement

zone of splay faults in the accretionary wedges (Carson et al., 1990; Martin et al., 1996; Moore & Vrolijk, 1992).

In parallel to the pore fluid expulsion during burial, several diagenetic reactions release mineral-bound water, among which smectite-to-illite transformation is the most important. This reaction occurs in the temperature range between 60°C and 150°C (Fig. I.1b; Saffer et al., 2008; Moore & Vrolijk, 1992; Kastner et al., 2014). The influence of diagenetic reactions onto chemical composition of interstitial fluids, such as smectite-to-illite or opal-to-quartz transformation, is well documented and understood via ODP/IODP programs (Kastner et al., 2014 and references therein). Released low-Cl⁻ fluid from smectite-to-illite transformation decreases the salinity of pore fluids (e.g., Brown et al., 2001).

At levels deeper than the downdip limit (at temperatures >400°C), several important dehydration reactions have been reported, such as the carpholite and chlorite breakdown in the blueschist facies or the glaucophane, lawsonite, and chlorite breakdown in the eclogite facies (Fig. I.1b; Agard et al., 2001; Angiboust & Agard, 2010; Bebout, 1991; Bebout et al., 2013; Becker et al., 2000; van Keken et al., 2002; Lefeuvre et al., 2020; Peacock, 1993; Simons et al., 2010; Spandler et al., 2003). These reactions have profound effect on global flux of volatile species and highly affect the chemical and isotopic composition of the mantle.

Also, several processes can highly affect the chemistry and isotopic composition of pore fluids in sediments, such as the cation exchange between clay minerals and fluids; precipitation (or conversely dissolution) of diagenetic and metamorphic phases. An example is provided for lithium and lithium isotopes in the fluid, where authigenic clay minerals tend to incorporate lithium (preferentially ⁶Li) from the fluid, leaving the fluid with higher $\delta^7\text{Li}$ than of the seawater (Fig. I.2; Chan & Kastner, 2000; Zhang et al., 1998). Conversely, dissolution of material and leaching of fluid-mobile elements tend to increase lithium concentration in the fluid, and as a consequence $\delta^7\text{Li}$ of fluids decreases towards the values of protolith (Fig. I.2; Chan et al., 1994; Scholz et al., 2010). The cation exchange is the controlling process in the low temperature diagenesis realm (Zhang et al., 1998), whereas dissolution-precipitation is of bigger importance at temperatures >150°C (Chan et al., 1994; Kastner et al., 2014).

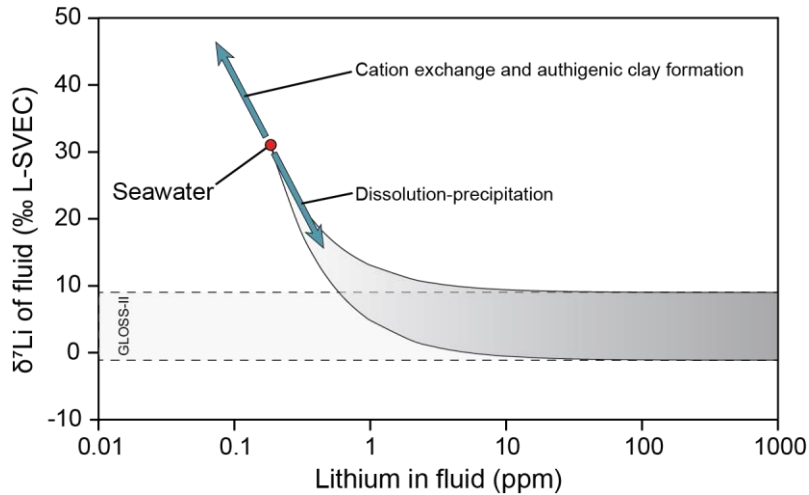


Figure I.2. Binary plot of $\delta^7\text{Li}$ vs lithium concentrations, indicating two opposite trends of fluids depending on the predominance of cation exchange and dissolution-precipitation processes. The mixing model is prepared with values of the seawater (Millot et al., 2004) and global subducted sediments (GLOSS-II; Plank, 2014).

I.3. Scientific context and motivations

As mentioned above, even the role of fluids along the seismogenic zones is of importance, the evolution of fluids in sediments subducted to the depths corresponding to the seismogenic zone is not well constrained. After the expulsion of majority of pore fluids, sediments discontinuously release water, depending on the stability fields of hydrous minerals (e.g., Aizawa et al., 1999; van Keken et al., 2002; Tatsumi & Kogiso, 2003). Only few metamorphic reactions has been identified in subducted sediments in the temperature range corresponding to the seismogenic zone (150-300°C), such as the formation of lawsonite (Goffé & Chopin, 1986; Lefeuvre et al., 2020). Although many exhumed sedimentary units have experienced sub-greenschist and greenschist facies (peak-metamorphism at 150-350°C) in subduction complexes, such as the Kodiak accretionary prism in Alaska (Brantley & Fisher, 1997; Fisher et al., 1995; Fisher & Brantley, 2014; Vrolijk et al., 1988) or the Shimanto belt in Japan (Nishiyama et al., 2021; Raimbourg et al., 2015, 2018), metamorphic transformation in the greenschist facies and the influence of reactions to the pore fluid budget is relatively poorly documented compared to deeper metamorphism. Furthermore, many (if not all) metasedimentary units in paleo-accretionary complexes contain evidence of ancient fluid pathways in form of metamorphic veins, also pointing to the occurrence of the mass transfer. However, the origin of veins remains the open debate. Contradictory explanations were proposed for different complexes: Quartz veins in the Kodiak accretionary

complex are considered as the product of local silica redistribution, without any significant input of external fluid (Brantley & Fisher, 1997; Fisher et al., 1995), on the contrary to quartz veins in the Otago Schist where an infiltration of external fluids is required (Breeding & Ague, 2002). Furthermore, vein-forming minerals commonly preserve high abundance of fluid inclusions, relicts of present fluids during their formation. Fluid inclusions in syn-subduction veins in metasedimentary complexes were subject of numerous studies. Majority of studies focused on changes in salinity across the prograde metamorphic path (Agard et al., 2000; Brantley & Fisher, 1997; Herviou et al., 2021; Raimbourg, 2015; Raimbourg et al., 2018; Rossetti et al., 2006; Vrolijk et al., 1988) or changes in the gas composition (Clément Herviou et al., 2021; Mullis et al., 1994; Raimbourg et al., 2018; Tarantola et al., 2007, 2009; Vrolijk et al., 1988). However, only few studies focused on actual chemical composition of fluids in subducted sediments (Rauchenstein-Martinek et al., 2016; Yoshida et al., 2015), and the knowledge about fluid-rock interaction in sediments subducted to the seismogenic zone is highly unexploited.

I.4. Thesis outline

This thesis aims to evaluate fluid-rock interaction in subducted sediments buried down to seismogenic depths (250-330°C) by (i) describing mineral reactions along the prograde path and (ii) describing fluid inclusions in syn-subduction veins, their salinity and the chemical composition. Then we evaluate the influence of proposed metamorphic reactions on the fluid budget and chemical evolution of the fluid in the given temperature range (major and trace elements as well as $\delta^7\text{Li}$ of fluids). Finally, we propose whether the system behave as open or closed. To do so, we focus in particular on metapelitic rocks from two paleo-accretionary complexes, the Kodiak accretionary complex, USA, and the Shimanto belt, Japan, whereas the study concerning $\delta^7\text{Li}$ of fluids is expanded as well to the Western Alps.

This study is divided into two parts: (1) Tectonic evolution of the Kodiak accretionary complex (Chapters II and III), and (2) petrological/geochemical characterization of metapelitic rocks and adjacent veins and fluid inclusions they contain (Chapters IV, V, and VI).

The chapters of the thesis are focused on:

Part 1

- As the Kodiak accretionary complex is the main field area, Chapters II and III concern the tectonic evolution of the complex (II) and thermal evolution across the complex (III). In chapter II, structural analysis was performed from collected structural data across five different units (basally accreted units and slope sediments).
- In Chapter III, in order to describe thermal history of the Kodiak accretionary complex, Raman Spectroscopy of carbonaceous material (RSCM) has been applied in nearly 100 samples across the complex, in basally accreted units and slope sediments. RSCM results were then used to estimate maximum burial depths, and in combination with structural data, a tectonic scenario of evolution is proposed, integrating in particular the different vein generations. A special focus is made on the vertical motion within the wedge, and two distinct events of exhumation in the complex are unraveled.

The combination of results from chapters II and III resulted in the submitted manuscript to the journal *Tectonics*: **Rajič, K., Raimbourg, H., Famin, V., Moris-Muttoni, B., Canizarés, A., Fisher, D., and Morell, K. *Exhuming the depths of accretionary prisms: A case study of the Kodiak accretionary complex, Alaska.***

Part 2

- Chapter IV focuses on mineral reactions and the fluid budget in metapelitic rocks from the Kodiak accretionary complex and the Shimanto belt in Japan. From each locality, two units were chosen according to the peak-metamorphic temperatures they experienced, presented as lower- and higher-grade units, corresponding to the peak metamorphic temperatures of ~250°C and ~330°C, respectively. In each unit the mineral composition was described by optical microscopy, SEM-BSE and XRD, followed by microstructural observations (SEM-BSE, Image analysis). The chemical composition of major minerals was determined by EPMA. From these results several mineral reactions were proposed along the prograde path as well as the evolution of chemical composition of major mineral phases. In parallel, the salinity and the chemical composition of fluid inclusions from associated veins were acquired by Raman Spectroscopy of OH band and by the decrepitation method combined

with SEM-EDS and EPMA. Combining these data, we discuss the influence and implications of proposed mineral reaction on the fluid budget along the seismogenic zone.

Chapter IV represents a basis for the manuscript submitted to the journal Tectonophysics: **Rajič, K., Raimbourg, H., Lerouge, C., Famin, V., Dubacq, B., Canizarés, A., Di Carlo, I., and Maubec, N. *Metamorphic reactions and their implication for the fluid budget in metapelites at seismogenic depths in subduction zones.***

- In Chapter V, fluid-mobile elements (FME, in first order Li, B, Rb, Sr, Cs, and Ba) behavior have been examined in the same samples as in Chapter IV. The FME whole-rock concentrations were measured by ICP-MS, whereas LA-ICP-MS was applied to estimate FME concentrations in individual mineral phases and in fluid inclusions. For the latter, we applied relatively new approach of bulk-microanalysis of small fluid inclusions population. We then explained the behavior of FME by looking into mineral reactions and modal proportion changes from Chapter IV. Based on these results, we were able to estimate W/R ratio and propose whether the system behave as open or closed.

From results of Chapter V, two manuscripts were prepared. The first is published in the journal Geochemistry, Geophysics, Geosystems, whereas the second is planned to be submitted to the journal Geochimica et Cosmochimica Acta:

Raimbourg, H., **Rajič, K.**, Moris-Muttoni, B., Famin, V., Palazzin, G., Fisher, D. M., et al. (2021). **Quartz vein geochemistry records deformation processes in convergent zones.** *Geochemistry, Geophysics, Geosystems*, 22.

Rajič, K., Raimbourg, H., Gion, A. M., Lerouge, C., and Erdmann, S. **Fluid-mobile elements behavior in subducted sediments: A case study from low- to moderate-P/T metapelitic rocks.** Submitted to *Geochimica et Cosmochimica Acta*.

- Chapter VI focuses on lithium isotopes of fluid inclusions and quartz by applying crush-leach technique in 21 syn-subduction quartz-dominated veins. Beside extensively studied veins from the Kodiak complex and the Shimanto belt in Chapters IV and V, here we

examined as well veins from the Western Alps. Also, remaining quartz powder is analyzed as well for Li isotopic composition, in order to test the existence of temperature-dependent Li isotopic fractionation. Finally, $\delta^7\text{Li}$ of fluid inclusions were combined with reconstructed Li concentrations to explain the origin of fluids and to discuss the implications for the fluid evolution during subduction.

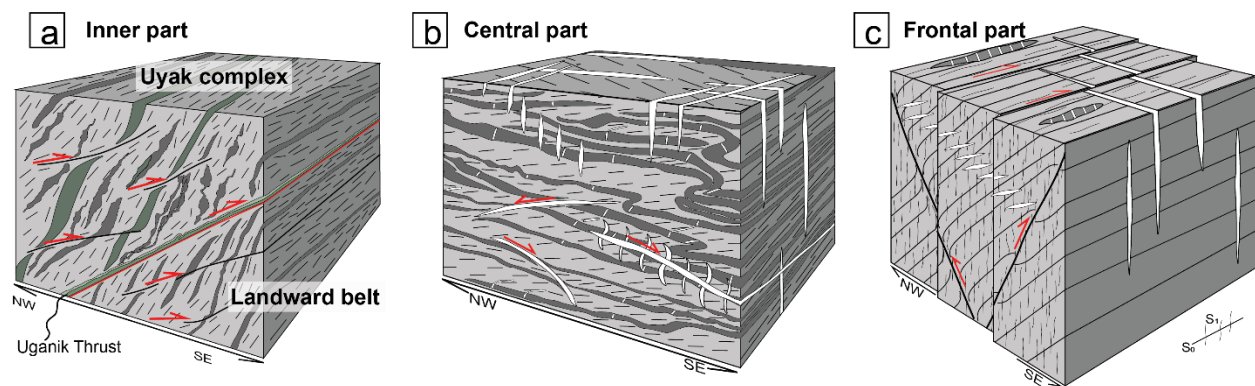
*This chapter is a basis for the manuscript which will be submitted to the journal Earth and Planetary Science Letters (EPSL): **Rajič, K., Richard, A., Raimbourg, H., Lerouge, C., Millot, R., Magna, T., Herviou, C. Lithium isotopic analysis of fluid inclusions in quartz from syn-subduction veins.***

The manuscript ends with general discussion and conclusion (Chapter VII) as a combination of all presented results, and point to perspectives for work in the future.

Preface

Rocks constituting paleo-accretionary complexes record a wide range of deformation structures formed either along plate-boundary interface during underthrusting, as intra-wedge deformation, or during exhumation. In spite of numerous studies conducted in paleo-accretionary complexes in order to discriminate between different deformation structures and their occurrence at the specific stage of tectonic history, no uniform consensus exists. In order to overcome this issue, in this chapter we report observed deformation structures along several units (including tectonic mélanges, accreted coherent units and slope sediments) in the Kodiak accretionary complex, followed by grouping either as underthrusting-related or as intra-wedge deformation, and proposing the relative age of each tectonic stage. Importantly, this chapter represents a basis for the interpretation at which stage examined veins formed.

CHAPTER II – Tectonic evolution of the Kodiak accretionary complex



CHAPTER II – Tectonic evolution of the Kodiak accretionary complex

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II.1. Introduction

Accretionary wedges grow horizontally through the frontal accretion of tectonic slices of sediments and vertically through the basal accretion combined with horizontal shortening (e.g., Dahlen, 1990; Davis et al., 1983; Menant et al., 2020; Moore et al., 2001; Moore, 1989). A large number of seismic studies and deep sea drilling programs in modern subduction zones have demonstrated tectonic processes, in particular the shallow, frontal accretion of tectonic slices by the propagation of in-sequence, land-ward dipping thrusts (Moore et al., 1990; Moore et al., 2001; Moore, 2000; Shipboard Scientific Party, 1994; von Huene et al., 1998). In addition to frontal processes, tectonics along the basal surface of the wedge also modifies its shape and volume: wedge thickness is increased by underplating of coherent units and mélanges beneath the wedge (e.g., Byrne & Fisher, 1987; Fisher & Byrne, 1987; Platt, 1986; Sample & Fisher, 1986) or decreased by basal erosion along the subduction interface (Vannucchi et al., 2001; Clift & Vannucchi, 2004; von Huene & Lallemand, 1990). In contrast to the border of the wedge, the deformation *within* the accretionary wedge is far less clear, because seismic reflection imaging cannot fully resolve deformation structures in the thick and strongly tectonized sediment sequences that constitute most of the wedge.

Fossil subduction zones exhumed to the surface provide additional information as to the tectonics active on the boundary and within accretionary wedges. Accretionary complexes, such as Shimanto belt of Japan (Raimbourg et al., 2014, 2017) or the Franciscan Complex (Meneghini et al., 2009; Wakabayashi, 2015), show exhumed rocks, either mélanges or coherent units, that experienced non-coaxial deformation due to intensive shearing along or in vicinity to the plate-boundary interface (e.g., Fagereng & Sibson, 2010; Meneghini et al., 2009; Raimbourg et al., 2019). Further deformation occurs after the incorporation of material into the wedge, mostly as out-of-sequence thrusting and formation of damage zones in the footwall of the thrusts, both processes being highly influenced by fluids (e.g., Fisher & Byrne, 1987; Kondo et al., 2005; Rowe et al., 2009; Smeraglia et al., 2019).

One of the largest accretionary prism worldwide is in the southern Alaska extending from Sanak Islands to the west to the Alexander Archipelago to the east, and is bordered to the north by the Wrangellia composite terrane along the Border Ranges Fault System (Plafker et al., 1994). The complex consists of trench-parallel trending metasedimentary packages and igneous intrusions,

where the age of intrusions decrease from west towards east (Farris & Paterson, 2009). As a part of it, the Kodiak accretionary complex represents well studied and exposed paleo-accretionary complex with the modern equivalent further to the southeast as the Aleutian Trench (Byrne & Fisher, 1987; Plafker et al., 1994). The complex consists of metaturbidites and metamafic units which, before exhumation, experienced subduction-related and intra-wedge deformation during multiple phases of accretion (Byrne & Fisher, 1987), providing the opportunity to study accretion-related processes. Even though the Kodiak accretionary complex was the subject of numerous studies, its deformation kinematics are poorly understood at the scale of the whole complex.

In this chapter we report the results of an extensive field survey across the Kodiak accretionary complex, viewed as an archetypal example of an ancient accretionary wedge, with the aim to unravel deformation variations since the Cretaceous to the present. We describe deformation structures and kinematics of each unit and relate them to plate-boundary interface and intra-wedge deformation dynamics, with particular emphasis on the relative chronology of each type of deformation during building of the prism.

II.2. Anatomy and lithostratigraphy of the Kodiak accretionary complex

The sedimentary terranes that form the Kodiak paleo-accretionary prism are exposed on the northwestern side of the archipelago to the youngest Miocene units on the southeast coast (Fig. II.1; Byrne & Fisher, 1987; Connelly, 1978; Moore et al., 1983; Roeske et al., 1989; Sample & Moore, 1987). The metamorphic grade is compatible with the aging trend, from blue- and greenschist facies at the northwest (Roeske et al., 1989), through prehnite-pumpellyite and greenschist in the middle part (Brantley & Fisher, 1997; Connelly, 1978; Sample & Moore, 1987; Vrolijk et al., 1988) to the zeolite facies and mildly deformed sedimentary rocks at the southeastern side (Moore et al., 1983; Moore & Allwardt, 1980).

The Uyak Complex, described as a tectonic *mélange* with block-in matrix texture, consists of lenses of greywacke, chert, mafic rocks, tuff and limestones within sheared argillitic layers (Connelly, 1978). The stratigraphic ages indicate it was deposited on top of the oceanic plate during most of the Mesozoic up to the Early Cretaceous as testified by the youngest fossil dated late Valanginian to late Aptian (Clift et al., 2005; Connelly, 1978; Pavlis et al., 1988). The Uyak

Complex was deformed during underthrusting between the Valanginian and the Maastrichtian (Connelly, 1978). The metamorphic conditions recorded in basalt lenses are up to the prehnite-pumpellyite facies (Connelly, 1978). Fluid inclusion studies in extensional veins documented trapping temperature of 270-290°C and pressure of 3.3 kbar (Vrolijk et al., 1988). The Uyak Complex is in tectonic contact with the Kodiak Formation along the Uganik Thrust (Moore, 1978; Rowe et al., 2009).

The Kodiak Formation is a sequence of turbidites – slates, siltstones and sandstones, interpreted as oceanic trench sediments accumulated during the Late Cretaceous (Byrne & Fisher, 1987). The age of sedimentation is determined as Maastrichtian (~70 Ma) by the occurrence of *Inoceramus kusiroensis* (Byrne & Fisher, 1987). The dominant deformation structure in the Kodiak Formation is a slaty cleavage distinctly organized across the package. Sample & Moore (1987) subdivided the Kodiak Formation into a Landward Belt (with a northwest-dipping slaty cleavage), a Central Belt (sub-horizontal cleavage) and a Seaward Belt (northwest-dipping cleavage; Fig. II.1). Vitrinite reflectance in the Kodiak Formation has an average value of 3.73, corresponding to a temperature of ~225°C (Sample & Moore, 1987). Based on cogenetic CH₄- and H₂O-rich fluid inclusions from syn-cleavage quartz veins in the Landward Belt, minimum temperature and pressure are estimated as 215-250°C and 2.8 kbar (Myers & Vrolijk, 1986). The Kodiak Formation is separated from the Ghost Rocks Formation to the southeast along the Contact Fault (Farris, 2010).

Dominant lithologies in the Ghost Rocks Formation are shales and sandstones, with minor conglomerates, volcanic rocks and limestones (Byrne, 1982; Moore, 1989). Pelagic foraminifera from limestone indicate Late Cretaceous-early Paleogene age (Moore et al, 1983 and references therein). The southeastern part of the Ghost Rocks Formation is described as a tectonic mélange, named Ghost Rocks mélange, whereas the northwestern part is represented as a coherent portion of the unit (Byrne, 1982). Vitrinite reflectance (R_0) on samples from the Ghost Rocks Formation is in the range of 2.15% to 2.95%, suggesting the peak temperatures of 225-250°C (Moore et al., 1983). The minimum temperature from fluid inclusion studies from syn-tectonic extensional veins at Jap bay and Pasagshak area is $250 \pm 20^\circ\text{C}$, with a trapping pressure of ~3 kbar (Vrolijk et al., 1988).

II.2. Anatomy and lithostratigraphy of the Kodiak accretionary complex

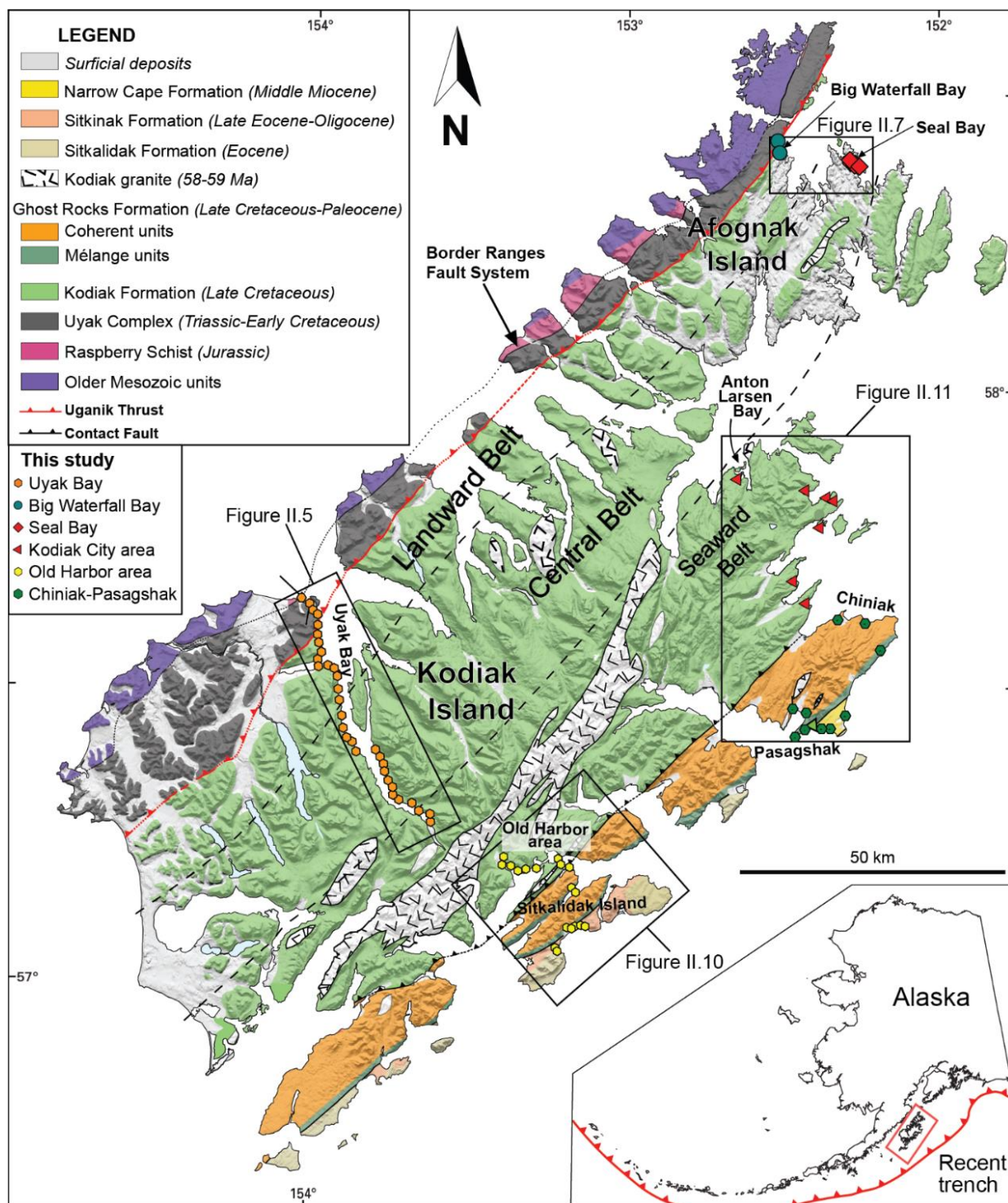


Figure II.1. Geological map of the Kodiak archipelago modified after Wilson (2013) with areas/localities where two field surveys were conducted. Dashed line in the Kodiak Formation are estimated borders between the Landward, Central and Seaward Belts.

The Kodiak and the Ghost Rocks Formation have been intruded by andesite and granodiorite plutons, dated at 58-59 Ma by U-Pb on monazite and zircon (Farris et al., 2006). It is proposed that both the Kodiak Formation and the Ghost Rocks Formation were basally accreted prior to the intrusive event (Byrne & Fisher, 1987; Sample & Fisher, 1986; Sample & Moore, 1987).

The Sitkalidak Formation, exposed along the southeast side of the archipelago, consists of sandstone and shale layers (Byrne & Fisher, 1987; Moore et al., 1983; Moore & Allwardt, 1980). The sedimentation age of the Sitkalidak Formation is Eocene (Moore et al., 1983; Moore & Allwardt, 1980). Unlike all other units, it contains abundant thrust faults with a landward vergence (Moore & Allwardt, 1980). Based on vitrinite reflectance, Moore & Allwardt (1980) inferred peak temperature of 100-125°C in the frontally accreted Sitkalidak Formation.

Tertiary sediments are unconformably deposited onto the Ghost Rocks Formation and Sitkalidak Formation. The Oligocene Sitkinak Formation consists of nonmarine to shallow marine sediments overlying the Sitkalidak Formation (Moore & Allwardt, 1980 and references therein). The metamorphic temperatures inferred from vitrinite reflectance are in the range 100-125°C (Moore & Allwardt, 1980). Middle Miocene slope sediments of the Narrow Cape Formation are composed of mildly deformed shallow water sediments, unconformably overlying the Ghost Rocks Formation (Moore et al., 1983).

II.3. Methods

II.3.1. Kinematic analysis of deformation structures

The attitude of micro- and meso-structures was measured in the field and used to reconstruct the deformation history of the accretionary prism. Structures include kinematic indicators (meter-scale striated faults, shear bands, fractures), indicators of finite strain (schistosity, crenulation, slaty cleavages and fold axes) as well as of stress orientations (dykes and extension fractures typically filled with syn-deformation minerals - calcite and/or quartz $\pm$ chlorite $\pm$ oxides $\pm$ sulfides). Bedding or foliations were measured at each site together with deformation structures. The measured data were processed following Delvaux & Sperner (2003) and Sperner & Zweigel (2010), which includes the search for chronological relationships in the field, the attribution of a categorical confidence level to each datum (certain, probable, supposed, unknown), and the nonautomated

separation of data into mechanically compatible subsets. Structural data were manually sorted according first to their crosscutting relationships, and then according to their kinematics and orientation.

We limited our kinematic analysis to the determination of shortening (P), intermediate (B) and extension (T) axes. The kinematic analysis was performed using the PBT method of the WinTensor program (Delvaux et al., 2013), which determines the statistical distribution of kinematic axes for a given subset of data.

II.4. Deformation structures

In what follows we describe each studied unit from the northwest to the southeast of the Kodiak archipelago. In addition, deformation structures around the Uganik Thrust are presented. All structural data for each locality is in Supplementary Table S2.1.

II.4.1. Uyak Complex

Lenses of basalts, cherts and sandstones are boudinaged and embedded within strongly sheared shale. Basalt lenses show a penetrative foliation and locally a lineation (average 47/313). NW-dipping shear bands with top-to-the-SE sense of shear are the dominant deformation structures (Fig. II.2a), filled with quartz or unmineralized. We classify these shear bands as D1 shear bands. Close to the contact with the Raspberry Schist (Site 19KO24), conjugate extensional shear bands have been observed (slickensides 39/301) indicating a NW-SE extension.

The dominant type of veins in the Uyak Complex are extension (categorized as Mode 1) veins (Fig. II.2b), filled with quartz in chert and sandstone boudins, and less common meter-scale veins filled with calcite in basalts. The orientation of Mode 1 veins is nearly perpendicular to the orientation of chert boudins, also when chert layers are folded. The concentration of veins increases from the center of boudin towards the neck where in some cases the neck is completely formed out of quartz. Sub-vertical calcite or quartz veins that crosscut several layers are locally observed but without particular orientation.

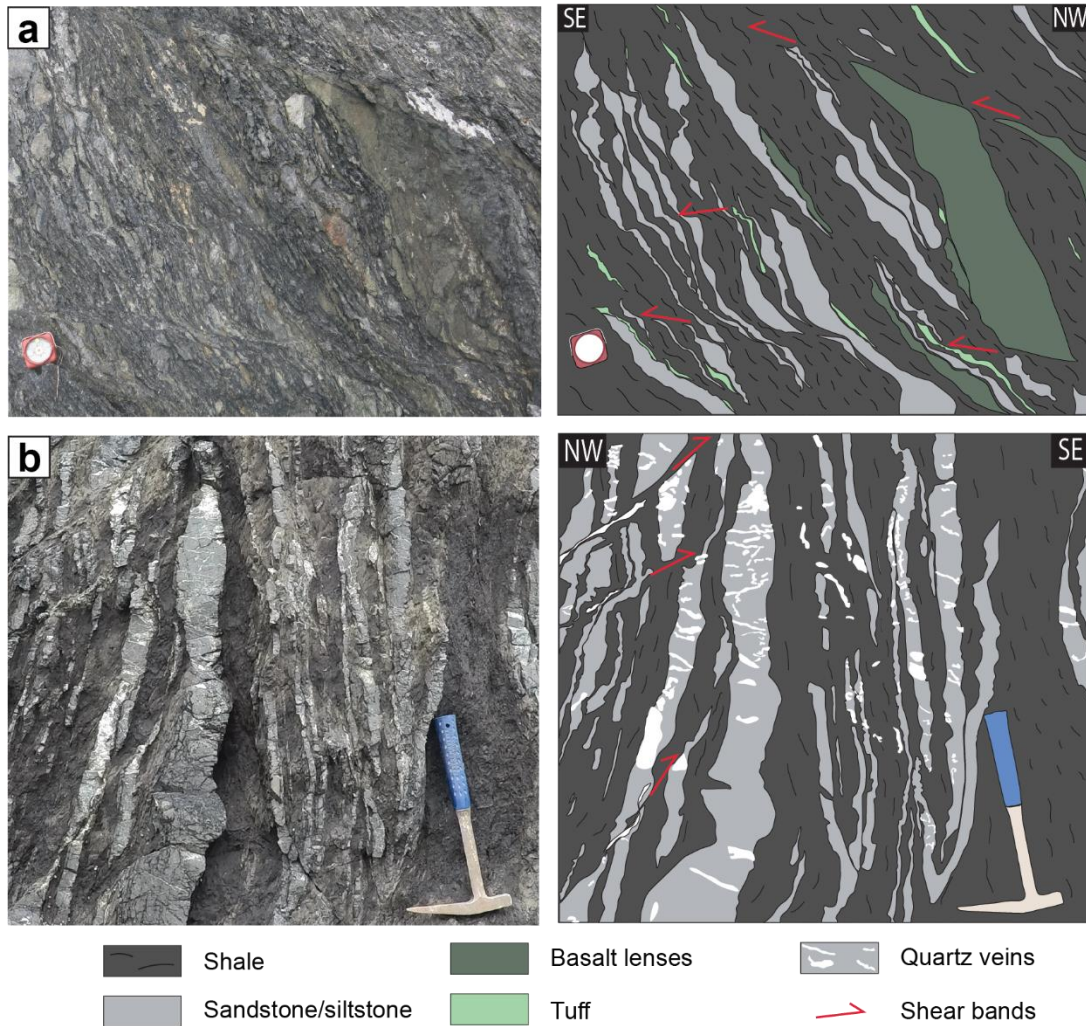


Figure II.2. Characteristic deformation structures in the Uyak Complex. (a) Top-to-the-trench shear bands with sandstone and basalt lenses embedded in a pelitic matrix. (b) Sub-vertically oriented sandstone layers with Mode 1 quartz veins sub-perpendicular to the bedding orientation.

II.4.2. Uganik Thrust

In Big Waterfall Bay, the fault core of the Uganik Thrust is characterized by a 0.15-0.30 m thick cataclastic zone in the footwall belonging to the Kodiak Landward Belt, and a 1-2 m thick mylonite in the hanging wall belonging to the Uyak Complex (Fig. II.3a). A damage zone, several meters thick, is observed in the footwall below the cataclastic zone (Fig. II.3b). The fault plane bordering the cataclastic zone is oriented 34/305, with a N170 slickenline and top-to-the-trench sense of shear. Asymmetric folds within the hanging wall mylonite confirms this sense of motion (Fig. II.3c; for more details see Rowe et al., 2009). The mylonite in the hanging wall is cut by a granitic

II.4. Deformation structures

dyke (Fig. II.3a), but it is not clear whether the dyke crosscuts the fault plane or not. In the foot wall close to the thrust, the damage zone contains NW-dipping shear bands with top-to-the-SE sense of shear, consistent with the kinematics of the fault plane (Figures II.3d, II.7a-b). A few meters away from the Uganik Thrust in the Kodiak Landward Belt footwall, schists display a very dense network of quartz veins. The density of shear bands and veins decreases with increasing distance from the fault.

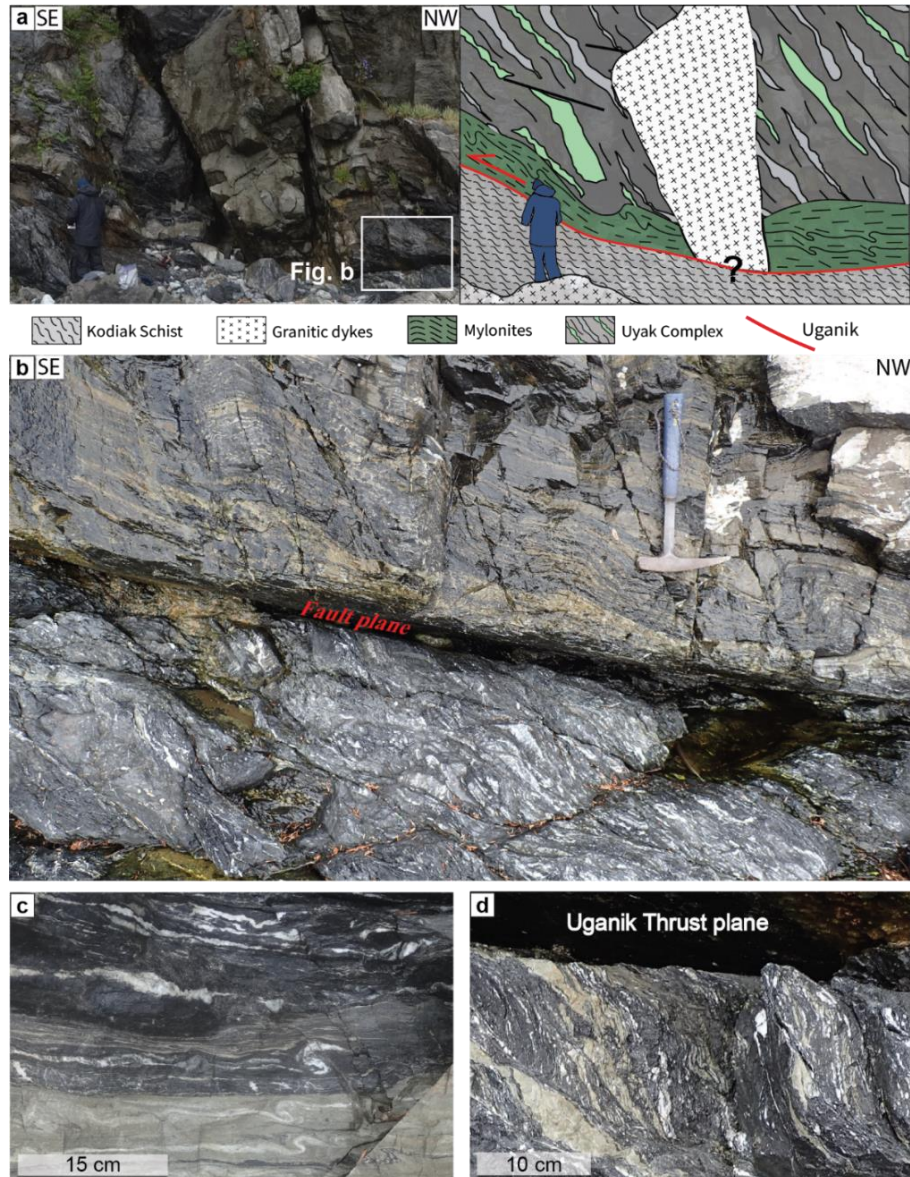


Figure II.3. (a) The Uganik Thrust at Big Waterfall Bay. (b) Uganik Fault plane with a mylonitic hanging wall (Uyak Complex) and highly sheared sediments in the foot wall (Kodiak Formation). (c) Asymmetric folds in the mylonite indicating a top-to-the-SE sense of shear. (d) Highly sheared sediments in the foot wall.

In the foot wall far from the damage zone, the dominant structures are conjugate sets of shear bands showing a SE-NW shortening direction, with sporadic only shear bands with the top-to-the-trench sense of shear (Fig. II.7b). Shear bands more often contain quartz than calcite.

II.4.3. Kodiak Formation

II.4.3.1. Uyak Bay

In the two studied localities where the Kodiak Formation contacts the Uyak Complex (Uyak Bay and Big Waterfall Bay), the top-to-the-SE (D1) shear deformation (Figures II.4a, II.5) vanishes below the Uganik Thrust and becomes almost absent a few hundred meters away from the thrust, leaving a well-preserved stratification bedding (Fig. II.4b). Away from the Uganik Thrust in the Landward Belt, quartz veins are restricted to sandstone layers and boudins, with an orientation perpendicular to the bedding (Fig. II.4c). Less common, layer-perpendicular meter-scale calcite and quartz veins are also locally observed.

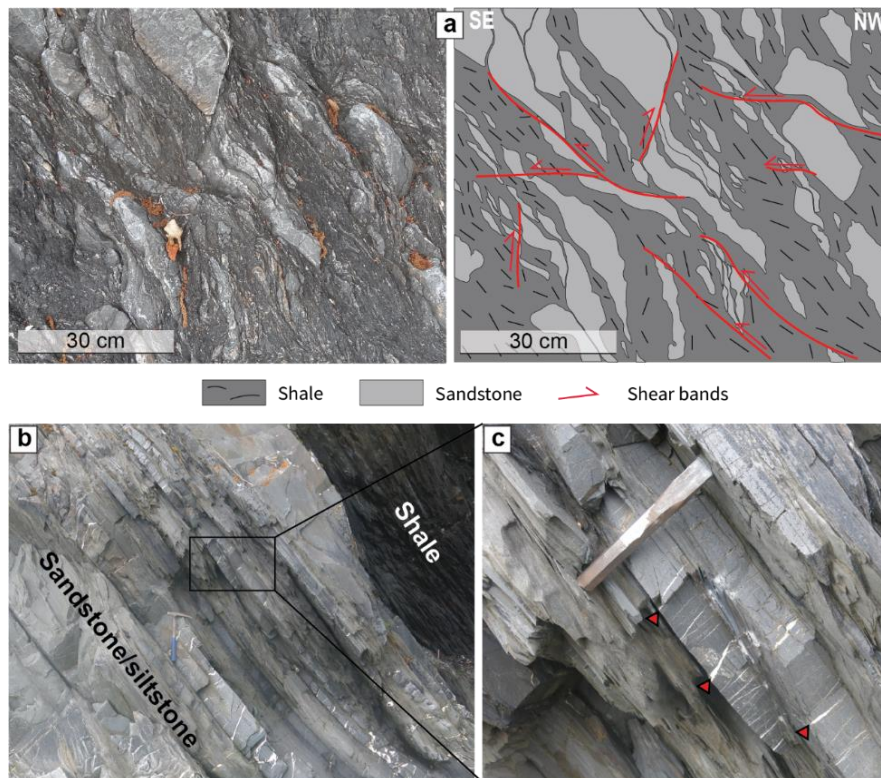


Figure II.4. Deformation structures of the Kodiak Landward Belt: (a) Top-to-the-trench shear bands in the Kodiak Landward Belt (Site 19KO17). (b) Coherent part of the Kodiak Landward Belt with shale and sandstone/siltstone beds. (c) Mode-1 quartz-calcite veins in sandstone beds.

II.4. Deformation structures

Further in Uyak Bay, from Larsen Bay towards southeast, the deformation style is different from the Kodiak Landward Belt. Hence, the rest of Uyak Bay is assumed to be part of the Kodiak Central Belt. In the Central Belt, the bedding stratification and slaty cleavage dip towards northwest but at slightly lower angle than in the Landward Belt. A pervasive slaty cleavage is at low-angle to the bedding stratification (Fig. II.5). Also, unlike the Landward Belt, deformation is non-coaxial rather than coaxial. At localities with sub-horizontal slaty cleavage, a set of conjugate normal shear bands

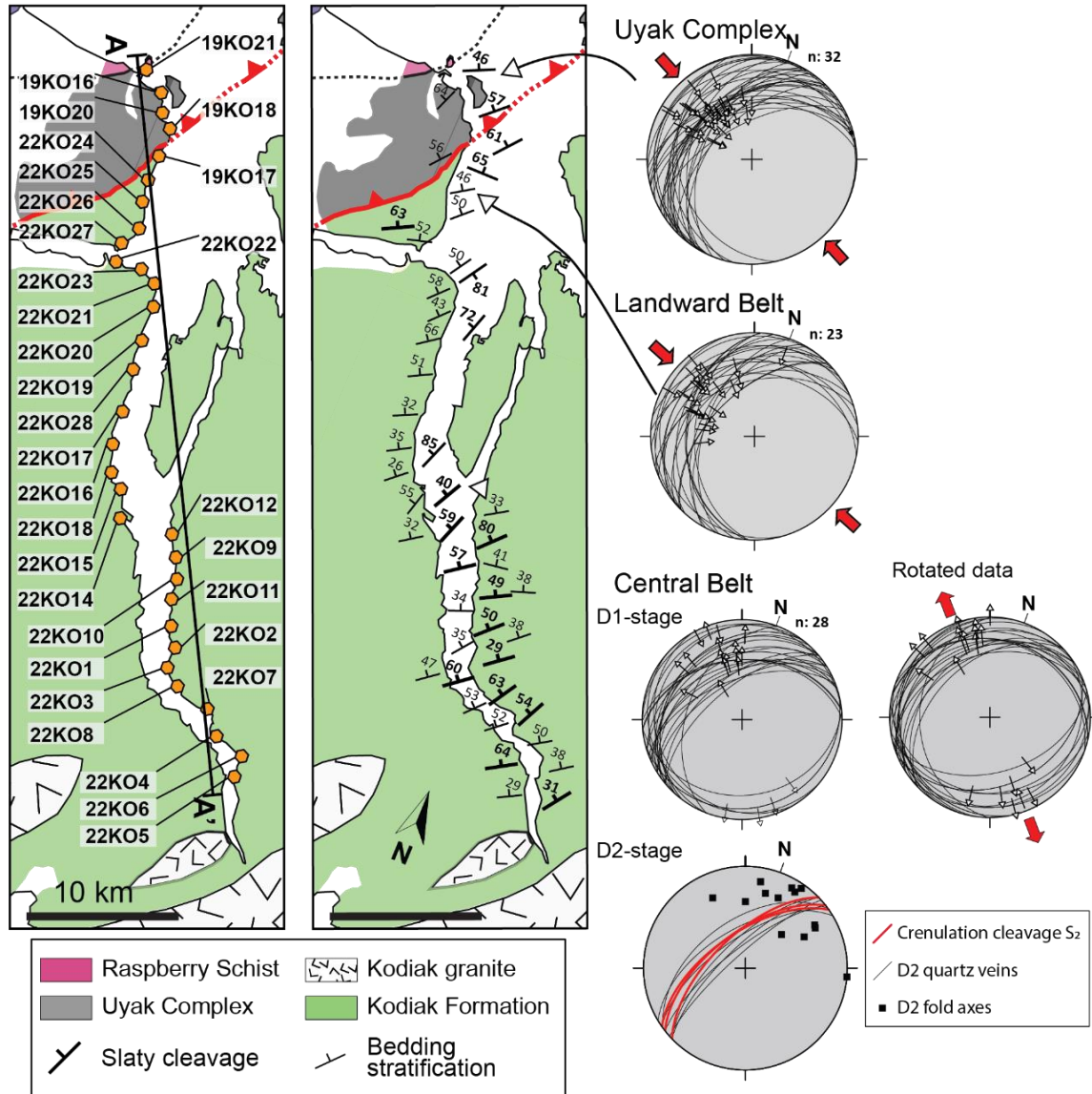


Figure II.5. Geological map of Uyak Bay with locations of samples, the orientation of a bedding stratification and foliation and pole figures of representative deformation structures. From top to the bottom, pole figures represent top-to-the-SE shear bands in the Uyak Complex; top-to-the-SE shear bands in the Kodiak Landward Belt close to the Uganik Thrust; normal and thrust faults in inner part of Uyak Bay (left) and their orientation after the restoration of foliation to the horizontal position (right); and folds, crenulation cleavage S_2 and D2-veins.

II.4. Deformation structures

are observed (Fig II.6a). We classify these shear bands as D1 shear bands as well. Quartz is the main mineral phase in D1 shear veins, sporadically calcite is observed. At localities characterized by steeper slaty cleavage, a set of high-angle normal and low-angle reverse shear bands have been found. When the slaty cleavage is rotated back to the horizontal position, these two sets appear as a set of conjugate extensional shear bands (Fig. II.5).

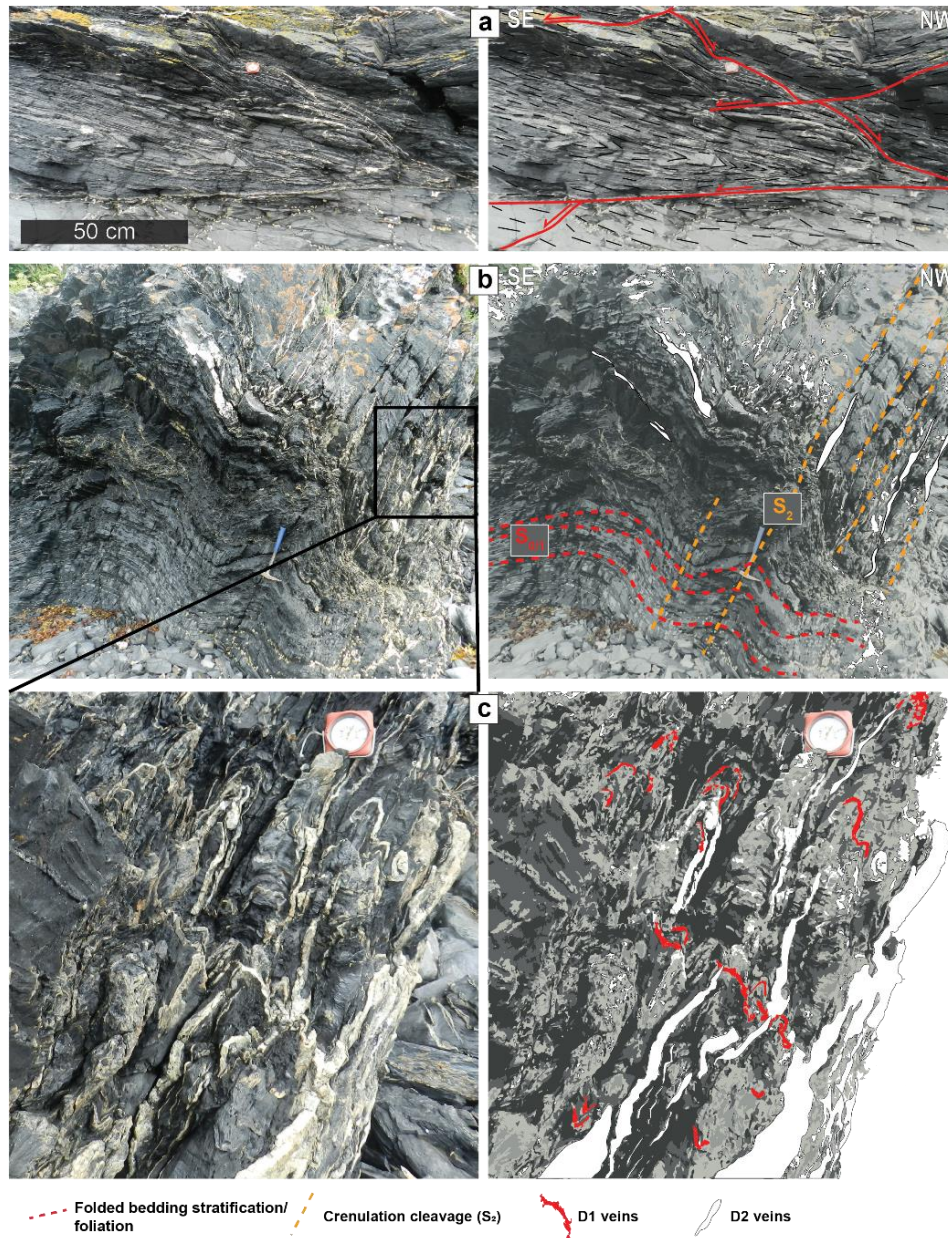


Figure II.6. (a) Conjugate extensional shear bands cutting across the bedding stratification at low angle (Site 22KO16). (b) Folded strata with fold axes parallel to the crenulation cleavage (S_2) and D2 quartz veins. (c) An example of earlier quartz shear bands at low angle to the stratification bedding and later D2 veins. Earlier D1 veins are folded and cut across by D2 veins.

Occasionally, the bedding stratification/slaty cleavage is folded with the orientation of fold axial plains SW-NE (Fig. II.6b). Fold axial plains are generally parallel to the NE-striking sub-vertical crenulation cleavage plains (S_2). In zones with pervasive crenulation cleavage S_2 , quartz veins parallel to S_2 plains are observed (Figures II.5, II.6c). These quartz veins are classified as D2 veins. At localities where folding is observed, D1 veins are folded and D2 veins cut across D1 veins (Fig. II.6c).

II.4.3.2. Seal Bay

The Central Belt in Seal Bay is characterized by a sub-horizontal bedding stratification with a low-dip towards the south or southwest (average 27/194). The pervasive slaty cleavage (average 10/204) is at low angle to the bedding (Fig. II.8a-b). Shear bands show a dominant normal sense of shear, which corresponds to horizontal extension in their present-day attitude (Figures II.7c, II.8d). Occasionally recumbent folds are observed at localities around Seal Bay (Fig. II.8a).

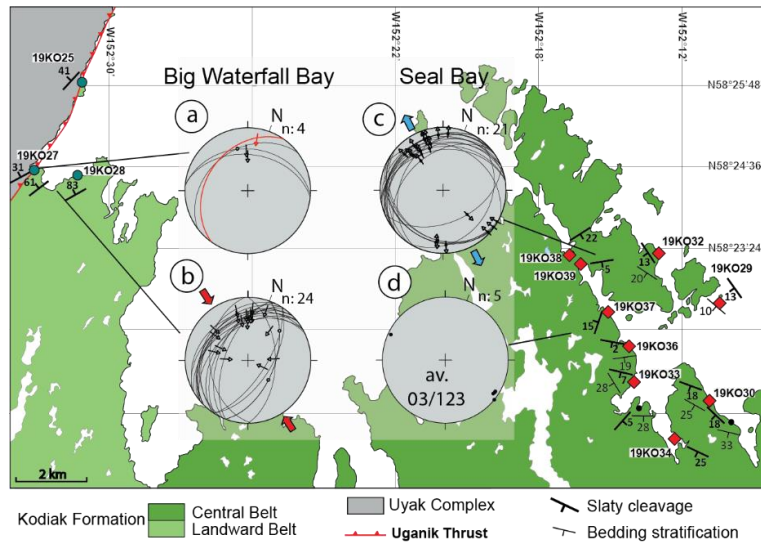


Figure II.7. A map of Seal Bay and Big Waterfall Bay with the orientation of the stratification bedding and the slaty cleavage. Stereographic plots: (a) Shear bands in the damage zone of the Uganik Thrust (black) and the thrust plane itself (red). (b) Shear bands from the Kodiak Landward Belt. (c) Extensional shear bands from the Kodiak Central Belt indicate a N156-N336 extension. (d) Asymmetric folds in the Kodiak Central Belt have an average orientation of fold axis 03/123.

Four different sets of veins have been distinguished in the Central Belt: (1) highly deformed Mode 1 veins with a preserved original orientation only in sandstone and siltstone layers. In the less resistant layers such as shales, these veins are completely deformed and rotated towards the

II.4. Deformation structures

orientation of the slaty cleavage (Fig. II.8a). The dominant mineral phase in these veins is quartz, but calcite is locally observed; (2) sub-vertical NE-striking quartz veins often forming en échelon arrays, the majority of which dip toward the southeast, to a lesser extent toward the northwest (Fig. II.8b-c). The length of individual vein can reach up to 1 m; (3) quartz shear veins with stretched quartz fibers in the NW-SE direction (Fig. II.8d). (4) Sub-vertical NW-striking quartz veins, up to 30 cm long. NE- and NW-striking sets of veins show mutual crosscutting relationship.

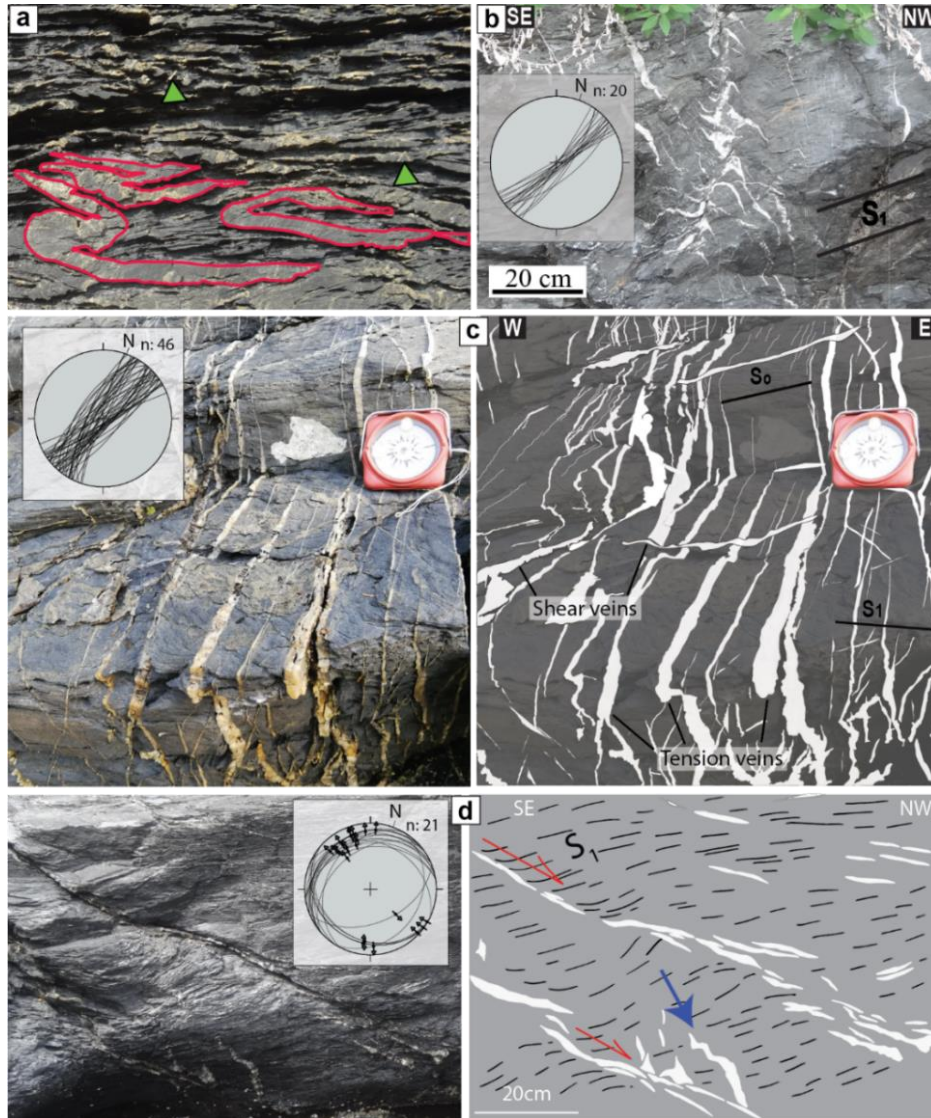


Figure II.8. Deformation structures in the Kodiak Central Belt: (a) Preserved stratification bedding and the slaty cleavage at low angle to stratification bedding (S_0). Marked layers represent recumbent folds. Early-stage extension veins are shown with green triangles, with their original orientation locally preserved in the most competent layers. (b) En échelon array of veins with a SE dipping direction. (c) Thick subvertical quartz veins with similar orientation to en échelon veins. (d) Normal shear bands.

II.4.3.3. The Kodiak Seaward Belt

The localities around Kodiak city and in Old Harbor area show identical deformation structures. Hence, both areas were treated as a single group called the Kodiak Seaward Belt. The Seaward Belt is characterized by a preserved bedding with a 40° to 90° dip dominantly to the northwest (Fig. II.9). The sub-vertical slaty cleavage is well developed at low angle (20 - 40°) with the bedding. Common structures in the Seaward Belt include conjugate sets of NW- and SE-dipping thrust faults filled with quartz fibers (Figures II.9a, II.10a, II.11a-b). Conjugate thrust faults, either NW- or SE-dipping, are up to 5 m in length and often form anastomosing network (Fig. II.9a). Upright folds are observed sparsely throughout the Seaward Belt (Figures II.9c, II.10a). Other frequently observed structures in the Seaward Belt are strike-slip faults, dominantly dextral (Figures II.9b, II.10a, II.11a-b). Within the granite pluton of Anton Larsen Bay, strike-slip faults are observed, but contrary to other sites in Seaward Belt most of them are sinistral (Fig. II.11f). Occasionally, the bedding and the slaty cleavage planes are reactivated as dextral strike-slip faults.

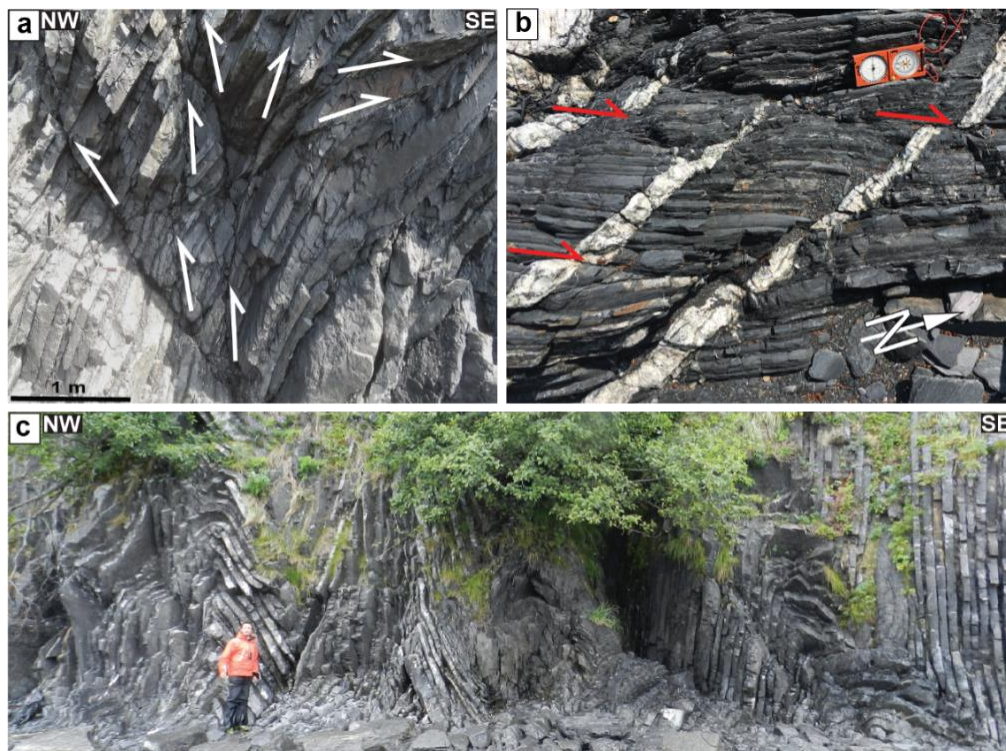


Figure II.9. Preserved deformation structures in the Kodiak Seaward Belt: (a) Conjugate set of thrust faults indicating NW-SE shortening direction (Site 19KO44). (b) Late-stage dextral strike-slip faults offsetting subvertical quartz-calcite-chlorite veins (Site 19KO12). (c) Isoclinal folds in the Kodiak Seaward Belt, Old Harbor area (Site 22KO42).

II.4. Deformation structures

Three different sets of veins have been observed in the Seaward Belt: (1) highly deformed Mode 1 veins as seen in the Central Belt in Seal Bay. (2) Sub-vertical quartz + calcite $\pm$ chlorite veins up to 15 cm thick and 0.5-2 m long (Fig. II.9b). Their average orientation is 84/229. Whenever present, chlorite is always found in association with quartz on the outer edge of the veins, whereas euhedral quartz and calcite occupy their middle part. This set of sub-vertical quartz veins is also observed in the Kodiak granite intruding the Seaward Belt, with the average strike of N124. (3) Sub-horizontal en échelon veins arranged in arrays dipping toward the southeast. These veins commonly contain euhedral quartz crystals.

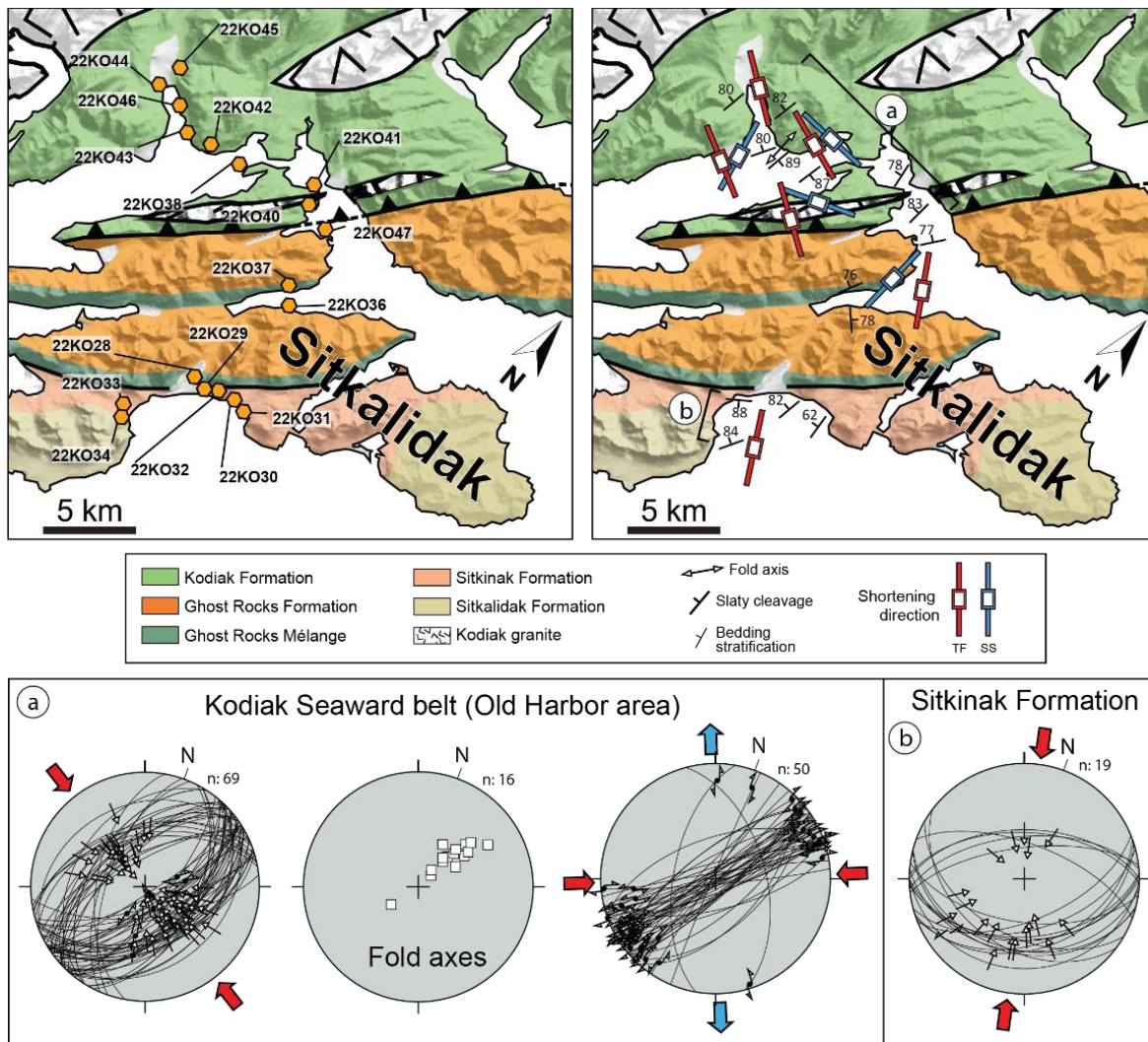


Figure II.10. Geological map of the Old Harbor area with measured bedding stratification and shortening directions derived from thrust and strike-slip faults. (a) Pole figures of main deformation structures in the Kodiak Seaward Belt: Conjugate thrust faults (left), isoclinal folds (center), and strike-slip faults (right). (b) A pole figure of measured thrust faults in the Sitkinak Formation at Sitkalidak Island.

II.4. Deformation structures

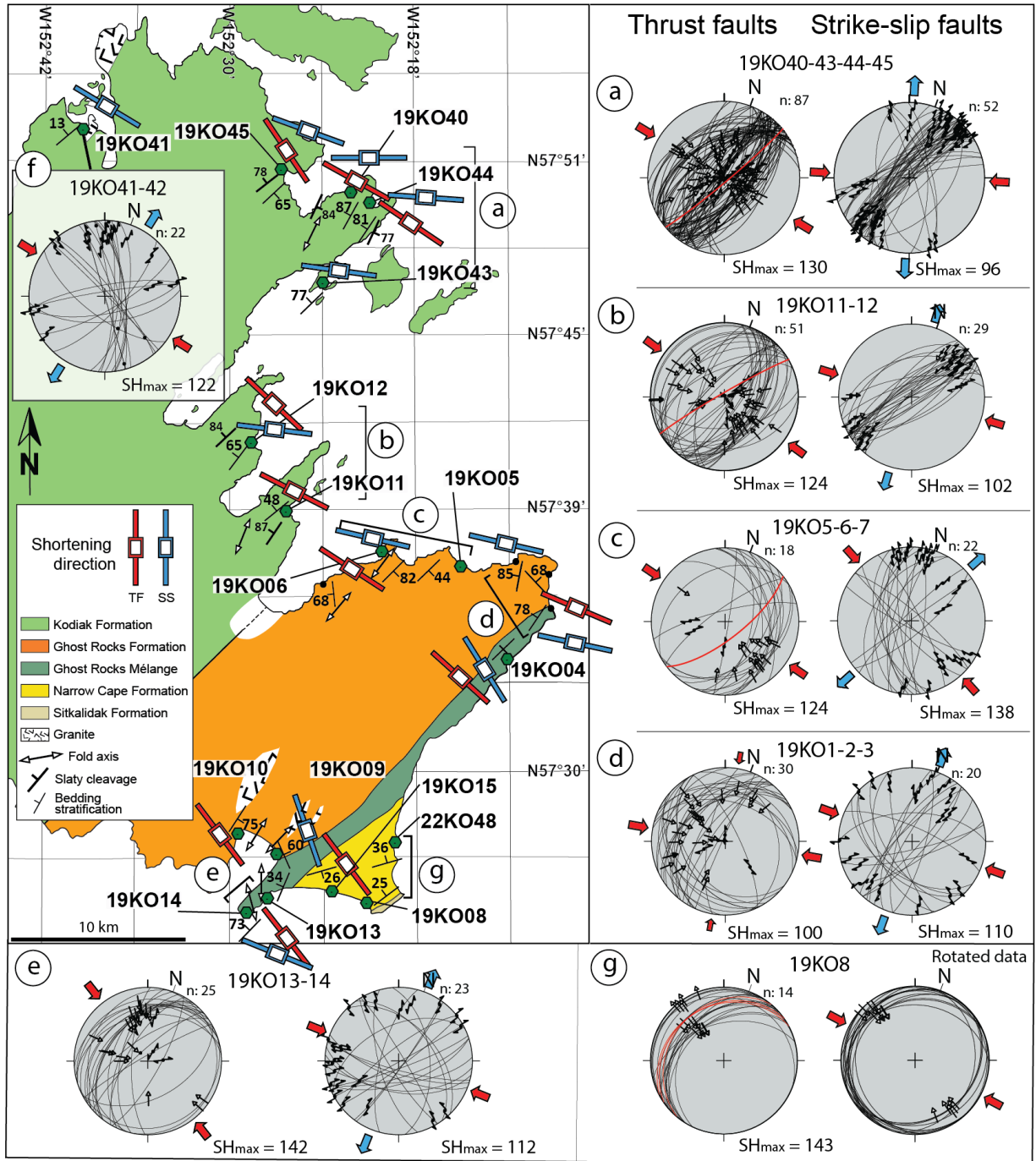


Figure II.11. Geological map of the Kodiak Seaward Belt in the Kodiak city area and the Ghost Rocks Formation with measured bedding stratification and slaty cleavage. Structural analysis indicates two deformational styles across both formations: earlier, conjugate thrust faults with a SE-NW shortening direction, and later strike-slip faulting. (a) and (b) represent structural data for the Kodiak Seaward Belt, (c) and (d) for the Ghost Rocks Formation in the Chiniak area, and (e) for the Ghost Rocks Mélange in the Pasagshak area. (f) Pole figure of strike-slip faults in both the Kodiak granite and the surrounding schists. The red line on pole figures represents the average slaty cleavage for each area. (g) Orientation of normal and thrust faults in the Narrow Cape Formation on the left pole figure. When the stratification bedding is rotated back to horizontal, all faults become conjugate thrust faults as on the right pole figure.

II.4.4. Ghost-Rocks Formation

II.4.4.1. Coherent unit

Coherent units observed in the Chiniak area are characterized by the bedding stratification dipping 44-90° toward the northwest or southeast, rarely to the east. Thrust faults are the main structures. Most of the large thrust faults have up to 50 cm thick gouges cutting the units with NW- and SE-dip. Minor faults, either strike-slip (dominantly dextral) or thrusts, filled with calcite, occur with a dominant NE-strike (Fig. II.11c-d). A crenulation cleavage is observed as well as isoclinal symmetrical folds with axes oriented 27/037 on average (Fig. II.12a).

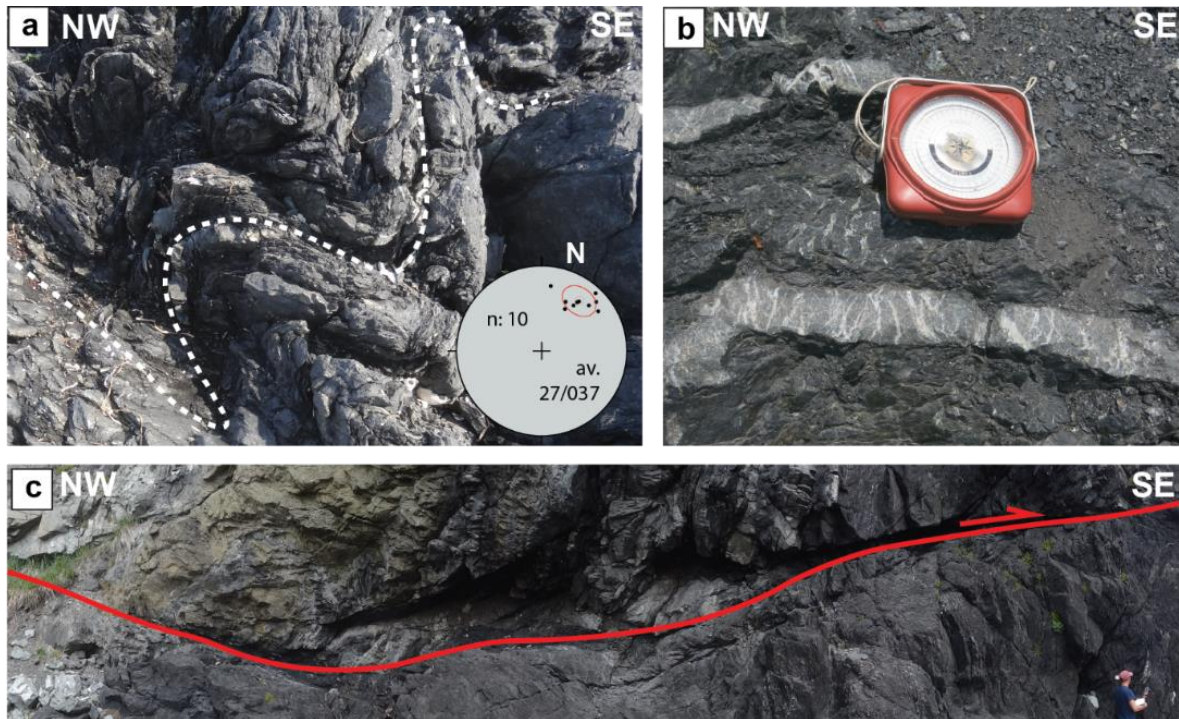


Figure II.12. Deformational structures in the Ghost Rocks Formation. (a) Symmetrical folds in a shale-dominant part, with a fold axial plane dipping towards NNE. (b) Extensional quartz veins in sandstone layer with sub-perpendicular orientation to the layer. (c) Large-scale top-to-the-SE thrust fault in the Ghost Rocks mélange, Pasagshak area.

Extension veins are observed in sandstone and siltstone layers, almost perpendicular to the stratification bedding (Fig. II.12b). Contrary to veins from other units, calcite is more common than quartz in the Ghost Rocks Formation. Wherever layers are folded and deformed, the orientation of veins is always close to perpendicular to the folded layers.

II.4.4.2. Mélange unit

The Ghost Rocks Mélange is nicely exposed in the Pasagshak area, with a block-in-matrix texture made of sandstone and basalt boudins embedded in a shale matrix (Fig. II.12c). When preserved, the bedding is oriented 43/293 on average and 06/322 for the pressure solution cleavage (Fig. II.11). The majority of thrust faults are dipping toward the northwest (average 45/312) with a top-to-the-SE sense of shear, while a minority of faults have a southeast-dip and a top-to-the-NW sense of shear (Fig. II.11e). As in the case of the Ghost Rocks Formation and the Kodiak Seaward Belt, NE- and NW-striking strike-slip faults are observed, with a dominant dextral slip.

II.4.5. Slope sediments

II.4.5.1. Narrow Cape Formation

Middle Miocene sediments of the Narrow Cape Formation, deposited above in unconformity onto the Ghost Rocks Formation, are characterized by different bedding attitudes (25/323, 26/164, and 36/344 for sites 19KO08, 19KO15, and 22KO48, respectively). Deformation is relatively discrete, and deformation structures include calcite-filled, m-scale normal and thrust faults (Fig. II.13a) with similar strikes and opposite dips. On the site 19KO08, both types of faults have NW-dip, and in site 19KO15 they have SE-dip (Fig. II.11g). After restoration of the bedding stratification back to the horizontal on both sites, these faults become conjugate thrust faults (Fig. II.11g).

II.4.5.2. Sitkinak Formation

The Oligocene Sitkinak Formation, unconformably overlying the Sitkalidak and Ghost Rocks Formations, is nicely exposed in the southern part of Sitkalidak Island. The bedding stratification is sub-vertical, 83/344 on average, with small variations in strike, from W-E to NE-SW. A weak foliation is observed as well oriented 85/322 on average. Thrust faults are dominantly characterized by S-dip and northward motion (Fig. II.13b), and smaller group of faults have N-dip with southward motion (Fig. II.10b). In their present attitude, these two groups of faults are forming conjugate set of thrust faults (Fig. II.10b).

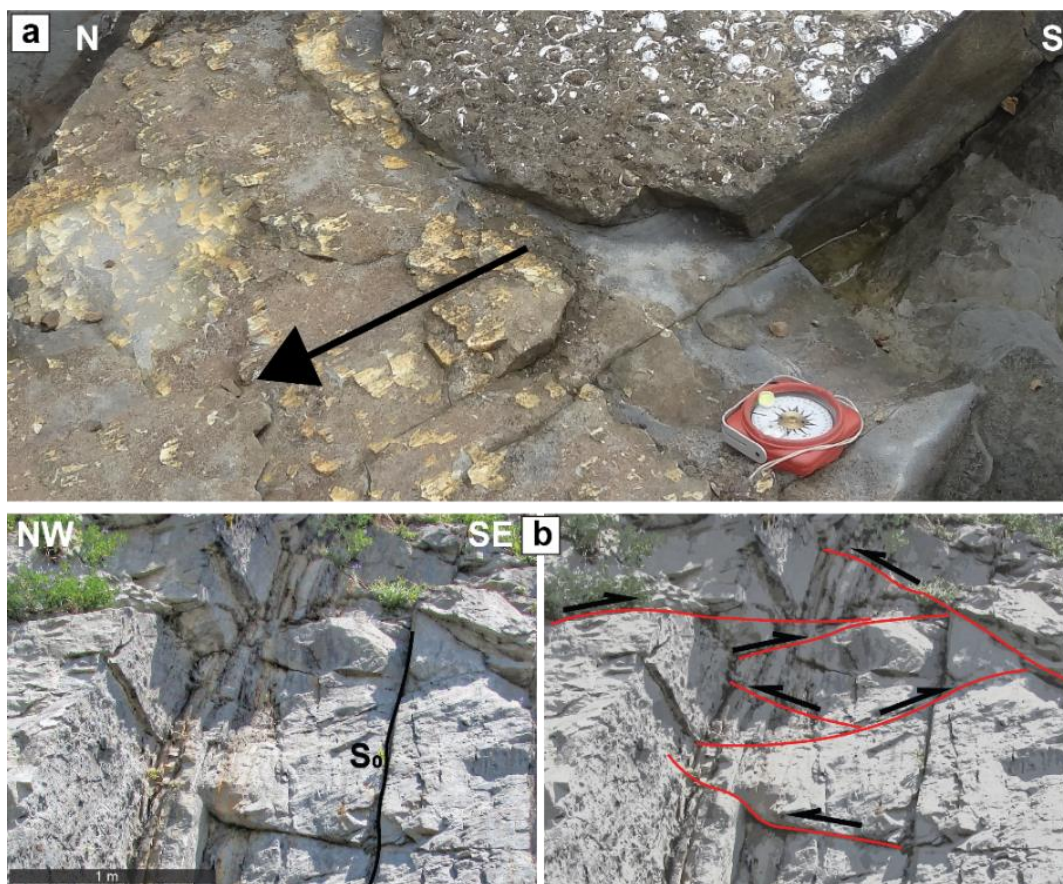


Figure II.13. Representative deformation structures in slope sediment units of the Kodiak accretionary complex. (a) An example of low-angle normal fault in the Narrow Cape Formation (Site 19KO08). (b) Sub-vertical bedding stratification and conjugate reverse faults in the Sitkinak Formation (Site 22KO29).

II.5. Discussion

II.5.1. Deformation kinematics across the complex

Our structural analysis points to constant deformation kinematics perpendicular to the strike of the belt, consistent with present-day kinematics across the complex. Top-to-the-trench noncoaxial deformation is the dominant kinematics in tectonic mélanges (Ghost Rocks Formation at Pasagshak, the Uyak Complex at Uyak Bay and Waterfall Bay) and the Kodiak Formation in the footwall of the Uganik Thrust (Fig. II.5). In contrast, most of coherent units (the Kodiak Landward Belt few 100s meters from the Uganik Thrust, the Kodiak Central and Seaward Belts and coherent part of the Ghost Rocks Formation) are characterized by coaxial deformation (Figures II.6, II.8, II.9). The Kodiak Formation is characterized by a plane of strain constantly oriented NW-SE, but with different kinematics, from newly recognized vertical shortening in the Kodiak Central Belt

to horizontal shortening in the Kodiak Seaward Belt. This was unexpected from the noncoaxial-only deformation previously described in the Kodiak Formation by (Byrne & Fisher, 1987; Sample & Fisher, 1986; Sample & Moore, 1987) as SE-verging thrusts interpreted as NW-directed underthrusting. Finally, the kinematics across slope sediments, the Sitkinak and Narrow Cape Formations, point to a later horizontal shortening in the frontal part of the wedge (post-Oligocene, post-Miocene?).

Combining the relative chronology of deformation structures with available stratigraphic and absolute ages, we decompose the deformation history into four stages. These are described and based as follows:

D1: The underthrusting phase. In the tectonic mélanges and the Kodiak Landward Belt, non-coaxial deformation occurred as a consequence of the vicinity to the plate-boundary interface. This stage represents as well a period of the Uganik Thrust activity as well. In the coherent units, such as Kodiak Central Belt in Seal and Uyak Bays, coaxial deformation is evidenced by sets of low-angle conjugate normal shear bands.

D2: Horizontal shortening within the wedge. This stage is responsible for compressional structures in the accreted units and tilting towards vertical position. The compression is more prominent in the frontal part of the prism, the Kodiak Seaward Belt and the Ghost Rocks Formation. As deformation structures possibly related to this stage are not observed in the Kodiak granite, a period of horizontal shortening possibly predates the intrusive event (between ~70 and 58-59 Ma).

D3: Ridge subduction and wide-spread magmatism at 58-59 Ma, when magmas of MORB affinity assimilated metasediments to yield granitic intrusions (Farris et al., 2006).

D4: Strike-slip faulting and NE-striking veining in the Kodiak Seaward Belt, the Ghost Rocks Formation and the Kodiak Granite.

In what follows, we discuss the origin and relative chronology of the main deformation structures across the Kodiak accretionary complex, from the structures related to the plate-boundary interface deformation to intra-wedge deformation.

II.5.2. Deformation structures related to underthrusting

In the tectonic *mélanges*, the deformation is distributed in form of a network of top-to-the-SE shear bands. As the deformation style is dominantly non-coaxial, such shear bands are interpreted as formed during underthrusting. This type of deformation in the tectonic *mélange* has been reported in several tectonic *mélanges* worldwide (e.g., Faghih et al., 2012; Raimbourg et al., 2019), including the Uyak Complex (Connelly, 1978) and Ghost Rocks *Mélange* (Byrne, 1984).

Contrary to the tectonic *mélange* units and the Kodiak Landward Belt (which experienced significant deformation due to their vicinity to the decollement), the coherent units recorded different deformation styles during underthrusting. In inner part of Uyak Bay and in Seal Bay where the Kodiak Central Belt is exposed, extensional shear bands (either in original position or restored back by tilting foliation/bedding to the horizontal), indicate NW-SE extension in the central part of the complex (Figures II.5, II.7c). The conjugate en échelon sets of arrays in Seal Bay are consistent with such a NW-SE extension, where most of the arrays dip towards the southeast and a minority towards the northwest. Recumbent folds are compatible as well with normal shear bands. This finding is at variance with previous structural analysis in the Kodiak Central Belt (Sample & Fisher, 1986; Sample & Moore, 1987), where only top-to-the-SE shear bands were reported. Sample & Moore (1987) reported normal faults, often in conjugate sets, but they proposed that such normal faults formed after the intrusive event. However, their occurrence in form of conjugates and at low-angle to the stratification bedding/slaty cleavage indicates that they formed in flat-lying position. This finding is clear indication that these thick turbiditic sequences were underthrust under strong (sub)-vertical stress, as proposed for tectonic *mélanges* of the Kodiak accretionary complex (Fisher & Byrne, 1990). Observed normal shear bands are compatible with the slaty cleavage and recumbent folds, all together indicating strong vertical shortening.

Furthermore, the deformation style in the Kodiak Central Belt is at variance with the style observed in the Kodiak Landward Belt (top-to-the-trench shearing). This can be simply a result of underthrusting of a thick pile of sediments, where only the top of a pile experienced plate-boundary interface deformation. Furthermore, it is not clear whether conjugate thrust faults in the Kodiak Seaward Belt formed as well during underthrusting as proposed for the Central Belt and later tilted to present position during a period of horizontal shortening.

II.5.2.1. A map-scale fault zone – the Uganik Thrust

The Uganik Thrust, interpreted as an out-of-sequence thrust (Rowe et al., 2009), is the only exposed large-scale fault zone on northwestern side of the accretionary prism. Deformation on both sides of the Uganik thrust is characterized by top-to-the-trench shear bands (Fig. II.5). In the Kodiak Landward Belt, top-to-the-trench simple shear only occurs close to the Uganik Thrust (Figures II.4a, II.5). The kinematics of the Uganik Thrust is very similar to the kinematics recorded in shear bands in the Kodiak Landward Belt (Fig. II.7a-b), where we have measured several south-verging thrust faults with N-S striking slickenlines, almost identical to that of the Uganik Thrust fault plane (Fig 1.7a). Fisher & Byrne (1987) suggested that the *mélange* in the Kodiak Landward Belt, known as the Big Waterfall *mélange*, was formed due to shearing in the vicinity to the major décollement on top of a thick sedimentary pile, while the Uganik Thrust was active after the intrusive event since a dyke is offset by the fault. However, the mylonite in the hanging wall is intruded by granitic dyke as well (Fig. II.3a). If the mylonite was formed during fault activity, as it is proposed by Rowe et al. (2009), the main activity of the fault predates the intrusive event. However, the cataclastic zone probably formed during reactivation rather than simultaneously to the mylonite in the hanging wall. We propose that the Uganik Thrust firstly acted as a plate-boundary interface during underthrusting of the Kodiak Formation beneath the Uyak Complex, before later reactivation as an out-of-sequence thrust without significant offset.

II.5.3. Intra-wedge deformation

After incorporation into the wedge by underthrusting and basal accretion, the accreted coherent units recorded further deformation in the wedge. This occurred mostly in the coaxial régime with conjugate thrust faults, symmetric folds, and associated slaty cleavage indicating horizontal shortening with variable intensity across the complex. In what follows we discuss relative ages of different deformation structures formed within the wedge.

II.5.3.1. Compression regime in the frontal part of the complex

The frontal part of the prism (the Kodiak Seaward Belt and Ghost Rocks Formation) are characterized by strong horizontal shortening, evidenced by sub-vertical slaty cleavage, conjugate thrust faults and folds with vertical/sub-vertical axial planes (Figures II.10, II.11). While Sample

& Moore (1987) described top-to-the-SE thrust faults only, we observed in those two formations an equal amount of top-to-the-NW thrust faults pointing to a strong NW-SE horizontal shortening (Figures II.10, II.11). Furthermore, the orientation of isoclinal folds is compatible with such shortening (Fig 10a). The lack of thrust faults in the Kodiak granite indicate that the formation of thrust faults in metasediments predates intrusion emplacement (between ~70 and 58 Ma). However, it is still unclear whether the conjugate thrust faults in the frontal part formed as well during underthrusting as in the case of the Kodiak Central Belt, and was later tilted to the present position during a period of horizontal shortening.

In the inner part of the complex, the Kodiak Central and Landward Belt, the horizontal shortening is less pervasive, with local folds and associated crenulation cleavage S_2 . This event (D2-stage) is responsible for partly tilting the strata in their present position.

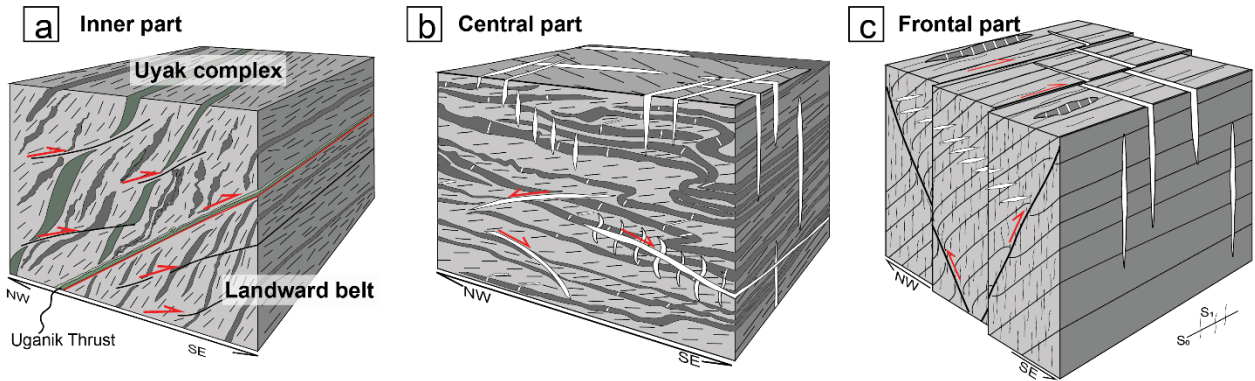


Figure II.14. 3D model showing the variations in observed deformation structures across the accreted units, from top-to-the-trench non-coaxial shearing in the Uyak Complex and the Kodiak Landward Belt, over (b) vertical shortening in the Kodiak Central Belt, to (c) horizontal shortening in the Kodiak Seaward Belt and Ghost Rocks Formation.

II.5.3.2. Strike-slip faulting

Another compatible set of deformation structures observed across the Kodiak Seaward Belt and the Ghost Rocks Formation are strike-slip faults (often conjugate) indicating W-E to WNW-ESE shortening (Figures II.10, II.11). We also observed strike-slip faults with similar shortening direction in the Kodiak Granite of Anton Larsen Bay (Fig. II.11f). Sample & Moore (1987) proposed such strike-slip faulting occurred either by oblique subduction or northward translation of the Kodiak accretionary complex. Hence, a potential explanation for strike-slip faulting lies in

the relative motion between the North American and Kula plates and an ancient ridge on the Kula plate (Molnar & Stock, 1987; Morgan, 1971; Torsvik et al., 2017; Wilson, 1963). Right after the accretion of the Kodiak and Ghost Rocks Formations, a ridge subduction occurred. Based on spatial variations in pluton spacing and geochronology of magmatic intrusions in southern Alaska, Farris & Paterson (2009) proposed that the ridge was segmented, with oblique subduction below the Kodiak accretionary complex. This may be responsible for strike-slip faulting in the frontal part of the complex. This interpretation is supported by structural analysis of the Valdez Group in the Kenai Peninsula (equivalent to the Kodiak Formation at the Kenai Peninsula; Plafker et al., 1994). Kusky et al. (1997) described mutual crosscutting relationship between magmatic dykes, mineralized veins and strike-slip faults, suggesting strike-slip faulting contemporaneous with the ridge subduction. In the Kodiak complex, no mutual crosscutting relationship has been observed between intrusions and strike-slip faulting. Hence, we propose that the event of strike-slip faulting postdate the intrusive event (post-58 Ma).

II.5.3.3. Post-Oligocene horizontal shortening

Closer to the trench, the slope sediments of the Sitkinak and Narrow Cape Formations record similar horizontal shortening, with variable intensity. The Sitkinak Formation experienced significant horizontal shortening and complete tilting of strata to the vertical position (Fig. II.10b). On the contrary, the Narrow Cape Formation experienced less intense deformation, but still under compressional régime (Fig. II.11g). Hence, both formations record a period of horizontal shortening post-dating Oligocene, possibly even Miocene.

II.5.4. The occurrence of veins

In the Uyak Complex, Kodiak Landward Belt, and Ghost Rocks Formation, only mode-1 quartz-calcite veins occur in more competent units, sandstones and cherts (Figures II.4c, II.12b). These veins were interpreted as a consequence of dissolution of feldspars and quartz in the host rock and local reprecipitation of fluid-mobile elements during underthrusting, during D1 stage (Fisher et al., 2021). The D1 veins from the Kodiak Landward Belt (Fig. II.4c) are extensively studied in Chapters IV and V.

In contrast, in the Kodiak Central and Seaward Belts diverse vein systems occur, from sub-vertical straight quartz veins to shear veins with strained and stretched quartz fibers. In the Kodiak Central Belt, two sets of vertical Mode 1 veins (NW- and NE-striking) show mutual crosscutting relationships, and based on structural analysis the NE-striking veins formed simultaneously with shear veins. Hence, three different sets of veins occurred simultaneously, at the burial, potentially during the D1 stage. Mode 1 veins cut across the foliation, but are folded as well perpendicular to the orientation of the foliation, interpreted as formed at the peak metamorphic conditions (Raimbourg et al., 2021). Based on oxygen isotopes, geochemical signatures of veins as well as host rock and textures presented in veins, the formation of veins in the deeper part of a prism is related to local diffusion of silica from the host rock (Brantley & Fisher, 1997; Fisher & Brantley, 1992, 2014). The origin of D1 veins from the Kodiak Central Belt, either Mode 1 veins or mineralized extensional shear bands, is extensively studied in Chapters IV, V, and VI.

Another set of veins, vertical and NW-striking, is found within the Kodiak Seaward Belt and the Kodiak granite. These veins crosscut both the granite and metasediments pointing to their formation after the intrusive event. The occurrence of vertical NW-striking veins has been described as well in the Valdez Group, occasionally characterized by gold mineralization (Haeussler et al., 1995). The age of gold mineralization in quartz veins in the Kenai Peninsula (53 to 57 Ma) is contemporaneous with ridge subduction (Haeussler et al., 1995) and sporadically thrust and strike-slip faults are mineralized. Decreasing age of the near trench magmatism from Sanak Island to Baranof Island (Bradley et al., 2000, 2003; Haeussler & Bradley, 2003) is described for gold mineralization as well, suggesting that the gold mineralization is related to the ridge subduction. The authors proposed that the formation of NW-striking veins is contemporaneous with the strike-slip faulting and intrusive event. In the granite of Anton Larsen bay, the average orientation of NW-striking veins is N124, close to σ_1 derived from strike-slip faults. However, the outcrops with NW-striking veins in the Kodiak complex are limited. Hence, we cannot fully support whether NW-striking veins formed contemporaneous to the granitic intrusions (D3 stage) or related to the strike-slip faulting (D4 stage) postdating the intrusive event. In any case, these veins are not subduction-related.

II.6. Conclusion

The deformation kinematics of observed structures in all units of the Kodiak accretionary complex correspond principally to plane strain in the NW-SE direction from the Early Cretaceous to present. Simple shear is present in the tectonic mélanges as well as in the Kodiak Formation in the vicinity to the Uganik Thrust, formed during underthrusting. Unlike prior studies reporting non-coaxial shearing in the coherent units, we find that pure shear is dominant (the Kodiak and Ghost Rocks Formations), as indicated by conjugate extensional shear bands along the plate-boundary interface and then later as intra-wedge conjugate thrust faults. Additional deformation structures are strike-slip faults which postdate the main magmatic event at 58-59 Ma.

The D1 veins from the Kodiak Landward and Central belt are interpreted as subduction-related, and these veins represent the basis for fluid studies in following chapters.

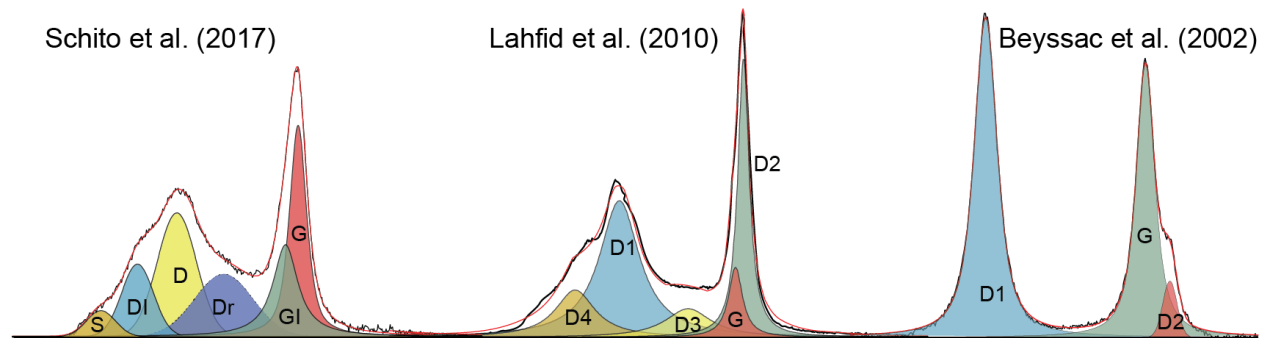
Overall, all studied units are characterized by deformation structures indicating compressional regime. As discussed below, on the basis of the few chronological constraints available, we propose two periods of horizontal shortening. The first one is recorded in basally accreted units and occurred prior to the intrusive event, and second Oligo-Miocene recorded in slope sediments.

Preface

The subject of this Chapter is the thermal structure of the Kodiak accretionary complex, by applying Raman Spectroscopy of carbonaceous material (RSCM). From each locality where deformation structures were described (Chapter II), the metasedimentary samples were taken in order to determine the peak-metamorphic temperatures across whole complex. The final temperature profile point to small variations in peak temperatures across basally accreted units (220-380°C), with highest temperatures in the central part of the complex. Among three unit-bound faults, only thermal discontinuity is reported for the Angular Unconformity between basally accreted Ghost Rocks Formation and slope sediments of the Sitkinak and Narrow Cape formations (100-140°C). These results were combined with previously published absolute and relative chronology, in order to (i) propose different periods of burial and exhumation, and (ii) to estimate exhumation/subsidence rates.

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CHAPTER III – Exhuming the depths of accretionary prisms: A case study of the Kodiak accretionary complex, Alaska



CHAPTER III – Exhuming the depths of accretionary prisms: A case study of the Kodiak accretionary complex, Alaska

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III.0. Abstract

To describe the thermal structure and decipher the processes of exhumation in the depths of accretionary prisms, we carried out an extensive structural study across the Kodiak accretionary complex in Alaska. The accretionary complex consists of a stack of tectonic mélanges and coherent units. Mélanges are characterized by subduction-related deformation with a pervasive network of top-to-the-trench shear zones, whereas coherent units are characterized by dominant coaxial deformation. Across the whole complex, most of the examined units, including basally accreted units and slope sediments, record compressional regime, except for relatively spatially limited outcrops in the Kodiak Central Belt. Peak burial temperatures estimated using Raman spectroscopy of carbonaceous material are bracketed within 220-400°C through most of the complex. The highest temperatures are recorded in the central part of the complex, pointing to a dome-like structure. Lower temperatures, around 120°C, are only recorded along the southeastern border of the complex, in the slope sediments unconformably overlying accreted units. Based on the combination of structural and thermal data, we conclude that the rocks constituting the Kodiak accretionary complex experienced at least 2 stages of burial then exhumation, with vertical motions up to ~10 km from the Paleocene to the present. Given the pervasive horizontal shortening within the wedge, exhumation resulted from prism thickening contemporaneous with surficial erosion, whereas subsidence stages may coincide with basal erosion. The rates of vertical motion are in range of 0.2-1.3 mm/yr, comparable with estimates in modern margins.

III.1. Introduction

As inferred from seismic reflection profiles, deep sea drilling in modern subduction zones and geodynamic models, sedimentary rocks from the subducting plate are transferred to the upper plate by principally two processes. First, the propagation of in-sequence, landward-dipping thrusts (e.g., Dahlen, 1990; Davis et al., 1983; Menant et al., 2020; Moore et al., 2001; Moore, 1989; Moore et al., 1990; Pajang et al., 2021) leads to the frontal accretion of tectonic slices of sediments at the trench. In addition to frontal processes, wedge thickness may increase by underplating of coherent units and mélanges below the wedge (e.g., Byrne & Fisher, 1987; Fisher & Byrne, 1987; Platt, 1986; Sample & Fisher, 1986). Unlike these two mechanisms that allow sediments or sedimentary rocks to be incorporated to the accretionary wedge and to be buried, their exhumation back to the surface is more enigmatic.

Deep underplating was proposed as one mechanism possibly leading to rock exhumation within the wedge (e.g., Guillot et al., 2009; Platt, 1986). In the conceptual framework of the critical wedge (Dahlen, 1990), as more material is underplated the wedge is experiencing thickening, which leads to its instability and triggers re-equilibration by the development of normal faults and extensional shear zones. In addition, surficial erosion removes the rock overburden and may contribute as well to exhuming deeper levels of the accretionary wedge (Platt, 1986; Ring et al., 1999). Exhumed fossil subduction zones provide additional information as to the tectonics active on the boundary and within the wedge. Accretionary complexes, such as Shimanto belt of Japan or the Franciscan Complex, are characterized by either mélanges or coherent units that experienced non-coaxial deformation due to intensive shearing along or in vicinity to the plate-boundary interface (e.g., Fagereng & Sibson, 2010; Meneghini et al., 2009; Raimbourg et al., 2019). The posterior deformation that occurred after the incorporation of material into the wedge is strongly localized in out-of-sequence thrust faults and their associated damage zones (e.g., Fisher & Byrne, 1987; Kondo et al., 2005; Rowe et al., 2009; Smeraglia et al., 2019). These contractive structures contribute only to prism thickening, so that additional processes are necessary to exhume rocks from the wedge depths.

In this chapter we report peak-metamorphic temperatures across the Kodiak accretionary complex, to unravel thermal history of units described in Chapter II. First, the thermal/burial history of the complex was studied by applying RSCM along the studied profile. Second, combining observed

deformation structures (Chapter II) and temperature results with available stratigraphic ages, absolute chronology as well as from cooling ages, we propose three different stages of the vertical motion and discuss models for such rock exhumation/burial within accretionary complexes.

III.3. Methods

III.3.1. Raman spectroscopy of carbonaceous material

From each locality where deformation structures were studied, an oriented thick section was prepared from a metasedimentary sample for the purpose of Raman Spectroscopy of Carbonaceous Material (RSCM). At several localities in the Ghost Rocks Formation and Uyak Complex, where magmatic lithologies are present, samples for RSCM were chosen few meters away from magmatic rocks. In prepared thick sections, analyzed particles were chosen away from any obvious shear bands to devoid shear-enhanced thermal maturation of carbonaceous material.

We performed RSCM using a Raman Renishaw InVia Reflex micro-spectrometer at the ISTO-BRGM and Renishaw InVia Qontor micro-spectrometer at CEMHTI CNRS, Orléans. The silicon standard was used for the calibration. The light source was a 514.5 nm Ar laser with a power of about 1 mV, focused by a Leica DM2500 microscope at the magnification 100x. The signal was analyzed by a CCD NIR/UV detector. 15-20 points were analyzed per sample on 150-200 μm polished thick sections. To avoid defects bands generated during preparation of the thin sections, particularly polishing, all analyzes were performed on subsurface grains by focusing laser beam through transparent minerals, generally quartz (Ammar & Rouzaud, 2012; Katagiri et al., 1988; Pasteris, 1989). The final deconvolution was made according to method of Lahfid et al. (2010) or Beyssac et al. (2002) according to following criteria: (1) If D4 band is present together with relatively high D3 and absent D2 band, Lahfid et al. (2010) method was applied. Raman spectra were processed with the software PeakFit 4.12 for the subtracting the baseline and fitting the obtained spectrum with five Lorentzian bands. From the area below five Lorentzian bands, RA1 ratio was calculated by the equation $RA1 = (D1 + D4) / (D1 + D2 + D3 + D4 + G)$. The final temperature was estimated following the equation $T (^{\circ}\text{C}) = 1250 \times RA1 - 469.75$ (Lahfid et al., 2010). (2) If the Raman spectra contains an obvious D2 band, low D3 band and absent D4 band, the deconvolution process was made according to Beyssac et al. (2002) procedure. Three Voight functions were applied to estimate the area, from where R2 ratio was calculated by the equation

$R2 = D1 / (D1+G+D2)$. The peak temperature was calculated following the equation $T (^{\circ}\text{C}) = 445 \times R2 + 641$.

For three samples from the Narrow Cape Formation and five samples from the Sitkinak Formation, the Raman spectrum was processed following the method by Schito et al. (2017), since the method by Lahfid et al. (2010) is valid only for temperatures higher than 200°C. After the subtracting the baseline and applying six mixed Gaussian-Lorentzian bands, RA2 ratio was calculated from the areas by the equation $RA2 = (S + DI + D) / (Dr + GI + G)$. Finally, RA2 value was correlated with Vr% (Schito et al., 2016) for which the linear correlation between RA2 and Vr% was found (Schito et al., 2017).

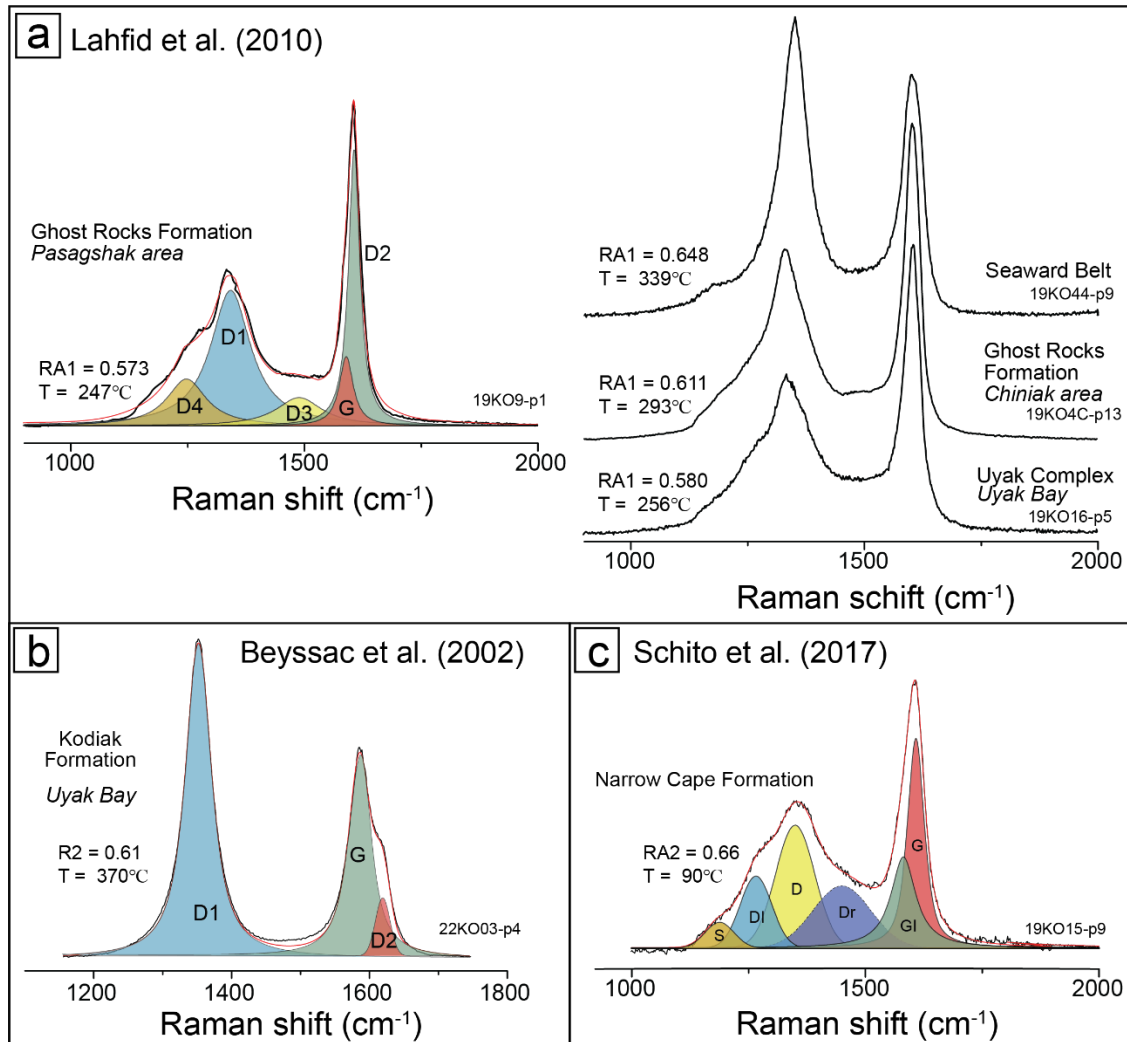


Figure III.1. (a) Representative Raman spectra for each accreted formation/belt deconvoluted according to the method of (a) Lahfid et al. (2010), (b) Beyssac et al. (2002), and (c) Schito et al. (2017).

III.4. Results – RSCM temperatures

Temperatures obtained by RSCM are reported in Table III.1. and representative Raman spectra of each formation/belt are plotted in Fig. III.1. The average values of each analyzed sample are plotted in Fig. III.2- Fig. III.4.

III.4.1. Accreted units

The average temperature for samples from the Uyak Complex in Uyak Bay is 256°C, in a range 239-281°C (Fig. III.2; Sites 19KO16, 19KO17F, 19KO18, 19KO19, 19KO20, 19KO21, and 19KO23). The Kodiak Landward Belt in Uyak Bay shows similar temperatures to the Uyak Complex several km from the Uganik Thrust (Fig. III.2), ranging 240-267°C. Further in Uyak Bay the Kodiak Formation is characterized by a discontinuous increase of temperature up to 382°C (Samples 22KO01-22KO28; Fig. III.2).

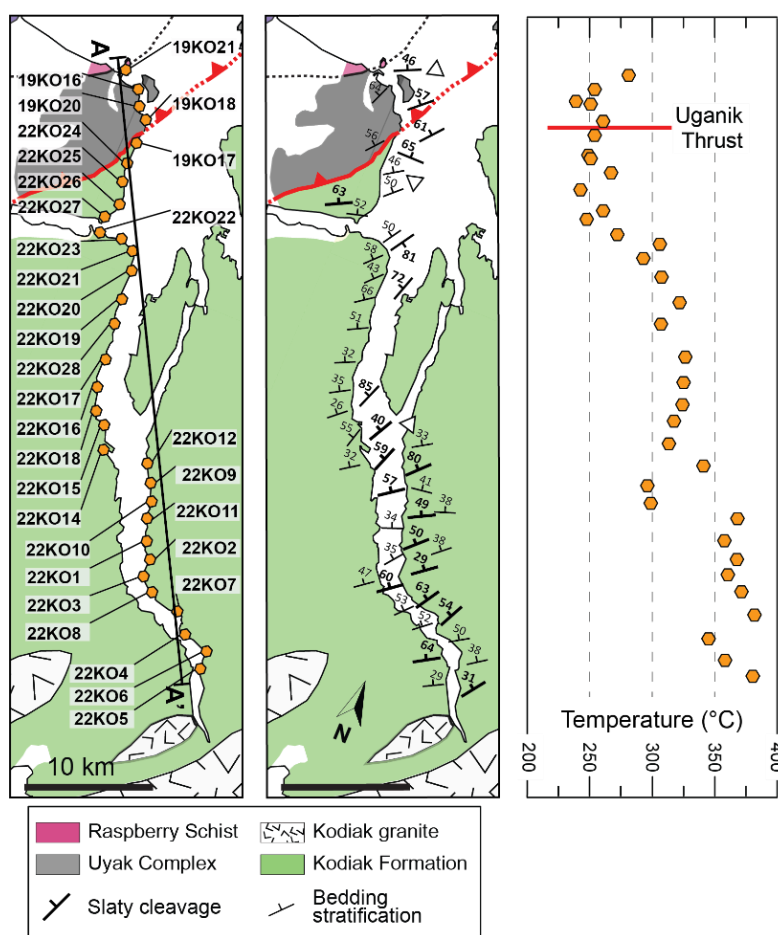


Figure III.2. The locations of analyzed samples, the orientation of bedding stratification and slaty cleavage, and estimated RSCM temperatures across the Uyak Complex and Kodiak Formation in Uyak Bay.

In Big Waterfall Bay where the Uganik Thrust is exposed, temperatures of the Uyak Complex in the hanging wall range 262-299°C (Sites 19KO25 and 19KO27), whereas the Kodiak Formation in the footwall shows a range of 275-296°C (Sites 19KO27 and 19KO28). The average values for both foot and hanging wall are identical (282°C). The Kodiak Central Belt in Seal Bay is characterized by temperatures 320-340°C (Sites 19KO29-19KO39). A wide range of temperatures is found in the Old Harbor area (Fig. III.3). Four samples (22KO38, 22KO41, 22KO44, and 22KO46) yielded temperatures in the range 310-354°C, whereas two samples show significantly lower temperatures of $217 \pm 14^\circ\text{C}$ (22KO42) and $222 \pm 8^\circ\text{C}$ (22KO43). The sample in the hanging wall of the Contact Fault (22KO40) in the vicinity to the granite intrusion yielded temperature of $557 \pm 16^\circ\text{C}$, similar to the sample 22KO45 ($536 \pm 18^\circ\text{C}$). For the Kodiak Seaward Belt in Kodiak city area obtained temperatures average at 325°C (305-348°C; Fig. III.4; sites 19KO11, 19KO12, 19KO40-19KO45). The lowest temperature among all samples from the Seaward Belt in the Kodiak city area is obtained in the schist from Anton Larsen Bay ($261 \pm 17^\circ\text{C}$; Site 19KO41), where the granitic intrusion is exposed.

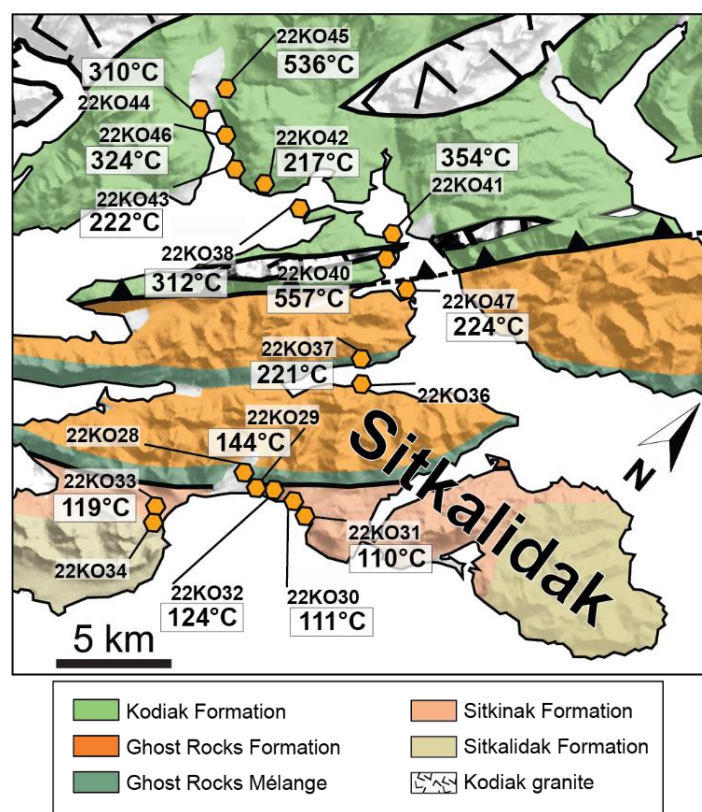


Figure III.3. The locations of analyzed samples and acquired temperatures in the Kodiak Seaward Belt, Ghost Rocks and Sitkinak Formations.

III.4. Results – RSCM temperatures

In the Ghost Rocks Formation, the Chiniak area (Fig. III.4) is characterized by an average temperature of 295°C (279-309°C; Sites 19KO4-19KO6), whereas Pasagshak area yielded average temperature of 227°C (218-241°C; Sites 19KO9, 19KO10, 19KO13 and 19KO14). At Sitkalidak Island (Fig. III.3) two analyzed samples show equal temperatures of $224 \pm 10^\circ\text{C}$ (22KO47) and $221 \pm 12^\circ\text{C}$ (22KO37).

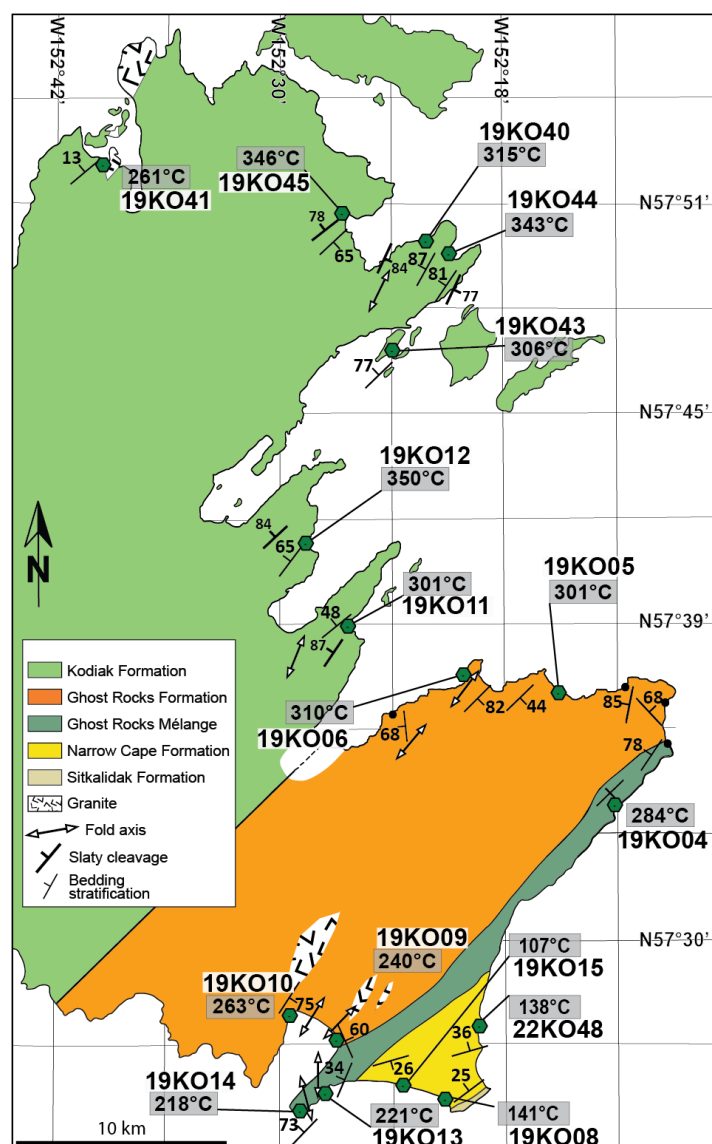


Figure III.4. The locations of analyzed samples, the orientation of bedding stratification and slaty cleavage, and acquired temperatures in the Kodiak Seaward Belt, Ghost Rocks and Narrow Cape Formations.

III.4. Results – RSCM temperatures

Table III.1. RSCM temperatures across the Kodiak accretionary complex with previously published results. VR - Vitrinite reflectance; IC - Illite crystallinity; FI - Fluid inclusion studies; MP – Mineral paragenesis.

Formation/Area	Sample	Longitude	Latitude	#	Method	RA1	T (°C)	SD	Reference
Narrow Cape Formation									
	19KO08	-152.3553	57.4276	13	Schito	0.72	100	13	This study
	19KO15	-152.3912	57.4342	18	Schito	0.82	119	14	This study
	22KO48	-152.3363	57.4546	13	Schito	0.98	138	19	This study
Sitkinak Formation									
<i>Sitkinak Island</i>	22KO29	-153.1794	57.0959	15	Schito	1.06	144	7	This study
	22KO30	-153.1432	57.1017	13	Schito	0.78	111	14	This study
	22KO31	-153.1318	57.1016	15	Schito	0.77	110	14	This study
	22KO32	-153.1703	57.0982	12	Schito	0.87	124	19	This study
	22KO33	-153.2192	57.0600	10	Schito	0.82	119	17	This study
					VR		100-125		Moore & Allwardt (1980)
Ghost Rocks Formation									
<i>Chiniak area</i>	19KO4C	-152.2079	57.5635	15	Lahfid	0.598	279	23	This study
	19KO4D	-152.2079	57.5635	15	Lahfid	0.603	284	16	This study
	19KO5	-152.2569	57.6186	15	Lahfid	0.616	301	21	This study
	19KO6	-152.3402	57.6271	14	Lahfid	0.624	310	10	This study
<i>Pasagshak area</i>	19KO9	-152.4489	57.4551	11	Lahfid	0.562	240	14	This study
	19KO10	-152.4913	57.4668	15	Lahfid	0.586	263	17	This study
	19KO13C	-152.4604	57.4300	15	Lahfid	0.553	221	20	This study
	19KO14A-BFR	-152.4804	57.4220	120	Lahfid	0.574	248	9	This study
	19KO14A-HR	-152.4804	57.4220	42	Lahfid	0.556	225	10	This study
	19KO14C	-152.4804	57.4220	20	Lahfid	0.55	218	9	This study
<i>Sitkinak Island</i>	22KO37	-153.1762	57.1670	12	Lahfid	0.552	221	12	This study
	22KO47	-153.1910	57.2032	12	Lahfid	0.554	224	10	This study
							225-		
Jap Bay; Pasagshak					VR		250		Moore (1983)
Kalsin Bay					FI		254		Vrolijk (1988)
Kodiak Formation									
<i>Kodiak City area</i>	19KO11	-152.4386	57.6516	15	Lahfid	0.61	301	19	This study
	19KO12	-152.4764	57.6875	15	Lahfid	0.656	350	29	This study
	19KO40	-152.3686	57.8291	20	Lahfid	0.627	315	19	This study
	19KO41	-152.6538	57.8639	13	Lahfid	0.584	261	17	This study
	19KO43	-152.3997	57.7775	12	Lahfid	0.618	306	16	This study
	19KO44	-152.3545	57.8213	20	Lahfid	0.65	343	11	This study

III.4. Results – RSCM temperatures

<i>Old Harbor area</i>	19KO45	-152.4385	57.8393	14	Lahfid	0.653	346	16	This study
	22KO38	-153.2856	57.1950	12	Lahfid	0.627	312	17	This study
	22KO40	-153.2144	57.2097	10	Beyssac	0.188	557	16	This study
	22KO41	-153.2207	57.2136	12	Beyssac	0.645	354	9	This study
	22KO42	-153.3197	57.1943	12	Lahfid	0.548	217	14	This study
	22KO43	-153.3423	57.1903	12	Lahfid	0.553	222	8	This study
	22KO44	-153.3890	57.1970	14	Lahfid	0.625	310	16	This study
<i>Seal Bay</i>	22KO45	-153.3938	57.2113	12	Beyssac	0.236	536	18	This study
	22KO46	-153.3674	57.2000	11	Lahfid	0.636	324	16	This study
	19KO29	-152.2180	58.3774	14	Lahfid	0.638	328	7	This study
	19KO30	-152.2228	58.3542	20	Lahfid	0.642	333	13	This study
	19KO32	-152.2450	58.3893	12	Lahfid	0.641	332	17	This study
	19KO33	-152.2568	58.3576	15	Lahfid	0.644	335	19	This study
	19KO34	-152.2397	58.3459	15	Lahfid	0.64	330	14	This study
	19KO36	-152.2586	58.3661	15	Lahfid	0.641	332	29	This study
	19KO37	-152.2696	58.3749	15	Lahfid	0.637	327	31	This study
	19KO38	-152.2865	58.3889	15	Lahfid	0.65	342	28	This study
	19KO39	-152.2815	58.3868	17	Lahfid	0.636	326	13	This study
									Brantley & Fisher (1997)
D2 veins in Central Belt					$\delta^{18}\text{O}$		280		
<i>Uyak Bay</i>	19KO17A	-153.9843	57.6094	10	Lahfid	0.559	251	10	This study
	19KO17B	-153.9843	57.6093	12	Lahfid	0.581	256	10	This study
	19KO17C	-153.9843	57.6104	10	Lahfid	0.58	255	9	This study
	19KO17D	-153.9855	57.6113	15	Lahfid	0.582	257	12	This study
	19KO17E	-153.9841	57.6119	12	Lahfid	0.568	240	9	This study
	22KO01	-153.7601	57.3443	15	Beyssac	0.637	358	4	This study
	22KO02	-153.7470	57.3309	12	Beyssac	0.615	368	5	This study
	22KO03	-153.7414	57.3190	15	Beyssac	0.631	360	7	This study
	22KO04	-153.6602	57.2948	15	Beyssac	0.665	345	5	This study
	22KO05	-153.6250	57.2787	12	Beyssac	0.585	381	10	This study
	22KO06	-153.6334	57.2904	12	Beyssac	0.636	358	7	This study
	22KO07	-153.6852	57.3077	16	Beyssac	0.583	382	13	This study
	22KO08	-153.7145	57.3093	10	Beyssac	0.606	371	8	This study
	22KO09	-153.7875	57.3861	12	Lahfid	0.613	296	18	This study
	22KO10	-153.7749	57.3758	12	Lahfid	0.616	299	18	This study
	22KO11	-153.7728	57.3652	12	Beyssac	0.614	368	10	This study
	22KO12	-153.7974	57.3977	9	Lahfid	0.650	341	18	This study
	22KO14	-153.8590	57.3969	11	Lahfid	0.627	313	12	This study
	22KO15	-153.8716	57.4105	12	Lahfid	0.631	317	18	This study
	22KO16	-153.9012	57.4324	12	Lahfid	0.637	325	13	This study
	22KO17	-153.9073	57.4525	12	Lahfid	0.638	326	11	This study

III.4. Results – RSCM temperatures

	22KO18	-153.8899	57.4180	12	Lahfid	0.636	324	15	This study
	22KO19	-153.9186	57.4942	12	Lahfid	0.634	322	12	This study
	22KO20	-153.9204	57.5163	12	Lahfid	0.623	308	7	This study
	22KO21	-153.9297	57.5337	12	Lahfid	0.611	293	11	This study
	22KO22	-153.9753	57.5379	12	Lahfid	0.594	272	9	This study
	22KO23	-153.9507	57.5392	10	Lahfid	0.621	306	4	This study
	22KO24	-153.9840	57.6021	10	Lahfid	0.590	267	7	This study
	22KO25	-153.9820	57.5835	10	Lahfid	0.569	243	12	This study
	22KO26	-153.9719	57.5688	13	Lahfid	0.584	261	5	This study
	22KO27	-153.9761	57.5532	10	Lahfid	0.574	248	6	This study
	22KO28	-153.9146	57.4805	12	Lahfid	0.622	307	15	This study
<i>Big Waterfall Bay</i>	19KO28	-152.5183	58.4075	12	Lahfid	0.607	296	8	This study
	19KO28-P1	-152.5183	58.4075	30	Lahfid	0.598	278	17	This study
	19KO28-P2	-152.5183	58.4075	27	Lahfid	0.602	283	27	This study
	19KO28-P3	-152.5183	58.4075	33	Lahfid	0.596	275	11	This study
									Rowe et al.
	Early stage extension veins				FI		280		(2009)
	Early stage extension veins				FI		280		Vrolijk (1988)
									Rowe et al.
	Shear veins parallel to Uganik Thrust				FI		230		(2009)
									Rowe et al.
	Late stage veins that postdate mélange formation				FI		200		(2009)
							290-		Rowe et al.
					VR		300		(2009)
									Sample &
					VR (R ₀)	3.73	225		Moore (1987)
					IC				Sample &
					(HBrel)	162	225		Moore (1987)
Uyak Complex									
<i>Uyak Bay</i>	19KO16	-154.0273	57.6456	15	Lahfid	0.579	254	8	This study
	19KO17F	-153.9828	57.6146	15	Lahfid	0.575	249	8	This study
	19KO18	-153.9809	57.6183	12	Lahfid	0.579	254	16	This study
	19KO19	-153.986	57.6267	12	Lahfid	0.584	261	7	This study
	19KO20	-154.0025	57.6391	33	Lahfid	0.576	251	7	This study
	19KO23	-154.0131	57.6448	12	Lahfid	0.581	239	18	This study
<i>Big Waterfall Bay</i>	19KO25D1	-152.5147	58.4305	62	Lahfid	0.627	315	7	This study
	19KO25D2	-152.5147	58.4305	134	Lahfid	0.611	294	11	This study
	19KO25E	-152.5147	58.4305	11	Lahfid	0.585	262	12	This study
	19KO25F	-152.5147	58.4305	10	Lahfid	0.59	267	11	This study
	19KO27A	-152.536	58.4096	15	Lahfid	0.599	279	17	This study
	19KO27B	-152.536	58.4096	15	Lahfid	0.602	283	7	This study

III.4. Results – RSCM temperatures

	19KO27A-1	-152.536	58.4096	22	Lahfid	0.607	288	20	This study
	19KO27A-2	-152.536	58.4096	27	Lahfid	0.61	293	19	This study
	19KO27A-3	-152.536	58.4096	14	Lahfid	0.597	276	28	This study
	19KO27A-4	-152.536	58.4096	43	Lahfid	0.602	282	19	This study
	19KO27A-5	-152.536	58.4096	32	Lahfid	0.601	281	20	This study
Early stage extension veins					FI		280		Vrolijk (1988)
							290-		Rowe et al.
					VR		300		(2009)
									Rowe et al.
Shear veins parallel to Uganik Thrust					FI		220		(2009)
Raspberry Schist									
<i>Uyak Bay - Bear Island</i>	KO21	-154.0328	57.6599	15	Lahfid	0.601	281	20	This study
									Roeske et al.
	Js1				MP		~350		(1989)
							360-		Roeske et al.
	Js2				MP		460		(1989)

III.4.2. Slope sediments

Samples from the Narrow Cape and Sitkinak Formation experienced peak-metamorphic temperatures below the limit of the method by Lahfid et al. (2010) and consequently they were treated following the method of Schito et al. (2017).

For three samples from the Narrow Cape Formation the average RA2 values are 0.72 ± 0.06 (19KO08), 0.82 ± 0.08 (19KO15) and 0.98 ± 0.14 (22KO48), with majority of points ranging 0.77-0.91. Estimated RA2 values are correlated to Ro (%) of 0.63-1.21 (0.92 ± 0.29 ; Schito et al., 2017), what further corresponds to the temperatures of $100 \pm 13^\circ\text{C}$ (19KO08), $119 \pm 14^\circ\text{C}$ (19KO15) and $138 \pm 19^\circ\text{C}$ (19KO15; Fig. III.4).

Five samples from the Sitkinak Formation revealed similar temperature results to the Narrow Cape Formation. In the sample 22KO29, RA2 value of 1.06 ± 0.14 corresponds to Ro% of 1.39 ± 0.29 , with final temperature of $144 \pm 7^\circ\text{C}$. Samples 22KO30 and 22KO31 have similar RA2 values, 0.78 ± 0.07 and 0.77 ± 0.07 , corresponding to Ro% of 0.80 ± 0.15 and 0.78 ± 0.15 , respectively. Yielded temperatures are $111 \pm 14^\circ\text{C}$ and $110 \pm 14^\circ\text{C}$. Samples 22KO32 and 22KO33 have RA2 values of 0.87 ± 0.15 and 0.82 ± 0.09 , what give Ro% values of 0.99 ± 0.3 and 0.89 ± 0.19 , finally corresponding to the temperatures $124 \pm 19^\circ\text{C}$ and $119 \pm 17^\circ\text{C}$, respectively (Fig. III.3).

III.5. Discussion

III.5.1. Temperature structure of the complex

Temperatures results from this study indicate that the relatively high temperatures (300-380°C) are recorded in the central part of the complex, the Kodiak Central and Seaward Belts, and decrease (220-300°C) towards the inner (Landward Belt and Uyak Complex) and outer (Ghost Rocks Formation) domains (Fig. III.5). This finding is at variance with previous studies where monotonous trenchward decrease is expected along the studied profile (Brantley & Fisher, 1997; Moore et al., 1983; Roeske et al., 1989; Rowe et al., 2009; Vrolijk et al., 1988). The only zone which potentially indicate trenchward cooling is observed in the Ghost Rocks Formation (Fig. III.5). Based on the orientation of the bedding stratification (sub-vertical in the Landward and Seaward Belts and sub-horizontal in the Central Belt), Fisher & Byrne (1992) proposed an antiformal structure within the Kodiak Formation, where the Central Belt represents its core and the Landward and Seaward Belts its limbs. Our temperature profile, where samples are plotted prior to the distance to the Contact Fault, suggests that the core of the antiform is located in the central portion of the Kodiak Formation, while the Kodiak Landward Belt/Uyak Complex and the Ghost Rocks Formation represent limbs on either side of the culmination related to the anticline (Fig. III.5). The orientation of the crenulation cleavage throughout the Kodiak and Ghost Rocks Formation suggests that the antiform is asymmetrical and inclined towards the trench. The wavelength of such folding is very large, at the scale of the whole belt, as it does not significantly rotate the preexisting upright folds of the Kodiak Seaward Belt and the Ghost Rocks Formation. Such antiform may formed during a period of horizontal shortening, which is the most pervasive in the frontal part of the complex. The influence onto central part is potentially formation of crenulation cleavage, whose orientation is sub-vertical throughout the central part of the complex (D2 stage from Chapter II).

The thermal structure of the Kodiak complex can be compared to several well-studied accretionary prisms across the globe. In the Franciscan complex (California) or the Shimanto and Sambagawa belts (southwestern Japan) for instance, metasedimentary units record a continuous increase in *P-T* conditions from the paleo-trench position to the inner domains (Ernst & McLaughlin, 2012; Osozawa & Wakabayashi, 2015; Palazzin et al., 2016; Raimbourg et al., 2014; Tagami & Dumitru, 1996; Wakabayashi, 2015). Contrary to the Franciscan complex and southwestern Japan, the Otago

Schists in New Zealand show an antiform structure, with pumpellyite-prehnite facies in outer parts of the antiform to garnet-biotite-albite zone in its core (Breeding & Ague, 2002; Mortimer, 2000). Forster & Lister (2003) suggested that the higher-grade metamorphic core of antiform is exhumed as a result of extensional tectonics and erosion. Distribution of our thermal data shown in Fig. III.5 suggest that the Kodiak accretionary complex is more similar to the Otago Schists, with temperature variations indicating structural relief associated with a post-accretion anticlinorium. However, extensional tectonics cannot be responsible mechanism for the antiform in the Kodiak complex due to lack of extensional structures. Hence, another mechanism should be considered.

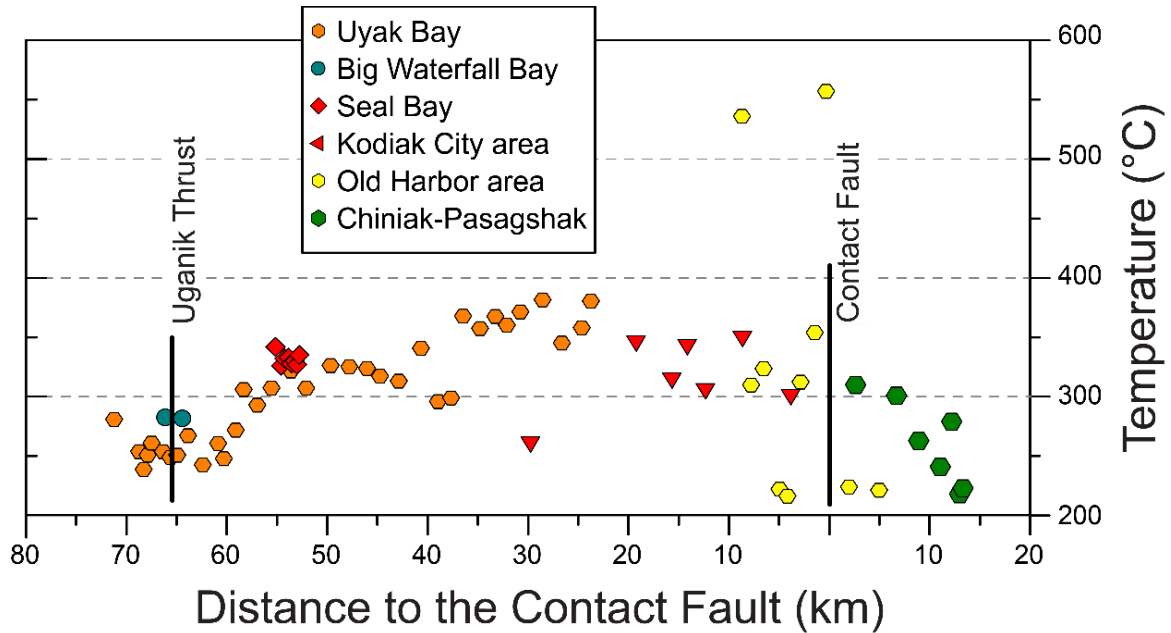


Figure III.5. A RSCM profile from all accreted units. For the Kodiak city area, Old Harbor area and Uyak Bay, results are plotted with respect to the distance to the Contact Fault, and for Big Waterfall and Seal Bay with respect to the distance to the Uganik Thrust.

III.5.2. Temperature structure around the Uganik Thrust

At the locations of the Uganik Thrust, in Uyak and Big Waterfall Bays, the paleothermometry results point to a lack of thermal gap. In Uyak Bay, the temperature gap of $\sim 10^{\circ}\text{C}$ in vicinity of the thrust is well below the uncertainty of temperature estimates by RSCM ($\sim 30^{\circ}\text{C}$, Lahfid et al., 2010) while the average temperatures from the Landward Belt and the Uyak Complex are identical (Fig. III.5). This relationship is also found in Big Waterfall Bay, where both sides of the thrust recorded a temperature of $\sim 285^{\circ}\text{C}$. RSCM temperature range for the Landward Belt in Big Waterfall Bay is

very close to the temperature results inferred from vitrinite reflectance (Rowe et al., 2009). A thermal gap across out-of-sequence thrusts (OOST) is reported in several accretionary complexes, caused by juxtaposition of rocks buried at different depths (e.g., Nobeoka Tectonic Line in the Shimanto belt; Kondo et al., 2005; Raimbourg et al., 2017). For the Uganik Thrust, Rowe et al. (2009) proposed that the thermal gap of 0-45°C existed between foot and hanging wall, but was later overprinted by a thermal peak caused by ridge subduction and focused flow of hot fluids along the faults. Such interpretation is ruled out by the thermal profiles (Fig. III.5), where the Uganik Thrust domain corresponds to much lower temperatures than the Kodiak Central Belt terranes. Therefore, the lack of thermal gap between foot and hanging wall, suggests that most of the slip occurred while the fault was a plate boundary décollement. Hence, combining deformation structures described in Chapter II with temperature results, we propose that the Uganik Thrust firstly acted as a plate-boundary interface during the underthrusting and accretion of the Kodiak Formation rather than as an out-of-sequence thrust as proposed by Rowe et al. (2009), and then later reactivated as the south-verging thrust fault without significant offset.

III.5.3. Vertical motion in the frontal part of the complex

Combining our results with previous publications, we were able to propose three different stages of vertical motion in the Kodiak accretionary complex (Fig. III.6). The approximate amplitudes of exhumation/rock subsidence are estimated from given geotherm of 30°C/km inferred from multi-phase equilibrium in the Kodiak Formation (Rajič et al., submitted; Chapter III) and based on vitrinite reflectance and porosity data in the Sitkalidak and Sitkinak Formations (Moore & Allwardt, 1980). The durations of each period are calculated based on relative chronology (Byrne, 1982; Byrne & Fisher, 1987; Moore et al., 1983; Moore & Allwardt, 1980).

The cooling and exhumation of the Late Cretaceous-Early Paleogene units is proposed to occur as a consequence of basal accretion of the Eocene sediments (Byrne, 1986; Byrne & Fisher, 1987). This is further supported by zircon and apatite fission tracks studies (Clendenen et al., 2003), which confirms that cooling of the Late Cretaceous-Early Paleogene units occurred during the Eocene (Fig. III.6). The exhumation is likely promoted by prism thickening in combination with surficial erosion, since normal faulting is scarcely observed throughout the complex. The lack of thermal gaps across the complex, in first order along the large-scale faults, point to the exhumation of all

units as a single rigid body. To exhume the deeply buried units, the Uyak Complex, Kodiak and Ghost Rocks Formations, 7-11 km of material must be removed from the top by surficial erosion. The estimated exhumation rate of the Kodiak and Ghost Rocks Formations through the Eocene is 0.25-0.5 mm/yr (for a duration of 22-26 My and the amplitude 7-11 km). Exhumation rates are similar to rates derived from zircon and apatite fission-track analyses in the Valdez Group (~0.5 mm/yr; Arkle et al., 2013), an equivalent to the Kodiak Formation at Kenai Peninsula.

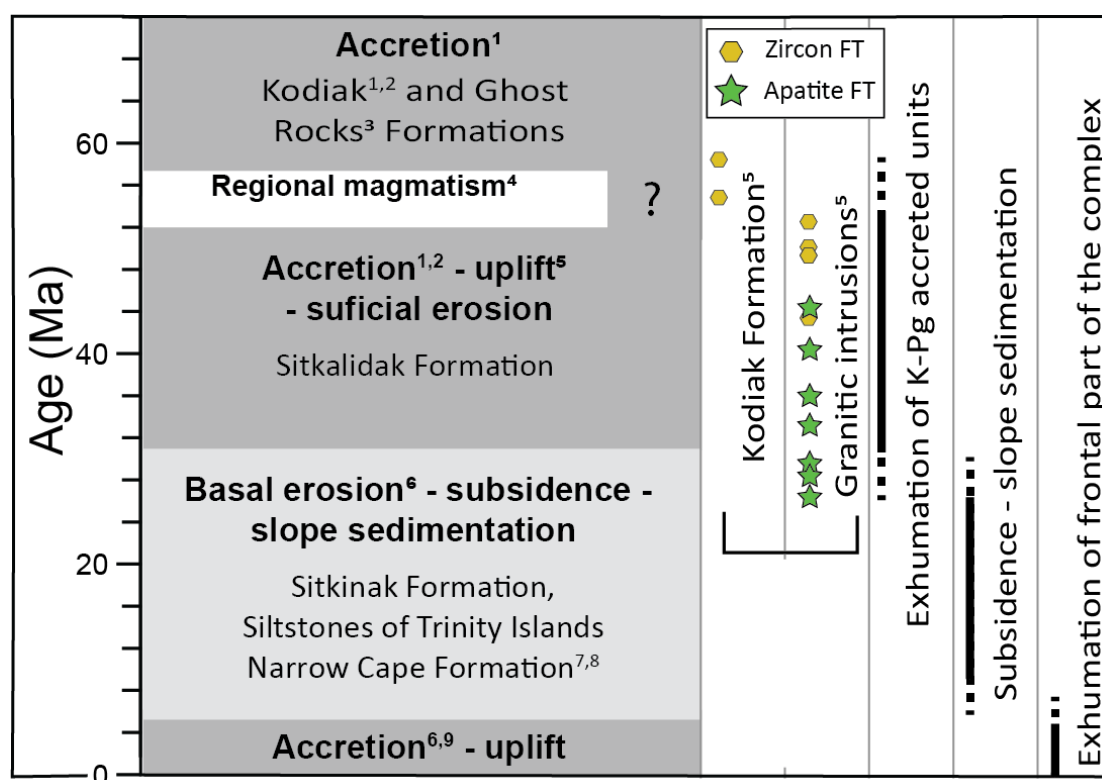


Figure III.6. Summary of different periods of basal accretion, slope sedimentation, combining with periods of exhumation and subsidence in the Kodiak accretionary complex. References: 1 - (Byrne, 1986); 2 - Byrne & Fisher (1987); 3 - Byrne (1982); 4 - Farris et al. (2006); 5 - Clendenen et al. (2003); 6 - von Huene et al. (2012); 7 - Moore & Allwardt (1980); 8 - Moore et al. (1983); 9 - Noda & Miyakawa (2017).

After the end of exhumation of the Cretaceous-Paleogene accreted units, deposition of slope sediments onto the accreted units represents the beginning of a wedge subsidence in the frontal part (Fig. III.6). The temperature gap along the angular unconformity between the basally accreted units and the slope sediments is about 100°C (Fig. III.7). The slope sediments, the Narrow Cape

and Sitkinak Formations, are characterized by temperatures 100-140°C, with the majority of measurements cluster around 120°C. The temperatures of 120°C points to a large amount of rock subsidence and burial down to ~4 km, considering a thermal gradient of about 30°C/km (Moore & Allwardt, 1980). The oldest record of slope sedimentation is from the Oligocene Sitkinak Formation, what is assumed to represent the beginning of subsidence. The end of subsidence is difficult to estimate, however, a plausible possibility is during Pliocene (3-6 Ma) when the sedimentation rate in the trench is significantly higher than during the Oligo-Miocene (von Huene et al., 2012; Noda & Miyakawa, 2017). Hence, the subsidence duration is estimated as 20-22 My, between the Oligocene and the Pliocene (3-6 Ma). Combined with the depth derived from the RSCM temperature results (4 km), the calculated rock subsidence rate ranges 0.18-0.2 mm/yr. To explain such subsidence, there are three possibilities: (1) The prism instability during a period of accretion, where a subsidence results from normal faulting. (2) Local subsidence in the footwall of out-of-sequence thrusts that cut across the fore-arc, leading to the formation of forearc basins. (3) A period of a subduction erosion instead of accretion (Clift & Vannucchi, 2004). To the extent of our observations, normal faulting is too rare to be a major contribution to the subsidence. Hence, the prism instability is not plausible mechanism to trigger such subsidence. In the slope southeast from the Kodiak archipelago, several basins have been formed, such as Tugidak (Fisher, 1980, 1979) or Albatross basins (Fisher & Holmes, 1980; von Huene et al., 2012), pointing to local (and recent) subsidence even though the margin is characterized by accretion. Hence, the processes that lead to the formation of recent offshore basins are another possible explanation for the Late Oligocene-Miocene slope sedimentation. The occurrence of such basins is still ambiguous, potentially related to the out-of-sequence thrusting and the consequent subsidence in the footwall of the thrust zone (Fisher & Holmes, 1980). In such scenario, the studied slope sediments are located in the footwall and the adjacent fault zone should be to the northwest from the place where the deposition occurred, in the Ghost Rocks Formation. However, the temperature profile shows no thermal gap, so that the presence of a large out-of-sequence thrust in the Ghost Rocks Formation is unsupported. Hence, the subduction erosion, i.e. erosion at the base of the wedge, during the Neogene is the most likely mechanism responsible for such subsidence. Also, the deposition of the Sitkinak and Narrow Cape Formations coincides with the proposed period of subduction erosion during the Miocene by Von Huene et al. (2012) based on the fact that the current slope is made of Eocene or older rocks in the contact with Quaternary sediments, suggesting that a large portion of

material is missing. This erosive subduction is supported as well by Deep Sea Drilling Project Leg 18, Site 178, which found another unconformity between the Pliocene and Miocene sediments of the slope (Kulm et al., 1973).

The final stage is the exhumation of previously buried units in the frontal part of the complex to the present position (Fig. III.6). The exhumation of the slope sediments buried down to $\sim 120^\circ\text{C}$ requires surficial erosion of ~ 4 km of material. The estimated exhumation rate is about 0.8-1.3 mm/yr. After slope sedimentation, strong horizontal shortening occurred in slope sediments, and significantly stronger in the Sitkinak Formation where the bedding stratification is fully tilted to the vertical position. Hence, the exhumation can be a result of horizontal shortening in the combination with surficial erosion. However, in the Narrow Cape Formation, a shortening is not as pervasive as in the Sitkinak Formation, and additional process is potentially required to exhume deeply buried sediments. Since the Pliocene, much larger sediment flux is observed in trench sediments (von Huene et al., 2012; Noda & Miyakawa, 2017), what can lead to the accretion and the prism growth. Also, Carver et al. (2013) point to higher recent uplift rate (~ 0.75 mm/yr) in the Narrow Cape Formation than in the rest of the Kodiak Island, related to the active upper crustal faulting in the Kodiak shelf fault zone (Fig. III.8). These faults are steep left-lateral with significant up-to-the-NW vertical component (Carver et al., 2013). Similar exhumation rates are reported in very frontal part of the Prince William Sound, Southern Alaska (Arkle et al., 2013). Based on zircon and apatite fission-track analyses calculated rates are 1.0-2.4 mm/yr since Pliocene (Arkle et al., 2013), related to a higher sediment input into the trench and consequently underplating of sediments.

As described in Chapter II, all deformation structures observed during this study are interpreted as formed along the plate-boundary interface or as intra-wedge deformation resulting mostly in horizontal shortening. Overall, we propose that the rock exhumation results from the combination of basal accretion, horizontal shortening and surficial erosion. Contrarily, periods of subsidence evidenced by slope sediments coincide with basal erosion (Fig. III.8).

III.6. Conclusion

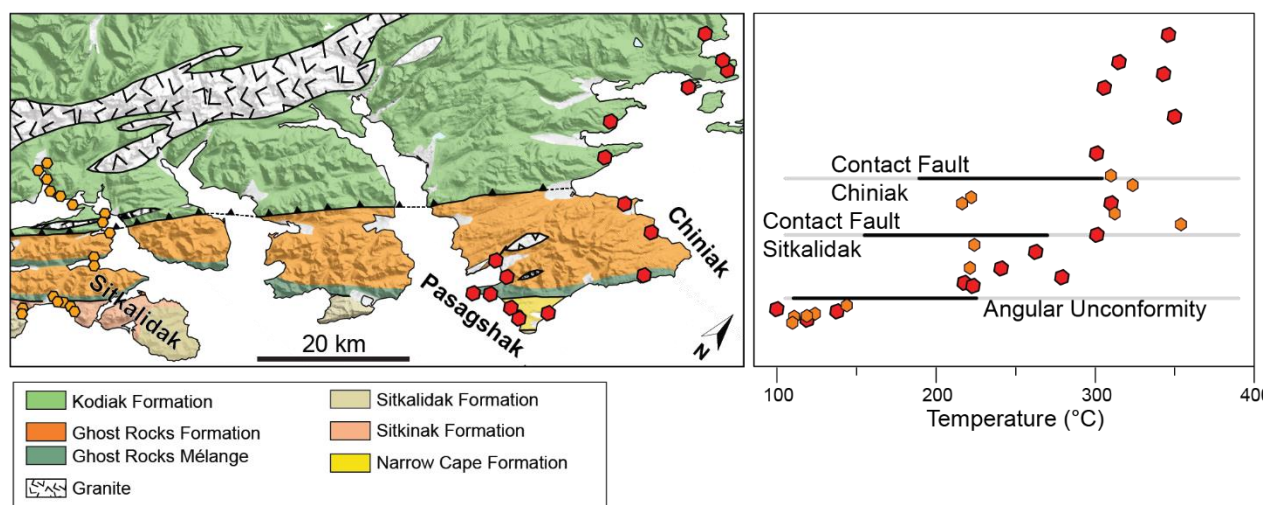


Figure III.7. A RSCM temperature profile in the frontal part of the complex. Note the thermal gap of ~100°C between basally accreted Ghost Rocks Mélange and slope sediment formations, the Narrow Cape and Sitkinak Formations.

III.6. Conclusion

Our regional RSCM study across the Kodiak accretionary complex shows temperature ranging from 220 to 400°C, without discontinuities across unit-bounding faults. The highest temperatures are measured in the Kodiak Central and Seaward Belts, which constitutes the central portion of the complex.

A gap in peak-metamorphic temperatures between accreted units and slope sediments suggest vigorous vertical motion within the wedge between the Paleogene and the Miocene (Fig. III.8). The period of exhumation of Cretaceous-Paleogene sedimentary units is related to the underplating of younger material, and the lack of significant extensional features indicates that the exhumation occurred as a result of horizontal shortening and surficial erosion. Later, a stage of subsidence in the Miocene is most likely related to a period of basal erosion. The final uplift of the Narrow Cape Formation is a result of the recent accretive character of the subduction zone and active upper crustal faulting. Estimated rates for the vertical motion are comparable with estimates from other paleo-accretionary prisms.

III.6. Conclusion

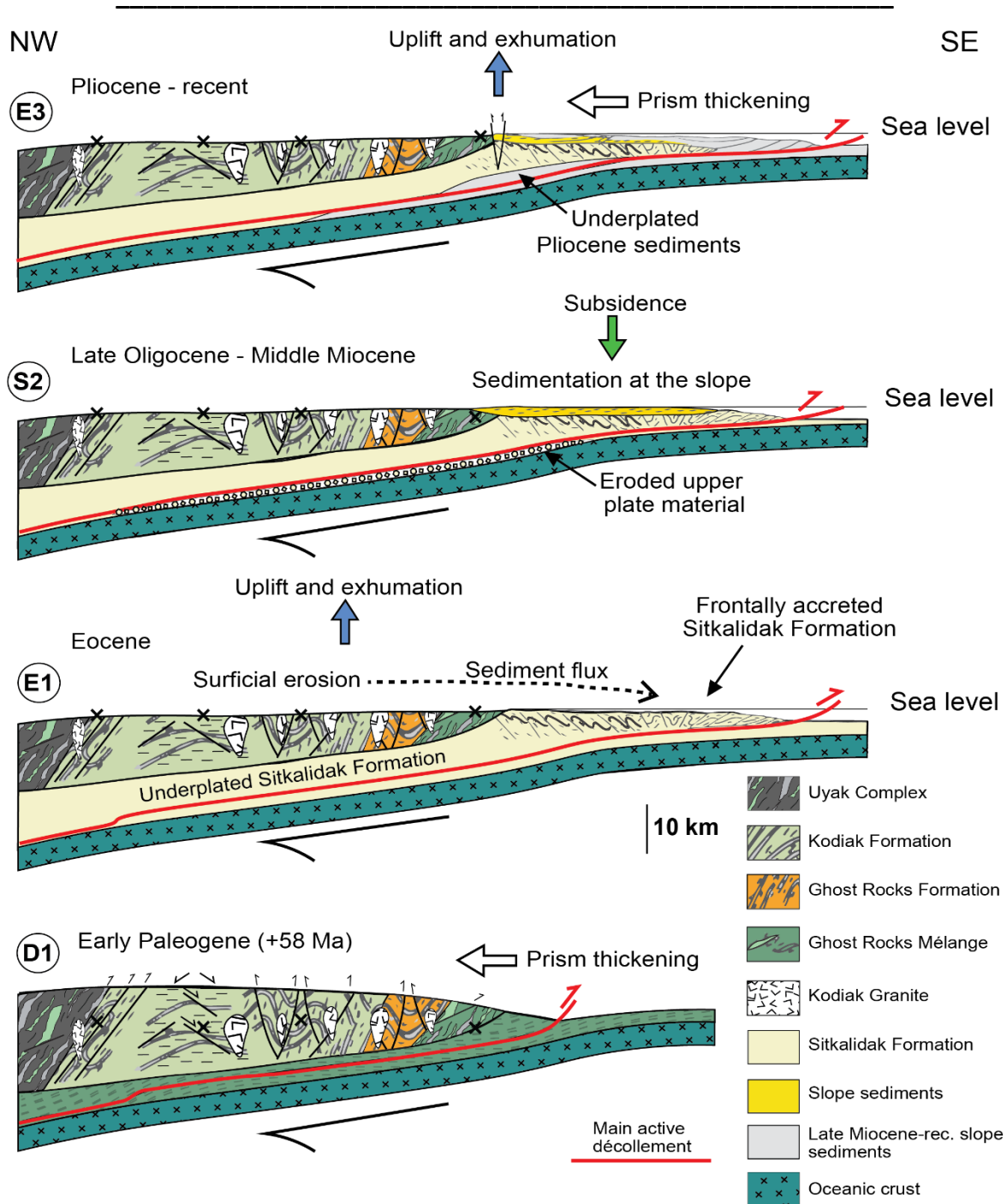


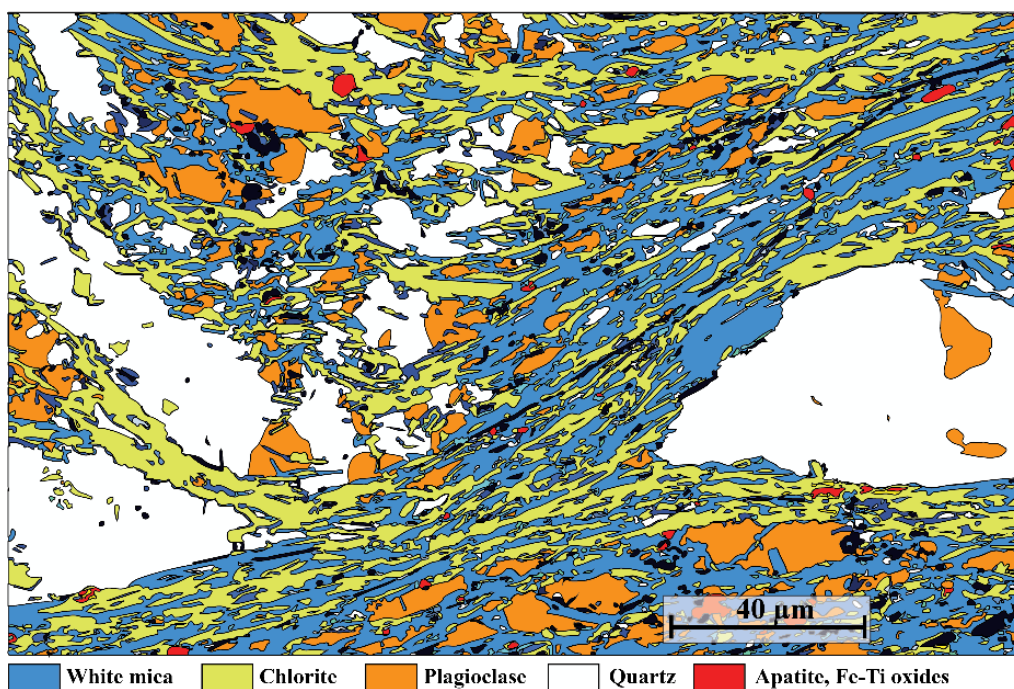
Figure III.8. Cross-section of the Kodiak accretionary complex evolution with three different stages of the vertical motion: (D1) A period of basal accretion during late Cretaceous-Early Paleogene, and associated deformation structures. (E1) The exhumation of accreted units by underplating of thick Eocene strata (Moore & Allwardt, 1980). The uplift is coeval with the surficial erosion and exposure of deeply accreted units to their nearly present position. (S2) Subsidence recorded in slope sediments in the frontal part of the prism, most likely due to the basal erosion. (E3) The exhumation of the frontal part of the complex. Recent profile is created based on seismic profiles (Fisher & Holmes, 1980; von Huene et al., 2012) as well as onshore observations (Carver et al., 2013).

Preface

In order to determine the fluid-mineral reactions and the fluid budget in subduction zones, we studied rocks spanning the base of the seismogenic zone in two accretionary complexes, the Kodiak (Alaska) and Shimanto (Japan). Burial maximum temperatures range from 230 to 350°C (based on Raman spectroscopy of carbonaceous material) in both examples, while pressures reached up to ~3 and ~4kbar in the higher-grade units of the Japanese and Alaskan complexes, respectively. At 230-260°C, the chlorite present is to a large extent interpreted as a coproduct from lower-grade smectite-to-illite transformation. Chlorite content increases as temperature rises up to 330-350°C, as a result of illite-to-chlorite transformation. Other reactions include pyrite oxidation and dissolution of titanite/precipitation of anatase. Whole-rock chemistry points to the absence of systematic changes between samples experiencing different temperatures, however, in restricted areas dissolution of quartz and albite caused SiO₂ and Na₂O depletion in the matrix, counterbalanced by reprecipitation within veins. Qualitative analysis of fluid inclusion chemistry using decrepitation method show that the composition of the fluid is significantly different from the original seawater trapped in the pores. In addition, fluid inclusions salinity in quartz veins at 230-260°C, analyzed using the Raman spectrum of water, is lower than seawater (~2 wt.% NaCl eq.) and interpreted as dilution of original seawater by fresh water released by smectite-to-illite transformation. In contrast, veins formed at 330-350°C contain fluid inclusions with a salinity of the order or higher than seawater. The increase in salinity for temperatures 250-350°C reflects hydration reactions, mostly controlled by chlorite crystallization. In contrast to the general trend of dehydration reactions occurring during rock burial in subduction zones, this study shows the base of the seismogenic zone is rather dominated by an uptake of pore fluid by mineral reactions.

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CHAPTER IV – Metamorphic reactions and their implication for the fluid budget in metapelites at seismogenic depths in subduction zones



CHAPTER IV – Metamorphic reactions and their implication for the fluid budget in metapelites at seismogenic depths in subduction zones

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IV.0. Abstract

In order to determine the fluid-mineral reactions and the fluid budget in subduction zones, we studied rocks spanning the seismogenic zone in two accretionary complexes, the Kodiak complex (Alaska) and Shimanto belt (Japan). Burial maximum temperatures range from 230 to 350°C (based on Raman spectroscopy of carbonaceous material) in both examples, whereas pressures reached up to ~3 and ~4kbar (based on multi-phase equilibrium model) in the higher-grade units of the Japanese and Alaskan complexes, respectively. At 230-260°C, the chlorite is interpreted as a coproduct from lower-grade smectite-to-illite transformation. Chlorite content increases as temperature rises up to 330-350°C, as a result of illite-to-chlorite transformation. Other reactions include pyrite oxidation and dissolution of titanite and precipitation of anatase. Whole-rock chemistry points to the absence of systematic changes between samples experiencing different temperatures. However, in restricted areas dissolution of quartz and albite caused SiO₂ and Na₂O depletion in the matrix, counterbalanced by reprecipitation within veins. Qualitative analysis of fluid inclusion chemistry using decrepitation method show that the composition of the fluid is significantly different from the original seawater trapped in the pores. In addition, the salinity of fluid inclusions in quartz veins at 230-260°C, analyzed using the Raman spectrum of water, is lower than seawater (~2 wt.% NaCl eq.) and interpreted as dilution of original seawater by fresh water released by smectite-to-illite transformation. In contrast, veins formed at 330-350°C contain fluid inclusions with a salinity of the order or higher than seawater. The increase in salinity for temperatures 250-350°C reflects hydration reactions, mostly controlled by chlorite crystallization. In contrast to the general trend of dehydration reactions occurring along rock burial in subduction zones, this study shows the base of the seismogenic zone is rather dominated by an uptake of pore fluid by mineral reactions.

IV.1. Introduction

Fluids are strongly involved in the majority of subduction zone processes: A presence of pore fluids highly impact rheological behavior of subducted lithologies (e.g., Fagereng et al., 2018; Hacker et al., 2003; Muñoz-Montecinos, Angiboust, & Garcia-Casco, 2021); influence seismic activity via the pore fluid pressure variations (Audet & Schwartz, 2013; D. Davis et al., 1983; Saffer & Tobin, 2011); dehydration reactions in deeply subducted lithologies are responsible for

arc magmas generation due to the melting action of volatile species of the mantle (Bebout, 1991; Elliott, 2003; Hacker, 2008; Stern, 2011). As fluids are reactants or products of metamorphic reactions, their abundance, nature and chemistry change with burial. Beyond the drilling reach limit of ODP/IODP programs (<5 km), our knowledge of fluid composition mostly relies on studies of fluid inclusions and mineral transformations in rocks from exhumed fossil subducted complexes (e.g., Agard et al., 2000; Herviou et al., 2021; Raimbourg et al., 2018; Scambelluri et al., 2015). In veins that trapped deep fluids as fluid inclusions, the most commonly retrieved property is salinity, converted in NaCl equivalent with an assumption that NaCl is the dominant salt (Agard et al., 2000; Brantley & Fisher, 1997; Herviou et al., 2021; Kondo et al., 2005; Nishiyama et al., 2021; Raimbourg, 2015; Raimbourg et al., 2018; Rossetti et al., 2006; Rowe et al., 2009; Sadofsky & Bebout, 2004). Only few studies have actually analyzed the chemistry of the occluded fluid (e.g., Scambelluri et al., 2004, 2015; Yoshida et al., 2015).

Sediments are major carriers of fluids (mostly water) into subduction zones (Jarrard, 2003; Plank, 2014; Stern, 2002), together with the altered and serpentinized oceanic lithosphere (Peacock, 1993; Schmidt & Poli, 2014; Reynard, 2013; Rupke, 2004). Average seafloor shales contain up to 70 vol.% of pore water chemically similar to sea water, and about 7 wt.% as crystal-bound H₂O (Plank, 2014). During burial, most of the interstitial water is expelled at shallow depths from sediments by compaction and cementation processes, leaving only <10 vol.% in pore spaces (Fagereng et al., 2018; Kastner et al., 2014; Kominz & Pekar, 2001; Saffer & Tobin, 2011). Following pore collapse, the occurrence of prograde metamorphic reactions controls the water budget (Rupke, 2004; Schmidt & Poli, 2014). The smectite-to-illite transformation occurring in the temperature range of 60-150°C and releases significant amount of H₂O bounded in minerals, thus, reducing the salinity of pore fluids (e.g., Kastner et al., 2014; Saffer et al., 2012). Upon further burial, several important dehydration reactions have been reported above 400°C, such as the carpholite and chlorite breakdown in the blueschist facies or the glaucophane, lawsonite, and chlorite breakdown in the eclogite facies (Agard et al., 2001; Angiboust & Agard, 2010; Bebout, 1991; Bebout et al., 2013; Becker et al., 2000; van Keken et al., 2002; Lefeuvre et al., 2020; Muñoz-Montecinos et al., 2021; Peacock, 1993; Simons et al., 2010; Spandler et al., 2003). Only few metamorphic reactions has been identified in subducted sediments in the range 150-400°C, such as the formation of lawsonite and Mg-Fe carpholite (Goffé & Chopin, 1986; Lefeuvre et al., 2020). Although many exhumed sedimentary units have experienced sub-greenschist and

greenschist facies (peak-metamorphism at 150-350°C) in subduction complexes worldwide contain evidence of ancient fluid pathways in form of metamorphic veins, such as the Kodiak accretionary prism in Alaska (Brantley & Fisher, 1997; Fisher et al., 1995; Fisher & Brantley, 2014; Vrolijk et al., 1988), the Shimanto belt in Japan (Nishiyama et al., 2021; Raimbourg et al., 2015, 2018), the Franciscan Complex in California, or the Otago Schists in New Zealand (Breeding & Ague, 2002; Fagereng et al., 2011), metamorphic transformation in the greenschist facies and the influence of reactions to the pore fluid budget is relatively poorly documented compared to deeper metamorphism (e.g., Fagereng & Cooper, 2010; Frey, 1978; Kameda et al., 2011; Rahn et al., 1994; Raimbourg et al., 2009; Schmidt et al., 1997; Wang, 1996).

The objective of our study is to fill this gap of knowledge, by describing the prograde evolution of mineral assemblages, the scale of chemical transport and the fluid budget in sediments subducted and buried down to greenschist facies. To do so, we targeted two accretionary prisms: Kodiak and the Shimanto belt, because peak-metamorphic conditions are well preserved and thoroughly constrained to 200-350°C at both localities (Brantley & Fisher, 1997; Palazzin et al., 2016; Raimbourg et al., 2014, 2021; Rowe et al., 2009; Vrolijk et al., 1988). First, we studied changes in microstructures, mineralogy and whole-rock chemistry with increasing temperature. Mineral chemistry was then used to test the mineral equilibrium for possible estimation of pressure-temperature conditions based on multiphase equilibrium model (Dubacq et al., 2010; Vidal et al., 2006). Finally, we studied fluid inclusions as fluid witnesses of the deep metamorphic reactions. Based on these results, we propose several mineral reactions and evaluate fluid-rock interaction as well as changes in the salinity among subducted rocks from the two paleo-accretionary complexes. Our results are of importance for quantifying the fluid budget of sediments undergoing burial in the greenschist facies realm during subduction.

IV.2. Geological settings and sampling strategy

We sampled metapelites and adjacent veins along various units of the two selected accretionary prisms (Fig. IV.1; Palazzin et al., 2016; Raimbourg et al., 2021) to investigate the dependence of fluid-mineral reactions on peak-metamorphic temperature and pressure. The list of samples and their peak-metamorphic conditions is presented in Table IV.1. In the Kodiak accretionary complex, metapelites and adjacent veins are sampled in the Kodiak Landward Belt in Uyak Bay and the

IV.2. Geological settings and sampling strategy

Kodiak Central Belt in Seal Bay, experienced peak-metamorphic temperatures of $\sim 250^{\circ}\text{C}$ and $\sim 330^{\circ}\text{C}$, respectively (Chapter III). Sampled veins are described as D1 veins in Chapter II. Briefly, the veins from the Landward Belt are Mode 1 quartz-calcite veins with an orientation almost perpendicular to bedding (Fig. IV.2a). In Seal Bay, two types of veins have been observed: D1 shear veins at low angle to the foliation with a fibrous structure parallel to the stretching direction on foliation plane, and Mode 1 quartz veins, often in form of en échelon arrays (Fig. IV.2c). En échelon veins cut across the foliation but are folded perpendicular to the foliation S_1 (Fisher & Brantley, 2014; Raimbourg et al., 2021).

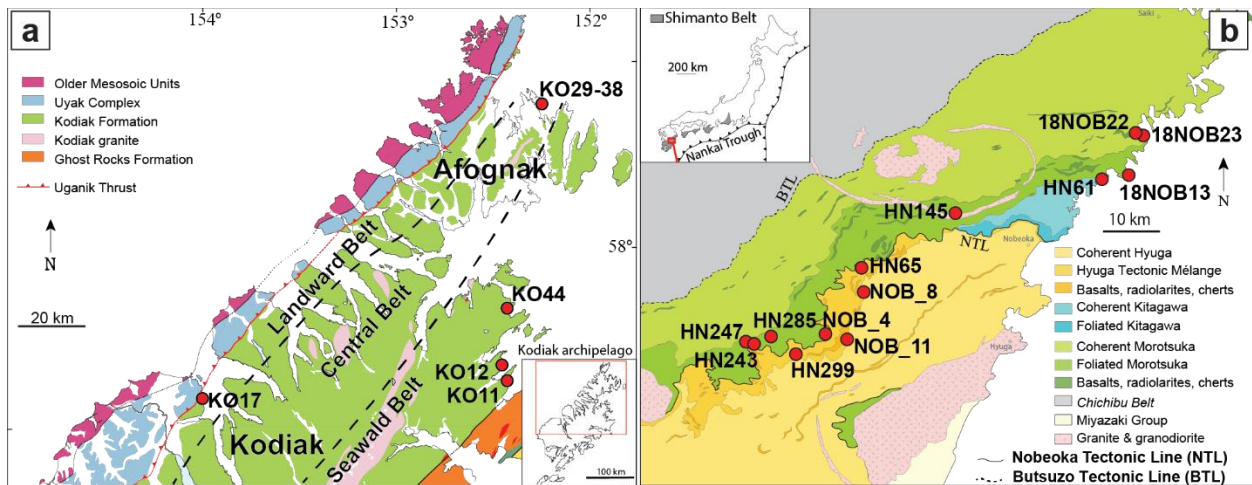


Figure IV.1. Geological map of (a) the Kodiak accretionary complex, Alaska, and (b) the Shimanto belt on Kyushu, Japan, with the locations of samples used in this study.

The Shimanto Belt is a paleo-accretionary wedge (Taira, 1988) exposed on islands of Honshu, Kyushu and Shikoku in Japan. It is composed of several units defining parallel belt striking to the SW-NE, such general trend is also consistent to the active Nankai Through. The Shimanto Belt in Kyushu is also divided into several units, among which are two units selected for the purpose of this study, the Foliated Morotsuka and the Hyuga Tectonic Mélange.

The Foliated Morotsuka (FM) is composed of sheared and strongly foliated lithologies, including deep-sea sediments and basaltic lenses embedded within metapelitic matrix. The sediment age range in Cenomanian-Turonian (Saito et al., 1996). A strong metamorphic foliation is present, along with a N-S and NNW-SSE stretching lineation (Raimbourg et al., 2009, 2014; Ujiie et al., 2018). RSCM revealed the maximum temperature of $345 \pm 30^{\circ}\text{C}$ (Palazzin et al., 2016). Based on metamorphic assemblages in basaltic lenses, pressure-temperature conditions in the Foliated

IV.2. Geological settings and sampling strategy

Morotsuka estimated to 3-5 kbar and 300-350°C (Toriumi & Teruya, 1988). The veins examined in this study are en échelon arrays (Fig. IV.2d), cutting across the foliation and are shortened perpendicular to the foliation (Raimbourg et al., 2021). The Foliated Morotsuka is separated from the Hyuga Group by the Nobeoka Tectonic Line (NTL; Teraoka & Okumura, 1992), an out-of-sequence thrust (Kondo et al., 2005).

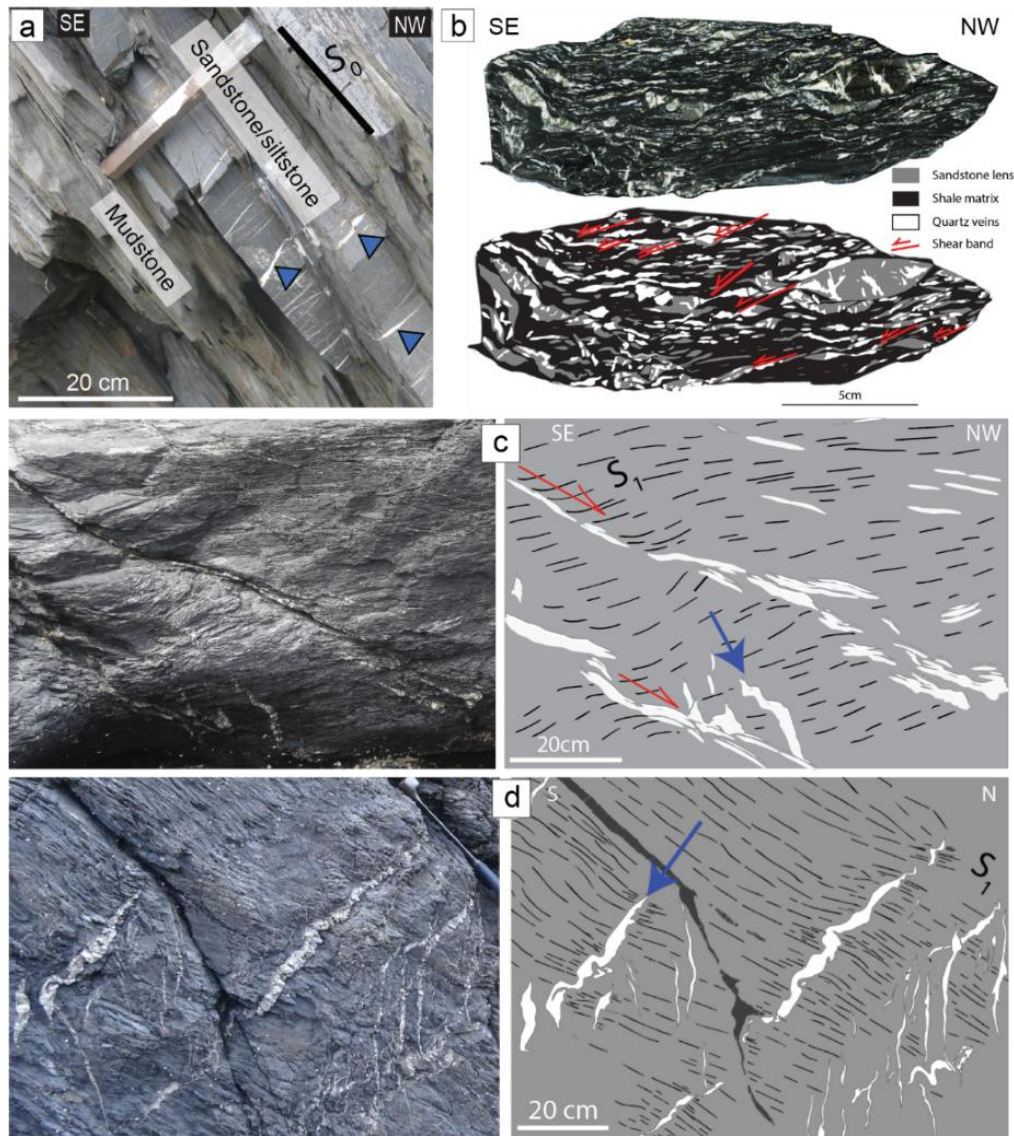


Figure IV.2. Field pictures of metasediments and veins used in this study from the Kodiak accretionary complex (a and c) and from the Shimanto belt (b and d). (a) Mode 1 quartz veins in coherent portion of the Kodiak Landward Belt (Alaska). Note that veins are restricted to sandstone/siltstone layers and absent in mudstone. (b) Quartz veins dominantly located in the sandstone lenses in strongly sheared shales from the Hyuga Tectonic Mélange (Shimanto belt, Japan). (c) Top-to-the-NW shear veins cutting across the foliation S_1 , Kodiak Central Belt (D1 shear bands in Chapter I). (d) Example of en échelon vein arrays in the Foliated Morotsuka (Shimanto belt, Japan).

IV.2. Geological settings and sampling strategy

The Hyuga Group is divided into Hyuga Tectonic Mélange (HTM) and Coherent Hyuga. In this study the Hyuga Tectonic Mélange is examined, which consists of strongly sheared sandstone lenses embedded in a pelitic matrix. Based on microfossil assemblages, the sedimentation age is determined from the Middle Eocene to the Early Oligocene (Nishi, 1988; Sakai et al., 1984). The dominant set of veins are mode 1 quartz veins oriented perpendicular to the orientation of the sandstone lenses stretched in NW-SE direction (Fig. IV.2b; Raimbourg et al., 2014). Based on RSCM, the peak-temperature of the deformation is $\sim 245 \pm 30^\circ\text{C}$ (Palazzin et al., 2016).

Table IV.1. Sample locations and pressure-temperature estimates based on Raman Spectroscopy of Carbonaceous Material and multi-phase equilibrium model. Literature: ¹Palazzin et al. (2016); ²Raimbourg et al. (2018); ³Raimbourg et al. (2021).

	Sample	Longitude	Latitude	RSCM		Multi-phase equilibrium				Ref.
Kodiak				T (°C)	SD	T (°C)	SD	P (kbar)	SD	
Landward Belt	KO17A	-153.9843	57.6094	251	9					This study
	KO17E	-153.9841	57.6119	240	9					This study
Central Belt	KO29A	-152.218	58.3774	327	7	349	17	3.5	0.8	This study
	KO30	-152.2228	58.3542	331	13	310	21	3.1	0.4	This study
	KO32A	-152.245	58.3893	330	16					This study
	KO32F	-152.245	58.3893	330	16					This study
	KO33C	-152.2568	58.3576	333	19	306	26	2.9	0.3	This study
	KO36A	-152.2586	58.3661	330	29					This study
	KO38	-152.2865	58.3889	340	28	329	16	3	0.4	This study
	Seaward Belt	KO11	-152.4386	57.6516	300	19				
	KO12B	-152.4764	57.6875	348	28					This study
	KO45C	-152.4385	57.8393	344	16					This study
Shimanto belt										
Hyuga Tectonic Mélange	HN65	131.4036	32.5452	240	6					1
	HN299	131.279	32.4033	228	16					This study
Foliated Morotsuka	18NOB13	131.5433	32.7211	323	19					This study
	18NOB22A	131.8556	32.7552	349	6					This study
	18NOB23	131.8786	32.7614	338	10					3
	HN61	131.8559	32.7202	348	6					2
	HN143	131.5583	32.6137	322	28	301	4	3.9	0.3	This study
	HN243	131.2075	32.4094	335	26	330	3	3.7	0.4	This study
	HN247	131.2026	32.3095	327	33					This study
	HN285	131.2392	32.4200	329	27	324	13	4	0.4	This study ¹

IV.3. Analytical methods

IV.3.1. Whole-rock chemistry

Samples for major element whole-rock analysis were crushed after removing any visible macro- and micro-veins in order to estimate the chemical composition of pelitic matrix. Major elements were analyzed by X-ray fluorescence (XRF) at ALS lab (Loughrea Galway, Ireland; analytical code ME_XRF26). To prepare glass beads, crushed samples (~0.5 g) were fused using a platinum mould into a fusion disk, mixed with lithium metaborate as a flux. The disks were then analyzed by XRF, where the concentrations of major elements (oxides) were determined in conjunction with loss-on-ignition (LOI) at 1000°C. Analyzed elements and parameters are Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K, P, S, Sr, Ba and LOI. Elements were calibrated in oxide weight percentage form.

IV.3.2. X-Ray Diffraction

X-ray diffraction (XRD) measurements were carried at BRGM, Orléans, France, using a BRUKER D8 Advance X-ray diffractometer equipped with a Cu K α radiation ($\lambda_{K\alpha} = 0.15406$ nm) operating at 40 kV and 40 mA.

X-Ray diffraction on bulk-powder was used for a first-order estimation of the mineralogy, including the nature of phyllosilicates. Samples were micronized in ethanol using an XRD Mill McCrone (Retsch), dried at 40°C and homogenized. XRD patterns were recorded on randomly oriented powder samples from 4 to 90°2 θ , with a step of 0.03°2 θ and a step time of 480 seconds. Quantitative analyses of X-ray diffractograms were carried out using the SiroQuantTM program, version 4 (Taylor & Clapp, 1991).

The <2 μ m fraction was then isolated from the bulk samples. To do so, the crushed powder was firstly treated with acetate (pH = 5.0) to dissolve carbonates, secondly with 0.01 M CaCl₂ to saturate interlayer space of clay minerals if present, and finally washed with pure water. Then clay particles were dispersed by ultrasonics in deionised water and the suspension was left to rest 100 minutes. Then <2 μ m fraction was isolated by sampling the upper part of the suspension and deposited on a thin section. X-ray diffraction patterns were acquired firstly on the oriented deposit dried at 50°C, then saturated with ethylene glycol under vapor tension at 60°C during at least 16

hours, to identify the clay mineral varieties. XRD patterns were recorded on oriented deposits from 2 to 35°2 θ , with a step of 0.03°2 θ and a step time of 1.5 seconds.

IV.3.3. SEM-Backscatter Electron images and Electron microprobe

Mineral petrography was carried by optical microscopy and a Merlin Compact ZEISS scanning electron microscope (SEM) equipped with backscattered electron (BSE) detector BSD4 at the Institut des Sciences de la Terre, Orléans (ISTO). The SEM-BSE was operated at 15 kV voltage and a dwell time of 50 ms. Backscattered electron images were further processed with the software ImageJ (Schneider et al., 2012) to semi-quantify the amount of each mineral phase and to prepare phase maps.

The chemical composition of main mineral phases was determined using a Cameca SX Five electron microprobe equipped with five wavelength-dispersive spectrometers (WDS), housed at ISTO-BRGM joint facilities in Orléans. The measurements were performed at 15 kV voltage, 10 nA beam current and 1 μ m spot size. Analyzed elements were Si, Ti, Al, Fe, Mn, Mg, Ca, Na and K. The used calibration standards were MgO (Mg), albite (Si, Al), andradite (Ca), orthoclase (K), MnTiO₃ (Mn, Ti) and hematite (Fe). For the elemental maps, step size and dwell time were 1 μ m and 150 ms. The maps were processed using the software XMapTools (Lanari et al., 2014).

IV.3.4. P-T estimates

The crystallization temperature of chlorite was estimated with the chlorite-quartz-H₂O thermodynamic model and the parameters described in Vidal et al. (2006), and the pressure was estimated via equilibrium with illite using the solid solution model from Dubacq et al. (2010). The approach relies on the phengite-chlorite-quartz model first presented by Vidal & Parra (2000) and applied to metapelites over a wide range of conditions, from LP-LT (Árkai et al., 2003; Battaglia, 2004) to HP-LT terrains (e.g., Plunder et al., 2012). In chlorite and mica, substitutions are modeled with end-members. The model accounts for the following substitutions: Fe=Mg²⁺; Tschermak [Si+(Mg,Fe²⁺)=Al^{IV}+Al^{VI}] in illite and chlorite; di/trioctahedral [$\square^{VI}$ +Al^{VI}+Al^{VI}=3(Fe²⁺,Mg)] in illite and chlorite, and pyrophyllitic [(Na,K)+Al= $\square^{XII}$ +Si] and paragonitic [K=Na] in illite (Dubacq et al., 2010; Masci et al., 2019; Vidal & Parra, 2000; Zane et al., 1998). Incorporation of water in

interlayer space of low-temperature illite is modeled via a vacancy-water [$\square=\text{H}_2\text{O}$] substitution (see Dubacq et al., 2010). The resulting set of solid solution end-members is pyrophyllite (Prl), hydrated pyrophyllite ($\text{Prl}\cdot\text{H}_2\text{O}$), muscovite (Ms), Mg- and Fe-celadonite (Mg-Cel and Fe-Cel) for illite, and clinochlore (Clin), daphnite (Daph), sudoite (Sud), Fe- and Mg-amesite (Fe-Am and Mg-Am) for chlorite. Additional phases are quartz (Qtz) and H_2O with activity set at unit value. With this set of phases, 124 reactions may be written, out of which six are independent. Equilibrium is inferred when independent reactions appear reasonably close to one another in P-T space (e.g., less than 20°C and 1 kbar).

IV.3.5. Raman Spectroscopy

From each locality where deformation structures were studied, a thick section oriented in the X-Z plane of kinematic referential was prepared from metasedimentary samples for the purpose of Raman Spectroscopy of Carbonaceous Material (RSCM). In the prepared thick sections, analyzed particles were chosen away from any shear bands to avoid shear-enhanced thermal maturation of carbonaceous material.

To estimate peak-metamorphic temperatures in metasediments, Raman Spectroscopy of Carbonaceous Material (RSCM) was used with a Raman Renishaw InVia Reflex microspectrometer at BRGM, Orléans. A silicon standard was used for calibration. The light source was a 514.5 nm Ar laser with a power of about 1 mW, focused by a Leica DM2500 microscope at the magnification 100x. The signal was analyzed by a CCD NIR/UV detector. 15-20 points were analyzed per sample on 150-200 μm thick, polished sections. The final deconvolution was made following the method of Lahfid et al. (2010), applicable for the temperature range from ~200°C to ~320°C. Raman spectra were processed with the software PeakFit 4.12 for subtracting the baseline and fitting each corrected spectrum with five Lorentzian bands. From the area below five Lorentzian bands, RA1 ratio was calculated by the equation $\text{RA1} = (\text{D1} + \text{D4}) / (\text{D1} + \text{D2} + \text{D3} + \text{D4} + \text{G})$. The final temperature was estimated following the equation $T\ (^{\circ}\text{C}) = 1217.6 \times \text{RA1} - 450.66$ (Lahfid et al., 2010). The uncertainty of the method is ~30°C (Lahfid et al., 2010). From 15-20 points in each analyzed sample, average values and standard deviations (1σ) were calculated.

The Raman spectrum of water originates from OH stretching vibrations, which vary as a function of salinity (e.g., Caumon et al., 2014, 2015). The salinity of water-rich fluid inclusions was estimated using a Raman Renishaw InVia Qontor micro-spectrometer at CEMHTI CNRS, Orléans. The silicon standard was used for the calibration, and the light source was a 514.5 nm solid state laser. Applied power was 50 mW, focused on standards or fluid inclusions with Leica DM2700 microscope at the 100x (0.9 NA) magnification. The signal was acquired by a CCD NIR/UV “centrus” detector. Acquiring time was 60 s for each point. For calibration, 12 solutions with known NaCl molarity were prepared (0.125 M, 0.25 M, 0.375 M, 0.5 M, 0.625 M, 0.75 M, 0.875 M, 1 M, 1.25 M, 1.5 M, 1.75 M and 2 M). The solutions were placed into the borosilicate circular capillaries with outer and inner radius of 0.33 and 0.2 mm, respectively. Borosilicate capillaries are transparent to Raman signal. Furthermore, the Raman Spectrum of OH stretching vibrations can be divided into two sub-bands (Sun et al., 2010), strong- (HBs, with the peak centered around 3200 cm⁻¹) and weak-hydrogen band (HBw, with the peak centered around 3450 cm⁻¹). For each solution, the deconvolution process is made following the method of Sun et al. (2010) using the software PeakFit 4.12. After the baseline subtraction, two Gaussian sub-bands were used to fit the obtained Raman Spectrum (Fig. IV.3a). Based on the intensity (I) and full width half maximum (FWHM) of each band, the equilibrium constant is calculated as:

$$K' = \frac{\left(\frac{I}{FWHM}\right)_{HBw}}{\left(\frac{I}{FWHM}\right)_{HBs}}$$

Finally, the linear correlation between K' value and salinity of prepared solutions (Table IV.2; Fig. IV.3b) leads to a formula for the salinity estimation in fluid inclusions:

$$\text{Cl}^- \text{ Molarity (M)} = -0.6843*(K')^2 + 5.6135*K' - 6.3693.$$

Fluid inclusions were analyzed with the same conditions as for the standards. To avoid biases due to the effect of host mineral birefringence (Caumon et al., 2015), circular polarization was applied to the beam. Also, the salinity of 22 fluid inclusions with wide range given by Raman Spectroscopy were measured as well by microthermometric measurements using a Linkam THMSG600 heating-cooling stage (Fig. IV.3c), and the salinity was estimated using the last ice-melting temperature (Bodnar, 1993).

IV.3. Analytical methods

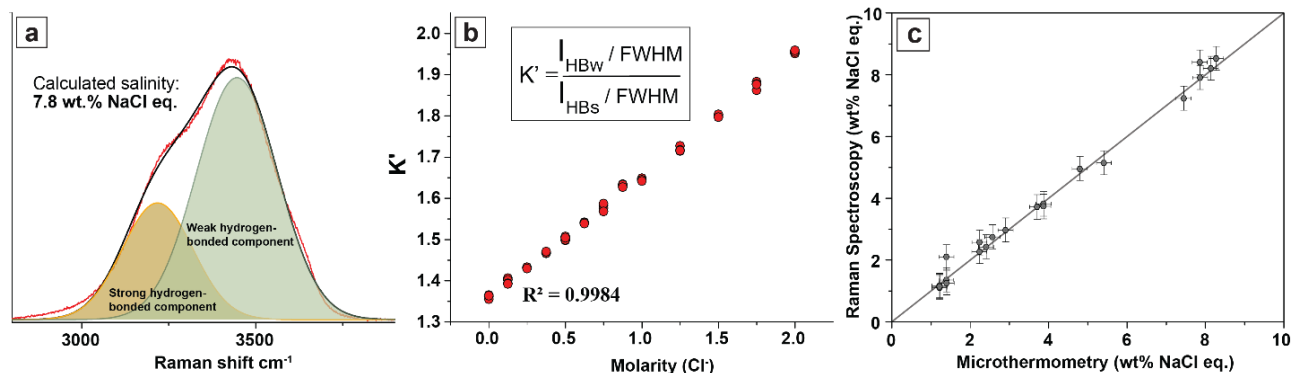


Figure IV.3. (a) Example of a H₂O Raman spectrum from fluid inclusion, decomposed into two Gaussian bands. (b) Calculated K' value from the standard solutions with known Cl⁻ molarity. (c) Salinity of 22 fluid inclusions estimated by Raman spectroscopy and microthermometry, showing the good agreement between the two independent measurements.

Table IV.2. The list of prepared standard solutions used for the calibration, the parameters of two Gaussian bands of OH stretching bands and derived K' value.

Solutions	Cl ⁻ molarity	Band 1				Band 2				K' value
		Intensity	Center	FWHM	Area	Intensity	Center	FWHM	Area	
0 M1	0.000	23137.4	3208.6	231.8	5708000	39610.0	3434.7	295.1	12443000	1.344
0 M2	0.000	23006.3	3209.1	231.8	5676900	39391.2	3434.6	295.1	12374000	1.345
0.125 M1	0.125	29400.4	3211.3	234.3	7333300	51986.9	3438.1	289.8	16039000	1.430
0.125 M2	0.125	29105.6	3211.0	234.2	7255200	51742.2	3437.9	290.1	15977000	1.435
0.25 M1	0.250	46874.2	3212.0	231.3	11540000	89008.1	3439.0	286.0	27093000	1.536
0.25 M2	0.250	46208.4	3211.7	230.4	11331000	88152.8	3438.8	286.0	26836000	1.537
0.375 M1	0.375	25792.6	3213.1	231.3	6349600	49605.3	3440.6	283.0	14945000	1.571
0.375 M2	0.375	25915.9	3214.1	232.8	6421100	49476.2	3441.2	281.9	14849000	1.576
0.5 M1	0.500	45019.9	3214.1	226.9	10874000	92965.2	3441.5	278.4	27546000	1.683
0.5 M2	0.500	45566.2	3214.4	227.4	11029000	93885.9	3441.6	278.0	27784000	1.685
0.75 M1	0.750	25350.3	3217.4	228.0	6153200	54404.0	3444.2	272.0	15749000	1.799
0.75 M2	0.750	25296.1	3217.4	228.8	6160200	54363.6	3444.3	272.2	15751000	1.806
1 M1	1.000	42210.5	3218.2	220.8	9919400	101020.0	3444.8	265.7	28575000	1.988
1.5 M1	1.500	21079.2	3222.3	214.6	4814700	57718.7	3447.5	256.1	15735000	2.294
1.5 M2	1.500	21169.4	3222.1	215.0	4845400	58077.1	3447.3	256.4	15849000	2.301
2 M1	2.000	33197.8	3224.6	196.9	6957800	116230.0	3448.1	243.8	30163000	2.828
2 M2	2.000	33030.0	3225.0	196.3	6900000	116860.0	3448.2	243.1	30239000	2.856

IV.3.6. Decrepitation of fluid inclusions

Qualitative chemical analysis of major cations and anions in individual fluid inclusions was carried out from evaporate mounds after decrepitating fluid inclusions, following the method by Kontak (2004). Double-polished quartz sections were rapidly heated by THMS-600 Linkam stage to 500-600°C and quenched for 5-15 minutes, until decrepitation was observed. The system was then rapidly cooled down to room temperature. The chemical maps of evaporate mounds were acquired by SEM-EDS at the voltage of 15 kV and a dwell time of 25 ms. In addition, the chemical composition of individual evaporate crystals was detected by a Cameca SX Five electron microprobe equipped with five wavelength-dispersive spectrometers (WDS), housed at ISTO-BRGM Orléans, at the conditions of 15 kV voltage, 10 nA beam current and 1 µm spot size. Up to 10 points were analyzed in each mound. Results were recalculated by removing SiO₂ as it is recognized as from the host quartz, and then normalized to 100%.

IV.4. Results

IV.4.1. Raman Spectroscopy of carbonaceous material

Peak-metamorphic temperatures obtained by RSCM are reported in Table IV.1.

A temperature for the sample HN65 from the Hyuga Tectonic Mélange a temperature is $228 \pm 16^\circ\text{C}$, whereas samples from the Foliated Morotsuka experienced peak-temperatures of $339 \pm 26^\circ\text{C}$. Results acquired during this study for samples from the Shimanto belt are consistent with previously reported RSCM results (Palazzin et al., 2016; Raimbourg, Famin, et al., 2017; Raimbourg et al., 2018).

Hereby, in what follows the Kodiak Landward Belt (KLB) and the Hyuga Tectonic Mélange (HTM) are grouped as lower-grade units, whereas the Kodiak Central Belt and the Foliated Morotsuka represent higher-grade units.

IV.4.2. Microstructures and mineral petrography

IV.4.2.1. Lower-grade units

In Kodiak and the Shimanto belt, lower-grade metapelites (230-260°C) show three different compositional and microstructural domains: pelitic matrix, quartz ribbons, and extension veins. Due to similarities in mineral compositions as well as present microstructures, samples from HTM and KLB are described together.

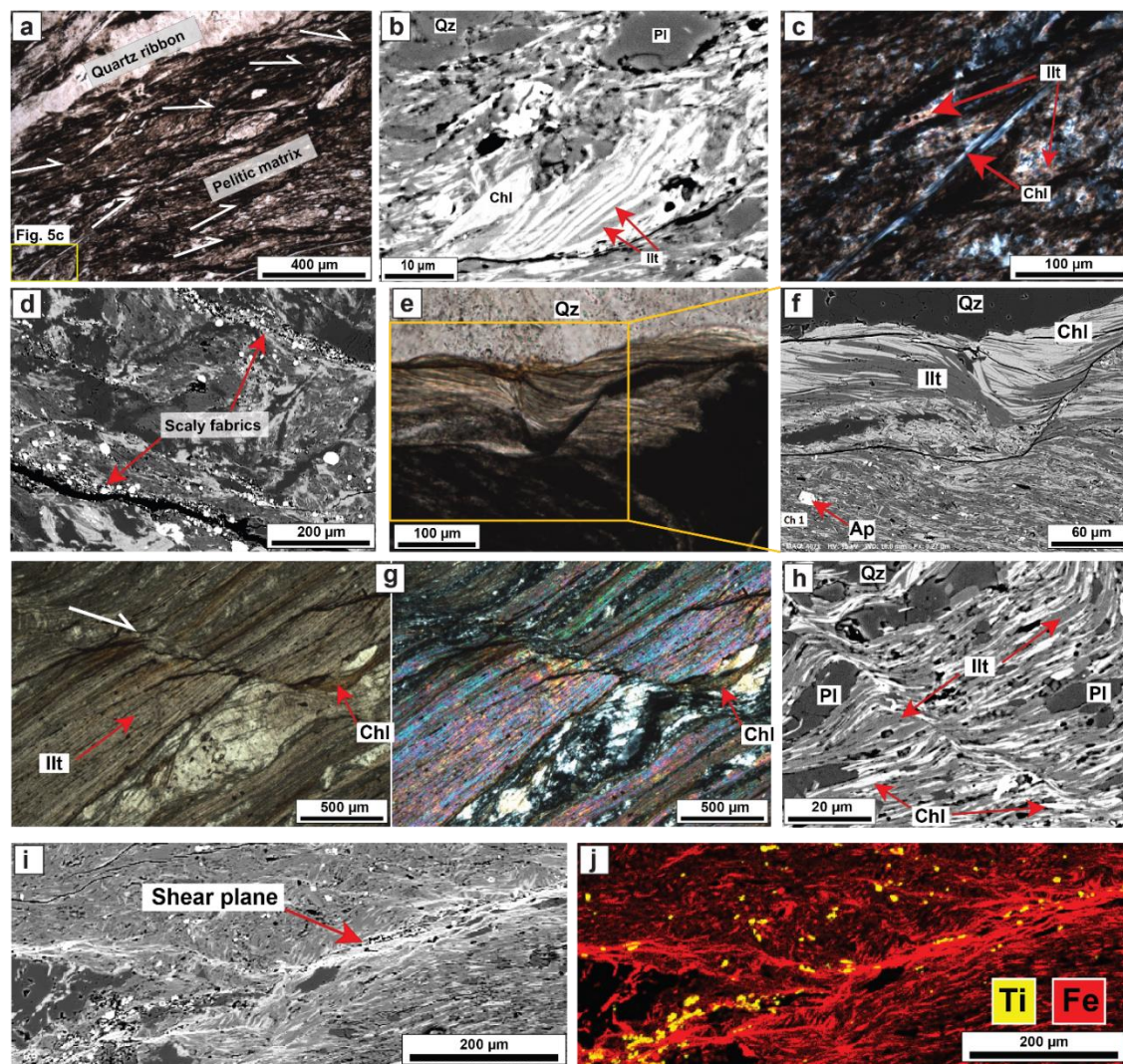


Figure IV.4. Main microstructures and mineral phases in lower- and higher-grade samples of the Kodiak accretionary complex and the Shimanto belt: (a) Photomicrograph of intercalated quartz ribbons and pelitic matrix rich in fine-grained phyllosilicates, plagioclase and quartz (Sample HN299C, Shimanto). (b) SEM-BSE image showing intertwined illite and chlorite (sample KO17E, Kodiak). (c) Photomicrograph (cross-polarized view) of chlorite shear band at low angle to the main foliation (Sample HN299A, Shimanto). (d) SEM-BSE image of a pelitic matrix with scaly fabrics enriched in Ti-oxides and sulfides (Sample HN299A, Shimanto). (e) Photomicrograph and (f) SEM-BSE image of the contact between a shear vein and the surrounding matrix. Note the rim of crystal size increase in the

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matrix in immediate contact with the vein compared to the host rock further away (sample KO38, Kodiak). (g) Optical photomicrograph (left: plain-polarized view; right: cross-polarized view) of illite+chlorite layers separated by scaly fabrics (Sample HN285, Shimanto). (h) BSE image of strongly foliated metapelite with the alignment of plagioclase and quartz parallel to the foliation (Sample HN247, Shimanto). (i) SEM-BSE image and (j) A mask image of EDS Ti and Fe maps of a shear zone enriched in titanium and iron (Sample HN145, Shimanto). Abbreviations: Qz – quartz; Pl – plagioclase; Chl – chlorite; Ill – illite; Ap – apatite.

Phyllosilicates are the most abundant phases in the matrix, with clusters of fine-grained illite (illite hereby refers to minute dioctahedral aluminous phyllosilicates with composition globally on the muscovite-pyrophyllite binary; Dubacq et al., 2010) and chlorite (Fig. IV.4b-c). The chlorite grain size varies between 2.5-60 μm (Fig. IV.4b), and increases up to 100 μm when in contact with quartz ribbons. Illite grain size is in the range 1-24 μm (Fig. IV.4b) in the matrix, whereas aggregates of illite up to 120 μm are present close to quartz ribbons. Detrital plagioclase and quartz are present in the matrix, as well as accessory phases such as framboidal pyrite, calcite, apatite and Ti-oxides. (Fig. IV.4b). The foliation (S_1) in the pelitic matrix is defined by compositional layering, including fine-grained layers enriched in phyllosilicates, Ti-oxides and sulfides (Figures IV.4a, IV.4d). The pelitic matrix also contains scaly fabrics (Ramirez et al., 2021; Vannucchi, 2019), enriched in sulfides, Ti- and Fe-oxides (Fig. IV.4d). Occasionally, thin shear bands are cutting across the main foliation at low angle, composed principally of elongated individual crystals of chlorite (Fig. IV.4c) and to a lesser extent illite and/or quartz grains. Such shear bands define a network of shear band, with non-coaxial shearing (Fig. IV.4a).

Extensional veins, commonly oriented perpendicular to the foliation, are made of blocky quartz and to a lesser extent calcite (Fig. IV.5a). Quartz crystals in lower-grade veins occasionally display growth rims, with crystal facets oriented towards the center of the vein. Occasionally quartz crystals are elongated parallel to the foliation (Fig. IV.5b). Bulging, as a mechanism of dynamic recrystallization, is observed sparsely. Calcite display characteristic undeformed twinning (Type I according to Ferrill et al., 2004).

Ribbons containing quartz $\pm$ calcite $\pm$ tiny flakes of chlorite, elongated parallel to the main foliation, are present within the pelitic matrix (Fig. IV.4a). Calcite, when present, occurs as late fill of the vein and is mildly altered. Quartz crystals in ribbons are characterized by incipient recrystallisation, with bulging grain boundaries.

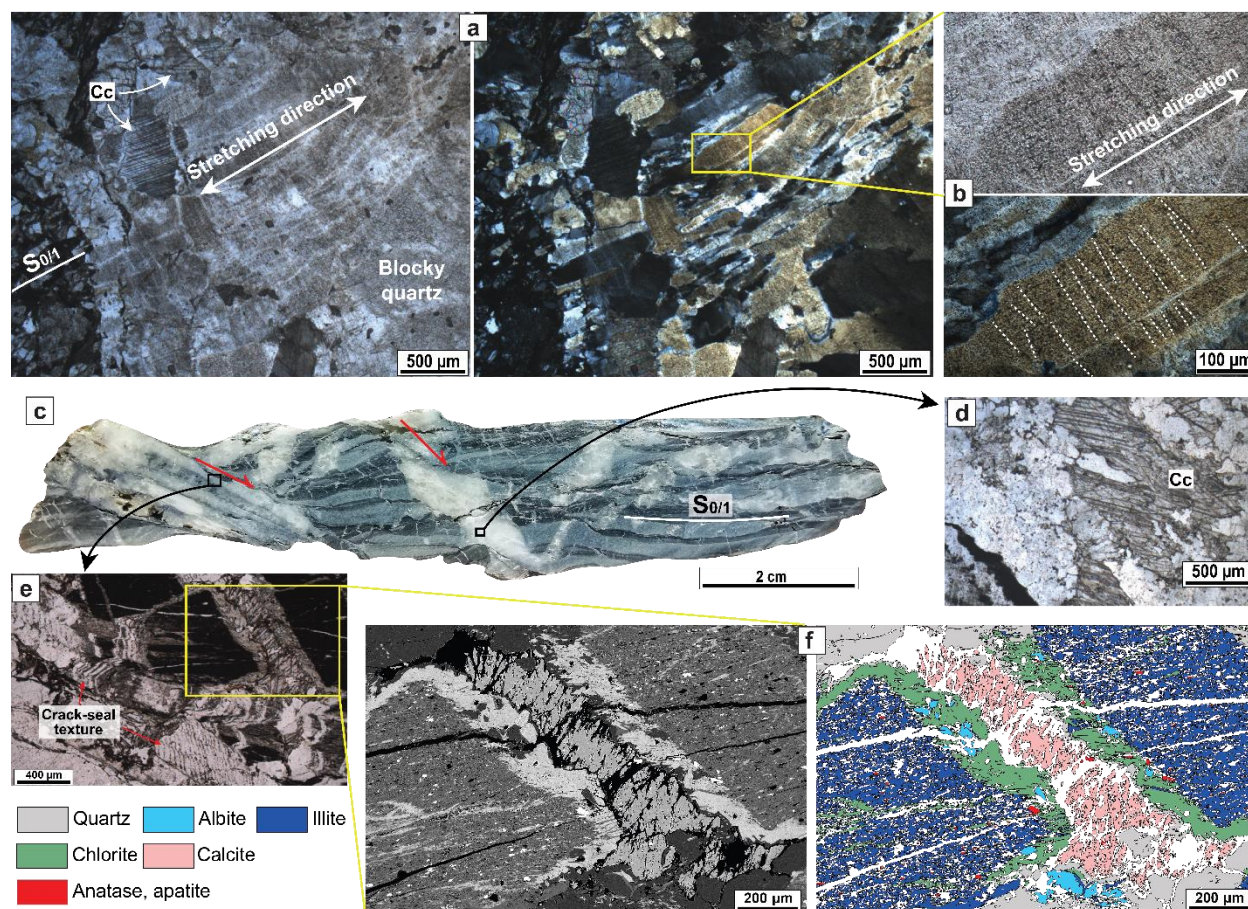


Figure IV.5. Characteristic vein textures in lower- and higher-grade samples: (a) A Mode-1 quartz-calcite vein with blocky and elongated quartz. (b) Elongated quartz with trails of pseudo-secondary fluid inclusions perpendicular to the stretching direction. (c) A sample slab with two extensional shear veins (Sample KO33C, Kodiak). (d) Deformed calcite in shear vein. (e) A part of shear vein characterized by crack-seal texture. (f) SEM-BSE image (left) and mask image (right) of an extensional vein connected to a shear vein from (c), showing chlorite rim along the contact vein and matrix. Note albite crystals in the vein and its absence in the matrix.

IV.4.2.2. Higher-grade units

In higher-grade samples, KCB and FM (Table IV.1; 320-350°C), the main mineral phases forming the matrix are illite, chlorite, quartz and plagioclase. The foliation (S_1) is penetrative and underlined by phyllosilicates (Fig. IV.5-b), and it is locally disturbed by 5-20 μm thick shear bands containing illite, chlorite, Ti-oxides, and sulfides. Whenever present, plagioclase and quartz crystals are flattened and elongated parallel to the foliation (Fig. IV.4h). A secondary crenulation

IV.4. Results

cleavage (S_2) is present only in the vicinity of shear bands. The average grain size in the pelitic matrix of higher-grade samples is larger than in lower-grade samples. In the KCB for instance,

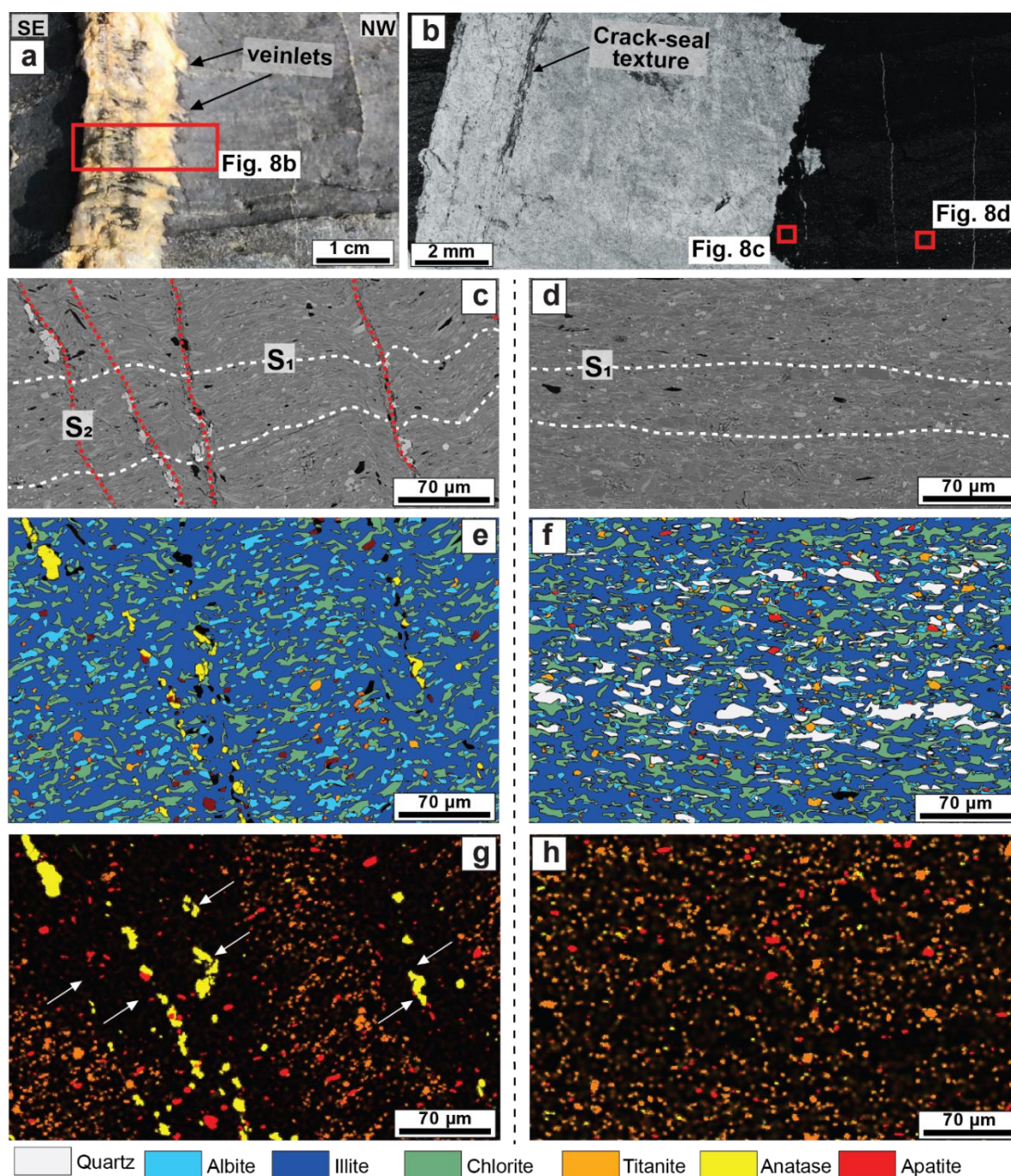


Figure IV.6. (a) A field photo of an example of quartz vein with veinlets only on the northwestern side (Site KO30, Kodiak). (b) Scan of the thin section from the vein of Fig. a. (c) SEM-BSE image of the host rock closer to the vein characterized by the presence of a foliation (S_1) and a crenulation cleavage (S_2), whereas away from the vein (d) only the foliation (S_1) is presented. (e-f) Mask images of (c-d). Note that away from the vein quartz is still present in the host rock, whereas closer to the vein it is completely absent. (g-h) Mask images of Ti- and Ca- bearing phases: titanite,

IV.4. Results

anatase and apatite. In zones showing crenulation cleavage, titanite is partly dissolved and anatase precipitates as indicated by white arrows, whereas titanite is still present in the host rock away from the vein.

chlorite crystals are in the range 5-400 μm in general and up to 775 μm in length when in contact with shear bands, whereas illite crystals reach 1-80 μm in the matrix and up to 320 μm closer to shear bands (Fig. IV.4e-f). In FM, illite and chlorite in the matrix are characterized by significantly bigger grain size than in KCB, ranging between 30-500 μm and 50-700 μm , respectively (Fig. IV.4f). Accessory phases in the matrix are apatite, pyrite, calcite, anatase and titanite. Sulfides are locally oxidized into goethite, with preserved pyrite crystal shapes. Scaly fabrics are enriched in micrometric anatase, apatite and locally in Fe-oxides (Fig. IV.4i-j), and occasionally act as shear planes that displace main foliation and quartz ribbons.

In higher-grade units, quartz ribbons are boudinaged and occasionally folded. The neck of boudins is composed of illite, chlorite and elongated quartz crystals. Shear veins and mode 1 quartz veins cutting across the foliation are dominantly made of quartz and display crack-seal microstructure (Fig. IV.5c). Bulging is recognized as a dominant mechanism of dynamic recrystallization in quartz from higher-grade veins. In KCB, to a lesser extent subgrain rotation is observed as well, whereas in FM a subgrain rotation is more prominent. In addition to quartz, veins contain to a lesser extent calcite, chlorite, and albite (Fig. IV.5e-f). Deformed calcite is characterized by curved and lensoid twins (Type III according to Ferrill et al., 2004). In few studied veins, clusters of vermicular chlorites are sparsely distributed, as well as euhedral albite crystals.

Locally, mineralogical variations are observed in correspondence with the microstructures. In the matrix in the contact with some shear bands, quartz and plagioclase grains are almost completely absent (Fig. IV.4c-d). Fig. IV.5f shows the host rock with few micrometric albite crystals, whereas larger crystals (up to 0.2 mm) are found in the shear band. Similar features were observed in the veins from the Kodiak Central Belt, with veinlets apparently located on one side of the main vein (Fig. IV.6a). On the side with veinlets, the crenulation cleavage (S_2) is found close to the contact (Fig. IV.6c), and disappears further from the shear band (Fig. IV.6d). The amount of quartz decreases towards the vein, and quartz is absent from the zone with crenulation cleavage (Figures IV.4e, IV.5e). Anatase also appears as formed synchronously with crenulation cleavage (Fig. IV.6g), it is concentrated in crenulation cleavage planes with apatite, whereas in zones with only main foliation present titanite is found instead (Fig. IV.6h).

IV.4.3. Whole-rock chemistry

Whole-rock major element compositions are presented in Table IV.3. In samples from the Kodiak complex, determined major elements and LOI are in the range of: SiO_2 - 54.76% to 69.90%; TiO_2 - 0.60% to 1.00%; Al_2O_3 - 12.22% to 20.27%; Fe_2O_3 - 6.87% to 8.82%; MgO - 1.94% to 3.29%; CaO - 0.33% to 1.28%; Na_2O - 0.97% to 2.77%; K_2O - 1.48% to 3.61%; SO_3 - 0.02% to 0.37%; and LOI - 3.16% to 5.23%. Major elements and LOI in samples from the Shimanto belt are in the range of: SiO_2 - 61.72% to 75.83%; TiO_2 - 0.34% to 0.70%; Al_2O_3 - 10.30% to 18.15%; Fe_2O_3 - 5.41% to 7.34%; MgO - 1.49% to 2.44%; CaO - 0.06% to 0.88%; Na_2O - 1.11% to 3.33%; K_2O - 1.44% to 3.29%; SO_3 - 0.01% to 1.89%; and LOI - 2.61% to 5.08%.

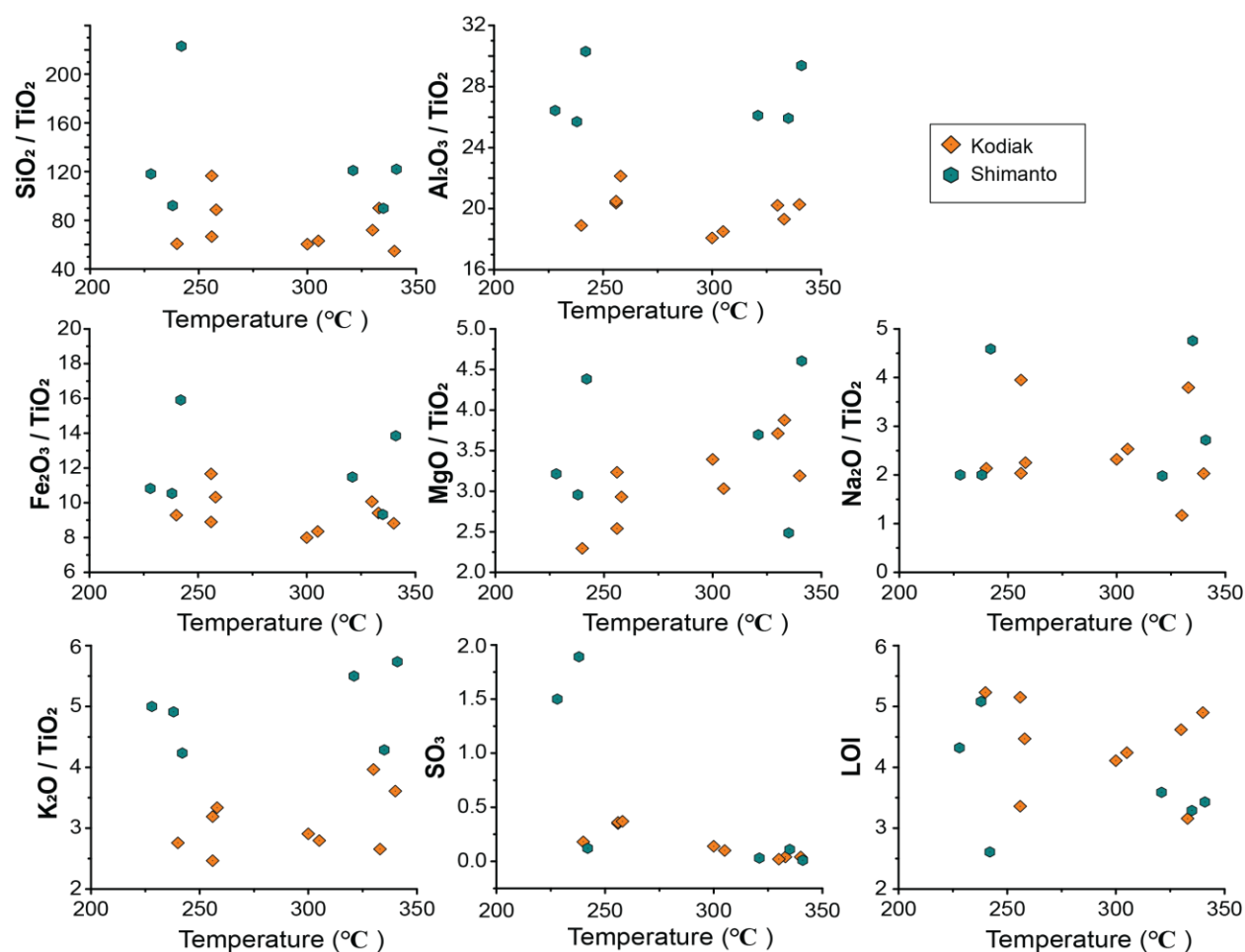


Figure IV.7. Major and minor element results analyzed by X-ray fluorescence normalized by TiO_2 versus peak-metamorphic temperature. SO_3 and LOI in are plotted without normalization.

No clear trend is apparent for the elements as a function of temperature, except for weak positive correlation of K_2O , MgO and Fe_2O_3 , and strong negative correlation for SO_3 . The normalization

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of oxides to TiO₂ (assumed as an immobile element) as a function of temperature of metamorphism, revealed no clear trends as well (Fig. IV.7).

Table IV.3. Major element compositions of metapelites expressed in wt.% from the Kodiak accretionary complex and the Shimanto belt of Japan.

	Kodiak Landward Belt				Central Belt			Seaward Belt		Hyuga Tectonic mélange			Foliated Morotsuka		
Sample	KO17B	KO17C	KO17D	KO17E	KO33A	KO36A	KO38	KO11C	KO43C	HN64	HN85	HN299	NOB_23B	HN145	HN243
SiO ₂	69.9	59.23	62.98	57.67	65.7	59.69	54.76	58.53	59.32	61.72	75.83	66.14	64.65	67.69	62.89
TiO ₂	0.6	0.89	0.71	0.95	0.73	0.83	1	0.97	0.94	0.67	0.34	0.56	0.53	0.56	0.7
Al ₂ O ₃	12.22	18.24	15.72	17.95	14.1	16.78	20.27	17.54	17.4	17.22	10.3	14.8	15.57	14.62	18.15
Cr ₂ O ₃	0.04	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.01	0.01	0.02	0.02	0.02	0.01
Fe ₂ O ₃	7	7.92	7.33	8.82	6.87	8.36	8.82	7.76	7.85	7.06	5.41	6.06	7.34	6.43	6.53
MnO	0.04	0.08	0.1	0.12	0.09	0.11	0.11	0.1	0.13	0.07	0.15	0.07	0.35	0.08	0.13
MgO	1.94	2.26	2.08	2.18	2.83	3.08	3.19	3.29	2.85	1.98	1.49	1.8	2.44	2.07	1.74
CaO	0.33	0.79	0.88	1.2	1	0.96	0.99	1.28	1.18	0.74	0.62	0.88	0.86	0.06	0.07
Na ₂ O	2.37	1.81	1.6	2.03	2.77	0.97	2.03	2.25	2.38	1.34	1.56	1.12	1.44	1.11	3.33
K ₂ O	1.48	2.84	2.37	2.62	1.94	3.29	3.61	2.82	2.63	3.29	1.44	2.8	3.04	3.08	3
P ₂ O ₅	0.16	0.26	0.22	0.28	0.22	0.25	0.27	0.44	0.36	0.1	0.08	0.09	0.09	0.07	0.11
SO ₃	0.35	0.36	0.37	0.18	0.04	0.02	0.04	0.14	0.1	1.89	0.12	1.5	0.01	0.03	0.11
SrO	0.02	0.02	0.02	0.02	0.03	0.02	0.01	0.02	0.03	0.02	0.01	0.02	0.02	0.01	0.01
BaO	0.05	0.11	0.08	0.1	0.12	0.14	0.15	0.11	0.12	0.07	0.03	0.06	0.05	0.06	0.06
LOI	3.36	5.15	4.47	5.23	3.16	4.62	4.9	4.11	4.24	5.08	2.61	4.32	3.43	3.59	3.29
Total	99.96	100.1	99.05	99.53	99.72	99.24	100.3	99.51	99.7	101.35	100.05	100.35	99.97	99.59	100.2

IV.4.4. X-Ray diffraction and phase quantification

X-Ray diffraction on bulk rocks confirmed the major phases observed using optical and electronic microscopy (Table IV.4; Fig. IV.8): illite, quartz, plagioclase and chlorite, and provided evidence of smectite-illite mixed layers in lower-grade samples and in higher-grade 18NOB23B sample. Accessory phases are calcite and pyrite, and serpentine in three lower-grade samples and in one higher-grade sample (Sample HN243). Magnesite, siderite and kaolinite are detected in individual samples (Table IV.4).

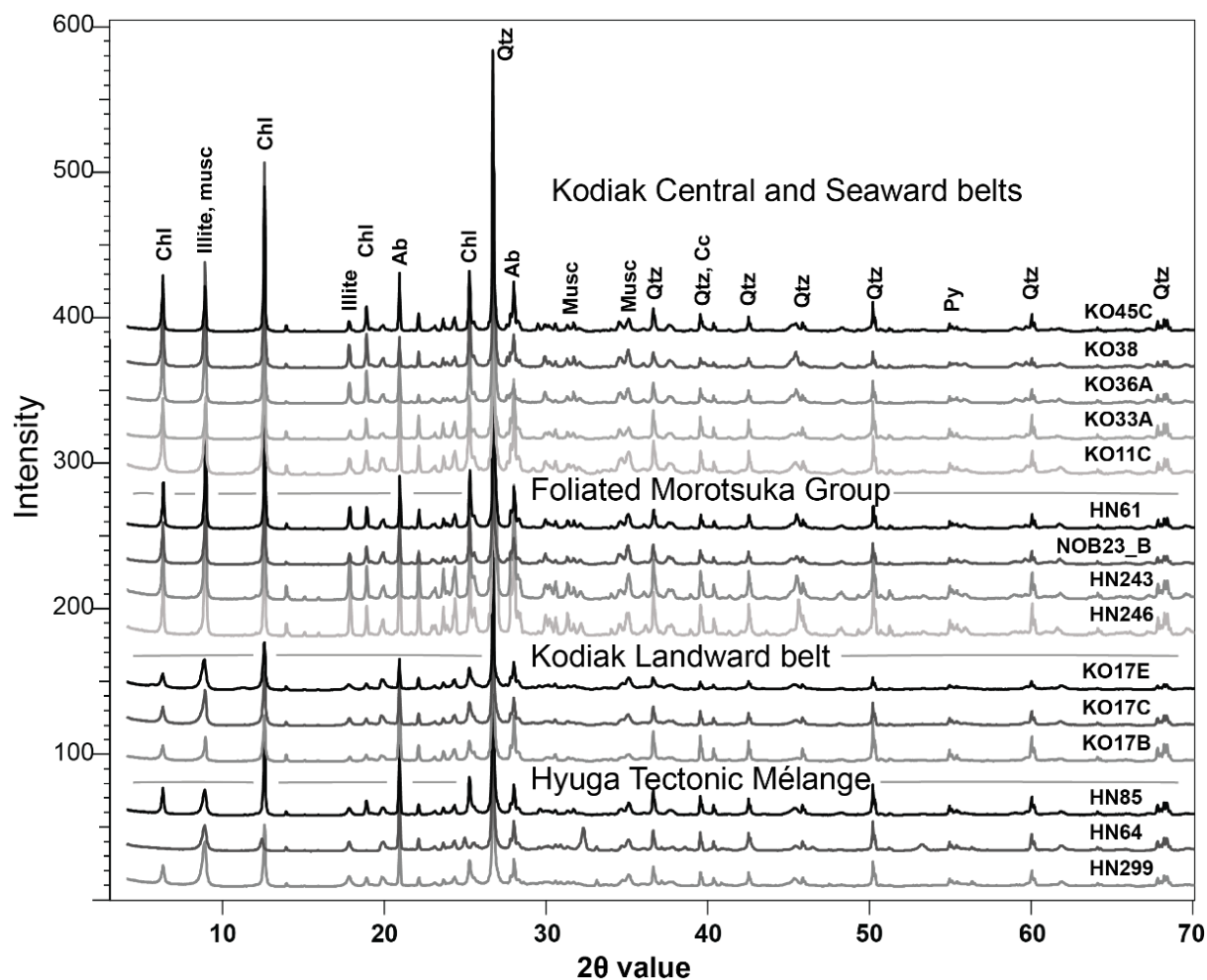


Figure IV.8. X-ray diffraction patterns of samples from the Kodiak Formation (Alaska), the Foliated Morotsuka, and the Hyuga Tectonic Mélange (Japan).

Quantitative phase proportions (Table IV.4) based on the method of Rietveld (1969) revealed that the main rock-forming mineral phases of lower temperature samples (230-260°C) are illite-mica (23-48 %), quartz (17-43 %), plagioclase (10-20 %), chlorite (0-14 %) and smectite-illite mixed layers (0-8 %). Minor phases include serpentine (detected in three samples, 1.6-3.4 %) and kaolinite (only in one sample - HN64, 4%). Higher temperature samples (~320-350°C) show similar proportions of main phases: illite/mica (21-42 %), quartz (16-34 %), plagioclase (5-25 %) and chlorite (15-24 %). The amount of smectite-illite mixed layers in the sample 18NOB23B is estimated as 1.5 % and 1.8 % of serpentine was estimated in the sample HN243.

IV.4. Results

Table IV.4. Mineral phase proportions based on X-Ray Diffraction patterns using the Rietveld method (Rietveld, 1969). I/S stands for smectite-illite mixed layers.

Formation	Landward Belt			Central Belt			Seaward Belt		HTM			Foliated Morotsuka			
Sample	KO17B	KO17C	KO17E	KO33A	KO36A	KO38	KO45C	KO11C	HN299	HN64	HN85	23B	61	HN243	HN246
Major phases															
Illite/muscovite	23.2	42.1	47.6	21	40.7	42.4	25.5	36.5	42.4	39.3	36.4	38.6	38.1	31.1	31.2
Chlorite	8.0	11.5	12.7	16.2	23.7	24.1	19.2	19.1	10.2	0.0	13.9	21.6	15.4	10.2	8.1
I/S	1.8	2.6	4.0	0.0	0.0	0.0	0.0	0.0	4.5	2.3	1.4	0.9	0.0	0.0	0.0
Quartz	43.1	27	17.3	34.2	25.7	15.8	29.4	22.7	27.7	32.9	35.1	23.9	25.2	30	30.0
Plagioclase	19.5	13.1	16.2	25.2	5.2	16.0	22.2	17.7	10.1	13.3	12.6	11.5	20.2	26.3	26
K feldspar	0.0	0.0	0.0	3.3	4.7	1.7	2.4	3.8	0.0	0.0	0.0	2.4	0.0	2.3	2.2
Phyllosilicates	33	56.2	64.3	37.2	64.4	66.5	44.7	55.6	57.1	41.6	51.7	61.1	53.5	41.3	39.3
Chl / (Chl+mus)	24.2	20.5	19.8	43.5	36.8	36.2	43.0	34.4	17.9	0.0	26.9	35.4	28.8	24.7	20.6
I/S / phs	5.5	4.6	6.2	0.0	0.0	0.0	0.0	0.0	7.9	5.5	2.7	1.5	0.0	0.0	0.0
Accessory phases															
Calcite	0.9		0.6				1.2		0.5	<0.5	< 0.5	0.9			
Magnesite													0.8		
Serpentine	3.4	2.8							1.6					1.8	
Pyrite	< 0.5	0.9	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.5	0.9	< 0.5			< 0.5	< 0.5
Dolomite									1.1	1					
Siderite										6.1					
Kaolinite										4					

IV.4.5. Mineral chemistry

Representative analyses of each major mineral phase are listed in Table IV.5. and all acquired point analyses are in Supplementary Table S4.1. In all lower- and higher-grade samples plagioclase is pure albite ($X_{Ab} > 0.98$), with only traces of K and Ca. In contrast, K-bearing phyllosilicates and chlorites show compositional variations correlated with peak-metamorphic temperatures.

IV.4.5.1. K-bearing phyllosilicates

More than 20 crystals of mica were analyzed in the matrix of each sample. Calculation of structural formulae based on 11 oxygen atoms shows that analyses correspond to dioctahedral mica, in agreement with XRD data. The layer charge is heterogeneous, ranging between 0.45 and 0.95 in lower-grade samples, and between 0.77 and 0.95 in higher-grade samples (Fig. IV.9a). The values lower than 1.0 indicates that illite-smectite mixed layers are probably involved.

In lower-grade samples (from KLB and HTM units), K is the major alkali (KLB: 0.43-0.81 apfu; HTM: 0.43-0.88 apfu), with secondary Na (KLB: 0.02-0.38 apfu; HTM: 0.01-0.32 apfu; Fig.

IV.9a). Mica crystals contain 0.27 vacancies pfu in average for KLB (0.09-0.44 pfu) and 0.26 pfu for HTM (0.05-0.55 pfu). Higher-grade samples (from KCB and FM units) show homogenous composition between different samples (Fig. IV.9e). The proportion of K increases in comparison with lower-grade samples (KCB: 0.74-0.89 apfu; FM: 0.74-0.96 apfu), whereas the amount of Na decreases (KCB: 0.01-0.04 apfu; FM: 0.01-0.06 apfu). Remaining interlayer vacancies are estimated around 0.09-0.22 apfu for the KCB and 0.1-0.24 apfu in the case of FM (Fig. IV.9a).

Octahedral position is dominantly occupied by Al, without correlation with the temperature increase (lower-grade: KLB av. 1.79 apfu, range 1.55-1.92; HTM av. 1.82 apfu, range 1.62-1.92; higher-grade: KCB av. 1.77 apfu, range 1.64-1.82; FM av. 1.73 apfu, range 1.54-1.81). Remaining position is occupied by Fe and Mg. In KLB, Fe is more abundant than Mg (av. FeO 2.25 wt.% and av. MgO 1.6 wt.%), whereas in HTM the proportion of Fe and Mg are similar (av. FeO 1.4 wt.% and av. MgO 1.45 wt.%). There is similar amount of Fe and Mg in higher-grade samples (KCB: av. FeO 1.71 wt.% and av. MgO 1.73 wt.%; FM: av. FeO 2.2 wt.% and av. MgO 1.9 wt.%).

In tetrahedral site, there is no systematic changes in Al-Si substitution with the temperature increase. The average SiO₂ in lower-grade samples is 49.62 wt.% (3.13-3.65 apfu) and 49.74 wt.%

IV.4. Results

Table IV.5. Representative electron microprobe data for illite (Ilt) and chlorite (Chl) in metasedimentary units from the Kodiak accretionary complex (Alaska) and the Shimanto belt (Japan). The symbol □ represents remaining vacancies.

Spot	KO17A-										KO38-					
	KO17A-p3	47	KO17E-p24	KO17E-p15	HN65-p19	299Ap61	299Ap41	299A33	KO33Cp18	KO33Cp11	16	KO38p10	243-p8	243-p8	285-p55	285-11
Sample	KO17A		KO17E		HN65		HN299A		KO33C		KO38		243		285	
Unit	Kodiak Landward Belt				Hyuga Tectonic Mélange				Kodiak Central Belt				Foliated Morotsuka			
Phase	Ilt	Chl	Ilt	Chl	Ilt	Chl	Ilt	Chl	Ilt	Chl	Ilt	Chl	Ilt	Chl	Ilt	Chl
SiO ₂	51.61	26.59	48.01	26.39	50.60	25.28	50.27	25.51	50.02	25.22	49.41	24.23	48.31	23.80	47.17	24.59
TiO ₂	0.02	0.00	0.08	0.05	0.06	0.16	0.06	0.01	0.10	0.00	0.17	0.10	0.00	0.05	0.10	0.03
Al ₂ O ₃	31.01	20.83	31.26	21.58	31.92	20.94	30.93	20.23	32.10	21.49	30.71	21.32	31.44	21.68	29.82	20.45
FeO	3.19	29.09	2.52	30.87	1.17	28.29	1.38	28.70	1.49	29.26	1.76	30.39	1.45	31.69	1.52	27.87
MnO	0.05	0.17	0.00	0.08	0.00	0.09	0.00	0.00	0.01	0.54	0.01	0.30	0.09	1.00	0.12	1.13
MgO	1.89	10.10	1.66	8.87	1.42	10.79	1.41	10.67	1.52	11.39	1.87	10.47	1.54	9.74	1.95	10.65
CaO	0.14	0.10	0.10	0.05	0.04	0.00	0.05	0.05	0.00	0.00	0.01	0.05	0.00	0.04	0.00	0.03
Na ₂ O	1.19	0.00	0.61	0.06	0.39	0.01	0.54	0.01	0.33	0.00	0.17	0.00	0.17	0.01	0.14	0.02
K ₂ O	7.42	0.15	7.25	0.05	6.98	0.06	8.73	0.04	9.75	0.02	10.03	0.03	10.79	0.05	10.74	0.03
Total	96.53	87.04	91.48	87.99	92.59	85.61	93.36	85.22	95.32	87.91	94.15	86.89	93.79	88.07	91.54	84.79
Normalized major elements data (on basis of 11 oxygens for illite and 14 for chlorite)																
Si ^{IV}	3.35	2.87	3.27	2.84	3.36	2.77	3.36	2.82	3.31	2.71	3.29	2.66	3.26	2.60	3.27	2.74
Al ^{IV}	0.65	1.13	0.72	1.16	0.64	1.22	0.64	1.18	0.68	1.29	0.70	1.33	0.74	1.39	0.72	1.26
Al ^{VI}	1.72	1.52	1.79	1.57	1.86	1.49	1.79	1.45	1.74	1.43	1.79	1.42	1.77	1.40	1.72	1.43
Mg	0.18	1.63	0.17	1.42	0.14	1.76	0.14	1.76	0.19	1.82	0.15	1.71	0.15	1.59	0.20	1.77
Fe ²⁺	0.17	2.63	0.14	2.78	0.07	2.59	0.08	2.65	0.10	2.63	0.08	2.79	0.08	2.90	0.09	2.60
Mn	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.05	0.00	0.03	0.01	0.09	0.01	0.11
Ti	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Sum octa	2.08	5.78	2.10	5.78	2.07	5.86	2.01	5.86	2.03	5.93	2.02	5.95	2.01	5.98	2.02	5.91
Ca	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.15	0.00	0.08	0.01	0.05	0.00	0.07	0.00	0.02	0.00	0.04	0.00	0.02	0.00	0.02	0.00
K	0.61	0.02	0.63	0.01	0.59	0.01	0.74	0.01	0.86	0.00	0.82	0.00	0.93	0.01	0.95	0.00
Alkalis	0.77	0.03	0.72	0.03	0.64	0.01	0.82	0.01	0.88	0.00	0.86	0.01	0.95	0.01	0.97	0.01
□	0.23	0.18	0.28	0.20	0.36	0.13	0.18	0.13	0.12	0.07	0.14	0.05	0.05	0.02	0.03	0.09

IV.4. Results

(3.11-3.67 apfu) for KLB and HTM, respectively, whereas SiO₂ in higher-grade samples shows narrower concentration variations - 49.32 wt.% in average (3.24-3.37 apfu) for the KCB and 47.57 wt.% in average (3.10-3.37 apfu) for the FM. The remaining position in tetrahedral sites is occupied by Al.

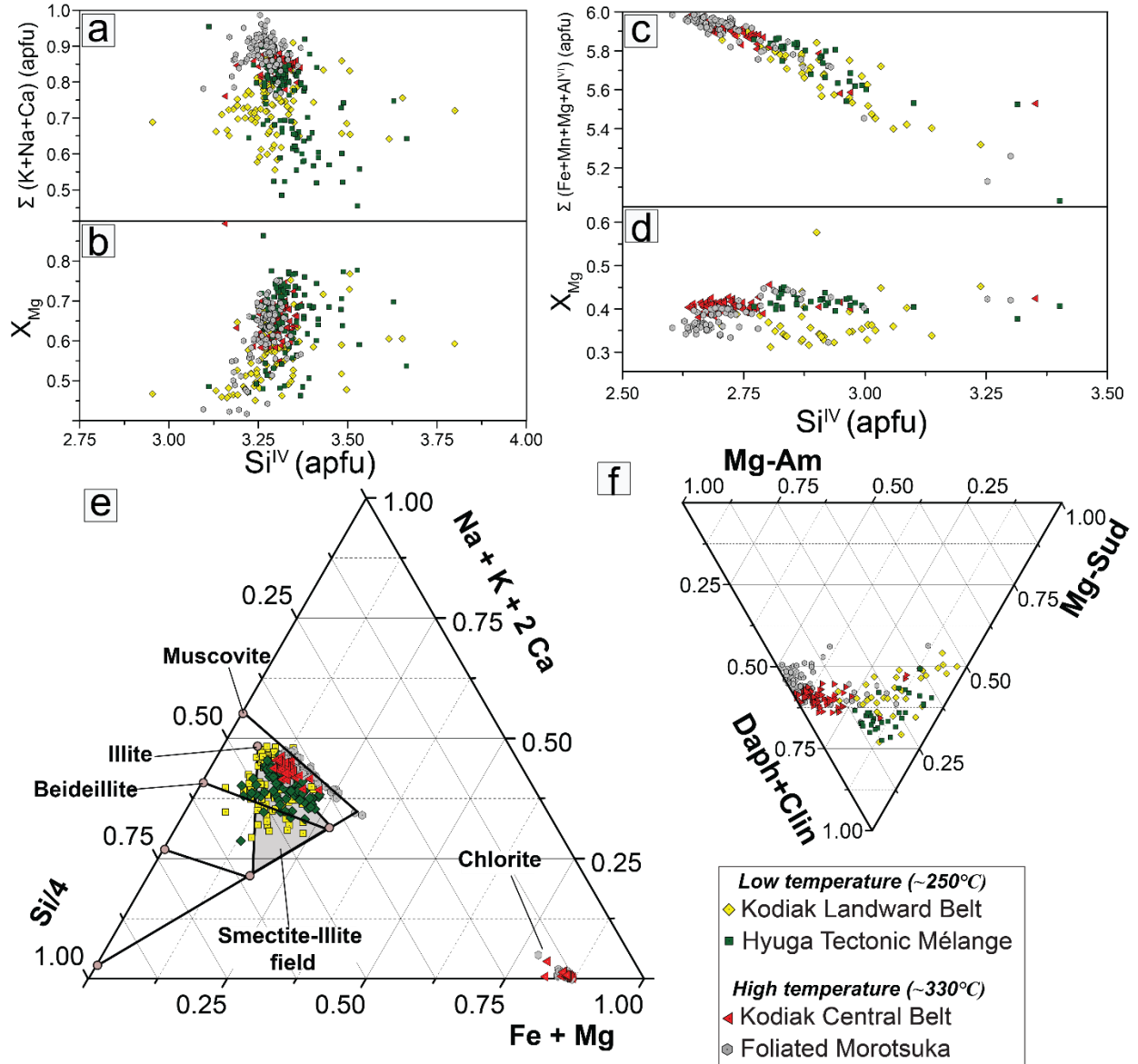


Figure IV.9. Chemical composition of illite and chlorite: Si^{IV} (apfu) in illite versus (a) total alkali (apfu) and (b) magnesium number (X_{Mg}). Si apfu in chlorite versus (c) sum at octahedral position and (d) magnesium number ($X_{Mg} = Mg^{2+}/(Fe^{2+}+Mg^{2+})$). (e) Composition of phyllosilicates shown in ternary diagram $Si/4 - (Na+K+2Ca) - (Mg+Fe^{2+})$ according to Velde (1985). (f) Composition of chlorite in amesite (Am) – sudoite (Sud) – clinocllore+daphnite (Clin+Daph) ternary diagram.

The ranges of each component in illite-mica expressed in form of structural formula are $\square_{0.09-0.22}\text{K}_{0.74-0.91}\text{Na}_{0.01-0.04}(\text{Al}_{1.64-1.82}\text{Mg}_{0.14-0.26}\text{Fe}_{0.06-0.21})(\text{Si}_{3.19-3.37}\text{Al}_{0.63-0.81})\text{O}_{10}(\text{OH})_2$ for the Kodiak Central Belt and $\square_{0.01-0.24}\text{K}_{0.74-0.96}\text{Na}_{0.01-0.06}(\text{Al}_{1.54-1.81}\text{Mg}_{0.14-0.37}\text{Fe}_{0.06-0.42})(\text{Si}_{3.10-3.37}\text{Al}_{0.62-0.90})\text{O}_{10}(\text{OH})_2$ for the Foliated Morotsuka.

IV.4.5.2. Chlorite

The structural formulae of chlorite are calculated based on 14 oxygen atoms. Chlorite in lower-grade samples exhibits chemical variations (Supplementary Table S4.1), with X_{Mg} generally in the range 0.3-0.45 (Fig. IV.9d). Higher-grade chlorite has similar X_{Mg} to lower-grade chlorite but appears more homogenous. Vacancies are in greater proportion in lower-grade chlorite (0.23 ± 0.08 and 0.21 ± 0.06 apfu in KLB and HTM, respectively) than in higher-grade chlorite (0.09 ± 0.06 apfu and 0.08 ± 0.06 apfu for KCB and FM, respectively; Fig. IV.9c). Tetrahedral Al increases with temperature from 0.60-1.27 to 1.02-1.39.

All analyzed grains in higher-grade samples show high clinocllore ($X_{\text{clin}} 0.24 \pm 0.01$ and 0.21 ± 0.03 for the KCB and the FM, respectively), daphnite ($X_{\text{daph}} 0.35 \pm 0.01$ and 0.34 ± 0.01 for the KCB and the FM, respectively), and amesite ($X_{\text{am}} 0.34 \pm 0.06$ and 0.38 ± 0.11 for the KCB and the FM, respectively) proportions, with a low sudoite proportion ($X_{\text{sud}} 0.07 \pm 0.06$ and 0.03 ± 0.03 for the KCB and the FM, respectively; Fig. IV.9f).

IV.4.5.3. Multi-phase equilibrium model for the higher-grade units

In higher-grade samples, based on the multi-phase equilibrium model equilibrated pairs of illite and chlorite have been determined (Fig. IV.10a). Fig. IV.10b shows the pressure-temperature conditions for equilibrium of illite-chlorite pairs sampled from Fig. IV.9e-f. The results from samples from the Central Belt spread over the range 250-350°C and 2-4 kbar, with a well-defined cluster, overall averaging at $327 \pm 21^\circ\text{C}$ and 3.0 ± 0.4 kbar. In the Foliated Morotsuka, the results spread over the range 300-350°C and 3-4.5 kbar, with average values of $320 \pm 14^\circ\text{C}$ and 3.9 ± 0.4 kbar (Fig. IV.10b).

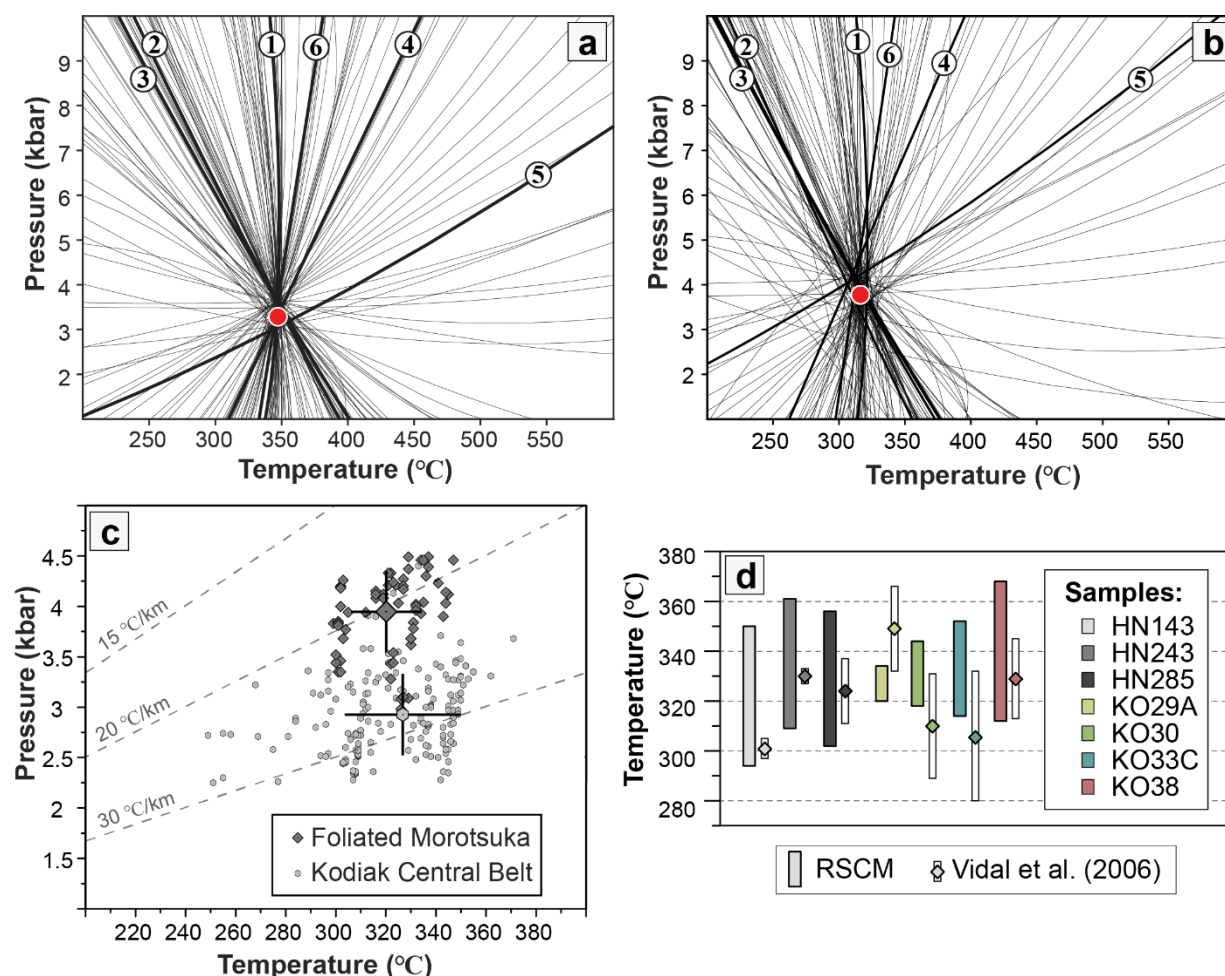


Figure IV.10. Examples of illite-chlorite equilibrium calculations in samples from (a) the Kodiak Central Belt (KO38, Kodiak) and (b) the Foliated Morotsuka (HN285, Shimanto). Bold lines represent independent reactions: (1) $(PrI)_{Phg} = (PrI)_{Phg} + H_2O$; (2) $4 Qtz - (Mg-Am)_{Chl} = 2 (PrI)_{Phg} + 2 (Sud)_{Chl}$; (3) $- 2 (Mg-Cel)_{Phg} + 15 Qtz + 2 (Ms)_{Phg} = 4 (PrI)_{Phg} + (Sud)_{Chl}$; (4) $- 5 (Mg-Cel)_{Phg} + (Clin)_{Chl} = (Fe-Am)_{Chl} + 4 (Fe-Cel)_{Phg} + (Ms)_{Phg}$; (5) $- 4 (Mg-Cel)_{Phg} + 4 (Daph)_{Chl} = 5 (Fe-Am)_{Chl} + (Mg-Am)_{Chl} + 4 (Ms)_{Phg}$; (6) $4 (Mg-Cel)_{Phg} + (Daph)_{Chl} = 5 (Fe-Cel)_{Phg} - (Mg-Am)_{Chl} + (Ms)_{Phg}$. (c) Pressure-temperature results from each of equilibrated illite-chlorite pair. (d) Comparison of the peak-metamorphic temperatures inferred from RSCM and the chlorite thermometry using the method by Vidal et al. (2006).

IV.4.6. Fluid inclusions

IV.4.6.1. Petrography of fluid inclusions

Quartz in the veins is characterized by high abundance of fluid inclusions (Fig. IV.11a-b). Veins from lower-grade units contain two types of primary fluid inclusions (Fig. IV.11c) interpreted as the result of fluid immiscibility (Raimbourg, 2015; Vrolijk et al., 1988): (1) 1-phase CH_4 -rich fluid inclusions with the size up to 20 μm and the negative crystal shape. These CH_4 -rich fluid inclusions

are randomly oriented in host quartz. (2) Smaller ($<10\text{ }\mu\text{m}$) 2-phase H_2O -rich fluid inclusions with various shape from roundish, squared to irregular (Fig. IV.11c). The small vapor bubble is dominated by CH_4 (Raimbourg et al., 2018). In zones characterized by stretched quartz, fluid inclusions (both CH_4 -rich and H_2O -rich) appearing as pseudo-secondary and are commonly in fracture healing planes perpendicular to the orientation of quartz elongation direction (Fig. IV.5b; Palazzin et al., 2016; Raimbourg et al., 2018).

In the higher-grade quartz veins, only one set of primary fluid inclusions is observed, two-phase H_2O -rich with a V/L ratio of 0.1-0.15 (Fig. IV.11d). The vapor bubble contains CO_2 and CH_4 to lesser extent (Raimbourg et al., 2018). Inclusions rarely exceed $10\text{ }\mu\text{m}$. Secondary fluid inclusions are common, aligned as healed fractures or trails of tiny one-phase fluid inclusions without systematic orientation of trails.

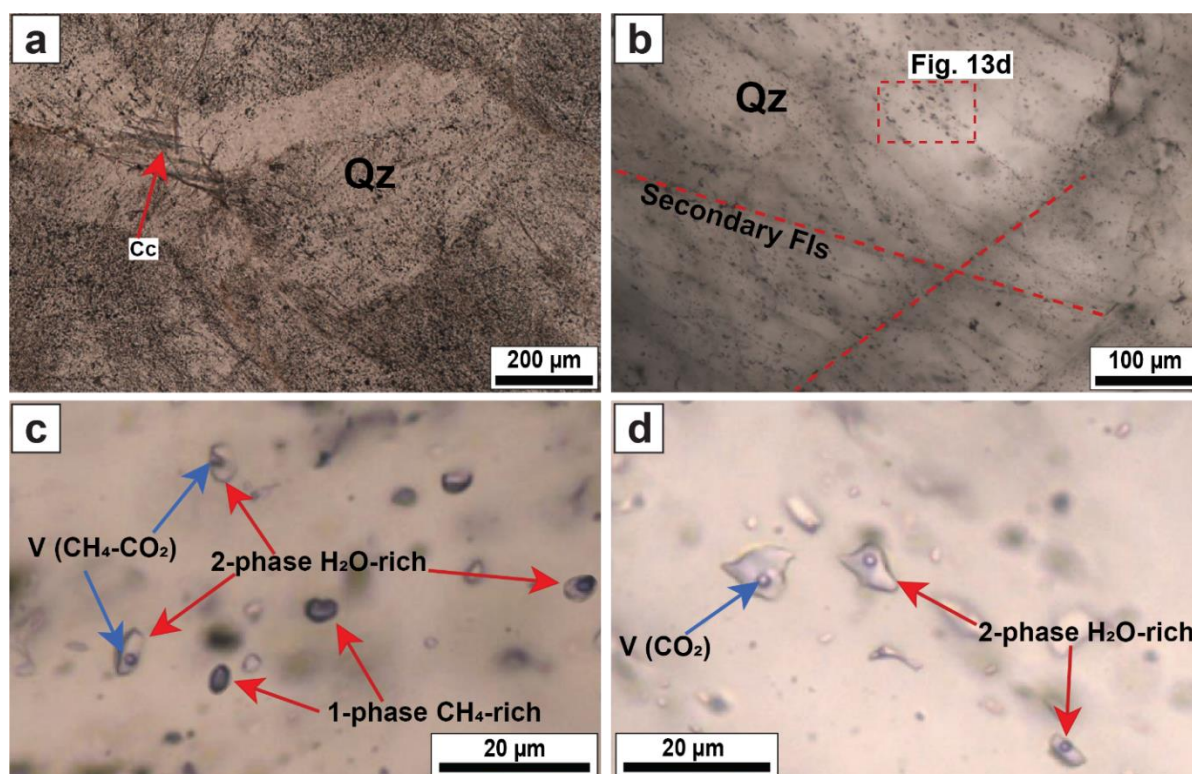


Figure IV.11. (a) Quartz with high fluid inclusion density from the Kodiak Landward Belt (Sample KO17H). (b) Quartz from higher-grade shear vein from the Kodiak Central Belt (Sample KO32F). Dashed lines represent trails of secondary fluid inclusions. (c) Two types of coexisting fluid inclusions in lower-grade veins: One-phase CH_4 and two-phase H_2O -rich with $\text{CH}_4\text{-CO}_2$ vapor bubble (Kodiak Landward Belt, sample KO17H). (d) two-phase H_2O rich fluid inclusions from quartz vein in the Kodiak Central Belt. Vapor bubble is composed of CO_2 .

IV.4.6.2. Fluid inclusion salinity

The salinity of fluid inclusions has been estimated in primary two-phase fluid inclusions and in a few secondary fluid inclusions (Fig. IV.12; Supplementary Table S4.2). On the one hand, in veins formed at lower temperatures, the salinity of primary fluid inclusions is often lower than ~3.5 wt. % NaCl eq. content of seawater (Fig. IV.12). In the Landward Belt for instance, primary fluid inclusions in samples: KO17A and KO17H yield average salinities of 2.1 ± 0.9 wt.% NaCl eq. and 2.1 ± 1.1 wt.% NaCl, respectively. Similarly, primary fluid inclusions in samples NOB_11C and NOB_8B of the Hyuga Tectonic Mélange yield average salinities of 2.2 ± 0.9 wt.% NaCl eq. and 1.2 ± 0.6 wt.% NaCl eq., respectively. A small proportion (<10%) of measured primary fluid inclusions show higher salinity than seawater.

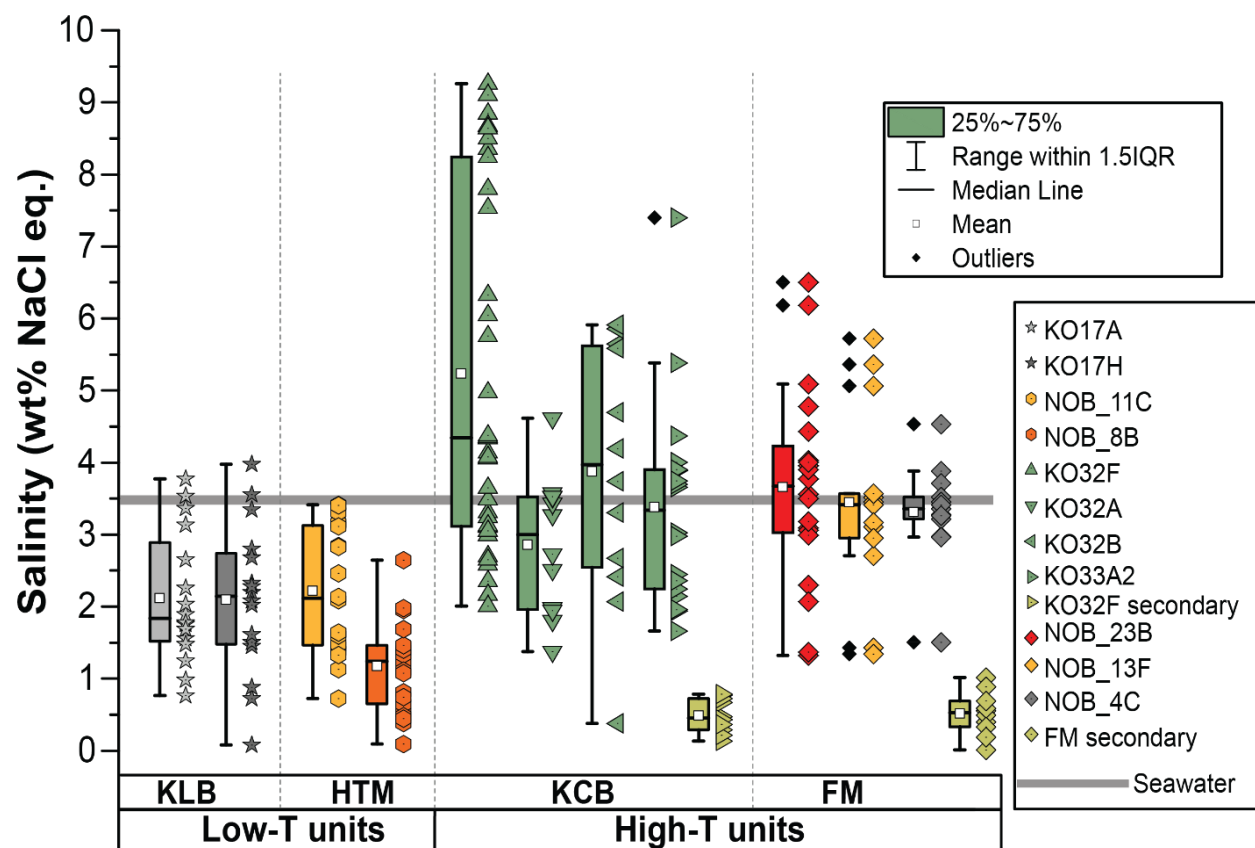


Figure IV.12. Box plots of estimated salinities of primary fluid inclusions and to a lesser extent of secondary inclusions in all the studied samples. Points next to each box plot correspond to the salinity of individual fluid inclusions in a given sample.

On the other hand, in higher-grade veins the average salinity of primary fluid inclusions is more variable and higher than in those of lower-grade veins, often exceeding the salinity of seawater (Fig. IV.12). This is the case in the Kodiak Central Belt, for which primary fluid inclusions in samples KO32F, KO32A, KO32B, and KO33A2 yield average salinities of 5.2 ± 2.5 wt.% NaCl eq., 2.9 ± 0.9 wt.% NaCl eq., 3.9 ± 1.8 wt.% NaCl eq., and 3.5 ± 1.4 wt.% NaCl eq., respectively. In the Foliated Morotsuka, samples NOB_23B, NOB_13F and NOB_4C yield average salinities of 3.7 ± 1.4 wt.% NaCl eq., 3.4 ± 1.3 wt.% NaCl eq., 3.3 ± 0.7 wt.% NaCl eq., respectively.

The salinity of secondary fluid inclusions from both localities is below 1 wt.% NaCl eq., in average 0.5 ± 0.3 wt.% NaCl eq. (Fig. IV.12).

IV.4.6.3. Fluid inclusion chemistry

SEM-EDS analyses of fluid inclusions in evaporite mounds in lower-grade veins show the presence of Na, K, Ca, Mg and Fe for cations, and Cl and S for anions (Supplementary Table S4.3).

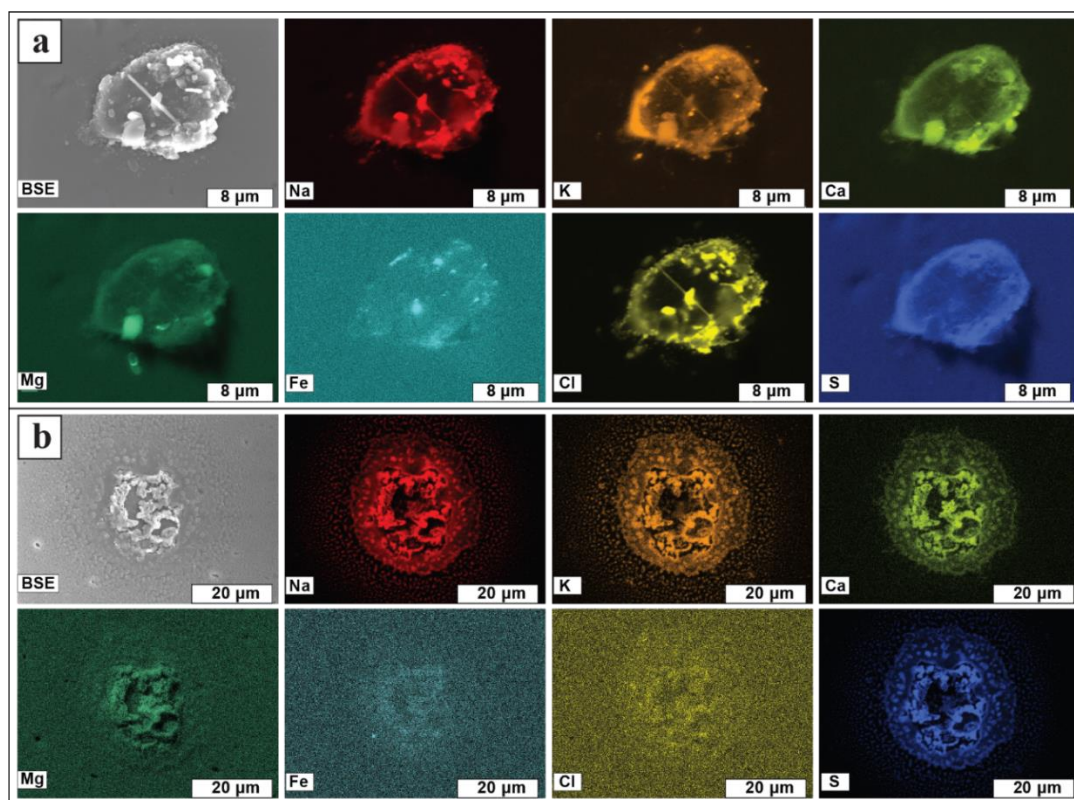


Figure IV.13. Examples of salt mounds formed due to decrepitation of fluid inclusions: SEM-BSE image as well as EDS elemental maps from (a) Lower-T quartz vein (Sample NOB_11C) and (b) higher-T quartz vein (sample KO30D).

Examples of two decrepitated mounds are presented in Fig. IV.13. EPMA point analysis revealed that the Na/Ca ratio is dominantly <1 (Fig. IV.14b), except for the sample NOB_13F and one evaporate mound in the sample NOB_23B where NaCl is the dominant compound (Fig. IV.14a). The amount of Fe and Mg varies between each analyzed mound (Fig. IV.14b), ranging from ~ 1.5 to $\sim 47\%$ and from ~ 1.5 to $\sim 42\%$, respectively. S and Cl are dominant anions, and the largest group of evaporate mounds ($\sim 75\%$) are characterized by SO_2/Cl ratio equal or higher than 1 (Fig. IV.14a). However, only few mounds are characterized by a presence of either Cl or SO_2 (Fig. IV.14c).

IV.5. Discussion

IV.5.1. Mass transfers

Whole-rock chemistry revealed no significant chemical variations on sample scale as a function of peak-metamorphic temperatures (Fig. IV.7), except for significant decrease is of SO_3 (further discussed in 5.2.). However, specific zones of the matrix, such as in the vicinity of the veins, are characterized by changes in mineralogy and thus pointing to the mass transfer on smaller scale. In such zones, as presented in Fig. IV.6, the matrix in the contact with veins is characterized by the absence of quartz and lower proportion of albite than in unaffected zones. Mass-balance calculations for specific zones of the higher-grade samples (zones with crenulation cleavage in the contact with veins and further from veins; Supplementary Table S4.4), e.g. like presented in Fig. IV.6, after normalization to TiO_2 show a decrease of SiO_2 and Na_2O counterbalanced by an increase of FeO , MgO , K_2O and LOI . Hence, SiO_2 loss is simply the result of removal of SiO_2 from the matrix and preservation of other mentioned elements, what can be interpreted as following mineralogical changes in pelitic matrix in vicinity to the veins (e.g., Fig. IV.6), where the depletion of quartz ($\pm$ albite) is observed with higher abundance of chlorite and illite (Fisher et al., 1995; Fisher & Brantley, 1992). The zones with noticeably different mineralogy are limited to <2 cm thickness from the contact with veins. Even though the length of diffuse mass transfer is difficult to trace, mass balance calculations as well as textural observations in examined samples point to limited mass transfer at a mm- to cm-scale. Other zones in the pelitic matrix where mass transfer operated are scaly fabrics (Fig. IV.4a; Fig. IV.5d), as enriched in Fe- and Ti-oxides with fine-grained illite and chlorite and characterized by the absence of quartz and albite. Similar observations were made in metapelites from the Shimanto belt (Kawabata et al., 2007; Ramirez et

al., 2021), where the progressive formation of scaly fabrics (their abundance and depletion in mobile elements) is described as facilitated by the temperature increase and deformation. For the elements depleted in scaly fabrics, such as SiO_2 or Na_2O , Ramirez et al. (2021) proposed that the mass transfer occurred along the scaly fabrics plains to the veins, where quartz and albite precipitated. A similar process is observed in the present work, with mass transfer from the host rock in the immediate vicinity of the vein towards the vein itself, interpreted as a site of dilation and preferential precipitation by Brantley & Fisher (1997).

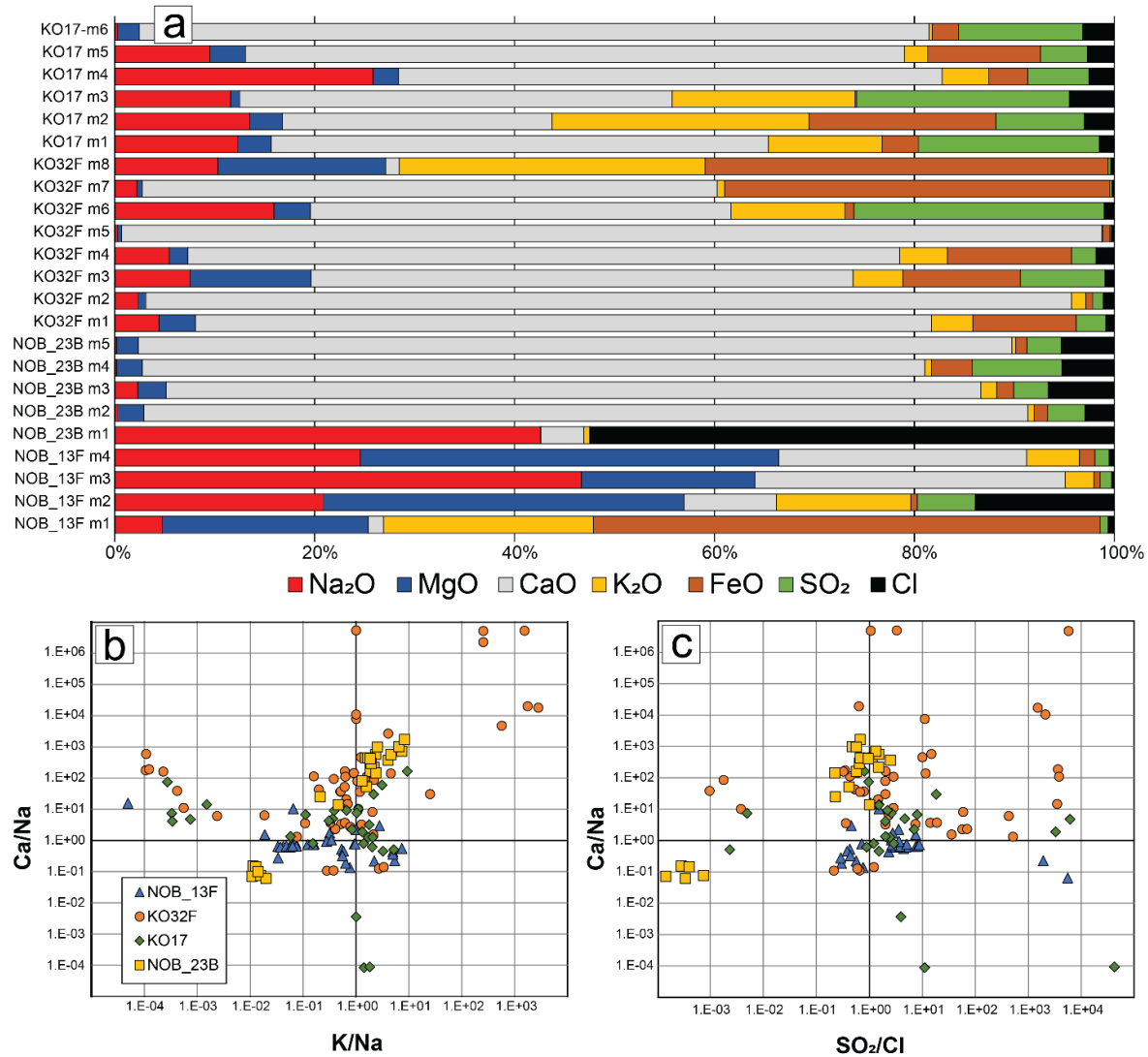


Figure IV.14. (a) Relative proportions of Na_2O , MgO , CaO , K_2O , FeO , SO_2 and Cl in evaporate mounds from decrepitated fluid inclusions. Each line represents the average composition from 3-10 points analyses acquired by EPMA in individual evaporate mounds. (b) Ca/Na vs. K/Na binary diagram and (c) Ca/Na vs. SO_2/Cl binary diagram of each individual point analysis in all examined evaporate mounds.

Unlike in examples of similar lithologies where external source of fluid is required, such as the Otago Schist (Breeding & Ague, 2002) or the Catalina Schist (Bebout, 1991, 1993; Penniston-Dorland et al., 2012), this work further support the idea of locally derived material of the veins in the Kodiak complex and the Shimanto belt (Brantley & Fisher, 1997; Fisher et al., 1995; Ramirez et al., 2021).

IV.5.2. Changes in mineralogy as a function of temperature

Our analyses from Kodiak and Shimanto reveal that metapelites of two studied accretionary prisms underwent a similar evolution of mineral proportions with peak-metamorphic temperature. In both cases, the most prominent mineral change is an increasing proportion of chlorite relative to other phyllosilicates with temperature (Table IV.4; Fig. IV.14). Ramirez et al. (2021) also reported an increase in the chlorite/phyllosilicates ratio with temperature in metapelites of Mugi and Makimine mélanges from the Shimanto belt having experienced peak-metamorphic temperatures of ~150-350°C. In addition, Kameda et al. (2011) described an increasing chlorite content from undeformed to deformed metasediments of the Kitagawa Group in the Shimanto belt, evolving in tandem with a more pervasive foliation. Because both undeformed and deformed part of the Kitagawa Group experienced same metamorphic temperatures (Kameda et al., 2011), the crystallization of chlorite must be facilitated not only by temperature increase, but also by deformation on the second order. The same conclusion was reached by Casciello et al. (2011) and Famin et al. (2021) for the transformation of smectite into illite, which is enhanced in deformation microstructures within metapelites even at isothermal conditions.

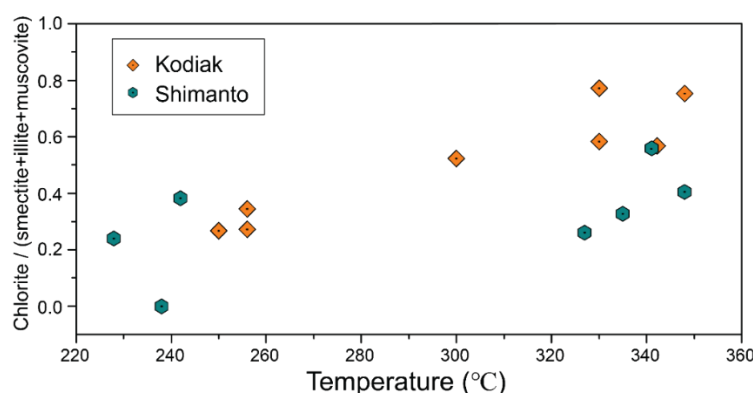


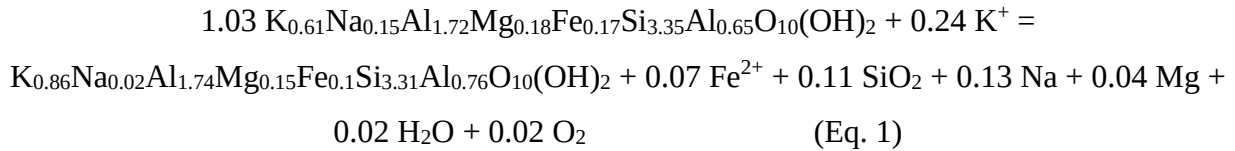
Figure IV.15. Compilation of chlorite vs. smectite + illite + muscovite ratio based on XRD. Note that for both localities there is an increase of chlorite proportion.

Last important observed mineral reaction is the pyrite oxidation. In lower-grade samples sulfides are dominantly represented by biogenic framboidal pyrite, whereas in higher-grade samples larger euhedral pyrite crystals are more dominant. However, in higher-grade samples, pyrite is also partly or completely oxidized into goethite. The enrichment of iron within shear bands is observed (Fig. IV.4i-j), and occasionally shear planes are connected to larger oxidized grains. Sulfide oxidations is matched by a significant drop of SO_3 on whole-rock scale with increasing temperature (Fig. IV.7). The main question is whether sulfide oxidation and the loss of sulfur occurred during metamorphism or due to surficial exposure of the samples. Goethite is reported as hydrothermal phase (e.g., Makvandi et al., 2021), what is further supported by experimentally derived work where it is shown that goethite is stable under low to moderate pressures (Majzlan et al., 2003). The progressive breakdown of pyrite in metasedimentary units is described as not only temperature-pressure dependent reaction, but also depending on the bulk composition and oxidation state of rocks (Dubessy et al., 1983; Ferry, 1981; Martin Frey et al., 1980; Hall, 1986). Furthermore, similar observations to ones from this study are reported in the external part of the Central Alps, where the oxidation of CH_4 to CO_2 and H_2O was associated with a reduction reactions in Fe-bearing phases, biotite and pyrite (Tarantola et al., 2007, 2009). To address this question, we have examined fluid inclusion chemistry to try to detect whether sulfur is released into the fluid. In decrepitated mounds in higher-grade veins, sulfur is detected and in many analyzed mounds is predominant over Cl (Fig. IV.14). Hence, the oxidation of pyrite possibly occurred at peak conditions, with sulfur remobilization into the fluid.

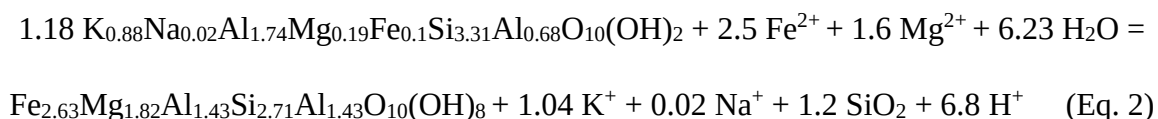
As previously discussed, the main mineralogical change occurring with temperature increase in metapelites of the two studied accretionary prisms is an increase in chlorite relative to other phyllosilicates (Fig. IV.15). Chlorite is the dominant Fe-Mg phase in metapelites, an important question is whether the local source of Fe and Mg is sufficient to support the transformation of phyllosilicates into chlorite, or if an external supply of Fe and Mg is needed. It is reported that diagenetic chlorite can form during burial at temperatures as low as 70°C , as a coproduct of smectite-to-illite transformation (Ahn & Peacor, 1985; Drief & Nieto, 2000; Hower et al., 1976; Muffler & White, 1969), or by the breakdown of smectite and kaolinite to form chlorite and illite (Boles & Franks, 1979). In both reactions described above illite is predominant product, with about 30% of chlorite (Boles & Franks, 1979; Hower et al., 1976). These reactions can explain the

formation of chlorite in lower-grade samples from this study (below 260°C), where chlorite content is 19-27% among all phyllosilicates (Table IV.4) and illite-chlorite intergrowth is observed (Fig. IV.4b). Also, among minor phases detected by XRD are smectite-illite mixed layers, serpentine and kaolinite in lower-grade samples (Table IV.4), which are proposed to be the precursor for chlorite (Boles & Franks, 1979). Kameda et al. (2011) proposed that chlorite crystallized from Fe-bearing berthierine, a category of inherited serpentine minerals which are metastable under low-metamorphic conditions. In this study, we have detected serpentine by XRD in lower-grade samples (Table IV.4). We propose that the chlorite in samples at 230-260°C is inherited from earlier smectite-to-illite transformation as well as a product of destabilization of serpentine.

With temperature increase, smectite-illite mixed layers transform into illite-muscovite during prograde metamorphism, occupancy of interlayer position is higher with the pressure-temperature increase and hence additional potassium is required (Fig. IV.9c). Taking illite composition from Supplementary Table S4.1 (Samples KO17A and KO33 as representatives), we propose the following reaction:



A small fraction of iron, magnesium and water are released during smectite-to-illite transformation. However, this reaction alone cannot explain further increase of chlorite amount at higher temperatures, nor textural observations such as chlorite rims around pelitic matrix or an enrichment in crenulation cleavage zones (Figures IV.4e, IV.5e). Several studies report the chloritization of micas during interaction with hydrothermal fluids (e.g., De Parseval et al., 1994; Komninou & Sverjensky, 1995; Tarantola et al., 2007, 2009), where muscovite reacts with Fe^{2+} , Mg^{2+} and H_2O , creating chlorite and releasing significant amount of K^+ and H^+ . During this study, we observed chlorite only as bimileralic chlorite-illite rims at the contact of the veins with the matrix (Figures IV.4e, IV.5f). These rims imply that fluids act at least as catalyzers of chlorite crystallization. As there are no systematic increase of magnesium and iron in the host rock as temperature increases, both elements originate rather locally. From the chemical composition of illite and chlorite from the zone with chlorite rims presented in Fig. IV.5f (Sample KO33), we propose that the crystallization of chlorite occurred through the following reaction:



where illite reacts with water, iron and magnesium creating chlorite and releasing silica, potassium and sodium in the fluid. As more potassium is required in illite in higher-grade samples (Fig. IV.9a), released quantity of potassium during this reaction is likely incorporated into remaining illite.

IV.5.3. P-T conditions of metamorphism

Due to several difficulties such as small grain size or the lack of equilibrium between newly formed phases, estimating pressure-temperature conditions in low-grade metamorphic rocks often represents a challenge. Despite these difficulties, our study succeeded in estimating peak-metamorphic temperatures in metapelites from two independent techniques, RSCM and chlorite thermometry, which yield similar results, confirming that chlorite formed at peak-temperatures (Fig. IV.10c). The illite-chlorite multi-equilibrium model indicates that both phases are metamorphic and not inherited. Also, textural observations then point to the precipitation of albite in veins at peak-metamorphic conditions, since it has been observed within chlorite rims (Fig. IV.5f). Furthermore, newly formed chlorite and albite are found at contact with and in the crack-seal veins, which indicates that the precipitation of chlorite and albite occurred contemporaneously with deformation. This confirms that the quartz in crack-seal veins crystallized also at peak conditions, as inferred from structural analysis of the veins (Fisher & Brantley, 2014; Raimbourg et al., 2021). As a consequence, the crack-seal structures described in these veins (Raimbourg et al., 2021; Ramirez et al., 2021) were also formed at temperatures ~300-350°C.

The RSCM temperature results in the Kodiak Landward Belt are around ~250°C, what is upper limit for homogenization temperatures (215-255°C) derived from fluid inclusions (Vrolijk et al., 1988). For the Kodiak Central Belt, our estimate of 2.5-3.5 kbar, 300-340°C is slightly higher than the average temperature of 280 °C obtained by Brantley & Fisher (1997) using $\delta^{18}\text{O}$ thermometry on quartz, mica, and chlorite (Brantley & Fisher, 1997). A possible explanation to this discrepancy is that $\delta^{18}\text{O}$ thermometry is more sensitive to low-temperature re-equilibration, due to intermineral oxygen diffusion (e.g., Farver & Yund, 1991), than RSCM and chlorite thermometry. In the case

of the Shimanto belt, our P-T estimate of 3.5-4.5 kbar and 300-350°C for the Foliated Morotsuka (Fig. IV.10b) is in match with Toriumi & Teruya (1988) who proposed a peak-metamorphic conditions at 3-5 kbar and 300-350°C based on mineral assemblages in metamafic rocks from the same unit.

P-T results in the Kodiak Central Belt estimated during this study point to a geotherm close to 30°C/km, in agreement with the previously proposed arguments for a warm geotherm in the subduction zone during the Cretaceous-Paleogene (Fisher & Byrne, 1992; Sample & Moore, 1987; Vrolijk et al., 1988), attributed to a ridge subduction less than 12 million years after the accretion of thick turbiditic sequences. Based on coexisting H₂O- and CH₄-rich fluid inclusions in extensional veins, Vrolijk et al. (1988) estimated geothermal gradient of ~20-25°C/km in the Uyak Complex, Kodiak and Ghost Rocks Formations, and concluded that these units were buried down to 10-14 km. Our geotherm estimate suggests that the Kodiak Central Belt has been buried down to 10-12 km. Furthermore, if the geothermal gradient remained constant during accretion, all the studied units were buried down to 7-12 km, depending on the peak-metamorphic temperature.

IV.5.4. Effect of mineral reactions on fluid composition

Initially during sediment burial, compaction and cementation reduce the porosity from several tens of vol.% to a few vol.% (e.g., Saffer & Tobin, 2011). Simultaneously, the pore fluid (originally seawater) becomes diluted by reactions such as smectite-to-illite transformations, which release fresh water (e.g., Colten-Bradley, 1987; Kastner, 1981; Kastner et al., 2014; Moore & Vrolijk, 1992; Perry & Hower, 1970; Spinelli, 2004). These transformations mostly occur in the temperature range 50-150°C, but may extent up to 250°C (Kastner et al., 2014). In several examples of metasedimentary rocks from paleo-accretionary complexes experiencing temperatures of ~250°C, fluid inclusion salinities in syn-subduction veins are lower than seawater (Herviou et al., 2021; Raimbourg et al., 2018; Figures IV.12, IV.16), which confirms this progressive dilution of the pore fluid during burial. Raimbourg et al. (2018) point to a difference in both salinities in fluid inclusions between rocks subducted to shallower and deeper than brittle-plastic transition (BPT). With increasing burial, another major change in fluid composition occurs at the brittle-plastic transition, in the 300-350°C temperature realm (e.g., Mullis et al., 1994; Raimbourg et al., 2018). At greater depth below this rheological limit, pore fluid salinities, as

inferred from fluid inclusions in various subduction zones worldwide, become highly variable and often higher than seawater (Herviou et al., 2021; Raimbourg et al., 2018 and references therein). This increase and scattering of salinities below the brittle-plastic transition, from ~250°C to 300-350°C, is not explained to date. Our fluid inclusion analyses show that the salinity increase and scattering also occurs in the metapelites of Kodiak and Shimanto (Fig. IV.12), thus our mineralogical and chemical results allow us to propose an explanation to these salinity variations. Indeed, for the pelitic rocks of the two accretionary prisms, burial between 230-260°C and 320-350°C was accompanied by an increase in chlorite proportion as previously discussed.

An important issue related to chlorite crystallization is that chlorite hosts more water than smectite-illite, ~13 wt.% to ~6-7 wt.%, respectively (Supplementary Table S4.1). Analyzed illite/smectite-illite at lower-grade contains about 7 wt.% of water. During formation of about 10% of chlorite, it is assumed that water from illite is placed into chlorite, but there is still a need for additional water. In 100 g of a rock with composition as of the sample KO38, 10% of chlorite (Table IV.5) contains ~1.3 wt.% H₂O. Potentially inherited water from 10% of illite is ~0.7 wt.% H₂O, hence there is a deficit of 0.6 wt.%, or 1.62 vol.% H₂O. Therefore, some of the pore fluid has to provide H₂O for chlorite crystallization, as a result of which the salinity of pore fluid increases (Figures IV.12, IV.15). The amount of pore water incorporated into chlorite is highly dependent upon the initial porosity and amount of illite in the metapelite protolith, which explains the scattering of salinity increases toward high-T samples. This amount of water incorporation by illite-to-chlorite transformation is also smaller than the variability of the initial water content of metapelite, which probably, beside the amount of the carbonates in the rock, masks any correlation between LOI and temperature (Fig. IV.7).

The oxidation of pyrite into goethite requires water as well. As an order of magnitude, the amount of initial pyrite is estimated roughly as 0.5-1% (Table IV.4). Since goethite contains ~10 wt.% of crystal-bound H₂O, the transformation of 0.5-1% of pyrite into goethite requires 0.05-0.1 wt.% H₂O, or 0.14-0.27 vol.%. Due to low abundance of pyrite, this reaction hardly affects the water budget. Combining the two described hydration reactions, the quantity of required fluid and the observed increase in salinity (~40%), the initial pore space is estimated at 4.4-4.7 vol.% and decreases down to 2.6-2.8 vol.%.

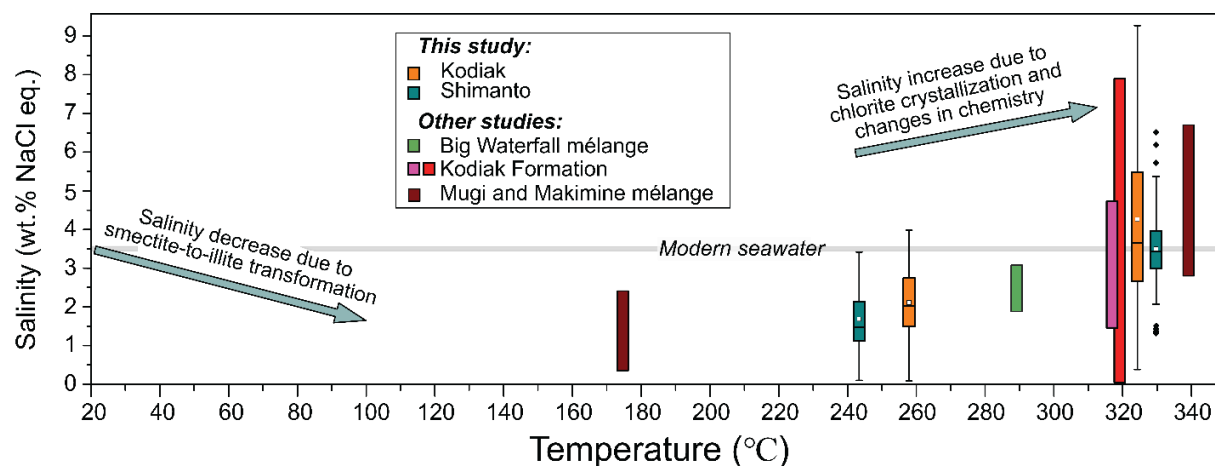


Figure IV.16. Box plots of fluid inclusion salinities in quartz veins from this study as well as from previous studies concerning salinity in the Kodiak accretionary complex and the Shimanto belt in Japan. Compilation of literature: Big Waterfall mélange, Kodiak (Rowe et al., 2009); Kodiak Formation, Alaska: pink – Afognak transect, red – Kodiak transect (Brantley & Fisher, 1997); Mugi mélange (Sakaguchi, 1999); Makimine mélange (Nishiyama et al., 2021).

IV.6. Conclusion

While at lower-grade the equilibrium is not yet postulated between metamorphic phases, our results point to the well-established equilibrium in higher-grade samples, at temperatures $>300^{\circ}\text{C}$. Chlorite thermometry revealed similar temperature of crystallization as RSCM, pointing to the occurrence of mineral reactions at the peak-metamorphic conditions.

Our study shows that during the prograde metamorphism of subducted metapelites, in the range of $230\text{--}260^{\circ}\text{C}$ to $300\text{--}350^{\circ}\text{C}$, the major change is an increase in chlorite/illite ratio as a result of illite-to-chlorite transformation. Other reactions include the oxidation of pyrite into goethite and dissolution of titanite and precipitation of anatase.

The bulk composition of the rock is not significantly modified in the range from $230\text{--}260^{\circ}\text{C}$ to $300\text{--}350^{\circ}\text{C}$, which suggests limited mass transfer. Local mass transport is nevertheless observed in the vicinity of veins formed at peak conditions. The matrix is depleted in quartz and albite, counterbalanced by their precipitation in the veins. Phyllosilicates growth is enhanced in the

vicinity of the veins. Textural observations point to all reactions occurring during the main deformation event.

The salinity of fluid inclusions in quartz veins that experienced 230-260°C, is constantly lower than that of seawater, as an inheritance of freshening from smectite-to-illite transformation. At higher temperatures the salinity is closer or higher to the seawater. Crystallization of chlorite is a possible explanation for a such salinity increase, as chlorite requires additional water.

Observed mineral reactions, in first order illite-to-chlorite transformation, affect the water budget in subducted sediments along the seismogenic zone where the pore fluid is transformed into crystal-bound water, potentially influencing the proportion of pore fluid and consequently pore fluid pressure.

Preface

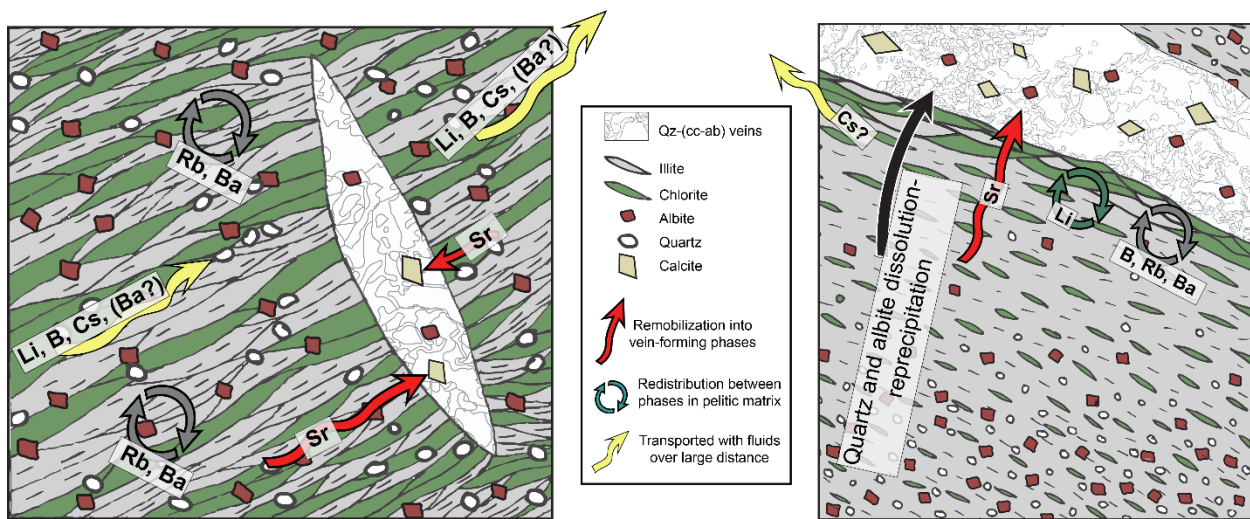
In this chapter we evaluate the fluid-mobile elements budget evolution in same units and samples examined in the Chapter IV: The Kodiak accretionary complex and the Shimanto belt. For this purpose, we combined and compared elemental concentrations in (i) bulk rock, (ii) individual mineral phases and (iii) populations of fluid inclusions trapped in syn-metamorphic quartz veins, using Inductively coupled plasma mass spectrometry (i) and Laser ablation Inductively coupled plasma mass spectrometry (ii and iii). Briefly, whole-rock concentrations as well as concentrations in individual mineral phases from the Kodiak accretionary complex suggest the preservation of fluid-mobile elements to temperatures of 330-350°C, whereas in the Shimanto belt a significant loss of all fluid-mobile elements is reported. Consequently, a closed system is proposed for units in Kodiak and open system in the Shimanto belt. The opposite behavior of two terranes results from their internal strain and from their proximity to large-scale faults that concentrate the fluid flow.

Results from this chapter represent a basis for one published article:

*Raimbourg, H., **Rajič, K.**, Moris-Muttoni, B., Famin, V., Palazzin, G., Fisher, D. M., et al. (2021). **Quartz vein geochemistry records deformation processes in convergent zones.** Geochemistry, Geophysics, Geosystems, 22.*

*And one manuscript currently in a review process in journal Geochimica et Cosmochimica Acta: **Rajič, K.**, Raimbourg, H., Gion, A. M., Lerouge, C., and Erdmann, S. **Fluid-mobile elements behavior in subducted sediments: A case study from low- to moderate-P/T metapelitic rocks.***

CHAPTER V – Fluid-mobile elements behavior in subducted sediments: A case study from low- to moderate-P/T metapelite rocks



CHAPTER V – Fluid-mobile elements behavior in subducted sediments: A case study from low- to moderate-P/T metapelitic rocks

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V.0. Abstract

This study examines the budget of fluid-mobile elements (FME: Li, B, Rb, Sr, Cs, and Ba) and evaluates fluid-rock interactions in metapelitic rocks from the Shimanto Belt (Japan) and the Kodiak complex (Alaska). Lower-grade rocks (~230-260°C) preserve a whole-rock FME signature that is similar to modern trench sediments. In contrast, at higher temperatures (~330-350°C) FME (in particular Li, B and Cs) are leached out of the rocks from Shimanto, whereas no significant loss is observed at Kodiak. The constant FME budget in Kodiak reflects a redistribution of elements between metamorphic illite and chlorite, whereas in Shimanto the loss is principally the result of a decrease in FME concentrations in illite and chlorite with temperature.

The composition of the metamorphic fluids, analyzed as fluid inclusions hosted in syntectonic quartz veins was combined with mass calculations for B, Cs, and Ba. In the Kodiak complex the mass balance calculations are consistent with closed-system behavior, wherein the fluid is an insignificant reservoir for FME. Conversely, in the Shimanto Belt the mass balance calculations are consistent with open-system behavior, wherein large amounts of fluid percolated through rocks and the water-rock ratios correspond to 0.3-1.7. We infer that such an open system behavior was promoted by a larger amount of internal strain and the proximity to a large-scale fault zone. Element ratios in the fluid differ significantly from seawater or sediment pore fluids, but have similar FME signature to mud volcanoes. This finding is consistent with the low-grade metamorphic reactions influencing the composition of deep fluids and contributing significantly to the chemistry of the fluids that are expelled through the subduction forearc.

V.1. Introduction

Subduction zones play a major role in element cycling between the different reservoirs of the Earth (Bebout et al., 1995, 2014, 2021; Hacker et al., 2003; Peters et al., 2017; Shervais & Jean, 2012; Tatsumi & Kogiso, 2003). In addition to serpentinites and altered oceanic crust (Deschamps et al., 2013; John et al., 2011; Reynard, 2013; Rupke, 2004; Scambelluri, et al., 2004a, 2019; Tenthorey & Hermann, 2004), sediments are an important carrier of volatiles and fluid-mobile elements (FME) at depth (Bebout et al., 2013; Bekaert et al., 2020; Kerrick & Connolly, 2001; Rea & Ruff, 1996). Many studies have focused on the composition of material entering subduction zones (e.g.,

GLOSS and GLOSS-II compilations; Plank, 2014; Plank & Langmuir, 1998), as well as high P-T metasedimentary units (e.g., Barnes et al., 2019a; Bebout et al., 1991, 1999, 2013; Busigny et al., 2003) in order to perform mass balance calculations. However, low- to moderate-P/T metasedimentary units have received less attention, even though low-temperature mineral reactions and the consequential fluid expulsion results in the loss of some of the mobile elements into the fluid coming through the overriding plate (Carson et al., 2003; Dia et al., 1999; Miriam Kastner et al., 2014; Lauer & Saffer, 2012; Ranero et al., 2008; Sahling et al., 2008).

Similarly to their host rocks, pore fluid chemistry in sediments experiencing burial and subduction at convergent margins, has been extensively studied as part of IODP/ODP programs and the chemical evolution of the fluid is related to specific mineral reactions, such as smectite-to-illite transformation (see a compilation by Kastner et al., 2014). In addition to chemical changes, the volume of the pore fluid is significantly reduced during burial due to compaction and cementation (Miriam Kastner et al., 2014; Kominz & Pekar, 2001; Saffer & Tobin, 2011), wherein expelled fluids are returned back to the ocean along the plate-boundary interface or splay faults in fore-arcs (Bangs et al., 1996; Bangs et al., 1999; Lauer & Saffer, 2012, 2015; Moore et al., 2001; Tobin et al., 2001; Ujiie, 2003; Vrolijk et al., 1991). Additionally, some of the fluids that are released at depths <15 km are believed to circulate through the subduction forearc along highly permeable zones and are expelled through mud volcanoes and springs back into the ocean (Carson et al., 1990, 2003; Kastner et al., 2014; Moore & Vrolijk, 1992). These fluids are characterized by elevated FME concentrations that are theoretically related to low-temperature dehydration reactions in subducted sediments (Barnes et al., 2019b; Dia et al., 1999; Dimitrov, 2002; Martin et al., 1996; Westbrook & Smith, 1983). Accretionary complexes such as the Kodiak accretionary complex, the Shimanto Belt in Japan, or the Otago Schist in New Zealand contain the mineral records of these low-grade reactions (i.e., 2-5 kbar, 250-350°C) and can therefore help to connect surface fluids to deep processes (Fagereng & Cooper, 2010; Kameda et al., 2011; Kawabata et al., 2007; Rajič et al., 2023; Ramirez et al., 2021). A prominent feature of those geological examples is the abundance of metamorphic veins, attesting to the ubiquitous presence of fluids during metamorphism (Brantley & Fisher, 1997; Breeding & Ague, 2002; Fagereng et al., 2018; Fisher & Byrne, 1990; Fisher et al., 1995; Herviou et al., 2021; Raimbourg et al., 2018, 2021; Vrolijk et al., 1988, 1991). These veins raise the question of the scale of the mass transfer, i.e. whether the

material is locally redistributed by dissolution-reprecipitation, as proposed for veins in the Kodiak accretionary complex (Brantley & Fisher, 1997; Fisher et al., 1995), or transported over large distances, through the prism upwards from the dehydrating slab as reported for the Otago Schist (Breeding & Ague, 2002).

Fluid-mobile elements are a major tool to help answer these questions. The FME budget is highly controlled by the thermal structure of the subduction zones. In warm subduction zones, such as the Catalina Schist, significant loss of boron and cesium and retention of rubidium and barium has been reported down to depths of ~45 km (Bebout, 1991, 1999). Conversely, in cold subduction zones such as those preserved in the Western Alps, no noticeable loss of FME down to ~90 km has been reported (Bebout et al., 2013; Busigny et al., 2003). In metapelites that have experienced low-grade metamorphic conditions (i.e., <350°C), scaly fabrics (or pressure-solution seams) are depleted in FME as compared to the surrounding pelitic matrix (Kawabata et al., 2007; Ramirez et al., 2021). Such depletion can be explained by different processes, such as FME incorporation into newly formed metamorphic phases in the pelitic matrix, local diffusive transport to low effective normal stress sites such as veins (Ramirez et al., 2021) or large-scale transport within a circulating fluid phase.

To study these issues, we have selected the Kodiak accretionary complex and the Shimanto Belt for the following reasons: (1) Both localities are paleo-accretionary complexes, with the majority of the exposed rocks being basally underplated (Byrne & Fisher, 1987; Ditullio & Byrne, 1990; Fisher & Byrne, 1987; Sample & Moore, 1987; Taira et al., 1982; Ujiie, 1997). (2) Both contain rock units that have experienced a range of peak-metamorphic temperatures that correspond to the seismogenic zone and its down-dip limit (from ~230°C up to ~350°C; (Palazzin et al., 2016; Raimbourg et al., 2014, 2021; Rajič et al., 2023; Rowe et al., 2009; Vrolijk et al., 1988). At each locality, syn-subduction veins with primary fluid inclusions associated with a main deformation event have been recognized (Raimbourg et al., 2021; Rajič et al., 2023). (3) Units at each locality have lithological and mineralogical similarities, even though they have experienced different peak-metamorphic temperatures.

In this work, we studied FME concentrations and budgets (Li, B, Rb, Sr, Cs, and Ba) in metasedimentary units from the two paleo-accretionary complexes, the Kodiak complex and Shimanto Belt, cited above. We examined the evolution of FME budgets as a function of the peak-

metamorphic temperatures, by using a combination of three datasets: analyses of whole-rock, individual metamorphic phases, and vein-hosted fluid inclusions. As a result, this study provides (i) insights into fluid-rock interactions in subduction zones and their impact on fluid chemistry as well as (ii) a framework of fluid circulations and mass transfers from the cm- to the multi-km scale.

V.2. Sample description

To evaluate the evolution of fluid-mobile elements budgets, their relationship to changes of concentrations in individual phases and to mineral reactions, the same set of samples was used as in Chapter III. In Table V.1. the list of samples and their locations is presented, as well as estimated peak-metamorphic temperatures and pressures, and salinities of fluid inclusions in vein samples.

V.3. Analytical methods

V.3.1. Whole-rock trace element composition

Whole-rock trace element compositions were acquired for 16 samples from the Kodiak Formation (Landward, Central and Seaward Belt) and the Shimanto Belt (the Hyuga Tectonic Mélange and the Foliated Morotsuka). Samples were crushed in a mortar and washed with doubly distilled water. Final powder samples were analyzed at Actlabs (Activation laboratories Ltd. Ireland) by inductively coupled plasma-mass spectrometry (analytical code ME-MS89L+B-MS89L).

V.3.2. Laser Ablation Inductively Coupled Plasma Mass Spectrometry

V.3.2.1. Trace-element concentration in mineral phases

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) was used to determine the trace elements concentrations in major mineral phases (illite, chlorite, and albite in the matrix, and quartz and calcite in the veins). LA-ICP-MS analyses were conducted at CNRS Institut de Sciences de la Terre d'Orléans (ISTO) using a RESOLUTION-SE 193 nm ArF excimer laser with a S155 ablation cell coupled to an Agilent 8900 QQQ mass spectrometer. To determine trace element concentrations in illite, chlorite, albite, and calcite, the laser was operated at 3 Hz and a fluence of $\sim 4 \text{ J/cm}^2$ on the sample surface, and a spot size of 10 μm in diameter. A SQUID

V.3. Analytical methods

Table V.1. Sample locations, pressure-temperature estimates based on RSCM and multi-phase equilibrium model, and salinity of fluid inclusions in vein samples. Literature: ¹Chapter II; ²Chapter III; ³Palazzin et al. (2016); ⁴Raimbourg et al. (2018); ⁵Raimbourg et al. (2021).

Locality	Longitude	Latitude	Rock type	RSCM		Multi-phase equilibrium				Ref.	Salinity ¹	
				T (°C)	SD	T (°C)	SD	P (kbar)	SD		Av.	SD
<i>Kodiak Landward Belt</i>												
KO17B	-153.9843	57.6093	Pelites	256	10					1		
KO17C	-153.9843	57.6104	Pelites	255	9					1		
KO17D	-153.9855	57.6113	Pelites	257	12					1		
KO17E	-153.9841	57.6119	Pelites	240	9					1		
KO17A	-153.9843	57.6094	Vein	251	9						2.1	0.9
KO17H	-153.9841	57.6119	Vein	240	9						2.1	1.1
<i>Kodiak Central/Seaward Belt</i>												
KO33	-152.2568	58.3576	Pelites	333	19	306	26	2.9	0.3	1		
KO36	-152.2586	58.3661	Pelites	330	29					1		
KO38	-152.2865	58.3889	Pelites	340	28	329	16	3.0	0.4	1		
KO11	-152.4386	57.6516	Pelites	300	19					1		
KO12B	-152.4764	57.6875	Pelites	348	28					1		
KO45C	-152.4385	57.8393	Pelites	344	16					1		
KO30D	-152.2228	58.3542	Vein	331	13	310	21	3.1	0.4	1	3.3	0.7
KO32B	-152.2450	58.3893	Vein	330	16					5	3.9	1.8
KO32C	-152.2450	58.3893	Vein	330	16					5	3.5	0.8
KO33A2	-152.2568	58.3576	Vein	333	19	306	26	2.9	0.3	1	3.5	1.4
<i>Hyuga Tectonic Mélange</i>												
HN64	131.4036	32.5452	Pelites	240	6					3		
HN85	131.3148	32.4287	Pelites	242	11					4		
HN299	131.2790	32.4033	Pelites	228	16					2		
NOB_5D	131.2561	32.4083	Vein	250	5					2	1.7	0.9
NOB_8B	131.3815	32.4904	Vein	233	24					2	1.2	0.6
NOB_11C	131.3147	32.4278	Vein	241	15					2	2.2	0.9
HN296B	131.2392	32.4201	Vein								1.7	0.9
HN298A	131.2541	32.4104	Vein								1.7	0.9
HN299	131.2790	32.4033	Vein	228	16					2	1.7	0.9
<i>Foliated Morotsuka</i>												
HN61	131.8559	32.7202	Pelites	348	6					4		
HN143	131.5583	32.6137	Pelites	322	28	301	4	3.9	0.3	2		
HN243	131.2075	32.4094	Pelites	335	26	330	3	3.7	0.4	2		
HN247	131.2026	32.3095	Pelites	327	33					2		
HN285	131.2392	32.4200	Pelites	329	27	324	13	4.0	0.4	3		
NOB13F	131.5433	32.7211	Vein	323	19					2	3.4	1.3
NOB13G	131.5433	32.7211	Vein	323	19					2	3.4	1.3
NOB13H	131.5433	32.7211	Vein	323	19					2	3.4	1.3
18NOB23	131.9935	32.9151	Vein	338	10					5	3.7	1.4

was used to homogenize the ablation signal. For each phase and spot, SiO₂ as measured by using an electron microprobe was used as an internal standard and NIST610 was used as an external standard, NIST612 and BCR2G were also analyzed as unknowns for quality control. The analyzed isotopes were: ⁷Li, ¹¹B, ⁵¹V, ²⁷Al, ²⁸Si, ⁵⁶Fe, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁹³Nb, ¹¹⁸Sn, ¹³³Cs and ¹³⁷Ba. Data reduction was performed with the software GLITTER™ (Van Achterbergh et al, 2001), wherein the background and ablation signals were manually selected and a linear fit was applied to all standard data.

V.3.2.2. Bulk microanalysis of fluid inclusion populations

The size of the fluid inclusions in quartz in the studied samples rarely exceeds 10 µm and thus, the classical approach of the laser ablation of individual fluid inclusion was not applicable. Instead a bulk microanalysis of fluid inclusion populations, following the approach of Tuba et al. (2019) was utilized. Tuba et al. (2019) showed that this approach is in a good agreement with other methods concerning the chemical composition of fluid inclusions, such as microthermometric studies, decrepitation method or crush-leach techniques.

Doubly-polished thick sections of quartz were prepared with a thickness of ~200-250 µm. To avoid heating and volatilization of the glue, all epoxy resin was removed after polishing by immersing samples in ethanol for up to ~24 hours and then rinsing repeatedly. The margins of the thick sections were subsequently fixed to a new glass plate with superglue. The laser operated at a frequency of 5 or 10 Hz and a fluence of 8 J/cm² on the sample surface. A laser spot size was 50 µm in diameter. The isotopes that were analyzed were ⁷Li, ⁹Be, ¹¹B, ²³Na, ²⁴Mg, ²⁷Al, ²⁸Si, ³⁹K, ⁴³Ca, ⁴⁷Ti, ⁵⁵Mn, ⁵⁶Fe, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁵Mo, ¹¹⁸Sn, ¹²¹Sb, ¹³³Cs, ¹³⁷Ba, ¹⁸²W, ²⁰⁸Pb and ²⁰⁹Bi. SiO₂ was used as an internal standard (100 wt. %), NIST610 was used as an external standard. NIST612 and BCR2G were also analyzed as unknowns for quality control.

Quartz from the examined veins is characterized by a high density of fluid inclusions with sporadic areas with a low density of fluid inclusions, but quartz is never “inclusion-free” (Fig. V.1a-b). By performing laser ablation analyses in fluid inclusion-rich (FI-rich) and fluid inclusion-poor zones in quartz (FI-poor), elements concentrated within fluid inclusions are distinguished from the elements hosted in the quartz crystal lattice. Due to the high FI density in FI-rich zones, elements

located in fluid inclusions are expected to show systematically higher concentrations than in FI-poor zones. The main limitation of this approach is the difficulty in determining the absolute concentrations of trace elements in the fluid inclusions. To do so, a charge-balance approach, widely used in classical LA-ICP-MS analysis of individual fluid inclusions (Allan et al., 2005), was applied by utilizing the measured element ratios with the salinity of the fluid inclusions (Chapter III; Raimbourg et al, 2018). Sodium was used as an internal standard for the fluid following the equation:

$$mNa = mCl \times \left(1 + \sum_i \frac{n_i \times mX_i}{mNa} \right)^{-1}$$

where concentration is expressed in molality (m , mol/kg), n_i represents the charge of each considered cation (X_i), and molal ratios ($\frac{mX_i}{mNa}$) are calculated from LA-ICP-MS data (Allan et al., 2005). The main problem in the quantification procedure arises if major elements (Na, K, or Ca)

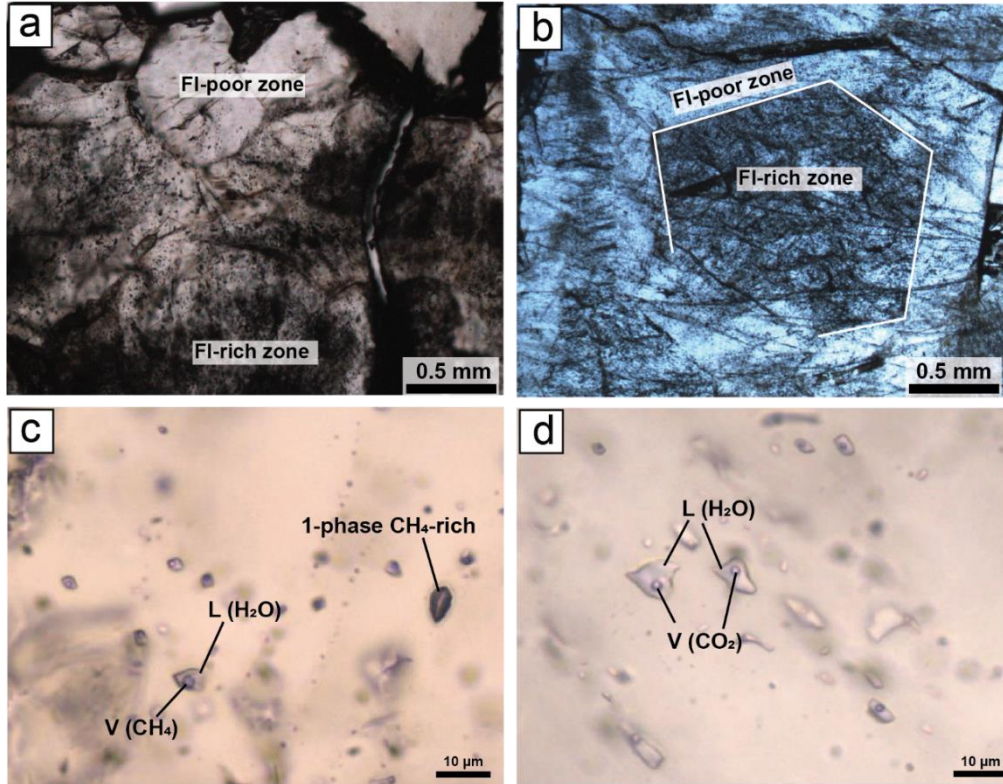


Figure V.1. Quartz and entrapped fluid inclusions from syn-subduction veins. (a-b) Quartz crystals characterized by FI-rich and FI-poor zone (Samples KO17 and KO33A2). Note that the FI-poor zone in (b) still contains high density of fluid inclusions, but in comparison with adjacent FI-rich zone significantly lower amount. (c) An example of coexisting one-phase CH₄-rich and two-phase H₂O-rich fluid inclusions in lower-grade veins (Sample KO17). (d) Primary two-phase H₂O-rich fluid inclusions with CO₂-(CH₄) vapor bubble in higher-grade veins (Sample KO33A2).

in the fluid inclusions are below the detection limit of the analyzed sample volume (which comprises various amounts of fluid inclusions and host quartz). Although, sodium and potassium are generally above detection limits, calcium was at times below the detection limit. Sodium was analyzed as ^{23}Na and potassium was analyzed as ^{39}K with isotopic abundances of 100 and 93.26%, respectively. Calcium was analyzed as mass ^{43}Ca which, in contrast, has a low isotopic abundance of 0.135%. More abundant Ca isotopes (e.g., ^{40}Ca , 96.941%; ^{44}Ca , 2.086) were not analyzed due to important interferences (e.g. from ^{40}Ar , $^{28}\text{Si}^{16}\text{O}$). Detection limits were 0.44-51.48 ppm for Ca, 0.1-0.4 ppm for Na, and 0.223-1.07 ppm for K. Because calcium is abundant in FIs in most of analyzed samples (Chapter III), the quantification for point analyses without estimated calcium value results in the concentrations of other elements being two or more times greater than in comparison with measurements where calcium is estimated. Thus, semi-quantitative results presented in this work are derived from only analyses where calcium is detected.

V.4. Results

V.4.1. Whole-rock trace element composition

Whole-rock trace element concentration data are presented in Table V.2 and the concentrations are plotted as a function of peak-metamorphic temperatures in Fig. V.2.

In metapelites from the Shimanto Belt, lithium concentrations range from 53 to 68 in HTM and 26 to 44 ppm in FM (Fig. V.2a; Table V.2). Boron concentrations range from 155 to 195 ppm in HTM and from 63 to 97 ppm in FM (Fig. V.2b). Concentrations of rubidium, strontium and barium are relatively consistent between the two units, with the range of all examined samples from 106 to 182 ppm, 110 to 150 ppm, and 430 to 704 ppm, respectively (Fig. V.2c-e). Cesium concentrations are 9 to 10.5 ppm in HTM and 4.9 to 6.2 ppm in FM. In samples from the Kodiak accretionary complex. Among all samples, lithium and boron range from 39 to 70 ppm and from 64 to 127 ppm, respectively. Concentrations of rubidium, strontium and barium range from 59.7 to 120.5 ppm, 110 to 280 ppm, and 555 to 1300 ppm, respectively. Cesium concentrations are in the range from 3.4 to 7.1 ppm (Table V.2).

V.4. Results

Table V.2. Whole-rock trace element composition of studied metapelites from the Shimanto Belt and the Kodiak accretionary complex.

Sample	T (°C) RSCM	K ₂ O wt.%	B ppm	Li ppm	Rb ppm	Sr ppm	Cs ppm	Ba ppm	B/K ₂ O	Li/K ₂ O	Rb/K ₂ O	Sr/K ₂ O	Cs/K ₂ O	Ba/K ₂ O	B/Li	Rb/Cs
<i>Shimanto</i>																
HN64	238	3.3	195.0	68.0	164.5	110.0	10.5	704.0	59.3	20.7	50.0	33.4	3.2	213.9	2.9	15.7
HN85	242	1.4	155.0	53.0	179	120.0	9.0	664.0	107.6	36.8	124.3	83.3	6.3	461.1	2.9	19.9
HN299	228	2.8	167.0	54.0	167.5	150.0	10.1	655.0	59.6	19.3	59.8	53.6	3.6	233.9	3.1	16.6
18NOB23	341	3.0	97.0	44.0	106.0	110.0	4.9	430.0	31.9	14.5	34.9	36.2	1.6	141.5	2.2	21.6
HN285	321	3.1	63.0	26.0	182.0	130.0	6.2	664.0	20.5	8.4	59.1	42.2	2.0	215.6	2.4	29.4
HN243	335	3.0	65.0	28.0	144.5	110.0	5.4	531.0	21.7	9.3	48.2	36.7	1.8	177.0	2.3	26.8
<i>Kodiak</i>																
KO17B	256	1.5	64.0	39.0	59.7	110.0	4.2	555.0	43.2	26.4	40.3	74.3	2.8	375.00	1.6	14.2
KO17C	256	2.8	118.0	40.0	120.5	110.0	7.1	1125.0	41.6	14.1	42.4	38.7	2.5	396.1	2.9	16.9
KO17D	258	2.4	78.0	57.0	96.3	280.0	3.8	1015.0	32.9	24.1	40.6	118.1	1.6	428.3	1.4	25.3
KO17E	240	2.6	139.0	55.0	105.0	190.0	5.8	978.0	53.1	21.0	40.1	72.5	2.2	373.3	2.5	18.1
KO33	333	1.9	115.0	52.0	93.1	130.0	4.2	1300.0	59.3	26.8	48.0	67.0	2.2	670.1	2.2	22.2
KO36	330	3.3	90.0	51.0	77.1	260.0	3.4	950.0	27.4	15.5	23.4	79.0	1.0	288.8	1.8	22.7
KO38	340	3.6	127.0	70.0	112	120.0	5.4	1195.0	35.2	19.4	31.0	33.2	1.5	331.0	1.8	20.7
KO11	300	2.8	122.0	54.0	83.4	200.0	3.7	923.0	43.3	19.2	29.6	70.9	1.3	327.3	2.3	22.5
KO12B	348	2.6	112.0	56.0	81.1	180.0	3.8	859.0	42.6	21.3	30.8	68.4	1.4	326.6	2.0	21.3
KO45C	345	2.6	78.0	51.0	68.5	230.0	3.5	818.0	29.7	19.4	26.1	87.5	1.3	311.0	1.5	19.6

The normalization of trace elements to K₂O wt.% (to normalize chemical heterogeneities among samples, and because that K-bearing phyllosilicates are the main host of FME) revealed different trends between samples from the Shimanto Belt and the Kodiak complex. In the Shimanto Belt, all elements exhibit a negative linear trend as a function of peak-metamorphic temperatures (Fig. V.2f-h). In the Kodiak complex, however, only cesium shows a strong negative linear trend as a function of peak-metamorphic temperatures, whereas all other elements have smaller changes in ratios between lower- and higher-grade samples (Fig. V.2f-h).

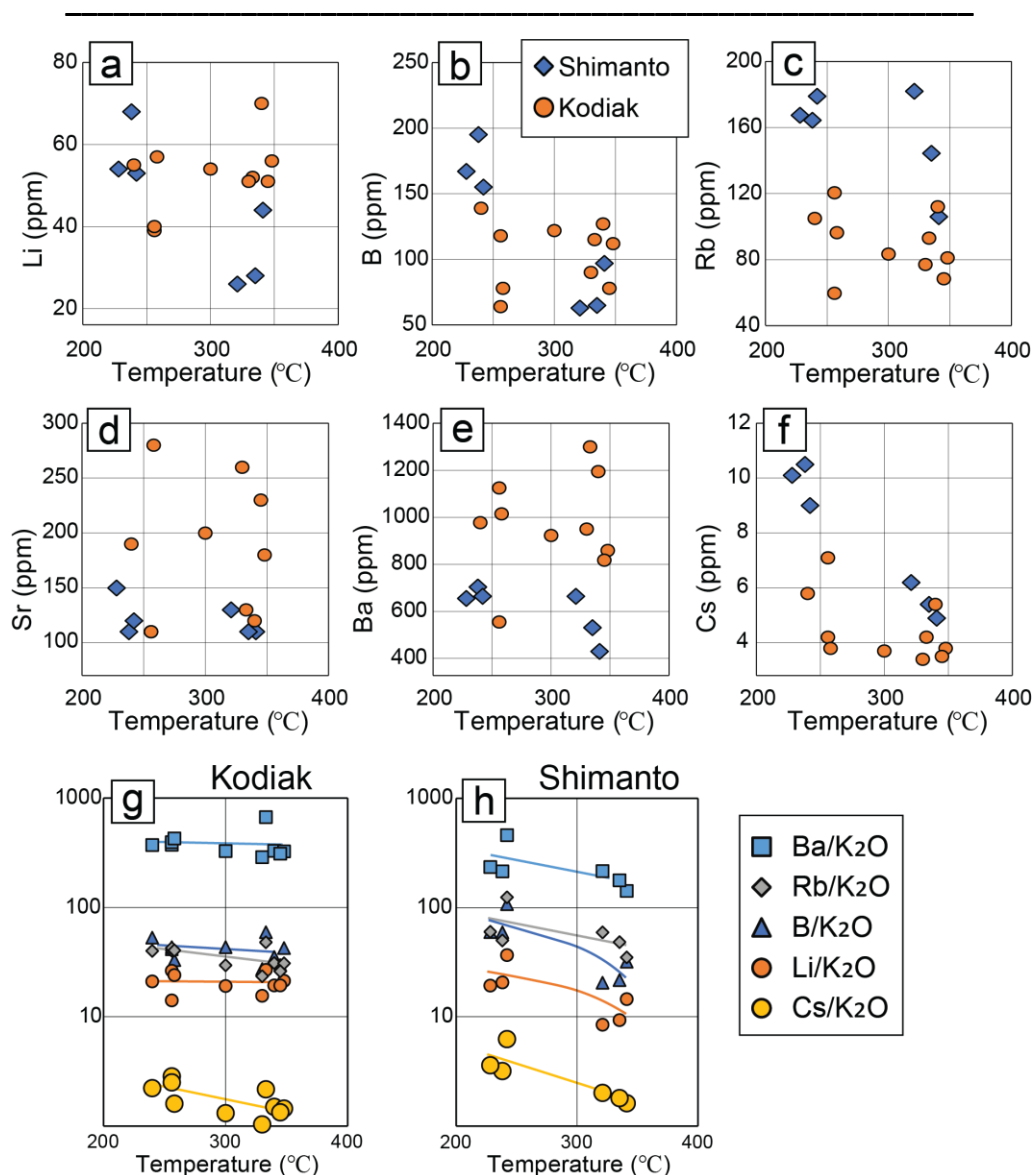


Figure V.2. Whole-rock trace element concentrations in metapelites from the Shimanto belt and the Kodiak accretionary complex as a function of peak-metamorphic temperatures: (a) Li; (b) B; (c) Rb; (d) Sr; (e) Ba; and (f) Cs. Mentioned elements normalized by K₂O and plotted against peak-metamorphic temperatures for (g) the Kodiak complex and (h) the Shimanto belt. All ratios in the Shimanto belt point to significant loss with T-increase, whereas in the Kodiak complex only Cs shows a loss.

V.4.2. Distribution of trace elements among mineral phases

The average FME concentrations and standard deviation of mineral phases in each sample are reported in Table V.3 and concentrations for illite and chlorite are also presented in Fig. V.3. All point analyses are presented in Supplementary Table S5.1.

V.4. Results

Table V.3. The average concentrations and standard deviation of trace elements in chlorite (chl), illite (ill), albite (ab), and calcite (cc) analyzed by LA-ICP-MS.

	#	Phase		Li ppm	B ppm	V ppm	Ni ppm	Cu ppm	Zn ppm	As ppm	Rb ppm	Sr ppm	Nb ppm	Sn ppm	Cs ppm	Ba ppm
Kodiak Landward Belt																
KO17A	34	ill	Av.	71	152	292	58	29	97	25	186	127	8	4	9	1429
			SD	40	79	75	33	16	61	17	50	276	8	2	3	355
	15	ab	Av.	5	21	12	57	11	14	-	21	244	-	-	-	174
			SD	2	14	12	24	8	10	-	18	220	-	-	-	115
KO17E	26	ill	Av.	71	145	298	59	33	101	32	202	100	4	3	8	1628
			SD	43	32	63	45	20	86	24	34	93	4	1	2	271
	6	chl	Av.	192	20	148	139	25	290	7	22	17	1	2	2	62
			SD	50	10	47	44	8	113	4	12	9	1	1	1	16
KO17H	15	cc	Av.	0.15	1.03	-	-	0.38	1.8	0.19	0.04	6244	-	-	-	20.7
			SD	0.07	0.36	-	-	0.28	0.6	0.07	0.02	923	-	-	-	3.5
Kodiak Central Belt																
KO29A	24	ill	Av.	98	208	354	88	45	126	9	307	58	1	6	17	2105
			SD	56	80	59	53	22	113	3	42	18	0	3	3	328
	27	chl	Av.	207	59	151	172	75	343	10	16	6	1	3	2	16
			SD	83	29	59	65	29	143	4	11	3	1	1	1	9
KO33C	24	ill	Av.	70	191	419	74	42	139	7	294	55	2	4	14	2266
			SD	57	33	45	61	55	120	1	39	41	5	2	3	293
	23	chl	Av.	221	18	142	206	29	470	3	1	4	0	1	2	2
			SD	79	13	40	85	23	179	1	1	3	0	0	1	2
KO38	23	ill	Av.	83	185	487	86	22	144	12	275	80	2	3	15	2142
			SD	64	34	56	69	19	111	11	51	23	4	1	3	402
	19	chl	Av.	168	38	201	159	30	308	14	3	8	0	1	4	1
			SD	65	23	54	52	25	103	15	3	6	0	1	2	1
KO32A	13	cc	Av.	0.2	1.4	-	-	0.1	1.3	0.3	0.04	7697	-	-	0.06	3
			SD	0.1	0.7	-	-	0.1	0.7	0.1		1187	-	-	0.03	1
KO32B	14	cc	Av.	0.9	3	-	-	0.3	2	0.3	0.1	8148	-	-	0.1	6
			SD	0.8	2	-	-	0.3	1.8	0.1	0.03	1324	-	-	0.1	2
Hyuga Tectonic Mélange																
HN299A	46	ill	Av.	95	249	220	54	49	87	39	312	109	6	5	16	1084
			SD	61	54	47	41	27	52	25	49	390	9	2	4	211
	47	chl	Av.	234	62	119	79	23	180	13	37	24	3	3	4	46
			SD	85	37	30	29	11	68	7	28	50	4	1	2	23
HN299C	8	ab	Av.	-	54	27	-	24	-	14	38	145	4	2	3	123
			SD	-	5	14	-	11	-	5	23	79	4	1	2	87
	26	ill	Av.	68	242	180	161	318	83	286	305	78	17	5	18	1075
			SD	40	54	39	490	465	102	160	54	79	54	3	5	231
HN65	21	chl	Av.	250	38	81	71	14	233	11	20	14	1	4	5	42
			SD	74	26	19	20	8	75	5	11	7	2	1	2	20
	17	ill	Av.	142	256	225	24	34	53	11	324	82	7	5	21	983
			SD	79	69	42	13	18	25	7	57	59	8	2	7	192
HN285	11	chl	Av.	440	130	100	22	17	45	7	146	12	5	3	7	280
			SD	355	46	27	15	8	33	4	43	6	9	1	2	97
Foliated Morotsuka																
HN145	52	ill	Av.	57	182	222	36	143	120	39	380	35	13	6	17	1336
			SD	22	74	20	17	78	59	26	19	10	20	3	4	104
	4	chl	Av.	78	83	111	110	366	377	21	-	-	3	4	-	-
			SD	38	40	28	52	170	194	14	-	-	4	2	-	-
HN243	29	ill	Av.	50	140	187	72	41	53	9	411	27	1	5	15	1280
			SD	21	65	58	28	23	48	4	106	14	0	2	5	370
	28	chl	Av.	120	67	105	74	52	288	18	8	3	1	3	3	5
			SD	46	18	27	32	27	128	14	5	2	1	1	2	3
HN285	35	ill	Av.	12	107	51	5	4	26	3	410	26	5	5	13	1338
			SD	2	9	20	2	2	4	1	24	10	13	1	2	110
	33	chl	Av.	137	7	80	114	53	511	8	2	3	0	1	1	6

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			<i>SD</i>	21	5	12	26	26	67	9	2	1	0	0	1	2
NOB_23B	15	cc	<i>Av.</i>	0.46	1.6	-	-	0.5	2	0.4	0.3	4744	-	-	0.05	2.8
			<i>SD</i>	0.14	0.8	-	-	0.4	0.5	0.2	0.2	1526	-	-	0.02	1

Lithium. Lithium is mainly hosted in chlorite and illite, and to a lesser extent in quartz from the veins (Raimbourg et al., 2021). In the Shimanto Belt, lithium concentrations in chlorite are 316 ± 41 ppm and 138 ± 21 ppm for samples from HTM and FM, respectively, and in illite are 86 ± 73 ppm and 19 ± 16 ppm for HTM and FM, respectively. In the KLB lithium concentrations in chlorite is 235 ± 18 ppm and in illite is 47 ± 24 ppm. In the KCB, chlorite has lithium a concentration of 245 ± 94 ppm and illite has a lithium concentration of 27 ± 18 ppm. In the Shimanto Belt, the lithium concentration decreases in both chlorite and illite as temperature increases (Fig. V.3; Table V.3). Conversely, in the Kodiak complex chlorite shows retention or even slight enrichment, and illite is characterized by statistically identical concentrations (Fig. V.3). Additionally, quartz from the studied veins shows a significant decrease in lithium concentrations as temperature increases, from <105 ppm in veins from HTM down to <4 ppm in FM, and <27 ppm in KLB down to <6 ppm in KCB. Calcite from veins contains <1 ppm of lithium, with majority of analyses being below detection limit.

Boron. Boron is dominantly carried by illite and to a lesser extent by chlorite and albite. In the Shimanto Belt, boron concentrations in Illite are 258 ± 56 ppm and 148 ± 68 ppm for samples from HTM and FM, respectively. In the Kodiak complex, illite is characterized by boron concentrations of 138 ± 50 ppm and 206 ± 43 ppm for KLB and KCB, respectively. Chlorite in units from the Shimanto Belt have fairly low boron concentrations of 35 ± 27 ppm and 5 ± 3 ppm in HTM and FM, respectively. In the Kodiak complex, chlorite has boron concentrations of 12 ± 5 ppm and 36 ± 31 ppm for KLB and KCB, respectively. Albite from the HTM has boron concentrations of 54 ± 10 ppm, and in KLB of 21 ± 14 ppm. Boron shows similar behavior to lithium in illite and chlorite. In the Shimanto Belt, boron concentrations decrease in both illite and chlorite, whereas in the Kodiak complex boron is retained with similar concentrations between lower- and higher-grade illite and chlorite (Fig. V.3). Calcite in veins contains boron concentrations of up to 15 ppm, with majority of analyses ranging between 0 and 5 ppm.

LILE (Rb, Sr, Cs, and Ba). Major carrier minerals of large ion-lithophile elements are illite and albite. Rubidium concentrations in illite from the Shimanto Belt are 321 ± 49 ppm and 402 ± 35

ppm in HTM and FM, respectively. Illite from the Kodiak complex shows slightly lower concentrations than in the Shimanto Belt and are 190 ± 51 ppm and 317 ± 34 ppm in KLB and KCB, respectively. Illite has strontium concentrations of 60 ± 38 ppm in the HTM, 30 ± 11 ppm in the FM, 85 ± 43 ppm in the KLB, and 69 ± 36 ppm in the KCB. Barium concentrations are generally higher in illite from the Kodiak complex than in illite from the Shimanto Belt. The average barium concentration in illite from HTM is 1095 ± 207 ppm and illite from FM has barium concentrations of 1348 ± 133 ppm. Illite from KLB has barium concentrations of 1525 ± 378 ppm and illite from the KCB has an average barium concentration of 2291 ± 296 ppm. Cesium

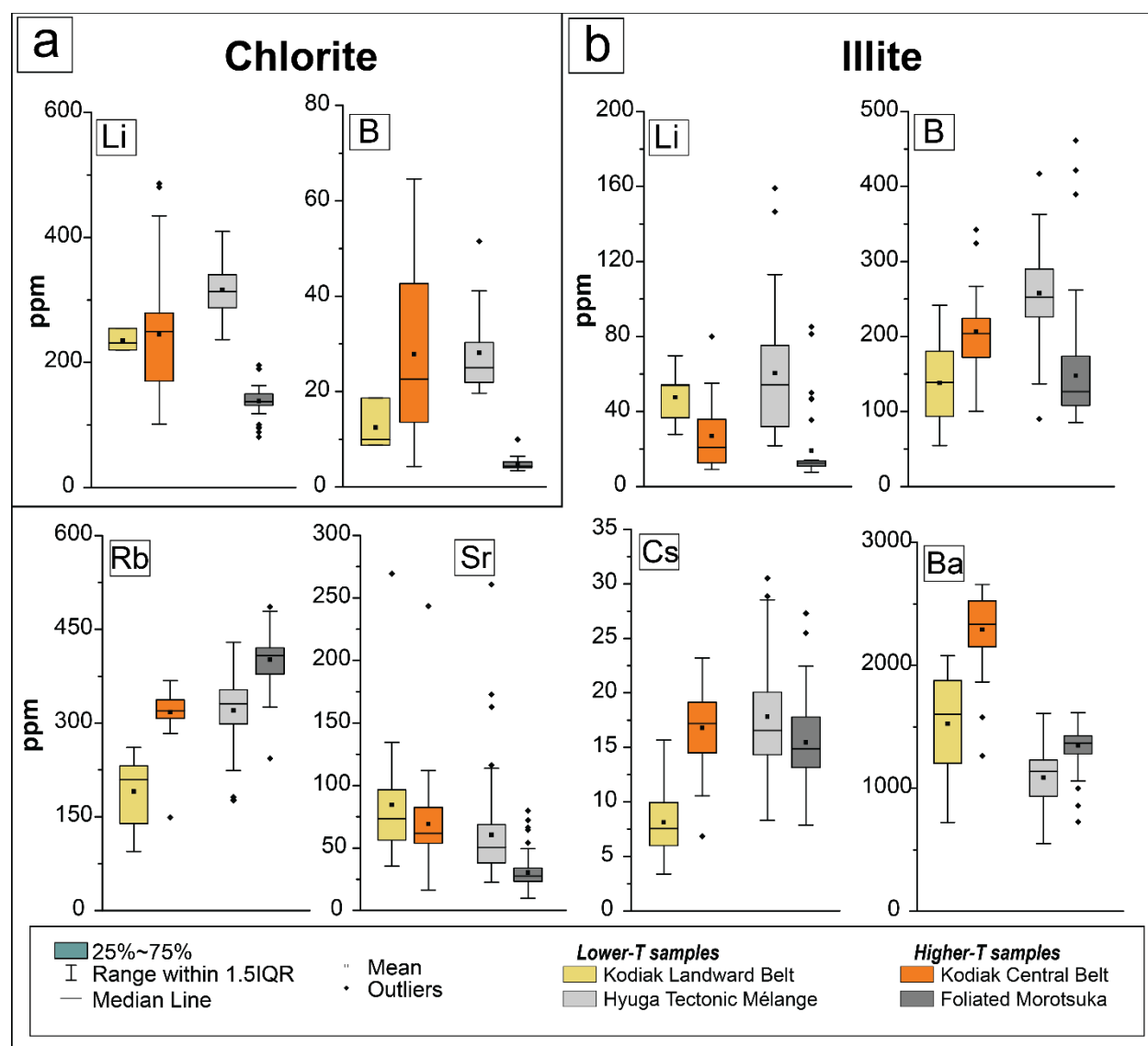


Figure V.3. Box plots of trace element concentrations of (a) chlorite (Li and B) and (b) illite (Li, B, Rb, Sr, Cs and Ba), from the Kodiak accretionary complex and the Shimanto belt, acquired by LA-ICP-MS.

concentrations in illite are 18 ± 5 ppm in samples from HTM, 15 ± 3 ppm from FM, 8 ± 3 ppm from KLB, and 17 ± 3 ppm from KCB. Albite hosts LILE as well, but due to small grain size only analyses on the lower-grade samples were performed. In samples from both HTM and KLB, albite contains low rubidium concentrations of 38 ± 23 ppm and 21 ± 18 ppm for HTM and KLB, respectively. Measured concentrations of strontium are 145 ± 79 ppm in HTM and 244 ± 220 ppm in KLB, whereas barium concentrations are 123 ± 87 ppm in HTM and 174 ± 115 ppm in KLB. The lowest concentrations among LILE are for cesium, which are 3 ± 2 ppm in HTM and <2 ppm in KLB. Calcite from the veins contain no rubidium or cesium. Less than 10% of measurements revealed concentrations above detection limit with concentrations <1 ppm. Barium concentrations in calcite range 1-45 ppm (average 9 ppm), whereas strontium concentrations are the highest in calcite among LILE, ranging 0.16-1.06 wt.%.

V.4.3. Major and trace elements of fluid inclusion populations

A total of 393 LA-ICP-MS spot analyses were performed in FI-rich quartz domains and 208 in FI-poor quartz (Supplementary Table S5.2) in order to determine which elements are hosted within fluid inclusions and which ones are hosted in the quartz crystal lattice.

Estimated concentrations of Be, Ni, Zn, As, Y, Mo, Sn, Sb, W, Pb, and Bi are below or very close to the detection limit without any systematic difference between FI-poor and FI-rich zones. FI-rich zones are characterized by systematically higher concentrations of B, Na, K, Ca, Rb, Sr, Cs, and Ba in comparison to FI-poor zones. An example of which elements are found in the fluid inclusions is presented in form of box plots for FI-rich zones and adjacent FI-poor zones (Fig. V.4). Lithium, aluminum and titanium show no systematic difference between two zones (Fig. V.4), and they are not generally considered for the fluid evolution studies due to inability to detect whether they are located in quartz crystal lattice or in both quartz and FIs.

V.4. Results

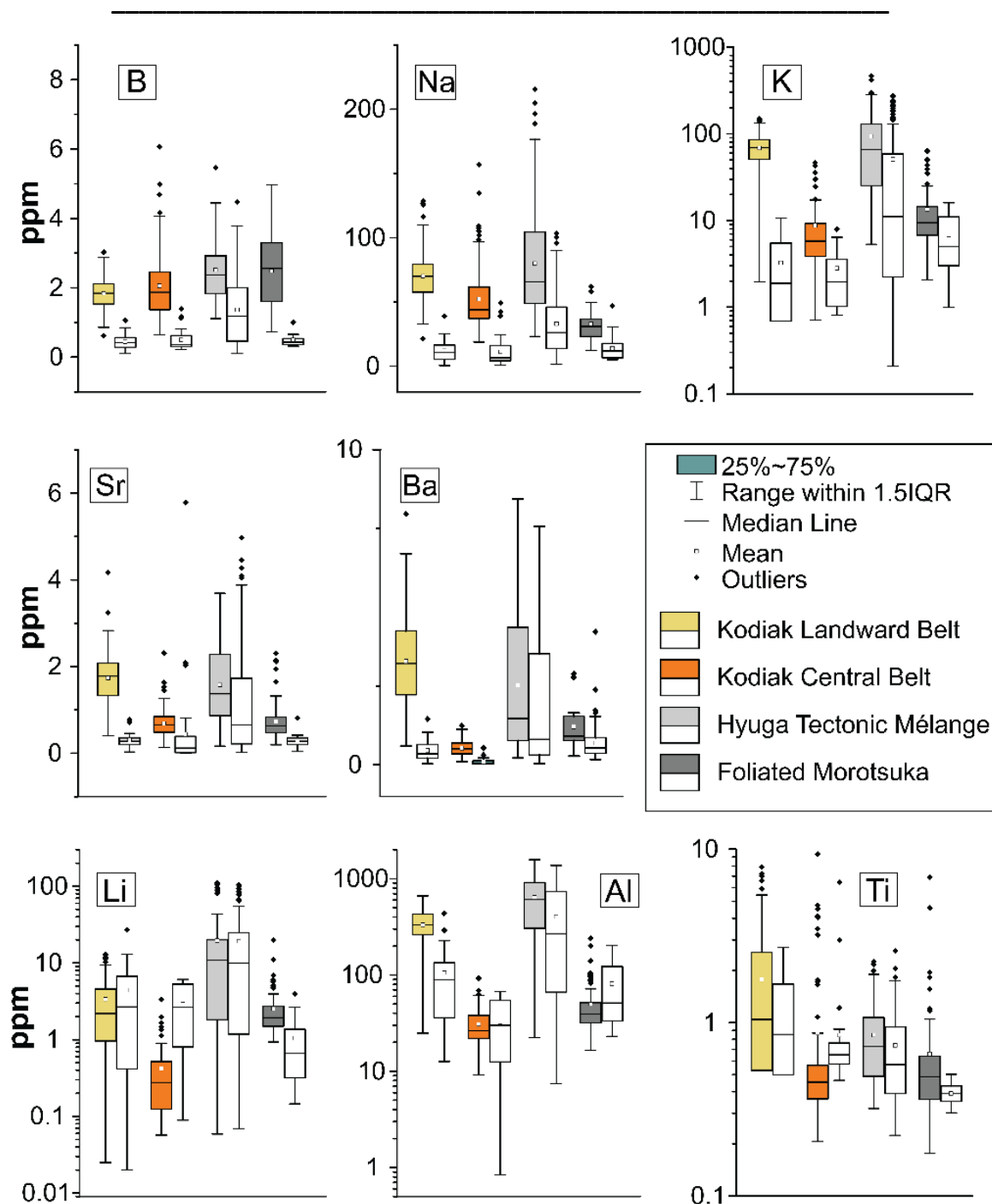


Figure V.4. The concentrations of B, Na, K, Sr, Ba, Li, Al, and Ti in quartz obtained with the LA-ICP-MS. Colored box plots correspond to the FI-rich quartz, whereas adjacent white box plots correspond to the FI-poor quartz. Note that FI-rich quartz is enriched in B, Na, K, Sr and Ba compared to FI-poor, whereas measured concentrations of Li, Ti and Al are fairly equal in both zones.

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Table V.4. Average values and standard deviation of recovered concentrations of major, minor and trace elements in fluid inclusion populations and molar ratios for each studied formation. Hereby, we report only point analyses where Ca was successfully measured.

	B	Na	Mg	K	Ca	Mn	Fe	Rb	Sr	Cs	Ba	B/Na	K/Na	Ca/Na	Rb/Na	Sr/Na	Cs/Na	Ba/Na
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	molal	molal	molal	molal	molal	molal	molal
<i>Kodiak Landward</i>																		
<i>Belt</i>																		
Av.	106	4121	115	5545	1034	-	113	6.0	103	1.0	185	0.07	0.82	0.37	0.0004	0.008	4.09E-05	3.61E-07
SD	29	980	61	1602	1064	-	98	2.9	35	0.5	82	0.01	0.36	1.54	0.0003	0.009	2.08E-05	1.87E-07
Min	8	333	31	657	415	-	17	1.0	46	0.4	28							
Max	204	7039	351	9088	6642	-	386	13.6	193	2.5	355							
#	60	60	60	60	60	-	47	59	60	21	60							
<i>Kodiak Central Belt</i>																		
Av.	232	6060	205	1206	4543	25	170	3.3	81	2.6	61	0.11	0.15	0.57	0.0002	0.005	8.32E-05	8.04E-08
SD	101	1963	223	800	1707	21	125	1.6	34	0.9	29	0.04	0.12	0.51	0.0003	0.009	4.57E-05	4.31E-08
Min	63	1565	16	270	1800	5	58	1.1	12	0.5	11							
Max	493	9346	941	3556	9229	89	427	6.7	177	3.9	134							
#	32	32	32	32	32	26	17	25	32	30	32							
<i>Hyuga Tectonic Mélange</i>																		
Av.	115	2790	123	5629	1555	6	162	12.7	74	2.0	120	0.09	1.16	0.32	0.0012	0.006	1.16E-04	2.83E-07
SD	53	788	98	3044	913	4	97	8.1	43	1.1	86	0.04	1.00	0.17	0.0013	0.004	7.84E-05	2.67E-07
Min	34	1606	5	240	358	1	38	0.4	16	0.4	8							
Max	276	5559	399	10259	4000	21	413	31.1	213	5.1	344							
#	36	36	36	36	36	34	27	36	36	36	36							
<i>Foliated Morotsuka</i>																		
Av.	273	3792	200	2196	6028	230	325	6.5	101	4.6	233	0.19	0.72	1.09	0.0011	0.007	0.0003	5.32E-07
SD	192	2074	244	2137	2494	355	374	7.4	56	3.1	428	0.08	2.86	1.99	0.0048	0.004	0.0002	8.60E-07
Min	4	47	10	13	978	2	64	0.0	18	0.1	1							
Max	865	9678	1241	10648	10784	1962	1519	38.9	383	11.9	1810							
#	62	62	62	62	62	61	40	61	62	62	62							

For elements present in the FIs, element ratios are in the range of: Ca/Na - 0.06 to 13.23; B/Na - 0.02 to 0.57; K/Na - 0.01 to 5.69; Rb/Na - 2.2×10^{-5} to 0.05; Sr/Na - 0.0005 to 0.09; Ba/Na - 1.1×10^{-8} to 5.3×10^{-6} ; and Cs/Na - 1.2×10^{-5} to 0.002 (Table V.4). Based on element ratios, semi-quantification of FI chemical composition by using a charge-balance approach was performed only in analyses where calcium, sodium and potassium were determined (Table V.4; Fig. V.5). Sodium, calcium and potassium are major elements in fluid inclusions. Their concentrations have a large range: Na – 333 to 9678 ppm; Ca – 358 to 10784 ppm; and K – 13 to 10648 ppm (Table V.4;

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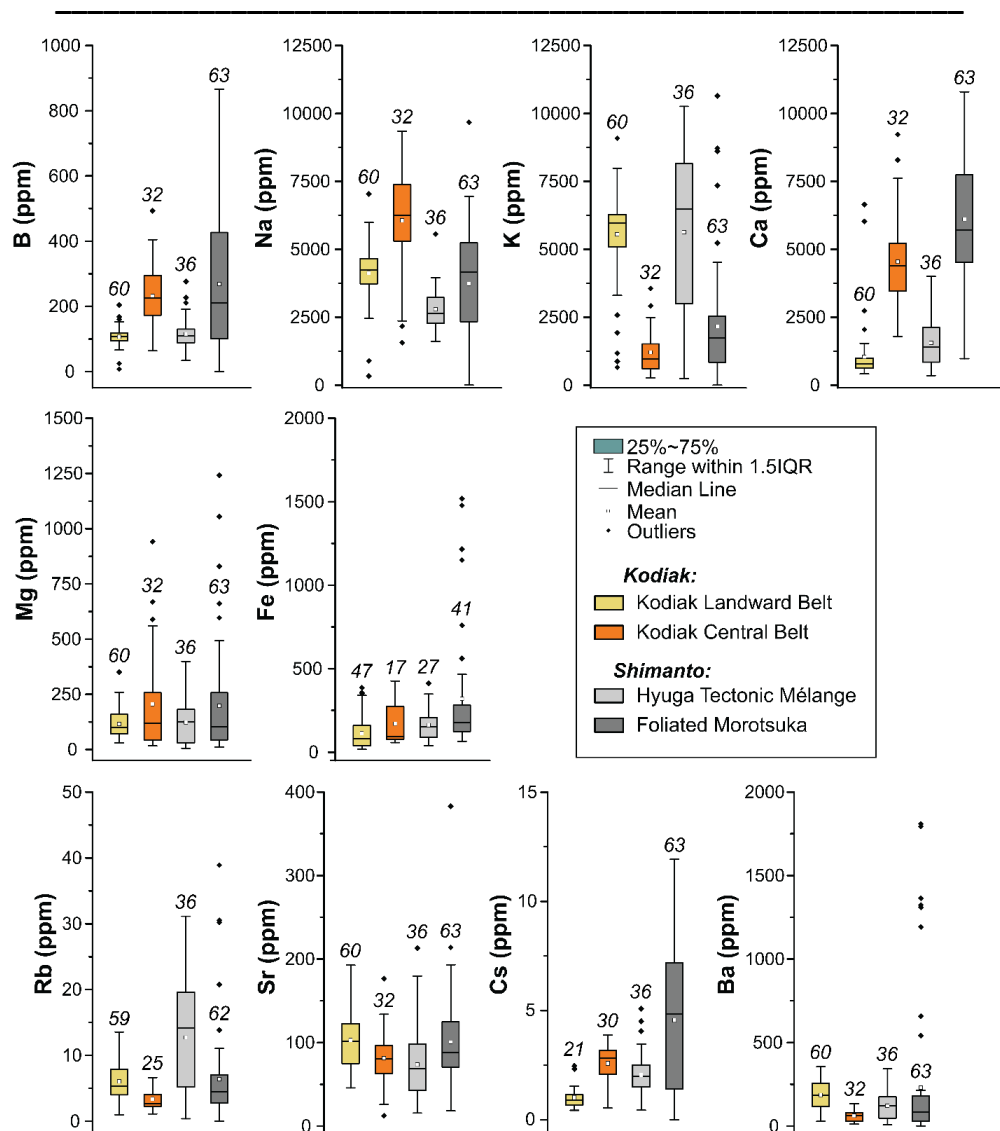


Figure V.5. Box plots of recovered concentrations for B, Rb, Sr, Cs, Ba, Na, and K based on charge balance with the average salinity.

Fig. V.5). Potassium is the predominant cation in fluid inclusions of lower-grade veins, and Ca and Na have higher concentrations in fluid inclusions of higher-grade veins. Magnesium and iron are minor elements with ranges of 10 to 1241 ppm and 17 to 1519 ppm, respectively, with noticeably higher concentrations in higher-grade FIs (Fig. V.5). The ranges of trace elements are: B – 4 to 865 ppm; Rb - 0.4 to 39 ppm; Sr – 12 to 383 ppm; Cs - 0.1 to 11.9 ppm; and Ba – 1 to 1810 ppm. Trace elements show a narrower range than major cations across examined veins for each unit (Fig. V.5).

V.5. Discussion

V.5.1. Fluid-mobile elements redistribution in the solid matrix upon metamorphism

V.5.1.1. Fluid element budget in the solid matrix

Although no significant changes in the whole-rock major element composition have been reported among the studied samples (Rajič et al., 2023), some of the FME concentrations vary as a function of temperature (Fig. V.2). In samples from the Kodiak complex, excluding the partial loss of cesium, all other FME are retained and the concentrations in higher-grade and the lower-grade samples are similar. Conversely, in the Shimanto Belt, FME show significant and systematic loss as temperature increases (Fig. V.2). The opposite trends between the Kodiak complex and the Shimanto Belt can be expressed by devolatilization indicators that have been extensively applied to other metasedimentary units (e.g., Bebout, 1995, 2013), such as Rb/Cs or B/Li. Both Rb/Cs or B/Li systematically decrease in the Shimanto Belt, whereas more scattered values are observed for samples from the Kodiak complex (Fig. V.6; Table V.2). The two opposing trends for FME budget can be accounted for by (i) changes in FME concentrations in the major minerals in the pelitic matrix, and (ii) mineral reactions and changes in phase proportions as a function of temperature.

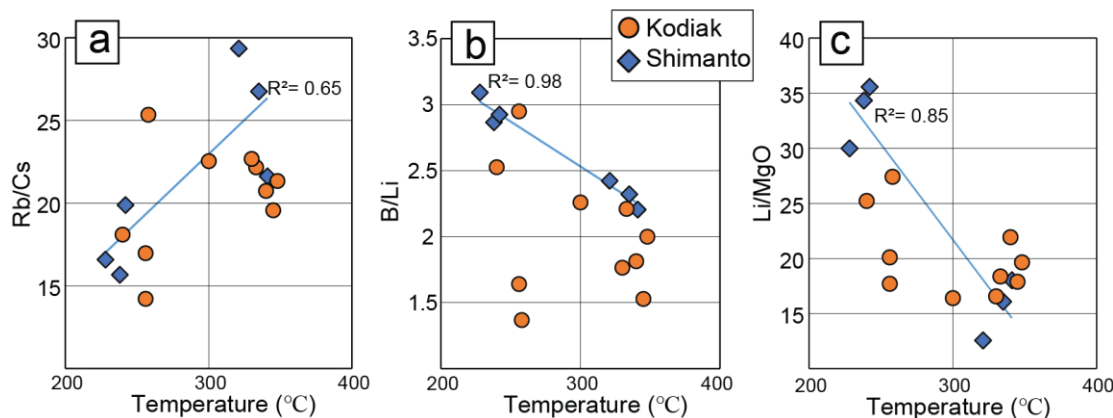


Figure V.6. (a) Rb/Cs, (b) B/Li and (c) Li/MgO ratios of metapelites from the Kodiak complex and the Shimanto belt, plotted against peak-metamorphic temperatures. These ratios are pointing to systematic devolatilization in the Shimanto belt and loss of cesium and boron, whereas in the Kodiak complex no systematic trend is obvious.

As noted by several studies, the FME budget in subducted lithologies is highly controlled by the abundance of phyllosilicates and their reactions during burial (e.g., Barnes et al., 2019a; Bebout et al., 1999, 2007, 2013; Busigny et al., 2003; Marschall et al., 2006). In the samples we have examined, the main FME carriers are illite (boron, rubidium, barium, cesium $\pm$ lithium, strontium) and chlorite (lithium $\pm$ boron), with lower concentrations of LILE in albite (strontium $\pm$ rubidium,

barium; Table V.3; Fig. V.7). Upon burial and P and T increase, these minerals present in the pelitic matrix are affected by three main mineral reactions that affect their composition and/or abundance: illite recrystallization, illite-to-chlorite transformation and the dissolution of albite (Rajič et al., 2023).

To examine the effects of these mineralogical reactions on FME budget, we performed mass balance calculations using the modal proportions of major minerals (XRD results; Rajič et al., 2023) and the FME concentrations of each major mineral (Fig. V.7). The calculated concentrations of lithium, rubidium, cesium, and barium are in fairly good agreement (within ~20% difference) with whole-rock concentrations. In contrast, for boron and strontium, the calculated concentrations are systematically underestimated for most of samples (from ~25% to ~50% and from ~35% to ~75%, for B and Sr, respectively, see Fig. V.7). The following discussion is therefore restricted to the elements for which the budget can be consistently estimated (i.e. Li, Rb, Cs and Ba), while the case of B and Sr is analyzed in V.1.2.

In the Kodiak complex, lithium concentration in chlorite, the main Li carrier, remains statistically identical as temperature increases (Fig. V.3). Therefore, in spite of minor modal variations due to illite-to-chlorite reactions, the whole-rock stock of Li remains constant upon T increase (Fig. V.2). In contrast, in the Shimanto Belt, both illite and chlorite show significant loss of lithium as temperature increases (Fig. V.3), which result in the whole-rock decrease in Li upon T increase (Fig. V.2).

In both localities, rubidium and barium show an increase in illite with increasing temperature (Fig. V.3). This is consistent with the illite-to-chlorite transformation, which results in the redistribution of rubidium and barium, whereby the elements are released from the illite fraction consumed to form chlorite and stored in the recrystallized illite. As a result, there is limited whole-rock variations in Ba and Rb concentrations upon T increase.

Finally, cesium shows contrasted behavior between the two geological examples. In Kodiak, similarly to Rb and Ba, cesium is redistributed within the illite fraction and the whole rock stock remains constant through T increase. In the Shimanto Belt example, illite concentrations remain constant, but the decrease in illite fraction led to whole rock decrease (Fig. V.2; Fig. V.3).

In summary, in most cases (all elements for Kodiak, Rb and Ba for the Shimanto Belt), elements are redistributed between mineral phases upon T increase, without affecting the whole rock stock. Contrarily to this, Li and Cs are leached out of the rock in the Shimanto Belt example, as a result of a decreasing concentration in (Li) or decreasing abundance of the main host mineral (Cs).

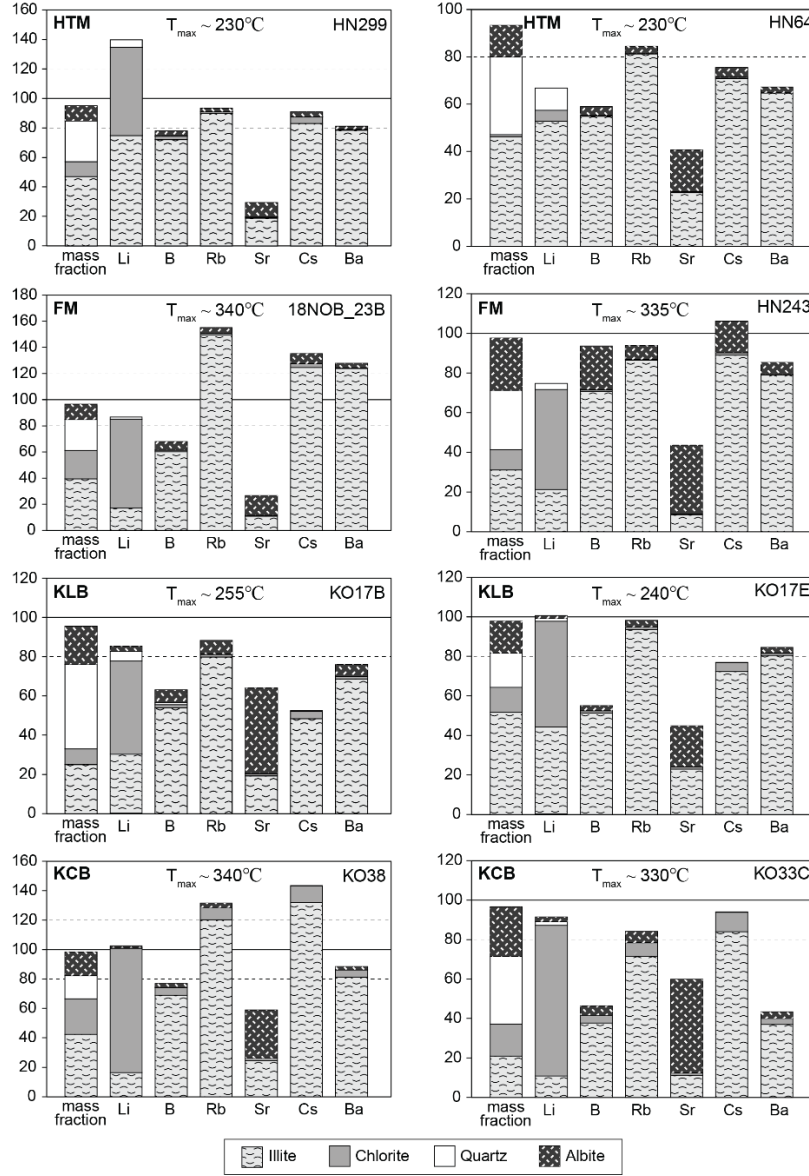


Figure V.7. Modal proportion of mineral phases and distribution of Li, B, Rb, Sr, Cs, and Ba among major mineral phases. The mass balance calculations of Li, B, Rb, Sr, Cs, and Ba were calculated from their concentrations in the major mineral phases (illite, chlorite, albite, and quartz) combined with XRD results (Rajič et al., 2023) and normalized to 100% of whole-rock concentrations. An example of mass balance calculation normalized to whole-rock concentrations is provided for lithium by the following equation: $c_{Li}^{mass\ balance} / c_{Li}^{rock} = \frac{\sum (x_i^{rock} \times c_{Li}^i)}{c_{Li}^{rock}}$, for measured lithium concentrations (c_{Li}^i) of the mineral phase (i) and its modal proportion (x). Dashed lines represent 20% variations from the whole-rock concentrations.

Consistent with the results of this study, Ramirez et al. (2021) described a similar depletion of FME in scaly fabrics in metapelites of tectonic mélanges from the Shimanto Belt and proposed that elements are remobilized by diffusion along grain boundaries into low, effective normal stress sites and incorporated into vein-forming minerals. However, vein-forming minerals (quartz and calcite) are small reservoirs for most FME, except for the limited incorporation of lithium in quartz (Raimbourg et al., 2021) or strontium in calcite. Therefore, for most FME the whole-rock depletion implies that these elements are transferred into a fluid phase and leached out of the rock.

V.5.1.2. Additional reservoirs for Sr and B

The mass balance calculations for strontium and boron are inconsistent with the whole-rock concentrations (Fig. V.7). Strontium behaves similarly to calcium, and the presence of calcium-bearing phases (which may incorporate large amounts of strontium) can highly influence the strontium budget. In the examined samples, calcite is observed in the host rock as a minor phase. However, due to its very small grain size, FME concentrations of calcite in the pelitic matrix were not obtained and not considered in the mass balance calculations (Fig. V.7). The modal fractions of calcite in the pelitic matrix range from ~0.5 to ~1.5% (Rajič et al., 2023). If calcite in the pelitic matrix has similar strontium concentrations to the vein calcite (Table V.3), it may contain 50-150 ppm of strontium, which resolves the strontium underestimation in mass balance calculations (Fig. V.7). Larger calcite crystals are observed in the veins (Rajič et al., 2023) and have strontium concentrations of up to 1 wt% (Table V.3). Thus, we propose that strontium was remobilized by the fluid into dilatation sites, where it is stored in newly precipitated calcite. The incorporation of strontium into vein-forming minerals was previously proposed for quartz-calcite-albite veins in tectonic mélanges of the Shimanto Belt (Ramirez et al., 2021).

Regarding the discrepancy in boron, several possibilities can be raised, such as boron being stored in organic material (Williams, Hervig, Wieser, et al., 2001) or the grain size of illite (N. Clauer et al., 2014; Norbert Clauer et al., 2018). First, although kerogen may contain significant boron (Williams, Hervig, Wieser, et al., 2001), the amount of carbonaceous material in metapelites is estimated to be ~0.5 wt% (Raimbourg, Thiéry, et al., 2017), i.e. it is a second-order reservoir. Second, Clauer et al. (2018) pointed out that the illitization progressed via dissolution-reprecipitation rather than by the solid-state substitution. As a consequence, newly precipitated

illite is characterized by larger grain size and lower boron concentrations than the older, smaller grains (N. Clauer et al., 2014; Norbert Clauer et al., 2018). During this study, only sufficiently large grains were analyzed by LA-ICP-MS (e.g., larger illite in the contact with the shear band shown in Fig. IV.4c) and the FME concentration of smaller illite in the pelitic matrix was not measured. Therefore, the underestimation of B content from individual mineral analyses (Fig. V.7) could be explained by the grain size dependence of B concentration in illite.

In spite of the discrepancy discussed above in the boron budget, the same general trend as Li can be observed. In the case of Kodiak, there is a slight increase in illite concentration in boron upon T increase. This increase, combined with the transformation of some illite into chlorite, is consistent with the redistribution of B within the remaining illite population, and a constant whole rock concentration. In contrast, both illite concentration in B (Fig. V.3) and illite abundance decrease upon T increase in the Shimanto case, resulting consistently with a decrease in whole-rock concentration in B. Therefore, unlike the close-system behavior observed for Kodiak, the high-T endmember in the Shimanto Belt was leached out by a circulating fluid.

V.5.2. Fluid-rock interaction

V.5.2.1. Chemical evolution of the fluid and fluid-rock interaction

To our knowledge, studies examining the chemical composition of FIs in subducted sediments that experienced peak-temperatures of 230-350°C are limited. The closest example are higher-grade metasedimentary and metamafic units from the Sambagawa Belt, Japan, where crush-leach technique was applied to syn-metamorphic quartz veins (Yoshida et al., 2015). Their results, in regards to element ratios, such as K/Na, Ca/Na, and B/Na, are consistent with those reported here (Fig. V.8). Another example are fissure veins from the Central Alps, which have experienced subgreenschist to amphibolite facies metamorphism (Rauchenstein-Martinek et al., 2016), wherein the chemical compositions of individual FIs were measured by LA-ICP-MS (Fig. V.8). The absolute concentrations of major elements (sodium, potassium, and calcium) and trace elements (boron, rubidium, strontium, cesium, and barium) are also in agreement with our results (Rauchenstein-Martinek et al., 2016; Table V.4). Similarities in the determined fluid compositions of the two previous studies (Rauchenstein-Martinek et al., 2016; Yoshida et al., 2015) and the

results from this study validate the approach of LA-ICP-MS bulk microanalysis of FI populations applied in this study (Fig. V.8).

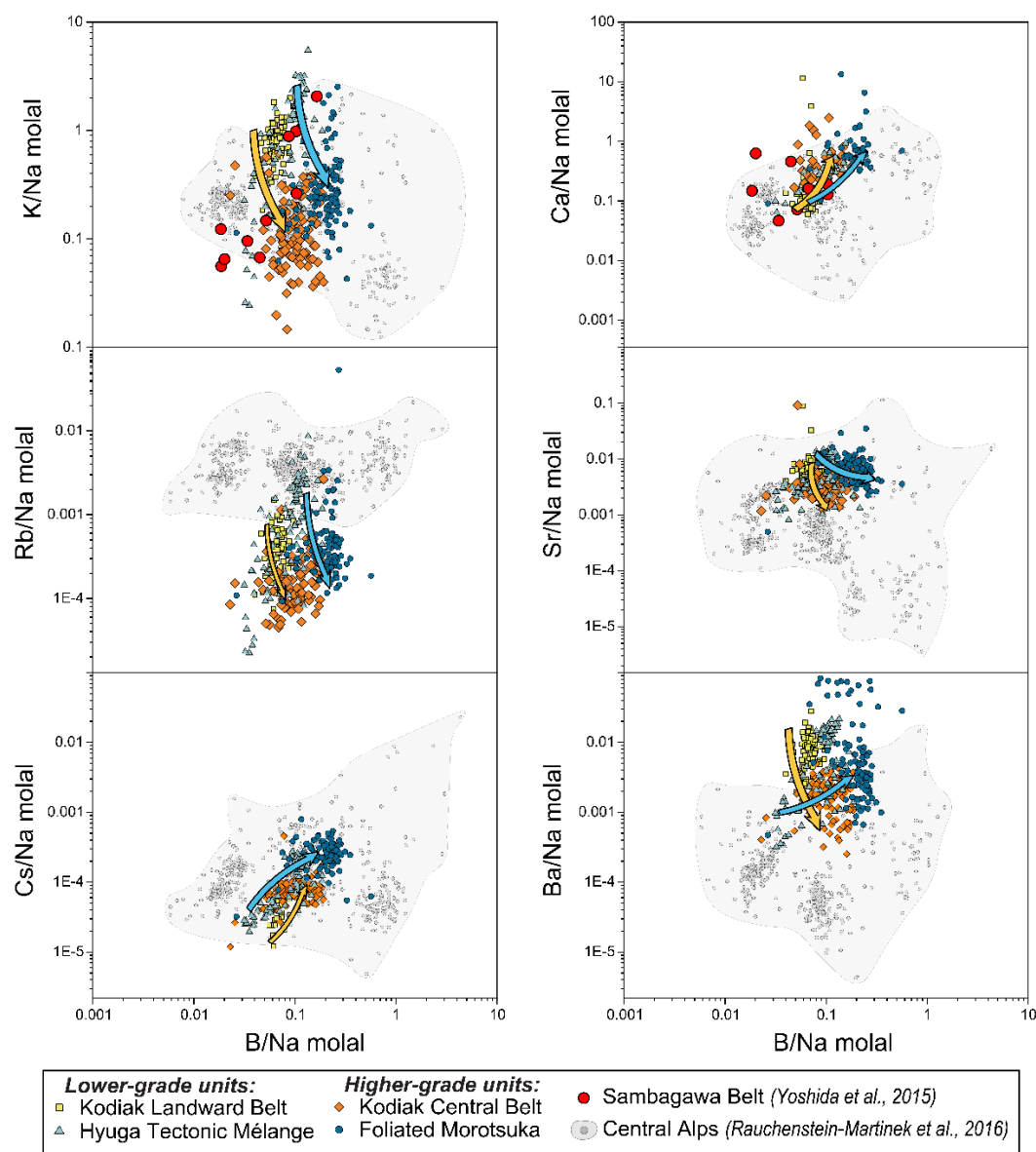


Figure V.8. Ca/Na, K/Na, Rb/Na, Sr/Na, Cs/Na, and Ba/Na molal ratios plotted against B/Na molal ratio of fluid inclusions, for each of studied formation. Arrows on the binary plots (orange – Kodiak; blue – Shimanto) represent the evolution of chemical composition as temperature rises. Gray areas represent fluid composition in units from the Central Alps determined by LA-ICP-MS on individual fluid inclusions (Rauchenstein-Martinek et al., 2016), whereas red points represent the chemical composition of fluid inclusions from the Sambagawa Belt determined by applying crush-leach technique (Yoshida et al., 2015).

Bulk-microanalysis of FI populations revealed high variations in the major elements (sodium, potassium, and calcium) composition of the fluid (Fig. V.4; Fig. V.5). Similar results were derived by using a decrepitation method for the same FIs, wherein the proportion of sodium, potassium

and calcium is highly variable and the majority of the analyzed evaporite mounds contained calcium as a major cation (Rajič et al., 2023). However, within a given geological unit, veins have similar chemical composition (Table V.4; Fig. V.8)

V.5.2.2. Water-rock ratio

In order to explain the chemical evolution of pore fluids from 250°C to 330°C, the proportion of the solid and the fluid reservoirs needs to be considered. The porosity of metapelitic rocks at the corresponding depths is expected to be up to 5 vol% (Bray & Karig, 1985; Neuzil, 1994; Tsuji et al., 2006), meaning that the mass of pore fluid (for a fluid density of ~0.7 g/cm³) may be 30-330 times smaller than that of the solid in given mass of a rock (Fig. V.9a). Thus, if the system is closed, minor changes in the FME concentrations of the solid caused by interaction with a fluid should have significant changes on the fluid composition. This may be the case in the Kodiak complex, where no loss of FME is observed from the solid with increasing temperature (Fig. V.2), whereas FIs record an enrichment, especially in boron and cesium (Fig. V.5). In order to calculate the extent to which FME need to be leached out of the solid to cause the measured enrichment in the fluid, mass balance calculations were performed. Because the system is conservative and only mass exchange between the solid and fluid is considered, the change in the mass of an element in the solid and the fluid can be defined as

$$\left| \frac{m_i^{F,f} - m_i^{F,0}}{m_i^{S,f} - m_i^{S,0}} \right| = 1 \quad (eq. 2)$$

where $m_i^{F,f}$ is the mass of element i in the final fluid, $m_i^{F,0}$ is the mass of element i in the initial fluid, $m_i^{S,f}$ is the mass of element i in the final solid, and $m_i^{S,0}$ is the mass of element i in the initial solid, where final and initial state refer to higher and lower temperature conditions of the present study, respectively. For both the solid and the fluid, the mass of element i can be expressed as a concentration by

$$m_{Total}^j \cdot c_i^j = m_i^j \quad (eq. 3)$$

where m_{Total}^j the total mass of phase j (fluid or solid), c_i^j is the mass of element i in phase j , and m_i^j is the mass of element i in phase j . Assuming that the total mass of the fluid and solid remains approximately constant at both final and initial stages, a valid approximation in conservative systems when considering trace elements, the concentrations of element i in the solid and the fluid can be expressed as

$$\left| \frac{(c_i^{F,f} - c_i^{F,0})m_{Total}^F}{(c_i^{S,f} - c_i^{S,0})m_{Total}^S} \right| = 1 \quad (eq. 4).$$

Finally, the concentrations of element i in the solid and the fluid are then related to the mass solid/fluid ratio with the following equation:

$$\left| \frac{(c_i^{F,f} - c_i^{F,0})}{(c_i^{S,f} - c_i^{S,0})} \right| = \frac{m_{Total}^S}{m_{Total}^F} \quad (eq. 5).$$

Kodiak Complex: Combining the theoretical mass solid/fluid ratios with measured concentrations of element i in the initial solid ($c_i^{S,0}$), initial fluid ($c_i^{F,0}$) and final fluid ($c_i^{F,f}$), concentrations in the final solid ($c_i^{S,f}$) can be calculated. In order to cause an enrichment in boron concentrations in the fluid (from ~110 ppm to 230-700 ppm; Table V.3), the required decrease in boron concentrations in the solid is from ~100 ppm down to ~91 ppm (Fig. V.9b) assuming a porosity of 1-5 vol%, which represents a <10% decrease. For cesium, in order to increase concentrations in the fluid from ~1 ppm to 2.6-7 ppm, the corresponding decrease in the cesium concentration in the solid is from 5.2 ppm down to 5.1 ppm (Fig. V.9c), hence less than 2%. Therefore, because of the small volume of the pore fluid reservoir (compared to the solid matrix), the concentration of FME is much more sensitive to rock/fluid exchanges than the solid matrix. Accordingly, in the case of Kodiak, a significant increase in the FME concentration in the fluid is observed with increasing temperature, whereas the FME concentration of solid matrix is relatively constant.

Shimanto Belt: Conversely, in the Japanese case study, significantly higher amounts of FME are released from the solid (e.g., Fig. V.9c-d). It is expected that the fluid will be drastically enriched in all released elements, however, the enrichment is on the same order as the fluids from the Kodiak complex (Fig. V.5). Thus, another mechanism should be considered, such as the percolation of externally derived fluids, which are responsible for leaching of FME out of the solid. In order to

calculate the required mass of fluid to leach FME from the solid, the mass solid/fluid ratio is calculated following the equation (5). Calculated solid/fluid ratios in the Shimanto Belt range from 0.29 to 0.97, 0.28 to 1.17, and 0.49 to 1.69 for boron, cesium, and barium, respectively (Fig. V.9f).

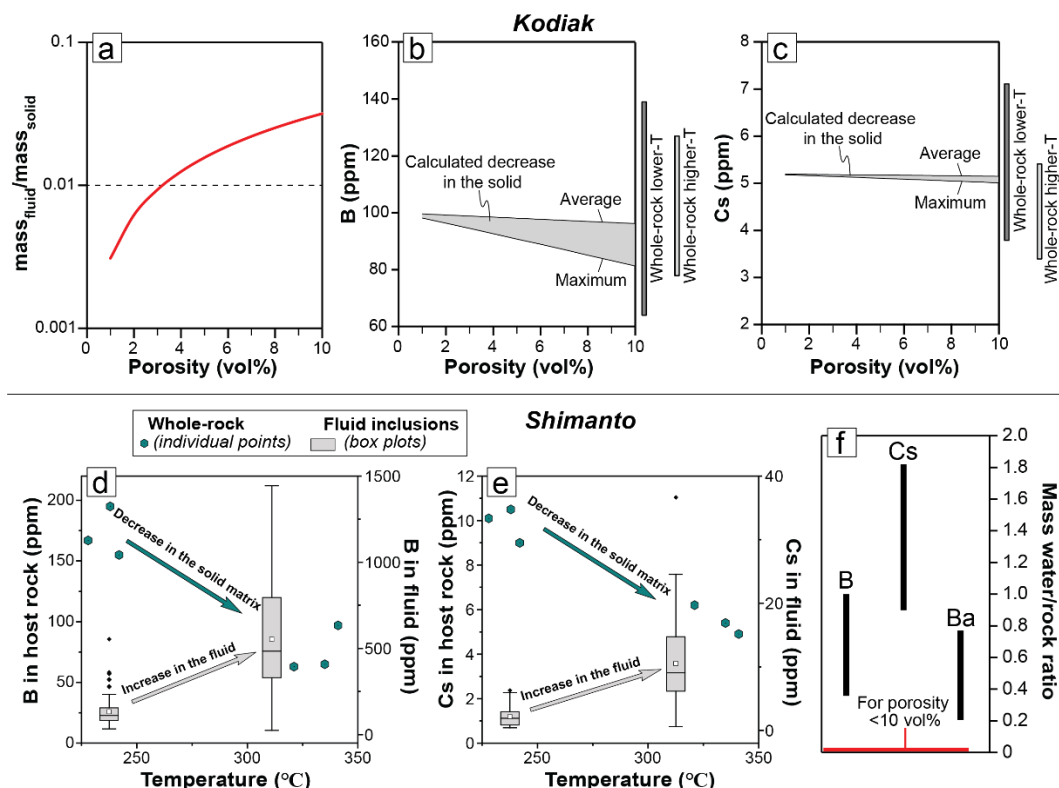


Figure V.9. (a) The mass fluid/rock ratio as a function of the porosity, showing that the fluid reservoir is significantly lower than the solid. Calculations of required decrease in concentrations of (c) B and (d) Cs from the rock in the Kodiak complex, in order to create the measured enrichment of B and Cs in the pore fluid. Adjacent box plots represent the range of measured whole-rock concentrations of boron and cesium in lower- and higher-temperature samples. The mass solid/fluid ratio for (a) boron and (b) cesium as a function of porosity in the Kodiak complex. The red line represents the general solid/fluid ratio as a function of porosity. (d) Boron and (e) cesium concentrations decrease at whole-rock scale (primary y-axis) as a function of temperature in the Shimanto Belt, whereas the fluid shows an enrichment (secondary y-axis). (f) Mass loss/gain ratio vs mass water-rock ratio for boron, cesium, and barium, indicated loss in the host rock and an enrichment in the fluid. Red area represents water-rock ratio to the actual porosity.

V.5.3. Closed vs. open system

Derived mass water-rock ratios in the Foliated Morotsuka (Shimanto Belt) are ~17 to ~105 times higher than expected for if the system was closed and characterized by porosity of lower than 5 vol% (for the porosity < 5 vol%, the water-rock ratio is < 0.016; Fig. V.9g). This implies that a large flux of water percolated through the rocks and leached the elements out of the minerals. Two factors can be invoked to explain why fluid percolation was present at Shimanto Belt and was not

observed at Kodiak. The first is the large amount of strain the rocks experienced in the Foliated Morotsuka (Raimbourg et al. 2014), wherein the pervasive network of shear zones greatly enhanced rock permeability (Cox, 2002, 2010; Wibberley & Shimamoto, 2003). The second is the proximity of large-scale fault zones, which may have acted as pathways for deeper and overpressurized fluid to drive water-rock interactions (Faulkner et al., 2003, 2010; Clement Herviou & Bonnet, 2023; Saffer & Tobin, 2011). The Foliated Morotsuka is located in the hanging wall of a large-scale fault zone, the Nobeoka Tectonic Line (Kondo et al., 2005), which may have promoted percolation of external fluid through these rocks. For these reasons, we propose that high water-rock ratios in the Foliated Morotsuka are the result of fluid flow from deeper levels, which was focused on the structural horizon where strain is the highest. Similar observations have been reported for the Glarus Thrust in the Eastern Helvetic Alps based on stable isotopes studies (Abart et al., 2002; Badertscher et al., 2002; Burkhard et al., 1992; Burkhard & Kerrich, 1988; Hürzeler & Abart, 2008).

In the case of the Kodiak Central Belt, textural evidence around crack-seal veins is consistent with local migration of SiO_2 due to pore-fluid diffusion of SiO_2 from the pelitic matrix (Fisher & Brantley, 1992; Rajič et al., 2023) and there is a lack of evidence to support long-distance transport (Brantley & Fisher, 1997; Fisher et al., 1995). In contrast to the Foliated Morotsuka, the Kodiak Central Belt is located in the central part of large turbiditic sequence far from any recognized large-scale faults (Fig. 1). Thus, we propose that the contrasting behavior between the closed system (with respect to FME) observed in the Alaskan terranes and the open system observed in the Japanese terranes is the result of their internal strain and their proximity to large-scale faults, which concentrated the fluid flow (Fig. V.10).

Thus, in the Kodiak complex, trace elements behaved as similar matter to major elements (Rajič et al., 2023): The system was open on a cm-scale, where FME were transported from the pelitic matrix towards the vein and the newly formed minerals (illite and chlorite) in contact with the vein (Fig. V.10). Conversely, there is a discrepancy between the behaviour of major and trace elements during prograde metamorphism in the Shimanto Belt. No systematic changes have been reported for major elements in HTM and FM, which indicates a closed system (Rajič et al., 2023). However, fluid-mobile elements examined during this study show systematic decrease as temperature increases, requiring high mass water-rock ratio to leach these elements out of the rocks. This study

further demonstrates that “classical” FME (Li, B, and LILE) are more sensitive to the fluid circulation than major elements.

V.6. Conclusion

This study provides an insight into the behaviour of fluid-mobile elements by examining whole-rock concentrations, concentrations in individual minerals, and fluid inclusions from syn-subduction veins in the Kodiak complex, Alaska, and the Shimanto Belt, Japan. The Kodiak complex exhibits closed system behavior and retention of all FME, except for limited loss of cesium at temperatures between ~230 and ~350°C. This retention reflects the redistribution of the FME between major mineral phases in the pelitic matrix. The Shimanto Belt exhibits open system behaviour and significant loss is observed for all FME at temperatures between ~230°C and ~350°C, except for barium and rubidium for which the variations are much more limited. In the Shimanto Belt strontium is transferred to calcite in the veins, whereas there is leaching of lithium, boron, cesium, and some barium into the fluid.

The fluid inclusions hosted in quartz in metasedimentary rocks that experienced temperatures 230-350°C from two localities show identical trends of evolution with temperature, such as increase in boron and cesium. In the Kodiak complex, the enrichment in boron and cesium in the fluid from ~230°C to ~350°C is consistent with a very small loss of boron and cesium from the solid, below that which can be detected by whole-rock analysis. In the Shimanto Belt, the loss between the low- and high-temperature rocks is significant, which is consistent with leaching of the solid by a percolating fluid and water-rock ratios ranging between 0.3 and 1.7. These high water-rock ratios are at least one order of magnitude larger than the *in situ* pore fluid. The difference between the closed (Kodiak) and open (Shimanto) system behavior is attributed to the variation in the amount of internal strain (controlling permeability) and the distance to large-scale faults (draining fluids).

Bulk microanalysis of fluid inclusion populations from metasediments in Kodiak complex and the Shimanto Belt show that these fluids have FME concentrations that are at least an order of magnitude higher than that of interstitial pore fluid in shallow sediments or seawater. Similarities in composition between FI trapped in metasediments and mud volcanoes or springs in subduction zone forearcs are consistent with the contribution of fluids being expelled from sedimentary units

V.6. Conclusion

forming the seismogenic plate interface along permeable zones through the subduction zone forearc.

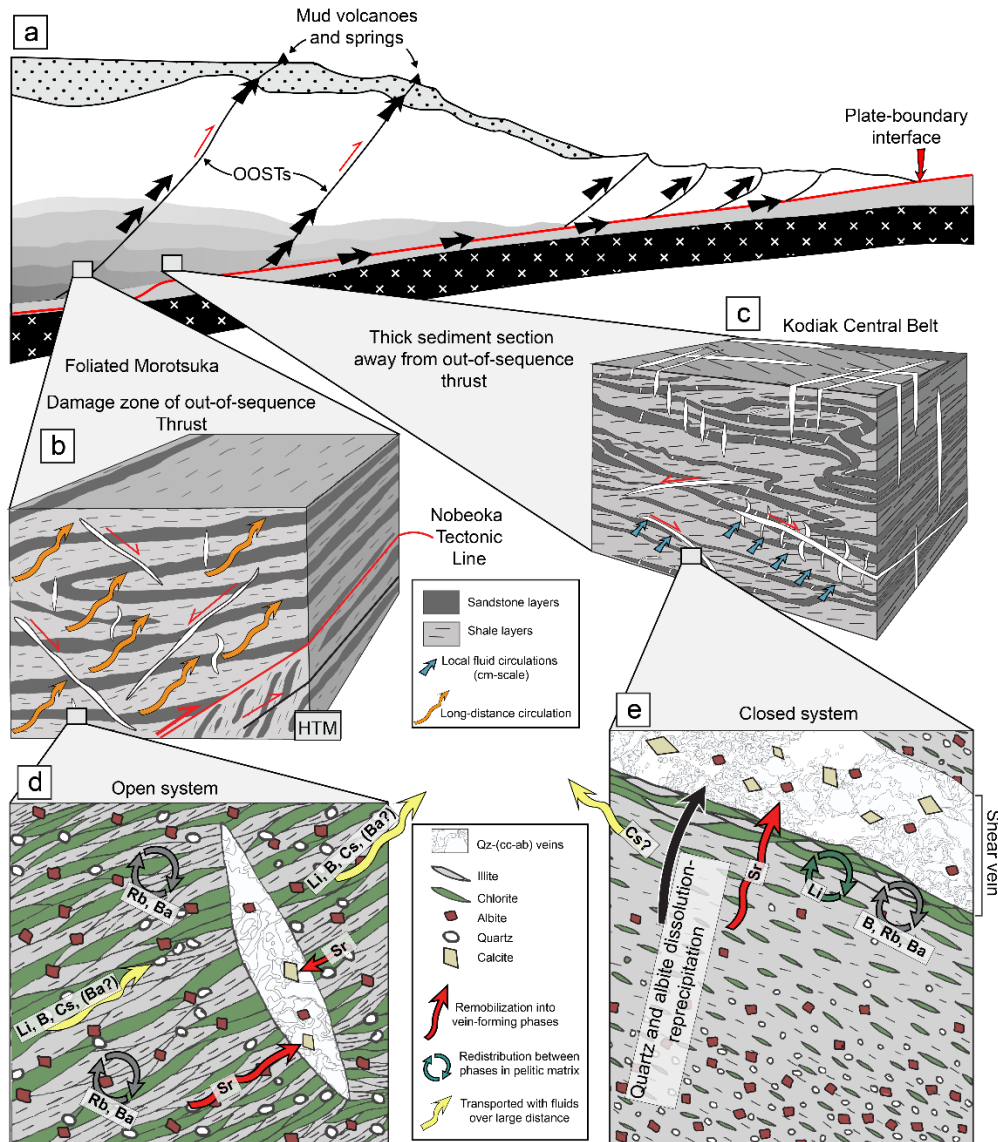


Figure V.10. The schematic scenario of FME budget evolution at studied sites, from the location within the wedge down to thin section: (a) A sketch of an accretionary wedge redrawn after Kastner et al. (2014) with the relative locations of studied units, the Foliated Morotsuka and the Kodiak Central Belt. The Foliated Morotsuka is located in the hanging wall of the out-of-sequence thrust (Nobeoka Tectonic Line), whereas the Kodiak Central Belt was underplated in the middle of thick turbiditic sequence far from any large-scale faults. A 3D sketch of (b) the Foliated Morotsuka and (c) the Kodiak Central Belt with presented deformation structures and possible scenarios for fluid flow. (d) and (e) show details of the mineralogy of metapelites from both localities and their influence on FME budget. In the Foliated Morotsuka (d), lithium, boron, cesium, and barium are leached from the host rock, with only strontium stored in vein-forming calcite. Conversely, (e) in the Kodiak Central Belt, lithium, boron, rubidium, and barium, are reorganized between illite, chlorite and albite. Only cesium is potentially lost over larger distance.

Preface

In this chapter, $\delta^7\text{Li}$ was determined in fluid inclusions by applying the crush-leach technique, and in the host quartz. Beside already described veins from the Kodiak complex and the Shimanto belt (Chapters III and IV), this chapter involves as well syn-subduction veins from Western Alps (from the Helmyntoïdes Flysch and the Schistes Lustrés).

The $\delta^7\text{Li}$ values of fluid inclusion leachates in combination with recovered lithium concentrations suggest fluid rock interaction changing $\delta^7\text{Li}$ of fluid towards the signature of the potential protolith.

*This chapter is a basis for the manuscript which will be submitted to the journal Earth and Planetary Science Letters (EPSL): **Rajič, K., Richard, A., Raimbourg, H., Lerouge, C., Millot, R., Magna, T., Herviou, C.: Lithium isotopes record fluid–rock interactions in subduction zone forearcs***

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VI.0. Abstract

Despite the recognition that fluids play important role in subduction zone processes, fluid-rock interaction and the extent of fluid circulation within subduction and accretionary complexes are still not fully understood. In this study we examined the chemical and $\delta^7\text{Li}$ isotopic compositions of (i) fluid inclusions, (ii) host quartz and (iii) the wall rocks of syn-subduction veins from three paleo-accretionary complexes (the Kodiak complex, Alaska, the Shimanto Belt, Japan, and the Western Alps), in the temperature range 250-400°C. $\delta^7\text{Li}$ value of fluid inclusion leachates shows distinguished signature between three localities, in the range from -1.54 to +17.07‰ overall. Heavier $\delta^7\text{Li}$ values of pore fluids in Kodiak (+8.1 to +17.07‰) are interpreted as a result of closed system, where lithium (^6Li dominantly) is preserved in illite and chlorite. Another example of closed system is in Western Alps (-1.5‰ to +9.5‰), where the fluids are buffered by the host rock, causing $\delta^7\text{Li}$ values of pore fluids shifting towards the values of the protolith. Relatively low $\delta^7\text{Li}$ values of pore fluids in Shimanto (+2.53 to +10.39‰) resulted in large flux of externally derived fluids which leached lithium out of the rock. The $\delta^7\text{Li}$ values of quartz are globally higher than those of paired leachates (+10.93 and +22.61‰) without temperature-dependent isotopic fractionation between quartz and fluid, attributed to significant drops in pore fluid pressure, which, in turn, facilitate the rapid crystallization of quartz.

Comparing the metamorphic fluids in the present study with seawater or pore water from deep sea sediments, elevated lithium concentrations in leachates and relatively light $\delta^7\text{Li}$ values suggest that lithium is progressively leached from sediments during burial, and consequently the $\delta^7\text{Li}$ value of fluids is shifted towards the signature of the protolith. Similarities in lithium concentrations and $\delta^7\text{Li}$ value between leachates and fluids expelled through springs and mud volcanoes in modern examples of subduction zone forearcs further confirm the origin of mud volcano and spring fluids dominantly from subducted sediments. This study further demonstrates the capability of lithium isotopes to effectively trace fluids across large distances within subduction zone forearcs.

VI.1. Introduction

Fluids are recognized to be of prime importance for subduction zone processes because they are among key factors for the formation of arc magmas, geochemical evolution of the mantle, or involvement into seismic cycles (Audet & Schwartz, 2013; Hacker et al., 2003; M. W. Schmidt & Poli, 2014). In subducted units and accretionary wedges, fluid circulation predominantly occurs within structures exhibiting high permeability, notably within the decollement zone and thrust faults within the wedge (Kastner et al., 2014; Moore and Vrolijk, 1992; Saffer and Tobin, 2011; Chan and Kastner, 2000; You et al., 1995). The questions of the origin of such fluids in subduction zones, the fluid-rock interactions they underwent, the pathways and the length-scales at which fluid circulation occurs are typically addressed by using fluid-mobile elements such as lithium and its isotopes (Barnes, Penniston-Dorland, et al., 2019; Gudelius et al., 2022; Hoover et al., 2022; Magna, Wiechert, Grove, et al., 2006; Penniston-Dorland et al., 2010, 2012). However, the knowledge of the behavior of lithium and its isotopes and how they could be used as fluid tracers in the subduction zones is still incomplete, as summarized below.

Global subducting sediments (GLOSS-II; Plank, 2014) contain 45 ppm Li on average, with the $\delta^7\text{Li}$ value ranges between -1.1 and +9.0‰. Since the Upper Cretaceous up to the present day, the $\delta^7\text{Li}$ value of seawater has undergone discontinuous changes, primarily driven by the rate of the continental weathering; ranging from the minimum value of +21‰ during the Paleocene-Eocene (Misra & Froelich, 2012) to present-day value of +31‰ (Millet et al., 2004). During early diagenesis, prior to sediment subduction, pore fluids exhibit highly variable $\delta^7\text{Li}$ (+7.5‰ to +45.7‰; Scholz et al., 2010). Two main processes in marine sediments which affect the $\delta^7\text{Li}$ value of fluids are (i) the cation exchange and Li uptake by authigenic clay minerals, and (ii) leaching of Li from Li-bearing mineral phases, either as a result of dissolution or a simple loss of Li due to the temperature increase (Berger et al., 1988; Scholz et al., 2010). Low-temperature alteration in sediment sequences rich in volcanic material is an example of cation exchange, where authigenic clay minerals tend to incorporate ^6Li , leaving the pore fluid with $\delta^7\text{Li}$ value higher than that of seawater (Chan & Kastner, 2000).

In cases when elevated temperatures linked with a hydrothermal process trigger dehydration of sediments, Li is released into a fluid phase, consequently decreasing $\delta^7\text{Li}$ value of fluids towards the signature of protoliths (Chan et al., 1994; James et al., 1999; Scholz et al., 2010; Zhang et al.,

1998). An example is reported in the Nankai accretionary prism, where the fluids circulating along the decollement zone are characterized by $\delta^7\text{Li}$ value lower than those of subducted sediments distal to the decollement zone (C.-F. You, Chan, et al., 1995). Another type of fluids migration within accretionary wedges is along the out-of-sequence thrusts (Carson et al., 2003; Lauer & Saffer, 2012), resulting in the fluid expulsion back to the surface through mud volcanoes or springs (Kopf, 2002). In the forearc region, these fluids are primarily attributed to subducted sediments at depths <15 km (e.g., Barnes et al., 2019a), while in the arc region, the contribution from the subducting slab is notably lower (e.g., Helper et al., 2023).

Due to the prohibitive depths of deep subduction processes, the knowledge about fluids at deeper levels of subduction (>5 km) mostly relies on exhumed rocks. Even though Li is considered a fluid-mobile element which should be removed from seafloor sediments at a relatively early stage of subduction, such as documented in the Catalina Schist (G. E. Bebout et al., 2007), it appears that in some cases lithium can be retained down to depths of ≥ 80 km in subduction zones (Barnes et al., 2019a; Bebout et al., 2013). In subducted metasedimentary rocks, such as the Catalina Schist (Penniston-Dorland et al., 2012), the Western Alps (Barnes et al., 2019), or the Otago Schist (Qiu et al., 2011), $\delta^7\text{Li}$ values show strong preservation of the protolith signature without any significant correlation to the metamorphic grade.

To further address the potential of lithium isotopes for tracing fluid circulation in sediments incorporated into accretionary wedge, samples from paleo-accretionary complexes in which evidence of fluid circulation through metamorphosed rocks is provided by syn-subduction quartz veins were targeted. In order to encompass temperatures ranging from $\sim 250^\circ\text{C}$ to $\sim 400^\circ\text{C}$, samples were taken from the Kodiak accretionary complex (Alaska; Fisher et al., 1995; Fisher & Brantley, 1992), the Shimanto Belt (Japan; Raimbourg et al., 2018), and the Western Alps (France; Agard et al., 2000; Herviou et al., 2021). Analysis of the chemical and isotopic compositions of quartz veins, their fluid inclusions and the wall rocks were carried out, allowing detailed investigation of lithium behavior at the sample scale and providing implications for tracing large-scale fluid pathways.

VI.2. Sample description

During this study 21 quartz-dominated vein samples were selected from three different paleo-accretionary complex (Table VI.1). The selected sets of veins are interpreted as syn-subduction veins and formed at peak-metamorphic conditions (Agard et al., 2000; Brantley & Fisher, 1997; Fisher et al., 1995; Herviou et al., 2021; Palazzin et al., 2016; Raimbourg et al., 2018, 2021).

Table VI.1. List of vein samples used during this study, their mineralogy, salinity of fluid inclusions, and P-T conditions. Qz – quartz, cc – calcite, chl – chlorite, car – carpholite, lws – lawsonite, ank – ankerite, sid – siderite.

Locality/sample	Longitude	Latitude	Mineralogy	Mean salinity	Salinity reference	T _{RSCM} (°C)	P (kbar)	P-T reference
Kodiak accretionary complex								
<i>Kodiak Central Belt</i>								
KO32B	-152.2450	58.3893	Qz+(cc)	3.2	This study	330 ± 16	3.7 ± 1.7	This study
KO32C	-152.2450	58.3893	Qz+(cc)	3.3	This study	330 ± 16	2.9 ± 1.0	This study
KO32F	-152.2450	58.3893	Qz+(cc)	5	This study	333 ± 19	4.3 ± 2.6	This study
KO36B	-152.2586	58.3661	Qz+(cc)	-	This study	330 ± 29	3 ± 0.4	This study
KO33C	-152.2568	58.3576	Qz+(cc)	3.3	This study	330 ± 19	3 ± 0.4	This study
KO33A	-152.2568	58.3576	Qz+(cc)	3.3	This study	330 ± 19	3.3 ± 1.3	This study
<i>Kodiak Seaward Belt</i>								
KO11	-152.4386	57.6516	Qz+cc	2.3	This study	300 ± 19	-	This study
KO12	-152.4764	57.6875	Qz+chl+cc	3	This study	348 ± 28	-	This study
KO42	-152.6538	57.8639	Qz	1.76	This study	261 ± 17	-	This study
Shimanto belt								
<i>Hyuga Tectonic Mélange</i>								
HN64	131.4630	32.5944	Qz	2.1	This study	240 ± 6	-	Raimbourg et al. (2018)
<i>Foliated Morotsuka</i>								
13D	131.5433	32.7211	Qz+(cc)	3.3	This study	323 ± 19	3.3 ± 1.3	This study
21_C	131.8556	32.7552	Qz+(cc)	-	This study	349 ± 6	3.9 ± 0.4	This study
23_B	131.8786	32.7614	Qz+(cc)	3.5	This study	338 ± 10	3.2 ± 0.7	This study
Western Alps								
<i>Helmyntoïdes Flysch</i>								
FH6	6.7259	44.5263	Qz+cc	2	Raimbourg et al. (2018)	292	-	Raimbourg et al. (2018)
FH16	6.6497	44.5119	Qz+cc	2	Raimbourg et al. (2018)	250	-	This study
FLY 17-26	6.70297	44.4253	Qz+cc	2	Raimbourg et al. (2018)	250	-	This study
<i>Schistes Lustrés</i>								
SL-15-01	6.8702	44.9858	Qz+car+cc	5.6	Herviou, unpublished data	330	12-13	Agard et al. (2001a, b)
SL-15-03B	6.8832	44.9984	Qz+lws	3.6	Herviou, unpublished data	343	12-13	Agard et al. (2001a, b)
SL-15-14	6.8720	44.9786	Lws-qz- Lws-qz-	2.9	Herviou, unpublished data	350	~16	Agard et al. (2001a, b) Schwartz et al. (2013);
PS1912	6.9901	44.6937	Ank	1.1	Herviou, 2021	373	13–16	Agard et al. (2001)

DS1802B	6.8062	44.9943	Qz+car+sid	11.7	Herviou, unpublished data	376	-	Herviou et al. (2022)
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From the Kodiak Central Belt, examined veins are D1 extensional quartz-(calcite) shear veins or Mode 1 quartz veins characterized by presence of crack-seal texture. Mode 1 veins are cutting across the foliation and are folded perpendicular to the foliation, suggesting their contemporaneous formation (Chapters II; Raimbourg et al., 2021). Multi-phase equilibrium model from illite and chlorite in the contact to the vein derived peak-metamorphic conditions of 3 ± 0.4 kbar and 320-340°C (Chapter IV). From the Kodiak Seaward Belt, examined veins are sub-vertical NW-striking quartz-calcite-chlorite veins (Chapter II). The origin of the NW-striking veins is still ambiguous, hypothetically related to the ridge subduction and late-stage magmatic fluids. The peak-metamorphic temperatures of the Kodiak Seaward Belt range 300-350°C (Chapter III).

In the Shimanto belt, examined veins from the Hyuga Tectonic Mélange are Mode 1 quartz veins from sandstone lenses embedded in highly sheared shale matrix (Palazzin et al., 2016; Raimbourg et al., 2018, 2021). The peak-metamorphic temperatures of the Hyuga Tectonic Mélange range 220-260°C derived from Raman Spectroscopy of carbonaceous material (RSCM; Palazzin et al., 2016; Raimbourg et al., 2018, 2021). Veins from the Foliated Morotsuka are Mode 1 quartz veins as well, often in form of en echelon arrays (Raimbourg et al., 2021). These veins cut across the slaty cleavage and are folded during shortening perpendicular to the slaty cleavage. The peak conditions in the Foliated Morotsuka are estimated at 3-5 kbar and 300-350°C based on multi-phase equilibrium in metapelites (Chapter IV), mineral assemblages in basalt lenses (Toriumi & Teruya, 1988) and RSCM (Raimbourg et al., 2021).

VI.2.1. Western Alps

The Western Alps are composed of metamorphic units formed during east to southeast-dipping subduction zone of Valais and Liguro-Piemont ocean below Adria/Apulia (Agard & Handy, 2021; Le Pichon et al., 1988; Schmid et al., 2017). The subduction occurred between Late Cretaceous to Late Eocene (Schmid et al., 2017; Stampfli et al., 1998), followed by continental subduction (Bonnet et al., 2022; Rubatto & Hermann, 2001) and finally continental collision (Simon-Labric et al., 2009). From the Western Alps, we have selected two units (Fig. VI.1a-b): The Flysch

Helminthoïdes (Kerckhove, 1963; Raimbourg et al., 2018) and the Ligure-Piemont Upper unit in the Schistes Lustrés (Agard et al., 2000; Herviou et al., 2021).

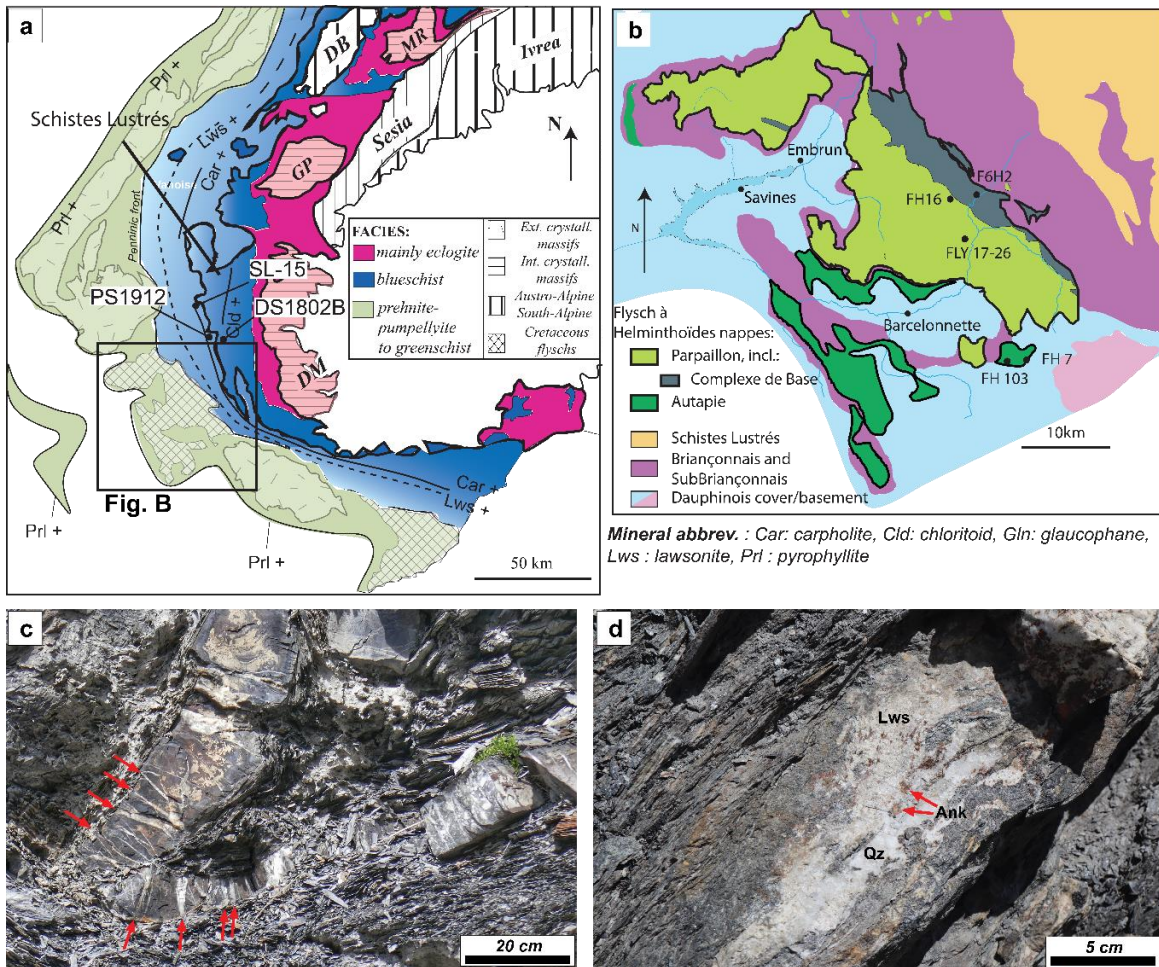


Figure VI.1. (a) A geological map of the Western Alps, with the sample locations from the Schistes Lustrés complex. (b) A closer look into The Helminthoïdes Flysch with the studied samples. (c) Folded chert layer in the Helminthoïdes Flysch with Mode 1 quartz veins perpendicular to the stratification bedding. (d) Quartz-lawsonite-ankerite vein from the Schistes Lustrés.

The Helminthoïdes Flysch composed of ~1000 m thick calcareous turbidites (Kerckhove, 1963; Raimbourg et al., 2018). The early stage deformation is recorded by isoclinal folding of turbidites beds and development of a schistosity as axial fold planes (Merle, 1982). Metamorphic conditions reach up to greenschist facies (Bousquet et al., 2012), with peak-metamorphic temperatures of 250-290°C derived by RSCM (Raimbourg et al., 2018). Examined veins in the Helmyntoïdes Flysch are Mode 1 quartz-calcite veins localized in thin folded turbidite beds with sub-

perpendicular orientation to the bedding (Fig. VI.1c), formed at peak temperatures of 250-290°C (Raimbourg et al., 2018).

The Schistes Lustrés complex consists of 200-400 m thick sequences of pelagic and hemipelagic calcschists, metapelites and marbles, with less abundant mafic and ultramafic lenses embedded in metasediments (Lemoine et al., 1984; Deville et al., 1992; Michard et al., 1996). The peak metamorphic conditions increase from blueschist to eclogite facies eastward, from 320-400°C and 1.2-1.9 GPa to 500-580°C and 2.2-2.8 GPa (Herviou et al., 2022 and references therein). The veins from the Schistes Lustrés (LPU1 unit in Herviou et al., 2021) are meter-scale foliation-parallel veins with quartz, carpholite and lawsonite (Fig. VI.1d; Agard et al., 2000; Herviou et al., 2021; Lefeuvre et al., 2020). For the LPU1 unit where veins were sampled for this study, the peak-metamorphic conditions are estimated at 330-380°C and 12-16 kbar (Agard et al., 2001; Herviou et al., 2022).

VI.3. Analytical methods

VI.3.1. Crush-leach

Selected veins were crushed to 1-2 mm fraction. From crushed material quartz was hand-picked under binocular loupe and all visible impurities were removed. Samples were then exposed to H₃PO₄ acid for an hour to dissolve remaining carbonates. Picked material was placed into a beaker with doubly distilled water and in ultrasonic bath for 2 hours, after they were rinsed and the procedure was repeated. Then samples were placed onto a hot plate, rinsed and then once more placed onto a hot plate. Finally, samples were rinsed twice with doubly-distilled water and let dried before crush-leaching.

Crush-leach procedure was performed at GeoRessources, Université de Lorraine, Nancy, France, following the technique of Banks et al. (2000). Cleaned quartz (1.55-14.8 g) was crushed to a powder in an agate pestle and mortar and the powder was covered with ~20 ml 18.2 MΩ deionized water. Leachates were filtered with 0.2 µm nylon filter after 24h when quartz powder deposited onto the bottom of a plastic box. After the extraction of leachates, the remaining quartz powder was rinsed three times and dried.

VI.3.2. ICP-MS

The chemical composition of fluid inclusion leachates was determined using an Inductively Coupled plasma mass spectrometry at BRGM, France. The detection limit of analyzed elements in fluid inclusion leachates is: Cl, 5 mg/L; Fe, 1 µg/L; Na, 1 µg/L; Al, 0.5 µg/L; Mg, 1 µg/L; B, 0.5 µg/L; Ba, 0.05 µg/L; K, 1 µg/L; Be, 0.01 µg/L; Ca, 10 µg/L; Cu, 0.1 µg/L; Li, 0.1 µg/L; Mn, 0.1 µg/L; Pb, 0.05 µg/L; Sr, 0.1 µg/L; Zn, 0.5 µg/L; Br, 1 µg/L; Rb, 0.1 µg/L; and Cs, 0.5 µg/L.

VI.3.3. Multi collector – inductively coupled plasma mass spectrometry (MC-ICP-MS)

The measurement of Lithium isotopic composition of fluid inclusion leachates, remaining quartz powder and host rock samples were performed using Neptune+ multi-collector ICP-MS (ThermoElectron) at BRGM, France (see Millot et al., 2004 for more details) and Neptune multi-collector ICP-MS (Thermo Scientific, Bremen, Germany) at the Czech Geological Survey, Prague, Czech Republic. The leachates were evaporated and recovered into 2 ml beakers in ~1 ml HNO₃ 2%. Two to three individual runs were performed for each sample, and determined average $\delta^7\text{Li}$ values are reported in per mil notation (‰). Aliquots of powdered quartz were weighed into Teflon beakers and digested in a mixture of 15M HNO₃ – 23M HF (1/6 v/v) for 72 hours on a hot plate (130°C). The evaporated samples were subsequently refluxed three times with small amounts of 15M HNO₃ and finally dissolved in 6M HCl for 24 hours on a hot plate (80°C) to ensure complete digestion and equilibration. The necessary amounts of these stock solutions were evaporated and re-dissolved in a mixture of 30% methanol–0.67M HNO₃. Lithium was isolated from the resulting solutions using a two-step cation exchange column chemistry, following the analytical procedures given elsewhere (Magna et al., 2004, 2006b; Millot et al., 2004). The first step employed 2.1-ml columns packed with BioRad AG50W-X8 (mesh 200–400) resin and 80% methanol–1M HNO₃ mixture as elution medium. The second step used 0.6-ml columns packed with BioRad AG50W-X12 (mesh 200–400) and 0.5M HNO₃ as elution medium. 30 ng of lithium is analyzed for the isotopic composition. The lithium concentrations and isotope compositions in clean Li fractions were obtained against the L-SVEC reference solution (Flesch et al. 1973). A standard–sample–standard bracketing method using the L-SVEC solution was employed to determine Li isotope variations in unknown samples. The results of Li isotope measurements are reported in

conventional delta notation relative to the L-SVEC reference solution and calculated as $\delta^7\text{Li} (\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000$. The reproducibility of Li isotope measurements was generally better than $\pm 0.3\text{‰}$ (2σ). The reliability of the analytical methods and instrumental approach was verified by analyzing international reference materials IRMM BCR-403 (seawater) and/or JB-2 (rock standard) at BRGM, and JCh-1 (chert, GSJ), IAPSO (seawater, OSIL) and NASS-6 (seawater, NRC–CNRC) at CGS. The accuracy of analyses is reported as $\pm 0.5\text{‰}$ (2σ , 2 standard deviation), after long-term measurements of standard solutions (Magna et al., 2004, 2006b; Millot et al., 2004). Four quartz samples (KO36B, FH6, SL15-3B, and DS1802B) were analyzed in both labs, yielding similar values ($\pm 1.5\text{‰}$).

VI.4. Results

VI.4.1. Chemistry of leachates

The chemical composition of fluid inclusion leachates is reported in Table VI.2. The analyzed elements are in the range: Cl, 0.34-29.29 mg/L; Fe, 1.2-38.6 $\mu\text{g/L}$ (five measurements b.d.l.); Na, 550-14778 $\mu\text{g/L}$; Al, 0.62-39.9 $\mu\text{g/L}$; Mg, 44-185 $\mu\text{g/L}$ (with one high value 6453 $\mu\text{g/L}$, Sample 23_B); B, 16.3-117 $\mu\text{g/L}$; Ba, 0.35-26.3 $\mu\text{g/L}$; K, 57-2140 $\mu\text{g/L}$; Ca, 1579-11474 $\mu\text{g/L}$ (with one high value – 40370 $\mu\text{g/L}$, sample 23_B); Cu, 0.58-5.73 $\mu\text{g/L}$; Li, 1.33-43 $\mu\text{g/L}$ (Fig. VI.3a); Mn, 0.76-133 $\mu\text{g/L}$ (with one high value – 2038 $\mu\text{g/L}$, sample 23_B); Pb, 0-1.38 $\mu\text{g/L}$; Sr, 12.5-549 $\mu\text{g/L}$; Zn, 0.87-16.2 $\mu\text{g/L}$; Br, 1.1-26.3 $\mu\text{g/L}$; Rb, 0.18-2.78 $\mu\text{g/L}$; Be, 0.003-0.004 $\mu\text{g/L}$ for three samples, for the rest of samples the value is below detection limit; and Cs, 0.04-1.41 $\mu\text{g/L}$ for four samples, for the rest the value is below detection limit.

From measured concentrations, calculated molar ratios range: Na/Li, 39.2-728.1; Na/K, 3.7-80.3; Na/Mg, 4.3-162.8; Na/Ca, 0.1-3.9; Na/Sr, 11.3-1137.1; Na/Ba, 496.9-41583.7; Na/B, 7.3-142.4; B/Li, 2.5-12.4; and Cl/Br, 486.5-5514.8. A Sample 23_B is not included due to significantly higher values than in the rest of samples.

Calcium is determined as a dominant cation in most of leachates (15 of 21), consistent with LA-ICP-MS or decrepitation methods conducted on the same vein samples (Chapters IV and V). In the rest of samples sodium is a dominant cation. Based on salinity estimates and charge-balance calculations (Allan et al., 2005), reconstructed fluid inclusion concentrations range are as follows:

Fe, 1-24 ppm; Na, 234-25898 ppm; Al, 0.3-50 ppm; Mg, 38-1433 ppm; B, 4-177 ppm; Ba, 0.1-46 ppm; K, 52-3083 ppm; Ca, 1558-14994 ppm; Cu, 0.2-6.4 ppm; Li, 2-24 ppm; Mn, 1-452.6 ppm; Pb, 0.03-1.5 ppm; Sr, 10-727 ppm; Zn, 0.4-8.3 ppm; Br, 1.5-46.1 ppm; Rb, 0.1-3.7 ppm; and Cs, 0.03-1 ppm.

VI.4.2. Li concentrations and $\delta^7\text{Li}$ of quartz veins and host rocks

The chemical composition of FI leachates is reported in Table VI.2. The lithium concentrations of FI leachates range between 1.33 and 43 ppm (Table VI.2). Based on salinity estimates and charge-balance calculations (Allan et al., 2005), reconstructed Li concentrations of FI leachates range between 2 and 24 ppm (Fig. VI.4a).

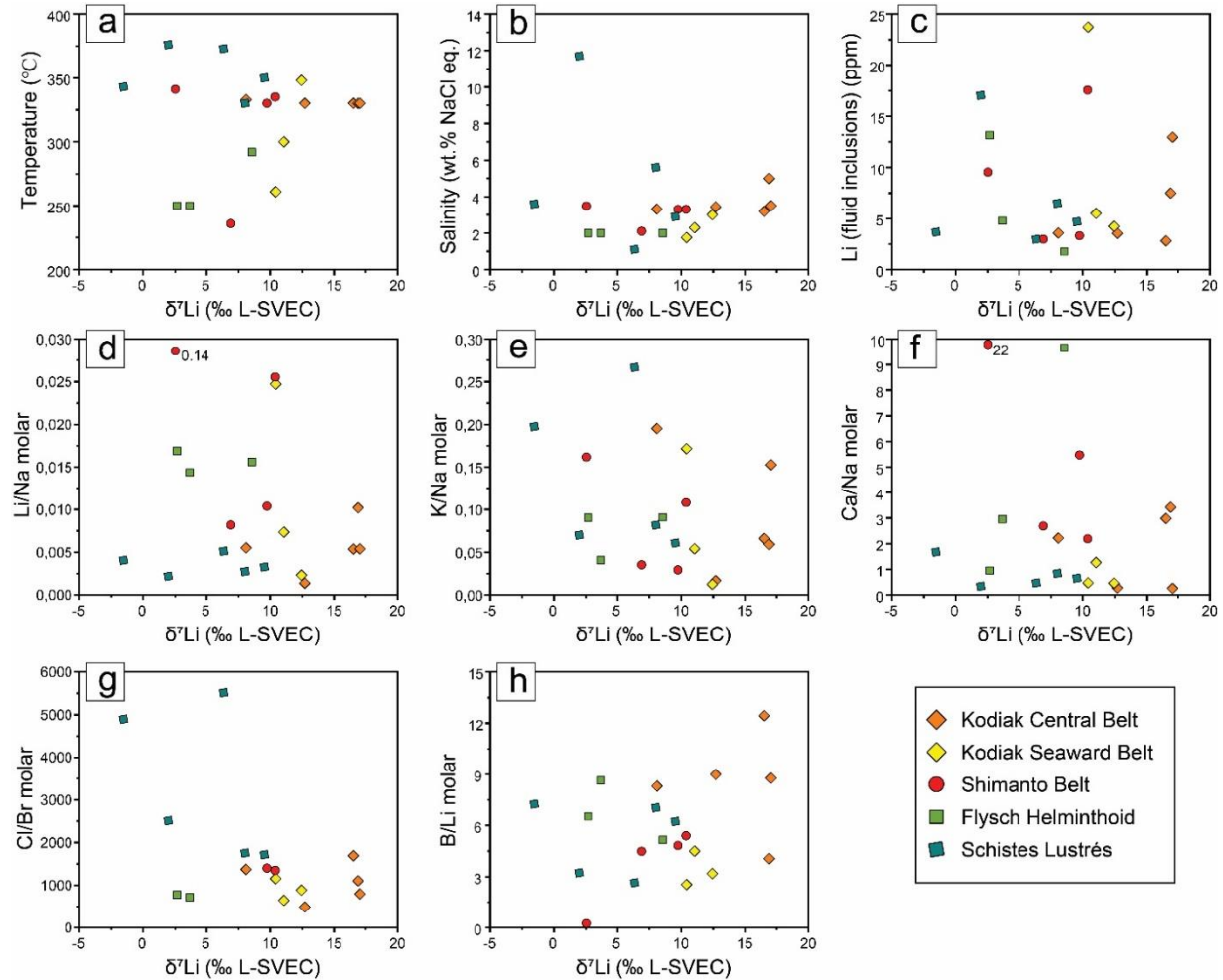
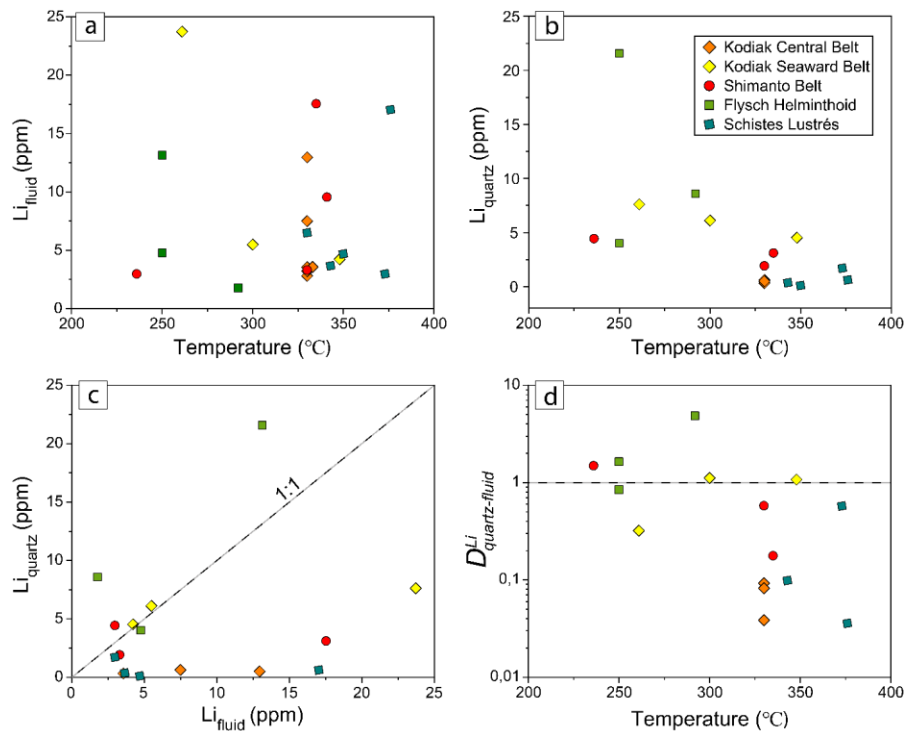


Figure VI.3. The $\delta^7\text{Li}$ of fluid inclusions leachates vs (a) peak-metamorphic temperatures, (b) salinity, (c) reconstructed lithium concentrations in fluid inclusions, (d) Li/Na, (e) K/Na, (f) Ca/Na, (g) Cl/Br, and (h) B/Li molar ratios.

Also, the majority of FI leachates have higher Li concentrations compared with paired quartz (Fig. VI.4c-d). Apparent partition coefficients between quartz and fluid ($D_{qz-fluid}^{Li}$) range from 0.0002 to 4.84 (Fig. VI.4d), with marginally higher values in lower-temperature samples (Fig. VI.4). Samples originating from the same units are characterized by similar values. For example, low $D_{qz-fluid}^{Li}$ values are found for the Kodiak Central Belt (0.04–0.09), in contrast to high values of the Helminthoid Flysch (0.84–4.84).

The $\delta^7\text{Li}$ values of individual FI leachates range between -1.54‰ and $+17.07\text{‰}$ (Fig. VI.2a; Table 1). The $\delta^7\text{Li}$ values are distinct for each locality: the Kodiak Central Belt, $+8.1$ to $+17.07\text{‰}$; Kodiak Seaward Belt, $+10.42$ to $+12.44\text{‰}$; the Shimanto Belt, $+2.53$ to $+10.39\text{‰}$; the Helminthoid Flysch, $+2.66$ to $+8.57\text{‰}$; and the Schistes Lustrés, -1.54 to $+9.54\text{‰}$. The $\delta^7\text{Li}$ values do not correlate with peak-metamorphic temperatures (Fig. VI.3), salinity, or molar ratios such as Li/Na, K/Na, Ca/Na, Cl/Br, or B/Li (Fig. VI.3), FI leachates are characterized by systematically lower $\delta^7\text{Li}$ values than those of quartz (Fig. VI.2a).



VI.4. Results

Figure VI.4. Binary diagrams of measured lithium concentrations in (a) fluid inclusions and (b) host quartz plotted against peak-metamorphic temperatures. (c) Lithium concentrations of quartz vs reconstructed lithium concentrations in fluid inclusions based on charge balance approach. (d) Quartz-fluid partition coefficient ($D_{quartz-fluid}^{Li}$) vs peak-metamorphic temperatures. Note that the partition coefficient is to some extent lower at higher temperatures.

Table VI.3. Lithium concentration and $\delta^7\text{Li}$ of whole-rock samples, quartz and fluid inclusion leachates. B and C stand for analysis locations, BRGM and Czech Geological Survey, respectively. All whole-rock samples were analyzed at BRGM.

Sample	Whole-rock				Lab	Quartz				Lab	FI leachates			
	[Li] ($\mu\text{g/g}$)	$\delta^7\text{Li}$ (‰)	2σ (m)	Average $\pm 0.5\text{‰}$ (2σ)		[Li] ($\mu\text{g/g}$)	$\delta^7\text{Li}$ (‰)	2σ (m)	Average $\pm 0.5\text{‰}$ (2σ)		[Li] ($\mu\text{g/L}$)	$\delta^7\text{Li}$ (‰)	2σ (m)	Average $\pm 0.5\text{‰}$ (2σ)
KO32B											2.61	16.56	0.26	16.56
KO32C					C	0.33	22.61	0.34		B	6.02	12.9 12.5	0.24 0.18	12.7
KO32F					C	0.62	20.36	0.28		B	4.78	16.96 16.89	0.2 0.24	16.93
KO36B	50.7	0.88 0.6 0.42	0.12 0.08 0.06	0.63	B	0.5	14.96 14.93	0.14 0.1	14.95	B	5.76	17.29 16.85	0.28 0.38	17.07
KO33A										B	1.33	8.1	0.42	8.1
KO11A					C	6.12	21.27	0.23		B	4.38	11.2 10.89	0.4 0.28	11.05
KO12B					C	4.53	19.59	0.22		B	10	12.64 12.24	0.24 0.24	12.44
KO42A					C	7.61	18.31	0.02		B	29.6	10.52 10.31	0.2 0.2	10.42
HN64	58.7	-1.92 -1.91	0.16 0.12	-1.92	B	4.43	15.17 15.39	0.14 0.16	15.28	B	2.35	6.91	0.2	6.91
21_C					C	3.10	21.19	0.36		B	9.18	10.3 10.47	0.34 0.36	10.39
23_B										B	43	2.67 2.38	0.18 0.24	2.53
13D	65.3	-0.06 -0.52	0.18 0.14	-0.29	B	1.91	17.88 17.45	0.16 0.12	17.67	C	5.17	9.74	0.25	
FH6	38.2	0.08 0.18	0.2 0.12	0.13	B	8.59	21.06 20.73	0.16 0.16	20.9	B	2.59	8.57	0.28	8.57
FH16	22.8	1.17 1.16	0.12 0.12	1.17	B	21.6	13.97 14.41	0.16 0.16	14.19	B	8.58	2.46 2.86	0.28 0.4	2.66
17_26					C	4.02	17.28	0.27		C	8.36	3.66	0.16	
SL-15-01										B	4.68	8.08 7.95	0.14 0.34	8.02
SL-15-3B	80.4	-3.09 -3.31	0.12 0.06	-3.2	B	0.36	11 10.77 11.03	0.14 0.08 0.08	10.93	B	2.01	-1.54	0.4	-1.54
SL-15-14										B	9.52	9.5 9.57	0.26 0.18	9.54
PS1912					C	1.70489	19.548	0.221		B	7.28	6.41 6.31	0.4 0.18	6.36
DS1802B	71.8	-2.1 -1.84	0.22 0.08	-1.97	B	0.61	-0.84 -0.86	0.18 0.14	-0.85	B	9.72	2.14 1.8	0.24 0.36	1.97
					C	0.52	0.44	0.33						

The Li isotopic fractionation between quartz and fluid in this study expressed as $\Delta^7\text{Li}$ ($\Delta^7\text{Li}_{\text{quartz-fluid}} = \delta^7\text{Li}_{\text{quartz}} - \delta^7\text{Li}_{\text{fluid}}$) ranges from +7.2‰ to +13.6‰ for 12 samples (Fig. VI.2b). Samples KO32F and SL-15-14 exhibit a rather low $\Delta^7\text{Li}_{\text{quartz-fluid}}$ of +3.43‰ and +3.14‰ (Fig. VI.2b), respectively, whereas samples DS1802B and KO36B are characterized by negative $\Delta^7\text{Li}_{\text{quartz-fluid}}$ values of -2.82‰ and -2.12‰, respectively. The sample DS1802B from Schistes Lustrés has a light Li isotopic composition of the fluid (+1.97‰), whereas samples KO32F and KO36B from the Kodiak Central Belt are characterized by the heaviest determined value of the fluid, +16.9‰ and +17.1‰, respectively.

VI.5. Discussion

VI.5.1. Do FI leachates retain the original fluid composition?

The crush-leach method has demonstrated its effectiveness in analyzing lithium isotopes of fluid inclusions (Richard et al., 2018; Yang et al., 2015). However, the analyzed samples exhibit notable variations in Li concentrations and $\delta^7\text{Li}$ for both quartz and FI leachates (Table 1). Therefore, it is necessary to address the validity of FI leachates in preserving original chemical composition of fluids during subduction.

In quartz, lithium is the main trace element which compensates the charge deficit of the Si–Al substitution (Neukampf et al., 2022; Peterková & Dolejš, 2019), with Li concentrations up to 3000 ppm in quartz crystallized at temperatures <300°C (Jourdan et al., 2009; A. Müller & Koch-Müller, 2009; Axel Müller et al., 2003; Pašava et al., 2023; Perny et al., 1992). In units subducted down to ~250°C, the Uyak Complex (Kodiak complex) and the Hyuga Tectonic Mélange (the Shimanto Belt), veins quartz is characterized by intercalation of geochemically distinguished zones with low- and high-luminescence (Raimbourg et al., 2021). High-luminescence zones are characterized by high FI density and are enriched in trace elements (mainly Al and Li), interpreted as a result of disequilibrium crystallization due to a large pressure drop, silica supersaturation in the fluid, and rapid growth of quartz (Raimbourg et al., 2021). At higher temperatures (>300°C), pressure variations are much lower (Raimbourg et al., 2022), hence the crystallization of quartz rather occurs under steady-state conditions. Thus, higher $D_{\text{qz-fluid}}^{\text{Li}}$ in lower-temperature quartz are explained by rapid out-of-equilibrium growth of quartz due to a pressure drop and consequent

supersaturation of silica (Fig. VI.4d). This opposite behavior is well illustrated when comparing samples from the Flysch Helminthoid and the Hyuga Tectonic Mélange (~250-300°C) with those from the Kodiak Central Belt, the Foliated Morotsuka or the Schistes Lustres (~330-380°C).

Furthermore, Li usually occupies two- and four-fold coordination sites in quartz (Larsen et al., 2004; Lynton et al., 2005). As ^7Li shows a preference towards the lower coordination number, it is to be expected that quartz is isotopically heavier than the coexisting fluid (Urey, 1947), where $\Delta^7\text{Li}_{\text{quartz-fluid}}$ tends to decrease towards 0 as temperature rises (Schauble, 2004).

Experimentally derived $\Delta^7\text{Li}_{\text{quartz-fluid}}$ values by Lynton et al. (2005) show a trend opposite to theoretical expectations: at 400°C, $\Delta^7\text{Li}_{\text{quartz-fluid}}$ ranges from +4‰ to +6‰, and increases at 500°C, ranging from +8‰ to +12‰. Similarly, temperature-dependent Li isotope fractionation between quartz and fluid is reported in the Gacun volcanogenic massive sulfide deposit, southern China (Yang et al., 2015), suggesting that quartz crystallized in equilibrium with fluid. Overall, the estimated $\Delta^7\text{Li}_{\text{quartz-fluid}}$ in our study is in an agreement with the experiments of Lynton et al. (2005), although no temperature-dependence has been observed in contrast to the findings of Lynton et al. (2005) and Yang et al. (2015).

The lack of temperature-dependent $\Delta^7\text{Li}_{\text{quartz-fluid}}$ fractionation may be explained as a consequence of: (i) disequilibrium crystallization of quartz from fluid; (ii) mixing of FI and quartz from different zones of quartz during the crush-leach; (iii) crystallization at equilibrium between quartz and fluid, later overprinted by re-equilibration due to dissolution–precipitation processes between FI and host quartz (Lambrecht & Diamond, 2014).

A relatively low $\Delta^7\text{Li}_{\text{quartz-fluid}}$ value in the sample SL-15-14 and a negative value in the sample DS1802B can plausibly be explained by the presence of micrometer-sized crystals of siderite and lawsonite in the vein. To our best knowledge, a study addressing Li isotopic composition in siderite or ankerite is lacking. The best approximation of Li isotopic fractionation between the fluid and carbonates (calcite, aragonite) at temperatures ranging between 4 and 30°C yielded $\Delta^7\text{Li}_{\text{carbonate-fluid}}$ values of –3‰ (calcite–fluid) and –12‰ (aragonite–fluid; Marriott et al., 2004), although more recent experiments by Fügler et al. (2022) indicate significant variability of $\Delta^7\text{Li}_{\text{carbonate-fluid}}$ linked with progressive changes of physico–chemical parameters. Nonetheless, we posit that the presence of carbonate phase may potentially explain unusually low $\Delta^7\text{Li}_{\text{quartz-fluid}}$ value for DS1802B.

A disequilibrium crystallization is well supported by other geochemical indicators in veins formed at temperatures $<300^{\circ}\text{C}$, such as zonation in quartz, variations in trace element concentrations, and the abundances of FI (Raimbourg et al., 2021, 2022). As discussed above, these characteristics are explained to have formed due to fluid pressure variations, and rapid growth of quartz during periods of large fluid pressure drops. In Fig. VI.5a these two zones are referred as FI-rich and FI-poor zones, respectively. However, in veins formed at temperatures $>300^{\circ}\text{C}$, it is less clear if quartz crystallized from the same medium because trace element concentrations in higher-T quartz are lower than in lower-T veins. Another possibility is that quartz crystallized in equilibrium with the fluid at any given point. In such case, variations in physico-chemical conditions, such as pore fluid pressure or changes in the composition of the fluid, may instantly change $\Delta^7\text{Li}_{\text{quartz-fluid}}$ with differences between slow and rapid crystallization of quartz. Such temporal and instant equilibrium between quartz and fluid cannot be resolved in this study, as during the crush-leach technique the different quartz zones and FI they contain are mixed.

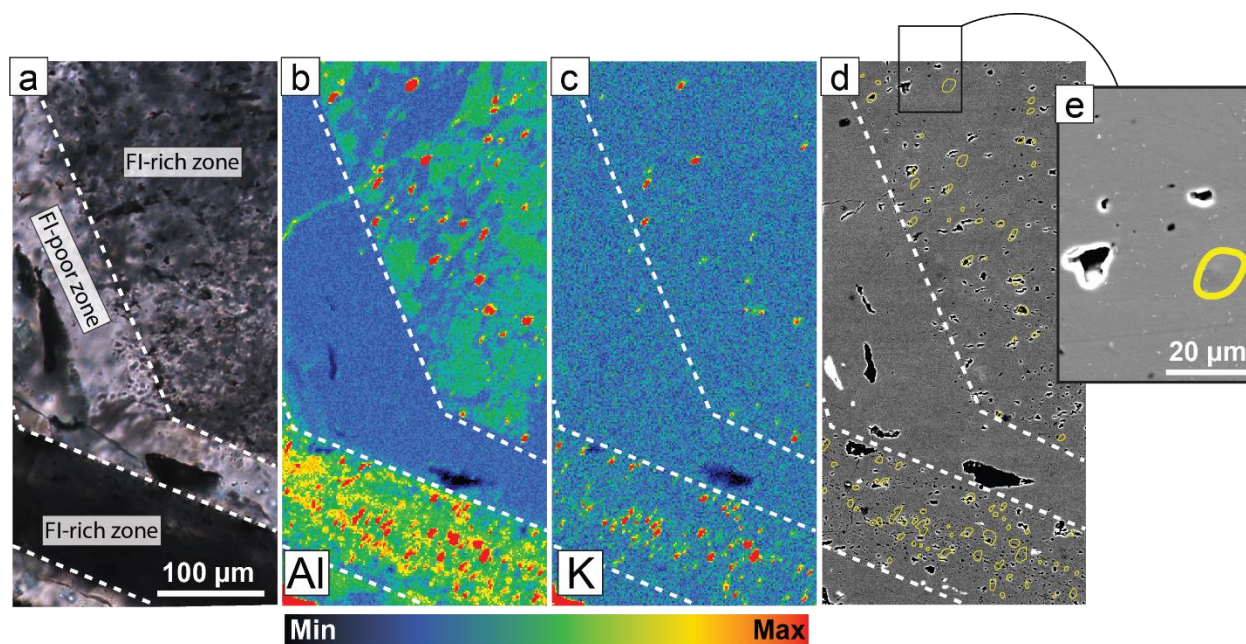


Figure VI.5. (a) Photomicrograph of a quartz crystal characterized by FI-poor and FI-rich zones. (b) and (c) represent EPMA Al and K maps of the quartz. Note the micro-sized high-Al and -K patches in comparison to surrounding quartz. (d) SEM-BSE image of the quartz surface reveals that the majority of these patches are linked to the halos of decrepitated fluid inclusions. There are a few instances where the patches are not correlated with halos, exemplified by the yellow circle marked in (d) and (e).

However, even if quartz crystallized at the equilibrium with the fluid, re-equilibration between FI and host quartz can occur as a result of dissolution–precipitation reactions and element transfer between FI and host quartz (Stern et al., 1995; Vityk et al., 2000). Diffusion of Li between FI and host quartz is unlikely, as it is expected to occur at temperatures $>500^{\circ}\text{C}$ (Zajacz et al., 2009). Re-equilibration of FI in metamorphic rocks has previously been documented as the pressure calculated based on microthermometry studies is significantly lower than that derived using other mineral-phase equilibrium models (Philippe Agard et al., 2000; Raimbourg et al., 2018). Furthermore, cathodoluminescence in quartz occasionally detects “CL patches” characterized by darker or brighter CL color than that of surrounding quartz. Such patches are associated with occurrence of FI, where the wall equilibrated with FI over distances of tens of μm up to few mm (Lambrecht & Diamond, 2014). In many of examined veins, micrometer patches in quartz are characterized by higher Al and K (Fig. VI.5b-c; Raimbourg et al., 2021). Majority of the patches are related to the haloes of decrepitated FI, and the density of the haloes is higher in FI-rich quartz (Fig. VI.5d). However, careful consideration of patches revealed that they are not only located around FI haloes, but also around FI located very close to the polished surface of the quartz (Fig. VI.5e), what is indeed a good indication that the dissolution–precipitation reactions occurred between quartz and FI.

However, to determine which mechanism, or a combination of mechanisms, is responsible for the lack of temperature-dependent fractionation between quartz and fluid remains to be investigated using dedicated studies. Even if quartz crystallized in equilibrium with the fluid, re-equilibration potentially influenced $\delta^7\text{Li}$ of FI and host quartz, but it remains difficult to quantitatively assess the implications for post-entrapment modifications of FI Li concentrations and isotope compositions (e.g., Neukampf et al., 2022). In any case, FI leachates likely preserve original signature of fluids entrapped within fluid inclusions. First, the chemical composition of FI leachates is very similar to results obtained by LA-ICP-MS method in the same veins (Chapter V). Second, the chemical composition of FI leachates as well as $\delta^7\text{Li}$ overlap with sediment-hosted hydrothermal fluids (Scholz et al., 2010) originating from the same temperature range. Lastly, as discussed in following lines, $\delta^7\text{Li}$ of FI leachates show expected trend in subducted sediments, suggesting that re-equilibration of quartz with fluid inclusions has only minor if any effect onto $\delta^7\text{Li}$ of FI.

VI.5.4. Controls on fluid chemistry and $\delta^7\text{Li}$ during sediment diagenesis and subduction

Whole-rock $\delta^7\text{Li}$ of analyzed metasedimentary samples are in the range of previously published data for subducted metasedimentary rocks such as those in the Schistes Lustrés (−4.6 to +7.3‰; Barnes et al., 2019b) and partially overlap those in the Otago Schist (−2.8 to +2.6‰; Qiu et al., 2011). No changes in whole-rock $\delta^7\text{Li}$ have been observed as a function of metamorphic temperature (Fig. VI.2a) nor Li concentrations. As whole-rock Li concentrations are significantly higher than in adjacent FI leachates, even slight variations in whole-rock concentrations can cause drastic changes in the fluid.

Variations in $\delta^7\text{Li}$ values between three localities can be explained by considering Li concentrations of main mineral carrier in the host rocks (chlorite and illite/phengite) and their isotopic fractionation during mineral–fluid interaction. The heavier isotope (^7Li) shows a preference for the lower coordination number and the higher bond energy (e.g., Magna et al., 2016). Consequently, ^7Li preferentially partitions into aqueous fluids where it resides in tetrahedral coordinated sites (Yamaji et al., 2001), contrary to octahedrally coordinated sites in chlorite and illite/phengite (Wunder et al., 2006). Thus, substantial loss of Li from phyllosilicates upon burial and metamorphism tends to decrease $\delta^7\text{Li}$ of pore fluids towards the values of the protolith.

Metapelites from studied units in the Shimanto Belt, the Hyuga Tectonic Melange and Foliated Morotsuka, record a decrease in Li concentrations as temperature rises, also supported by decrease of Li concentrations in chlorite and illite (Chapter V). Such loss, in parallel to other fluid-mobile elements (mainly boron and cesium), is interpreted as a consequence of large flux of external fluids along the Foliated Morotsuka which acts as a damage zone of the out-of-sequence thrust (Kondo et al., 2005). Thus, large flux of external fluids is responsible for the leaching of Li out of chlorite and illite, and as both mineral preferentially incorporate ^6Li , this will decrease $\delta^7\text{Li}$ of fluids.

In contrast to the Shimanto Belt, in studied units from the Kodiak complex and Western Alps the system is described as closed. Whole-rock concentrations of Li do not change as a function of temperature at both localities (Bebout et al., 2013; Chapter V), where for instance in the Schistes Lustrés Li is preserved in the subducted rocks down to depths of ~80 km.

In metapelites from Kodiak, illite and newly formed chlorite retain high Li concentrations up to 350°C (Chapter V). As both illite and chlorite preferentially incorporate ^6Li , a pore fluid is likely characterized by relatively high $\delta^7\text{Li}$. The preservation of high Li concentrations is attributed to the fact that system behaved as closed, as the studied parts of the Kodiak Formation were subducted as a part of thick sediment section away from the decollement zone and later accreted away from any large-scale fault system (Chapter II).

In studied samples from the Schistes Lustrés, Li is stored in chlorite and phengite, and released Li during chlorite breakdown is incorporated into stable phengite (G. E. Bebout et al., 2013). Such preservation of Li, among other fluid-mobile elements (N, B, Rb, Cs, Ba), suggests a rather closed system (G. E. Bebout et al., 2013), also suggested by isotopic and FI studies (Epstein et al., 2020; Henry et al., 1996). In parallel, $\delta^7\text{Li}$ values of metasediments show strong preservation of the original signature of the sedimentary assemblage (Barnes et al., 2019a). In this respect, $\delta^7\text{Li}$ values of fluids in the Schistes Lustrés are very similar to those of host rocks (Table 1; Barnes et al., 2019a). Because the system is proposed to behave in a closed-system fashion, the explanation for such low $\delta^7\text{Li}$ of fluids (as low as -1.5‰ ; Table 1) can be represented by dissolution of Li-bearing phases and crystallization of new Li hosts, which ultimately leads to the shift of $\delta^7\text{Li}$ of fluids towards that of the parent sediments.

Thus, the heavier $\delta^7\text{Li}$ of FI leachates from Kodiak in contrast to Western Alps can be elucidated by considering the reactive volume in metapelites and the progression of mineral reactions. In metapelites from Kodiak, the volume of rock that reached equilibrium under peak metamorphic conditions is notably restricted to the vicinity of veins (Rajič et al., 2023). Conversely, In Western Alps, subduction occurred to much greater depths (10-12 km in Kodiak as opposed to 30-40 km in the Schistes Lustrés). This significant difference in subduction depth resulted in a more extensive occurrence of metamorphic reactions within the units, where the bulk rock volume achieved equilibrium with the fluids and the fluid itself is significantly buffered by host rock.

In conclusion, the $\delta^7\text{Li}$ of pore fluids in subducting sediments at temperatures ranging from 250-400°C depends primarily on the initial composition of the sediments, occurrence of mineral reactions along the prograde metamorphic path, and the proximity of units to the main fluid conduits, both during subduction and within the wedge.

VI.6. Conclusion

By analyzing chemical composition and $\delta^7\text{Li}$ of FI leachates, quartz, and adjacent metapelites, this study offers valuable insight into the $\delta^7\text{Li}$ evolution of pore fluids in subducted sediments at temperatures ranging from 250 to 400°C. The chemical composition of FI leachates exhibits a notable enrichment in trace elements when compared to interstitial pore fluids and seawater, indicating substantial fluid-rock interaction and the leaching of elements (e.g., lithium and boron) from the host rock. FI leachates record a wide range of $\delta^7\text{Li}$ (-1.54 to +17.07‰) in fluids from subducted sediments, and show contrasting behavior between the three studied sites. Such variations likely resulted by (i) the proximity of studied units to the main fluid pathways – the decollement zone and out-of-sequence thrusts, and by (ii) the occurrence of mineral reactions occurring along prograde path. $\delta^7\text{Li}$ of FI leachates do not correlate with other parameters, such as temperature, salinity, or molar ratios such as Na/Li or Na/K.

Quartz is isotopically heavier than adjacent FI leachates (+10.93 and +22.61‰). $\Delta^7\text{Li}_{\text{quartz-fluid}}$ is fairly grouped (+7.15‰ to +13.63‰) and in agreement with experimentally derived values. However, $\Delta^7\text{Li}_{\text{quartz-fluid}}$ values do not correlate with the peak metamorphic temperatures. The lack of temperature dependent fractionation likely supports the dis-equilibrium crystallization of quartz from the fluid as a result of pore fluid pressure variations.

This study further demonstrates that lithium and $\delta^7\text{Li}$ of fluids can be used as fluid tracers and a tool to evaluate fluid-rock interactions in the subduction zone forearc.

CHAPTER VII – General discussion and conclusion

The objective of this work is to study the fluid-rock interactions at low metamorphic grade in subduction zones. We focused in particular on the evolution of metapelites from the base of the seismogenic zone ($\sim 250^{\circ}\text{C}$) to the down-dip transition to the aseismic domain ($\sim 330^{\circ}\text{C}$). In the two examples examined here (Kodiak Complex in Alaska, Shimanto Belt in Japan), we followed the variations in mineralogy, trace element budget, as well as fluid inclusion elemental and isotopic ($\delta^7\text{Li}$) composition. Prior to geochemical work, we carried out an extensive field survey to describe the kinematics and P-T conditions of deformation across the Kodiak accretionary complex.

VII.1. Tectonic evolution and thermal profile of the Kodiak accretionary complex

Field work has been conducted in Kodiak to describe tectonic evolution of the Kodiak complex and its thermal evolution. All basally accreted units record deformation formed during underthrusting (D1 stage). In tectonic mélanges and the Kodiak Landward Belt, top-to-the-trench non-coaxial shearing occurred as these units were in the vicinity to the decollement zone (Fig. VII.1). In contrast, in thick turbiditic sequences of the Kodiak Central Belt, which was further from the decollement zone in underthrust sediment pile, a coaxial extension occurred (Fig. VII.1). Later intra-wedge deformation (D2 stage) is characterized by coaxial horizontal shortening, with stronger shortening in the frontal part of the prism (Fig. VII.1).

Thermal profile point to small variations in temperatures in the Kodiak accretionary complex ($220\text{--}380^{\circ}\text{C}$), with highest temperatures in central part, Kodiak Central and Seaward Belts. The thermal gap is recorded around the unconformity that separates the basally accreted units and the slope sediments ($100\text{--}140^{\circ}\text{C}$), indicating vigorous vertical motion in the complex, with the amplitude of motion up to 10 km. Calculated exhumation and burial rates in this work ($0.2\text{--}1.3\text{ mm/yr}$) are comparable with previous estimations in exhumed paleo-accretionary wedges such as Chugach Terrane (Arkle et al., 2013) or the Cascadia accretionary wedge (Brandon et al., 1998), as well as with the exhumation of HP-LT of underplated duplexes (Agard et al., 2009; Guillot et al., 2009), or inferred from thermo-mechanical models (e.g., Angiboust et al., 2021; Menant et al., 2020). Also, rates are in an agreement with tectonically-induced exhumation, estimated to occurred at rates of $<4\text{ mm/yr}$ (e.g., Yamato et al., 2008). The burial depths ($7\text{--}12\text{ km}$ for basally accreted units

and 4 km for slope sediments) imply large amplitude of the burial/exhumation in the forearc. Similar vertical motions and temperature gap at the unconformity between accreted and slope sediment units has been observed in the Shimanto belt (Raimbourg, Famin, et al., 2017), implying three stages of motion: (1) exhumation of the basally accreted units (buried at peak temperature of 300-350°C) to the surface due to collision and surficial erosion removing about 3-8 km of material; (2) Subsidence and sedimentation of fore-arc Misaki Group on top of the previously exhumed units, and burial down to 170-250°C ; (3) exhumation of the Misaki Group to the surface. The results from both localities, the Shimanto belt and the Kodiak complex, are evidence for vigorous vertical motion within frontal portion of the prisms, which to date are not completely understood.

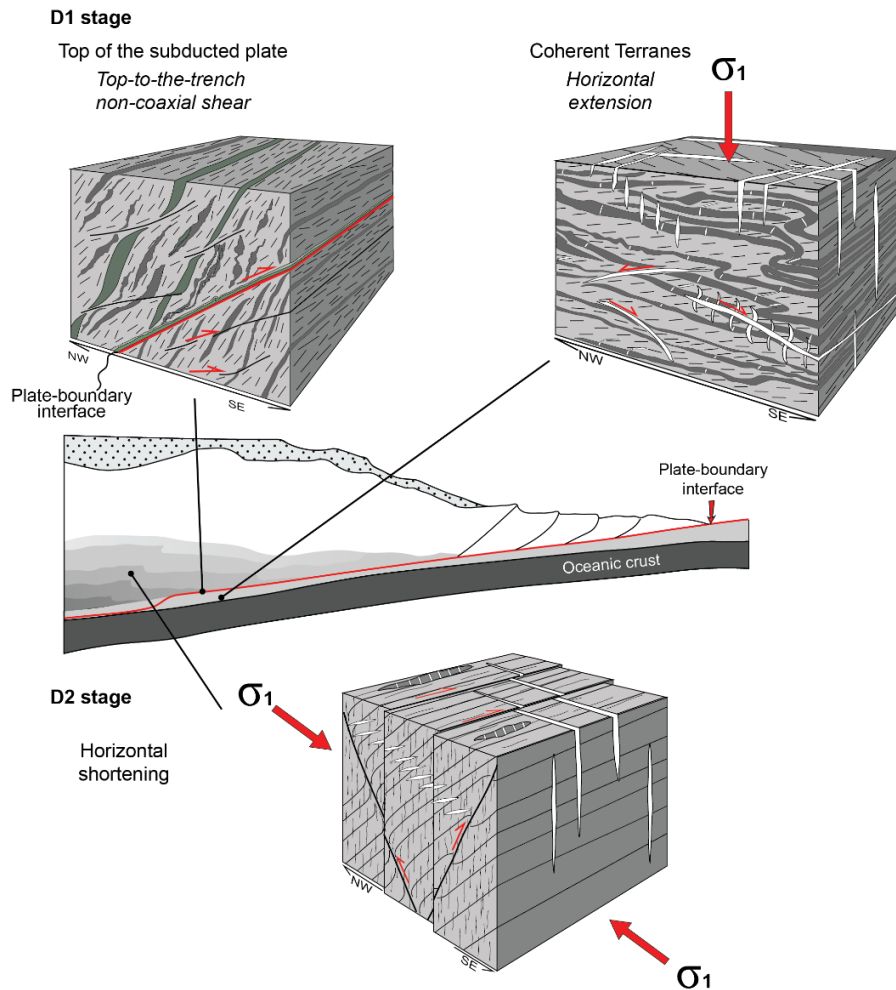


Figure VII.1. Schematic representation of deformation structures and their occurrences. At the top of subducting sediment pile, top-to-the-trench non-coaxial shearing occurred during underthrusting (D1 stage) as a consequence to the vicinity to the plate-boundary interface, whereas in coherent terranes (further away from the plate-boundary

interface) coaxial extension is reported. Later intra-wedge deformation (D2 stage) is characterized by horizontal shortening, with different intensity over the complex.

VII.2. Mineral reactions and water-budget

To evaluate fluid-rock interaction along the seismogenic zone and its downdip limit, we characterized metapelites from the Kodiak accretionary complex and the Shimanto belt in Japan, from the whole-rock scale, individual minerals as well as fluid inclusions (FI) in syn-subduction veins. As temperature increases (from 250°C to 330°C), we report an increase in chlorite/phylosilicates in metapelites from Kodiak and Shimanto. An increase in chlorite proportion is explained as a consequence of illite-to-chlorite transformation. Also, multi-phase equilibrium model using the chemical composition of foliation-forming minerals, illite and chlorite, derived similar temperature results to temperatures derived by RSCM method. This finding suggest that the described metamorphic reactions occurred at the peak metamorphic conditions. In the Shimanto belt, estimated temperature-pressure conditions ($320 \pm 14^\circ\text{C}$ and 3.9 ± 0.4 kbar) are in an agreement with previous estimates based on mineral assemblages in metamafic lenses (300-350°C and 3-5 kbar; Toriumi & Teruya, 1988). Furthermore, Raman spectroscopy of OH band has been applied to estimate the salinity of fluid inclusions trapped in quartz from syn-subduction veins. This method to estimate salinity of fluid inclusions is relatively new (Caumon et al., 2014, 2015; Clément Herviou et al., 2021; Sun et al., 2010), and provide the opportunity to overcome the issue of the salinity estimation in extremely small fluid inclusions ($<10\text{ }\mu\text{m}$) by classical microthermometric studies. Here we present the new and simple approach for the calibration, and preliminary results for few bigger fluid inclusions are in a good agreement with microthermometric studies. In summary, the salinity of fluid inclusions increases from $\sim 250^\circ\text{C}$ to $\sim 330\text{-}350^\circ\text{C}$, from $\sim 2\text{ wt.}\%$ NaCl eq. to $\sim 3.5\text{ wt.}\%$ NaCl eq., respectively. Assuming that the starting salinity of pore fluids, in seafloor sediments, is similar to that of seawater ($\sim 3.5\text{ wt.}\%$ NaCl eq.), the salinity of pore fluids in sediments buried to temperatures $\sim 250^\circ\text{C}$ is interpreted as dilution of initial seawater due to smectite-to-illite transformation, as large quantity of low- Cl^- fluids is released by such a reaction. Conversely, for the later increase in salinity, we connect the illite-to-chlorite transformation to the salinity increase, as such mineral reaction incorporate H_2O from the pore fluid.

Beside the influence of hydration/dehydration reactions (i.e uptake/release of H₂O from/into the pore fluid), the salinity might also reflect the uptake/release of solutes from/into the pore fluid. During this study, qualitative analysis of evaporite mounds of fluid inclusions revealed the large variability of the chemical composition of the pore fluid (Fig. IV.14). In analyzed evaporite mounds, instead of Na predominance (only in one analyzed evaporite mound; 23_B mound1 in Fig. IV.14a), in majority of analyzed mounds Ca is predominant cation with various amount of Na, K, Mg and Fe (Fig. IV.14). Also, sulfur is present in equal amount as Cl or as predominant anion (Fig. IV.14). This enrichment can be explained as a consequence of observed pyrite oxidation, what is also supported by iron oxides localization in shear planes and significant decrease of sulfur in whole-rock chemistry.

Another implication of our findings is that the composition of pore fluids in subducted sediments is not exclusively controlled by the intake or uptake of water in minerals. The chemical evolution of fluids in sediments undergoing subduction is often simplified as a suite of salinity changes occurring in response to the release or uptake of pure water by mineral reactions, assuming NaCl as the dominant species in solution (Herviou et al., 2021 and references therein). Our study shows that other reactions, such as the oxidation of pyrite, may profoundly change the composition of pore fluids, and that sulfur may become the dominant species in solution. Because sulfur is a highly reactive species under certain oxido-reducing conditions, this drastic evolution in the chemistry of pore fluids may generate other reactions, for instance with carbonates. Further work is required to investigate and quantify these reactions and their effect on the composition of subducted fluids.

An important implication of our study is that the transformation of illite into chlorite and the oxidation of pyrite are two reactions that transform pore water into structural water. By consuming pore fluids, these hydration reactions contribute to decrease the porosity of metapelites undergoing subduction. As they occur in the 250-350°C temperature range, these reactions also strongly contribute to trap water in minerals, and thus to restrict fluid circulation in the realm of the brittle-plastic transition. As oppose to large-scale circulation and infiltration of external fluids described in several exhumed blueschist and eclogite facies complexes (Muñoz-Montecinos, Angiboust, Garcia-Casco, et al., 2021; Spandler & Pirard, 2013; Taetz et al., 2016), results from this study rather support a hypothesis that the brittle-plastic transition is found to be a limit between a domain of large-scale circulation of external fluids above it, and a domain of small-scale transfers of local

fluids below it (Fagereng et al., 2018; Hyndman & Wang, 1993; Oleskevich et al., 1999; Raimbourg et al., 2018).

VII.3. Chemical composition of fluid inclusions

In this study, we applied three different techniques in order to determine the chemical composition of fluid inclusions. The three methods point to a high variability in the composition of fluid inclusions (Fig. VII.2). The LA-ICP-MS results show two distinct groups when plotted in Na-Ca-K ternary diagram, with higher concentrations of sodium and to some extent calcium in fluid inclusions from higher-grade veins, whereas fluid inclusions from lower-grade veins are potassium-rich (Fig. VII.2). The decrepitation technique of individual evaporate mounds points to higher content of calcium among majority of analyzed mounds, similar to results derived by crush-leach technique. However, the reason for such discrepancy in derived results is not well understood. In any case, this study points to the necessity to examine carefully the chemical composition of fluid inclusions. As sodium is not the dominant cation in majority of fluid inclusions examined during this study, the salinity estimation may result in wrong estimations, as the temperature of the last melt correspond to different salinity depending on the major cation (Davis et al., 1990; Steel-MacInnis et al., 2011).

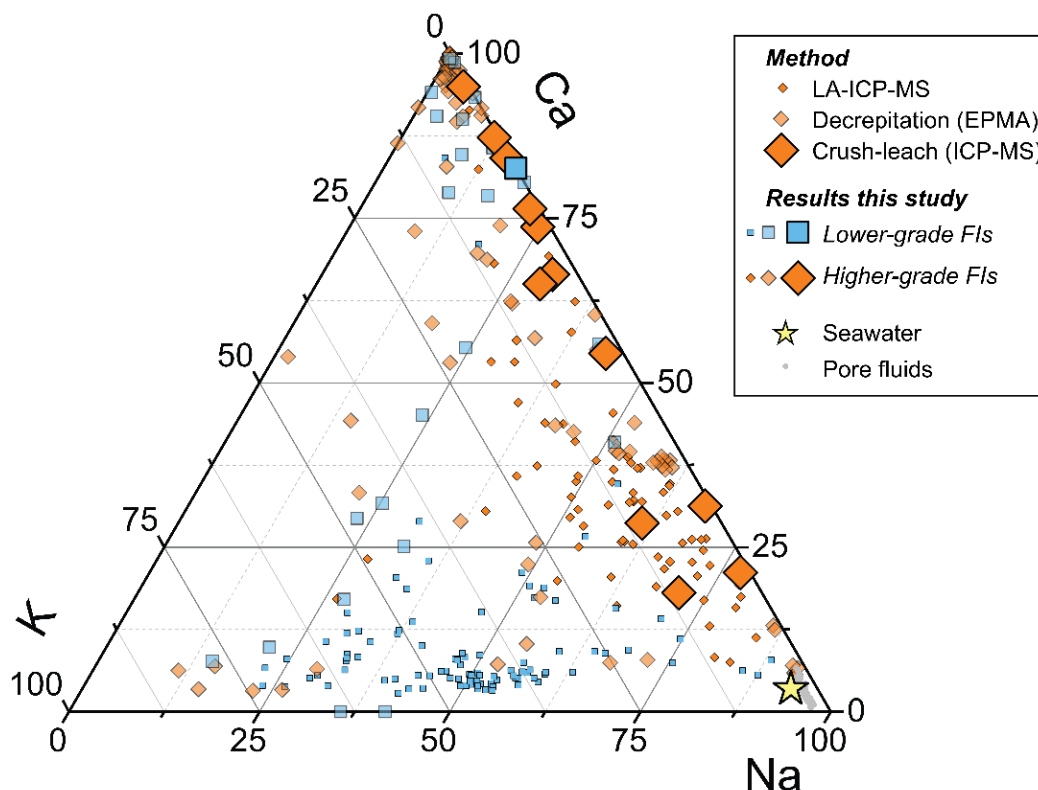


Figure VII.2. Na-Ca-K ternary diagram of fluid inclusions determined by three different methods (LA-ICP-MS, decrepitation method combined with EPMA, and crush-leach technique combined with ICP-MS).

The molal ratios obtained in the present work, such as K/Na, Ca/Na, B/Na, Rb/Na, or Ba/Na, are on average at least one order of magnitude higher than those of seawater and of the pore fluids of subducting sediments measured during IODP/ODP programs (Fig. VII.3). Only Cs/Na ratios are similar to the pore fluids to some extent (Fig. VII.3). This indicates that the fluids entrapped in Fls have chemical compositions that are significantly different from the initial pore fluid and that reflect the effect of diagenetic to low-grade metamorphic reactions. Upon burial of clay-rich sediments, the recrystallization of illite is the critical mineral reaction that influences the evolution of the fluid, because smectite-illite contains boron, lithium, and LILE in both the interstitial site and the mineral structure. At temperatures $>60^{\circ}\text{C}$, alkali metals (Li, Na, K, and LILE) preferentially go into the fluid phase (Miriam Kastner et al., 2014; Seyfried et al., 1998; Chen-Feng You & Gieskes, 2001). Most boron stored in clay minerals is released into the fluid phase at temperatures $\sim 150^{\circ}\text{C}$ (Hüpers & Kopf, 2012; Williams et al., 2001; You et al., 1995). Conversely, the depletion of potassium and rubidium in the fluid is expected when the transformation is completed, as illite incorporates higher concentrations of potassium and rubidium than smectite-

illite (Miriam Kastner et al., 2014). Thus, major changes in the composition of pore fluids is likely to occur at temperatures $<250^{\circ}\text{C}$, with smaller compositional variations upon further temperature increase.

Nevertheless, upon T increase from ~ 250 to $\sim 330^{\circ}\text{C}$, a few general geochemical trends are observed in veins from both the Kodiak complex and the Shimanto Belt (Fig. V.8): Ca/Na, B/Na, and Cs/Na ratios increase, whereas K/Na and Rb/Na ratios decrease as temperature increases (Table 3). The Sr/Na ratio remains relatively constant. Only the Ba/Na ratio shows different trends between the two localities, with a slight decrease in the Kodiak complex and a slight increase in the Shimanto Belt with a temperature increase.

The changes of element ratios as a function of temperature can be explained by examining the chemical evolution of the mineral phases and the mineral reactions in the pelitic matrix (Rajič et al., 2023). For example, the K/Na ratio decreases as temperature increases because illite becomes more potassium-rich as temperature increases, and the fluid becomes enriched in sodium at higher temperatures related to the dissolution of albite in the pelitic matrix.

Furthermore, the fluid in higher-grade veins from both case studies is characterized by an enrichment in trace elements, and in both localities the increase in FME concentrations are similar (Fig. V.5). In the Kodiak complex, there is no systematic loss of FME as temperature increases in whole-rock (Fig. V.2a-f). Conversely, in metapelites from Shimanto, FME show the most significant loss in whole-rock with increasing temperature (Fig. V.2a-f). Thus, as in both localities same trends in the fluid were observed as temperature increases, such as increase in boron and cesium concentrations, and opposite trends on whole-rock scale, the two case studies require different interpretation. The plausible explanations are (i) the difference in the size of fluid and rock reservoirs and (ii) the external influx of fluid responsible for leaching of FME from the rock.

VII.4. Open vs. closed system

Fluid-mobile elements are extensively used to determine fluid-rock interaction and to answer whether the system behaved as closed or open. In this study we describe two opposite observations, with the preservation of FME to higher-grade samples in the Kodiak complex, and significant loss in the samples from the Shimanto belt. These observations are further supported by analyzing

individual mineral phases. More precisely, high concentrations of lithium and boron are preserved in illite and chlorite in higher-grade samples from the Kodiak complex, whereas illite and chlorite from the Shimanto belt are characterized by significant loss of lithium and boron, likely released to a fluid phase. Rubidium and barium show redistribution between minerals (rubidium and barium released during albite dissolution are stored in remaining or newly formed illite) with potentially partial loss to a fluid phase. The lost quantity of cesium is likely released to a fluid phase. Furthermore, strontium is the only FME stored in vein-forming calcite in significant concentrations (to a lesser extent lithium in vein-forming quartz), suggesting that boron, lithium, cesium, as well as partially lost barium and rubidium, are the prominent fluid tracers.

In parallel, LA-ICP-MS micro-analysis of fluid inclusion populations has been proven as a powerful technique to determine the chemical composition of trapper fluids, as majority of analyzed elements are specifically located in fluid inclusions and not in quartz. Moreover, determined molar ratios and reconstructed concentrations are in an agreement with results from similar veins (Rauchenstein-Martinek et al., 2016; Yoshida et al., 2015).

This study further demonstrates that boron and cesium are the most prominent tracers of an origin of devolatilization processes in subducted sediments, as previously shown for prograde dehydration of altered oceanic crust (Angiboust et al., 2014; Bebout, 1991, 1993, 2007; Lafay et al., 2013; Marschall et al., 2006; Moran et al., 1992) or serpentinites (Deschamps et al., 2010, 2011, 2013; Hattori & Guillot, 2007; Lafay et al., 2013; Li & Lee, 2006; Scambelluri, et al., 2004a, 2004b). Furthermore, derived fluid-rock ratios suggest high quantity of focused fluid circulating through the Foliated Morotsuka. Such fluids may be expelled through the subduction zone forearc along permeable horizons.

Also, this study shows that “classical” fluid-mobile elements are indeed more sensitive to a high W/R ratio than major elements. Mass W/R ratios calculated for boron and barium are 0.36-0.68 and 0.21-0.77, where ranges are overlapping with wider range for barium to some extent. Cesium however point to much higher W/R ratio, 1.31-1.82. This discrepancy may be a result of low concentrations of cesium, where a standard deviation of ~1 ppm can result in significantly different ratios. For boron and barium, proposed W/R ratios are low in comparison to hydrothermal systems or ore-forming environments. However, for the clay-rich lithology that constitute a large

proportion of the studied rocks, calculated W/R ratios are significantly high and indicate that fluids do circulate in spite of the low permeability of the rocks.

VII.5. Implications for the fluid evolution during subduction

This study shows that boron and cesium are the most prominent tracers of devolatilization processes in subducted sediments, which is consistent with prograde dehydration of altered oceanic crust (Angiboust et al., 2014; Bebout, 1991, 1993, 2007; Lafay et al., 2013; Marschall et al., 2006; Moran et al., 1992) or serpentinites (Deschamps et al., 2010, 2011, 2013; Hattori & Guillot, 2007; Lafay et al., 2013; Li & Lee, 2006; Scambelluri, et al., 2004a, 2004b). Furthermore, derived water-rock ratios suggest that high quantities of fluid circulated through the Foliated Morotsuka. Such fluids may be expelled through the subduction zone forearc along permeable horizons.

In addition, similarities are observed between boron and cesium concentrations (or B/Na and Cs/Na ratios) in FIs acquired during this study and the chemical composition of fluids from mud volcanoes from Trinidad (Dia et al., 1999) or hot and cold springs from New Zealand (Barnes et al., 2019b) which have been interpreted to be derived from dehydrated subducted sediments based on high $\delta^{18}\text{O}$ and δD values in fluids flowing through the springs (Barnes, et al., 2019b; Giggenbach et al., 1993; Reyes et al., 2010). The fluids from mud volcanoes and springs (Dia et al., 1999; Barnes et al., 2019b) are characterized by a composition that is between that of the seawater and fluids from this study (Fig. VII.3), confirming the mixing of seawater percolating downwards and metamorphic fluids percolating upwards, as proposed for the Hikurangi accretionary prism (Reyes et al., 2010). Our study also confirms that compositionally altered pore fluids from the subducted sediments (coming from depths of the order of <15 km) travel along zones with high permeability back to the seafloor.

Additionally, the results from this study and the fluids from mud volcanoes and springs are characterized by different compositions compared to fluids derived from serpentinites (Fig. VII.3; Scambelluri et al., 2004a, 2015). This difference eliminates serpentinites as the main source for fluids circulating through overriding plate in subduction zones, at least in subduction zones where a significant amount of sediment is present.

Another example of fluids originating from dehydrated slab are cold springs that flow through serpentinite mud volcanoes across the Mariana forearc (Alt & Shanks III, 2006; Hulme et al., 2010;

Mottl, et al., 2003; Mottl et al., 2004; Wheat et al., 2020). It is proposed that chemical composition of fluids coming through serpentinite mud volcanoes can provide an insight into devolatilization processes of the subducting plate (Hulme et al., 2010; Mottl et al., 2004). The chemistry of sampled fluids from Mariana serpentinite mud volcanoes is significantly different from seawater (e.g., an enrichment in cesium; Mottl et al., 2004). However, in comparison to the results acquired during this study, as well as mud volcanoes/springs from Trinidad and New Zealand, fluids from Mariana serpentinite mud volcanoes are closer in composition to seawater and shallow sediment pore fluids, which is consistent with the mixing of deep fluids that are derived from the dehydrating slab and seawater that has percolated through the upper plate (Fig. VII.3).

VII.5. Implications for the fluid evolution during subduction

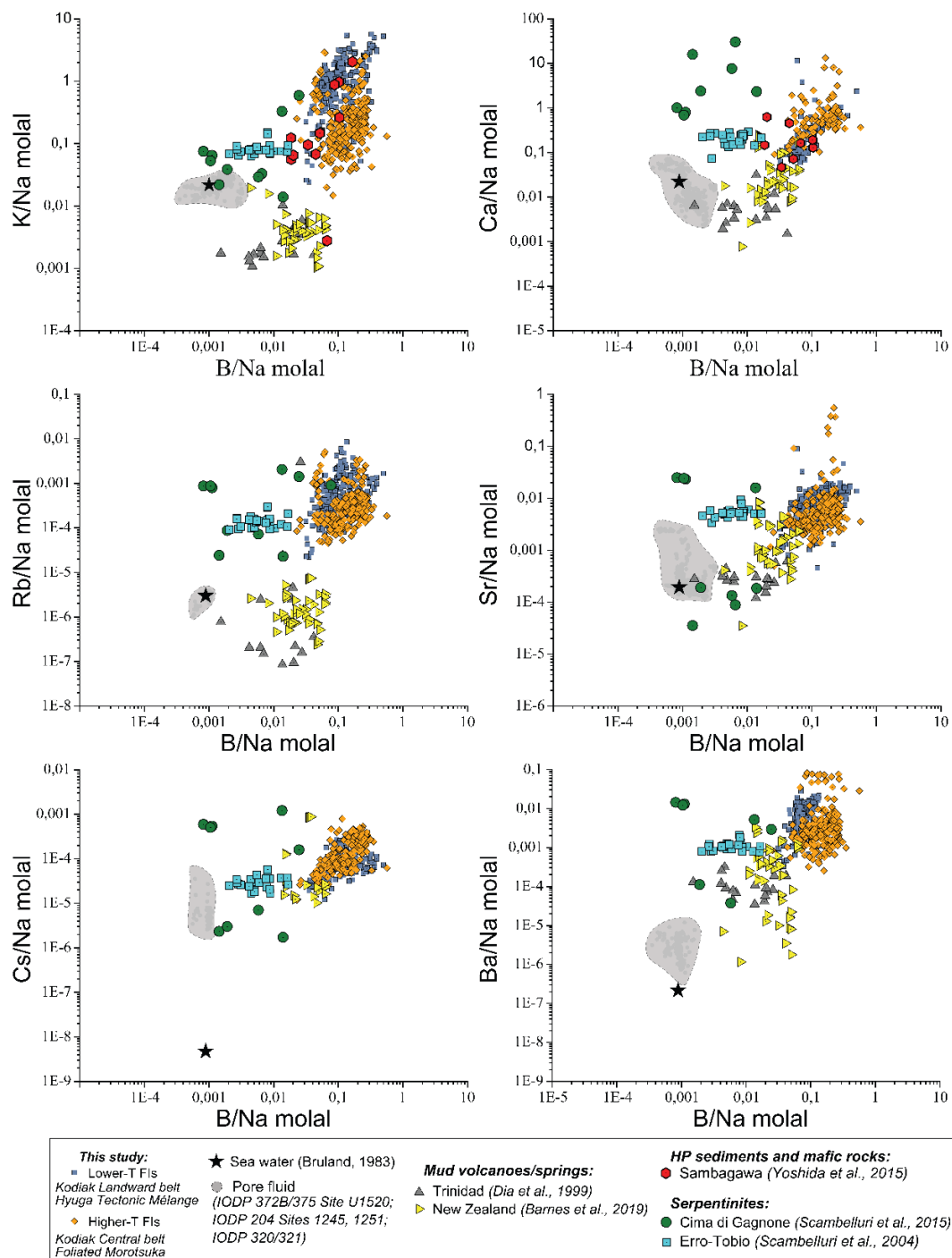


Figure VII.3. Binary diagram of B/Na vs. K/Na, Ca/Na, Rb/Na, Sr/Na, Cs/Na, and Ba/Na molal ratios of fluid inclusions examined in this study by LA-ICP-MS, with the compilation of possible fluid reservoirs involved into chemical evolution of subduction zone fluids in sedimentary units: The seawater composition (Bruland, 1983); The chemistry of pore fluid: IODP 372B/375 Site U1520 (Wallace et al., 2019); IODP 204 Sites 1245 and 1251 (Tréhu et al., 2003); IODP 320/321 (Pälike et al., 2010); Mud volcanoes and hot/cold springs (Barnes et al., 2019b; Dia et al., 1999); Crush-leach results from the Sambagawa belt (Yoshida et al., 2015); Serpentinities (Scambelluri et al., 2015; Scambelluri et al., 2004).

VII.6. $\delta^7\text{Li}$ of fluids

Finally, $\delta^7\text{Li}$ of FI leachates range from -1.54 to +17.07‰. In Kodiak, the fluid is relatively heavy (+8.1 to +17.07‰) in comparison to the fluid from Shimanto (+2.53 to +10.39‰). Such difference may be explained by looking into retention/loss of lithium in lithium-bearing minerals and predicted isotopic fractionation between minerals and fluid. Chlorite is the main host for lithium and it preferentially incorporates ^6Li . As chlorite from Kodiak shows no loss of lithium as temperature rises, the fluid remains isotopically heavier. In contrast, fluid from Shimanto is isotopically lighter, consistent with lithium loss from chlorite as temperature increases. The temperature dependent isotopic fractionation between quartz and fluid is not observed, which may be explained by disequilibrium crystallization of quartz from fluid, or as a result of dissolution-precipitation reactions postdating FI entrapment. Lithium concentrations and $\delta^7\text{Li}$ of FI leachates suggest constant interaction between fluid and sediments, where $\delta^7\text{Li}$ of fluids is shifted towards the signature of the protolith.

To track the chemical evolution of pore fluids in subducting sediments and the scale of their circulation, we integrate data on $\delta^7\text{Li}$ and Li concentrations across various reservoirs (Fig. VII.4a), starting from the seawater which is very initial pore fluid. Two critical processes need to be considered: (i) The formation of authigenic minerals, such as smectite, which have the affinity for Li, particularly the ^6Li . This results in the preferential adsorption of ^6Li , leaving the associated fluid depleted in Li and exhibiting a heavier $\delta^7\text{Li}$ compared to seawater (Fig. VII.4a). A nice example of such reactions is described in the Costa Rica subduction zone (Chan & Kastner, 2000), where alterations of volcanic material cause a depletion of Li in the fluid accompanied by heavier $\delta^7\text{Li}$ than that of seawater. (ii) The leaching of Li from minerals resulting in increased Li content within the fluid but concurrently lowers the $\delta^7\text{Li}$ values. Such case is documented in the Nankai Trough (C.-F. You, Chan, et al., 1995), where terrigenous material tends to release Li from minerals, causing an increase in Li concentrations of pore fluids and the decrease in $\delta^7\text{Li}$ (Fig. VII.4a). The formation of authigenic minerals plays important role very early during diagenesis, whereas in sediments experiencing higher temperatures (e.g., >100°C) the leaching of Li from minerals is the dominant process. Such progressive leaching of Li from minerals and its impact onto pore fluid composition are presented as a mixing model adapted from Scholz et al. (2010)

between seawater ($\text{Li} = 0.185 \text{ ppm}$, $\delta^7\text{Li} = 31 \text{ ‰}$; Millot et al., 2004) and GLOSS-II ($\text{Li} = 44 \text{ ppm}$, $\delta^7\text{Li} = -1.1$ to $+9.0 \text{ ‰}$; Plank, 2014).

In comparison to seawater and shallower pore fluids (Scholz et al., 2010), FI leachates from this study are enriched in Li and are isotopically lighter. Furthermore, our results are very similar to some of well-equilibrated pore fluids from sediment-hosted hydrothermal systems (Chan et al., 1994; Foustoukos et al., 2004). Moreover, results from this study are in agreement with a mixing model, pointing to a progressive evolution of fluid composition dominantly controlled by dissolution–precipitation processes, with a trend of $\delta^7\text{Li}$ of fluids towards values of the protolith (Fig. VII.4a).

During subduction and within the accretionary wedge, fluid flow becomes concentrated within regions of high permeability, such as the decollement zone or the out-of-sequence thrusts (Fig. VII.4b; Kastner et al., 2014). Along these pathways, fluids originating from deeper levels circulate back towards the surface, resulting in the development of chemical anomalies within these conduits. This phenomenon is effectively exemplified in the Costa Rica subduction zone (Chan & Kastner, 2000) and the Nankai Trough (C.-F. You, Chan, et al., 1995). In these two cases, pore fluids along the decollement zone exhibit distinctive characteristics, including anomalous $\delta^7\text{Li}$ and Li concentrations when compared to the pore fluids from sediments both above and below decollement zone (Fig. VII.4a). Furthermore, in the Costa Rica subduction zone, the thrust fault that traverses highly deformed sediments within the frontal accretionary wedge contains fluids with very the composition remarkably similar to those found along the decollement zone (Chan & Kastner, 2000). The fluids within the decollement show a slight depletion in Li when compared to FI leachates in this study (Fig. VII.4a). This observation implies that the leaching of Li is less pronounced at temperatures $>250^\circ\text{C}$, confirming that their origin likely stems from subducted sediments at temperatures $<150^\circ\text{C}$, associated with the smectite-illite transformation (Chan & Kastner, 2000; C.-F. You, Chan, et al., 1995).

An additional influx of fluids returning to the Earth's surface from subduction occurs through mud volcanoes and springs (Kopf, 2002; J. Casey Moore & Vrolijk, 1992), as documented in both offshore and onshore regions. These mud volcanoes are often related to the thrust faults within the overriding plate (Carson et al., 2003; Lauer & Saffer, 2012). Remarkably, these features have been observed at distances as far as $\sim 180 \text{ km}$ from the trench (e.g., Costa Rica subduction zone; Helper

et al., 2023; Hensen et al., 2004; Schmidt et al., 2005), extending into the arc region. Thus, these fluids provide an insight into devolatilization of the slab material and fluid circulation through the accretionary wedge.

The chemical composition of fluids from springs from the Hikurangi margin (Barnes et al., 2019b) show wide range of $\delta^7\text{Li}$ (-2.6‰ to $+29.0\text{‰}$) and Li concentrations (0.1 to 13.2 ppm), similar to the composition of FI leachates from this study (Fig. VII.4). These fluids were explained as originated from dehydrated sediments at depths <15 km (Barnes et al., 2019b). Thus, similarities between the Hikurangi spring fluids and FI leachates from this study further confirms the idea that fluids passing through the upper plate originate from subducted sediments. In the forearc region of the Costa Rica subduction zone, spring fluids show similar composition to the Hikurangi spring fluids and FI leachates from this study (Fig. VII.4; Helper et al., 2023), also confirming the origin of fluids as sedimentary-derived (Hensen et al., 2004). However, a systematic decrease in the $\delta^7\text{Li}$ values and an increase in Li concentrations of pore fluids is reported towards the arc region (Helper et al., 2023). Combining $\delta^7\text{Li}$ and $^3\text{He}/^4\text{He}$ of fluids, Helper et al. (2023) proposed that for the spring fluids within the arc region the slab shows only minor contribution to the fluids.

Hence, the combination of Li concentration and $\delta^7\text{Li}$ values in fluids can effectively serve as reliable tracers for fluid movements within subduction zones over substantial distances. Notably, these similarities become apparent in subducted sediments that have been buried to depths ranging from approximately 10 to 40 kilometers and subjected to temperatures below 400°C , as well as in fluids resurfacing through mud volcanoes. However, when the pore fluid composition gradually approaches the $\delta^7\text{Li}$ values of the protolith, determining the fluid source becomes challenging, as the $\delta^7\text{Li}$ values of sediments, basalts, altered oceanic crust, and serpentinites overlap (Fig. VII.4a).

VII.6. $\delta^7\text{Li}$ of fluids

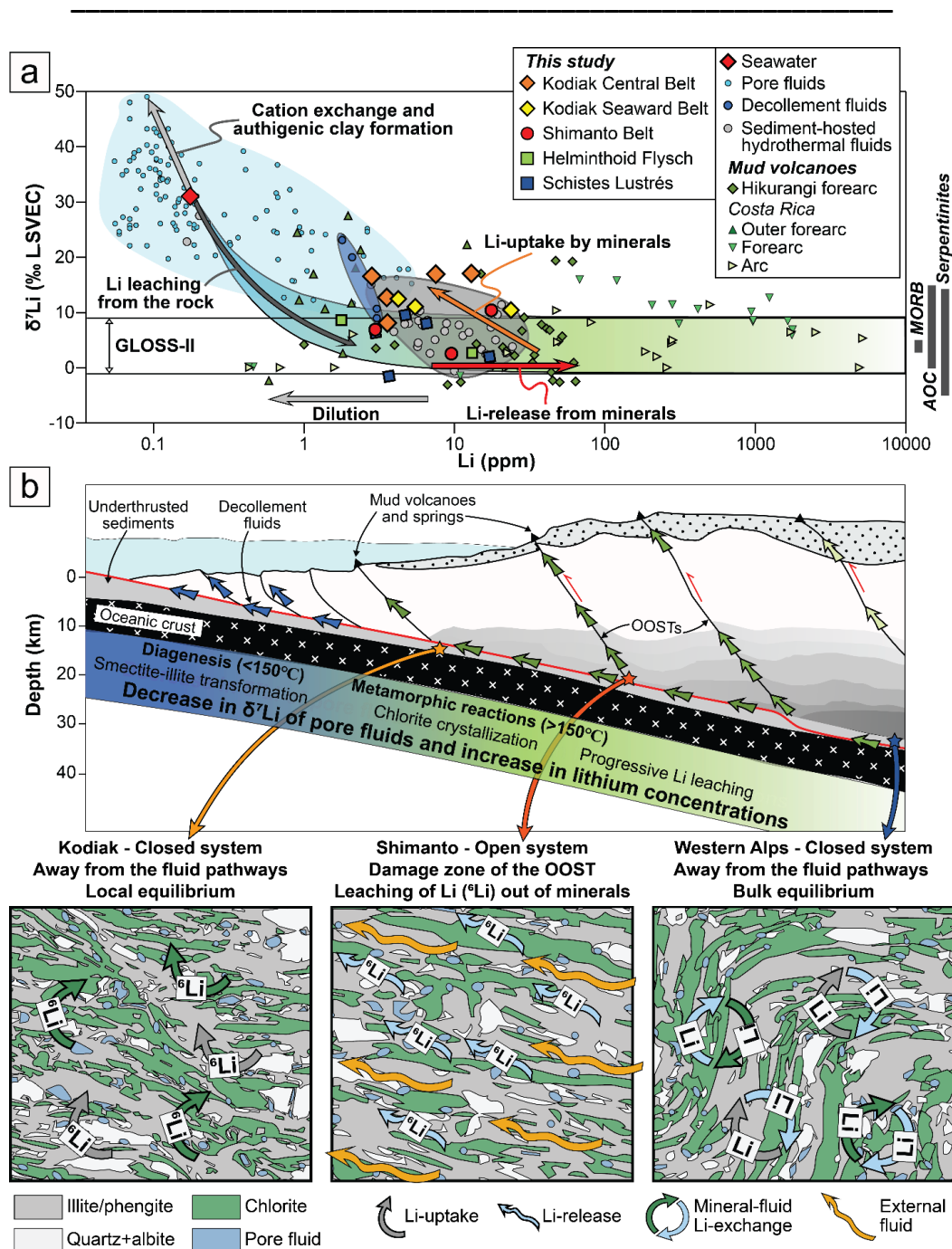


Figure VII.4. (a) A binary plot of Li concentrations and $\delta^7\text{Li}$ with a mixing model (Scholz et al., 2010) between Seawater (Millot et al., 2004) and GLOSS-II (T. Plank, 2014), with values of fluid inclusion leachates from this study, interstitial pore fluids (Scholz et al., 2010), decollement fluids (Chan & Kastner, 2000; C.-F. You, Chan, et al., 1995), sediment-hosted hydrothermal fluids (Chan et al., 1994; James et al., 1999), and mud volcanoes and springs (Barnes, Cullen, et al., 2019; Helper et al., 2023). (b) Schematic cross section showing accretionary prism and subducting plate with major tectonic elements (decollement zone, out-of-sequence thrusts) and arrows indicating the direction of focused fluid circulation. Stars denote an approximate depths and location of each studied complex and their proximity to the decollement zone or out-of-sequence thrusts, whereas adjacent sketch illustrates fluid-rock interaction and the fate of lithium in metapelites from these complexes.

Supplementary files

All Supplementary files are uploaded to the online repository *zenodo*. All files are available following the link: <https://doi.org/10.5281/zenodo.7505556>

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Supplementary Table S2.1. Structural data

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Supplementary Table S4.4. Mass balance calculations for specific zones of matrix

Chapter V

Supplementary Table S5.1. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) of individual mineral phases

Supplementary Table S5.2. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) of fluid inclusion-rich (FI-rich) and fluid inclusion-poor (FI-poor) quartz

References

- Abart, R., Badertscher, N., Burkhard, M., & Povoden, E. (2002). Oxygen, carbon and strontium isotope systematics in two profiles across the Glarus thrust: implications for fluid flow. *Contributions to Mineralogy and Petrology*, 143(2), 192–208. <https://doi.org/10.1007/s00410-001-0326-5>
- Agard, P., & Handy, M. R. (2021). Ocean Subduction Dynamics in the Alps. *Elements*, 17(1), 9–16. <https://doi.org/10.2138/gselements.17.1.9>
- Agard, P., Vidal, O., & Goffé, B. (2001). Interlayer and Si content of phengite in HP-LT carpholite-bearing metapelites: PHENGITE IN HP-LT METAPELITES. *Journal of Metamorphic Geology*, 19(5), 479–495. <https://doi.org/10.1046/j.0263-4929.2001.00322.x>
- Agard, P., Yamato, P., Jolivet, L., & Burov, E. (2009). Exhumation of oceanic blueschists and eclogites in subduction zones: Timing and mechanisms. *Earth-Science Reviews*, 92(1–2), 53–79. <https://doi.org/10.1016/j.earscirev.2008.11.002>
- Agard, Philippe, Goffé, B., Touret, J. L. R., & Vidal, O. (2000). Retrograde mineral and fluid evolution in high-pressure metapelites (Schistes lustrés unit, Western Alps). *Contributions to Mineralogy and Petrology*, 140, 296–315.
- Ahn, J. H., & Peacor, D. R. (1985). Transmission Electron Microscopy study of diagenetic chlorite in Gulf Coast argillaceous sediments. *Clay and Clay Minerals*, 33(3), 228–236.
- Aizawa, Y., Tatsumi, Y., & Yamada, H. (1999). Element transport by dehydration of subducted sediments: Implication for arc and ocean island magmatism. *Island Arc*, 8(1), 38–46. <https://doi.org/10.1046/j.1440-1738.1999.00217.x>
- Allan, M. M., Yardley, B. W. D., Forbes, L. J., Shmulovich, K. I., Banks, D. A., & Shepherd, T. J. (2005). Validation of LA-ICP-MS fluid inclusion analysis with synthetic fluid inclusions. *American Mineralogist*, 90(11–12), 1767–1775. <https://doi.org/10.2138/am.2005.1822>
- Alt, J., & Shanks III, W. (2006). Stable isotope compositions of serpentinite seamounts in the Mariana forearc: Serpentinization processes, fluid sources and sulfur metasomatism. *Earth and Planetary Science Letters*, 242(3–4), 272–285. <https://doi.org/10.1016/j.epsl.2005.11.063>
- Ammar, M. R., & Rouzaud, J.-N. (2012). How to obtain a reliable structural characterization of polished graphitized carbons by Raman microspectroscopy. *Journal of Raman Spectroscopy*, 43(2), 207–211. <https://doi.org/10.1002/jrs.3014>
- Angiboust, S., & Agard, P. (2010). Initial water budget: The key to detaching large volumes of eclogitized oceanic crust along the subduction channel? *Lithos*, 120(3–4), 453–474. <https://doi.org/10.1016/j.lithos.2010.09.007>
- Angiboust, Samuel, Pettke, T., De Hoog, J. C. M., Caron, B., & Oncken, O. (2014). Channelized Fluid Flow and Eclogite-facies Metasomatism along the Subduction Shear Zone. *Journal of Petrology*, 55(5), 883–916. <https://doi.org/10.1093/petrology/egu010>
- Angiboust, Samuel, Menant, A., Gerya, T., & Oncken, O. (2021). The rise and demise of deep accretionary wedges: A long-term field and numerical modeling perspective. *Geosphere*. <https://doi.org/10.1130/GES02392.1>
- Árkai, P., Faryad, S. W., Vidal, O., & Balogh, K. (2003). Very low-grade metamorphism of sedimentary rocks of the Meliata unit, Western Carpathians, Slovakia: implications of phyllosilicate characteristics. *International Journal of Earth Sciences*, 92(1), 68–85. <https://doi.org/10.1007/s00531-002-0303-x>
- Arkle, J. C., Armstrong, P. A., Haeussler, P. J., Prior, M. G., Hartman, S., Sendziak, K. L., & Brush, J. A. (2013). Focused exhumation in the syntaxis of the western Chugach Mountains and Prince William Sound, Alaska. *Geological Society of America Bulletin*, 125(5–6), 776–793. <https://doi.org/10.1130/B30738.1>
- Audet, P., & Schwartz, S. Y. (2013). Hydrologic control of forearc strength and seismicity in the Costa Rican subduction zone. *Nature Geoscience*, 6(10), 852–855. <https://doi.org/10.1038/ngeo1927>

- Badertscher, N. P., Beaudoin, G., Therrien, R., & Burkhard, M. (2002). Glarus overthrust: A major pathway for the escape of fluids out of the Alpine orogen. *Geology*, 30(10), 875–878. [https://doi.org/10.1130/0091-7613\(2002\)030<0875:GOAMPF>2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030<0875:GOAMPF>2.0.CO;2)
- Bangs, N. L., Shipley, T. H., & Moore, G. F. (1996). Elevated fluid pressure and fault zone dilation inferred from seismic models of the northern Barbados Ridge decollement. *Journal of Geophysical Research: Solid Earth*, 101(B1), 627–642. <https://doi.org/10.1029/95JB02402>
- Bangs, N. L. B., Shipley, T. H., Moore, J. C., & Moore, G. F. (1999). Fluid accumulation and channeling along the northern Barbados Ridge decollement thrust. *Journal of Geophysical Research: Solid Earth*, 104(B9), 20399–20414. <https://doi.org/10.1029/1999JB900133>
- Banks, D. A., Giuliani, G., Yardley, B. W. D., & Cheilletz, A. (2000). Emerald mineralisation in Colombia: Fluid chemistry and the role of brine mixing. *Mineralium Deposita*, 35, 699–713.
- Barnes, J. D., Penniston-Dorland, S. C., Bebout, G. E., Hoover, W., Beaudoin, G. M., & Agard, P. (2019). Chlorine and lithium behavior in metasedimentary rocks during prograde metamorphism: A comparative study of exhumed subduction complexes (Catalina Schist and Schistes Lustrés). *Lithos*, 336–337, 40–53. <https://doi.org/10.1016/j.lithos.2019.03.028>
- Barnes, J. D., Cullen, J., Barker, S., Agostini, S., Penniston-Dorland, S., Lassiter, J. C., et al. (2019). The role of the upper plate in controlling fluid-mobile element (Cl, Li, B) cycling through subduction zones: Hikurangi forearc, New Zealand. *Geosphere*, 15(3), 642–658. <https://doi.org/10.1130/GES02057.1>
- Battaglia, S. (2004). Variations in the chemical composition of illite from five geothermal fields: a possible geothermometer. *Clay Minerals*, 39(4), 501–510. <https://doi.org/10.1180/0009855043940150>
- Bebout, G. E. (1991). Field-Based Evidence for Devolatilization in Subduction Zones: Implications for Arc Magmatism. *Science, New Series*, 251(4992), 413–416.
- Bebout, G. E. (1995). The impact of subduction-zone metamorphism on mantle-ocean chemical cycling. *Chemical Geology*, 126(2), 191–218. [https://doi.org/10.1016/0009-2541\(95\)00118-5](https://doi.org/10.1016/0009-2541(95)00118-5)
- Bebout, G. E. (2014). Basic Considerations: Sampling, the Key for a Successful Applied Geochemical Survey for Mineral Exploration and Environmental Purposes. In *Treatise on Geochemistry* (Second Edition, Vol. 4, pp. 703–747). Elsevier. <https://doi.org/10.1016/B978-0-08-095975-7.01401-7>
- Bebout, G. E. (2021). Insights Into Subduction Zone Dynamics. In *Encyclopedia of Geology* (pp. 233–247). Elsevier. <https://doi.org/10.1016/B978-0-08-102908-4.00150-8>
- Bebout, G. E., Ryan, J. G., Leeman, W. P., & Bebout, A. E. (1999). Fractionation of trace elements by subduction-zone metamorphism — effect of convergent-margin thermal evolution. *Earth and Planetary Science Letters*, 171(1), 63–81. [https://doi.org/10.1016/S0012-821X\(99\)00135-1](https://doi.org/10.1016/S0012-821X(99)00135-1)
- Bebout, G. E., Bebout, A. E., & Graham, C. M. (2007). Cycling of B, Li, and LILE (K, Cs, Rb, Ba, Sr) into subduction zones: SIMS evidence from micas in high-P/T metasedimentary rocks. *Chemical Geology*, 239(3–4), 284–304. <https://doi.org/10.1016/j.chemgeo.2006.10.016>
- Bebout, G. E., Agard, P., Kobayashi, K., Moriguti, T., & Nakamura, E. (2013). Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps HP/UHP suites. *Chemical Geology*, 342, 1–20. <https://doi.org/10.1016/j.chemgeo.2013.01.009>
- Bebout, Gray E, Ryan, J. G., & Leeman, W. P. (1993). B–Be systematics in subduction-related metamorphic rocks: Characterization of the subducted component. *Geochimica et Cosmochimica Acta*, 57(10), 2227–2237. [https://doi.org/10.1016/0016-7037\(93\)90565-E](https://doi.org/10.1016/0016-7037(93)90565-E)
- Becker, H., Jochum, K. P., & Carlson, R. W. (2000). Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. *Chemical Geology*, 163(1–4), 65–99. [https://doi.org/10.1016/S0009-2541\(99\)00071-6](https://doi.org/10.1016/S0009-2541(99)00071-6)
- Behr, W. M., Gerya, T. V., Cannizzaro, C., & Blass, R. (2021). Transient slow slip characteristics of frictional-viscous subduction megathrust shear zones. *AGU Advances*, 2(3), 1–26. <https://doi.org/10.1029/2021av000416>

References

- Bekaert, D. V., Turner, S. J., Broadley, M. W., Barnes, J. D., Halldórsson, S. A., Labidi, J., et al. (2020). Subduction-Driven Volatile Recycling: A Global Mass Balance. *Annual Review of Earth and Planetary Sciences*, 49, 37–70.
- Berger, G., Schott, J., & Guy, C. (1988). Behavior of Li, Rb and Cs during basalt glass and olivine dissolution and chlorite, smectite and zeolite precipitation from seawater: Experimental investigations and modelization between 50° and 300°C. *Chemical Geology*, 71(4), 297–312. [https://doi.org/10.1016/0009-2541\(88\)90056-3](https://doi.org/10.1016/0009-2541(88)90056-3)
- Beyssac, O., Goffé, B., Chopin, C., & Rouzaud, J. N. (2002). Raman spectra of carbonaceous material in metasediments: a new geothermometer: RAMAN SPECTROSCOPY OF CARBONACEOUS MATERIAL. *Journal of Metamorphic Geology*, 20(9), 859–871. <https://doi.org/10.1046/j.1525-1314.2002.00408.x>
- Bodnar, R. J. (1993). Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. *Geochimica et Cosmochimica Acta*, 57(3), 683–684. [https://doi.org/10.1016/0016-7037\(93\)90378-A](https://doi.org/10.1016/0016-7037(93)90378-A)
- Boles, J. R., & Franks, S. G. (1979). Clay Diagenesis in Wilcox Sandstones of Southwest Texas: Implications of Smectite Diagenesis on Sandstone Cementation, 16.
- Bonnet, G., Chopin, C., Locatelli, M., Kylander-Clark, A., & Hacker, B. (2022). Protracted subduction of the European hyperextended margin revealed by rutile U-Pb geochronology across the Dora-Maira massif (W. Alps). *Tectonics*, 41(4).
- Bousquet, R. R. O., Goffé, B., Schmid, S. M., & Wiederkehr, M. (2012). Metamorphic framework of the Alps (1/1,000,000) (second edition). Paris, Commission for the Geological Map of the World.
- Bradley, D. C., Parrish, R., Clendenen, W., Lux, D., Layer, P. W., Heizler, M., & Donley, D. T. (2000). New Geochronological Evidence for the Timing of Early Tertiary Ridge Subduction in Southern Alaska. *US Geological Survey Professional Paper*, 1615, 5–21.
- Bradley, D. C., Kusky, T. M., Haeussler, P. J., Goldfarb, R. J., Miller, M. L., Dumoulin, J. A., et al. (2003). Geologic signature of early Tertiary ridge subduction in Alaska. In V. B. Sisson, S. M. Roeske, & T. L. Pavlis, *Geology of a transpressional orogen developed during ridge-trench interaction along the North Pacific margin*. Geological Society of America. <https://doi.org/10.1130/0-8137-2371-X.19>
- Brandon, M. T., Roden-Tice, M. K., & Garver, J. I. (1998). Late Cenozoic exhumation of the Cascadia accretionary wedge in the Olympic Mountains, northwest Washington State. *Geological Society of America Bulletin*, 110(8), 985–1009. [https://doi.org/10.1130/0016-7606\(1998\)110<0985:LCEOTC>2.3.CO;2](https://doi.org/10.1130/0016-7606(1998)110<0985:LCEOTC>2.3.CO;2)
- Brantley, S. L., & Fisher, D. M. (1997). Segregation veins: evidence for the deformation and dewatering of a low-grade metapelite. In *Deformation-enhanced Fluid Transport in the Earth's Crust and Mantle* (pp. 267–288). Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK.
- Bray, C. J., & Karig, D. E. (1985). Porosity of sediments in accretionary prisms and some implications for dewatering processes. *Journal of Geophysical Research: Solid Earth*, 90(B1), 768–778. <https://doi.org/10.1029/JB090iB01p00768>
- Breeding, C. M., & Ague, J. J. (2002). Slab-derived fluids and quartz-vein formation in an accretionary prism, Otago Schist, New Zealand. *Geology*, 30(6), 499–502.
- Brenan, J. M., Ryerson, F. J., & Shaw, H. F. (1998). The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: experiments and models. *Geochimica et Cosmochimica Acta*, 62(19–20), 3337–3347. [https://doi.org/10.1016/S0016-7037\(98\)00224-5](https://doi.org/10.1016/S0016-7037(98)00224-5)
- Brown, K. M., Saffer, D. M., & Bekins, B. A. (2001). Smectite diagenesis, pore-water freshening, and fluid flow at the toe of the Nankai wedge. *Earth and Planetary Science Letters*, 194, 97–109.
- Bruland, K. W. (1983). Trace Elements in Sea-water. In *Chemical Oceanography* (pp. 157–220). Elsevier. <https://doi.org/10.1016/B978-0-12-588608-6.50009-2>

- Burkhard, M., & Kerrich, R. (1988). Fluid regimes in the deformation of the Helvetic nappes, Switzerland, as inferred from stable isotope data. *Contributions to Mineralogy and Petrology*, 99(4), 416–429.
- Burkhard, M., Kerrich, R., Maas, R., & Fyfe, W. S. (1992). Stable and Sr-isotope evidence for fluid advection during thrusting of the glarus nappe (swiss alps). *Contributions to Mineralogy and Petrology*, 112(2–3), 293–311. <https://doi.org/10.1007/BF00310462>
- Busigny, V., Cartigny, P., Philippot, P., Ader, M., & Javoy, M. (2003). Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (western Alps, Europe). *Earth and Planetary Science Letters*, 215(1–2), 27–42. [https://doi.org/10.1016/S0012-821X\(03\)00453-9](https://doi.org/10.1016/S0012-821X(03)00453-9)
- Byrne, T. (1984). Early deformation in melange terranes of the Ghost Rocks Formation, Kodiak Islands, Alaska. In *Geological Society of America Special Papers* (Vol. 198, pp. 21–52). Geological Society of America. <https://doi.org/10.1130/SPE198-p21>
- Byrne, Tim. (1982). Structural evolution of coherent terranes in the Ghost Rocks Formation, Kodiak Island, Alaska. *Geological Society, London, Special Publications*, 10(1), 229–242. <https://doi.org/10.1144/GSL.SP.1982.010.01.15>
- Byrne, Tim. (1986). Eocene underplating along the Kodiak Shelf, Alaska: Implications and regional correlations. *Tectonics*, 5(3), 403–421. <https://doi.org/10.1029/TC005i003p00403>
- Byrne, Tim, & Fisher, D. M. (1987). Episodic growth of the Kodiak convergent margin. *Nature*, 325, 338–341.
- Carson, B., Suess, E., & Strasser, J. C. (1990). Fluid flow and mass flux determinations at vent sites on the Cascadia Margin Accretionary Prism. *Journal of Geophysical Research*, 95(B6), 8891. <https://doi.org/10.1029/JB095iB06p08891>
- Carson, B., Kastner, M., Bartlett, D., Jaeger, J., Jannasch, H., & Weinstein, Y. (2003). Implications of carbon flux from the Cascadia accretionary prism: results from long-term, in situ measurements at ODP Site 892B. *Marine Geology*, 198(1–2), 159–180. [https://doi.org/10.1016/S0025-3227\(03\)00099-9](https://doi.org/10.1016/S0025-3227(03)00099-9)
- Carver, G., Sauber, J., Lettis, W., Witter, R., & Whitney, B. (2013). Active Faults on Northeastern Kodiak Island, Alaska. In J. T. Freymueller, P. J. Haeussler, R. L. Wesson, & G. Ekström (Eds.), *Geophysical Monograph Series* (pp. 167–184). Washington, D. C: American Geophysical Union. <https://doi.org/10.1029/179GM09>
- Caumon, M.-C., Dubessy, J., Robert, P., & Tarantola, A. (2014). Fused-silica capillary capsules (FSCCs) as reference synthetic aqueous fluid inclusions to determine chlorinity by Raman spectroscopy. *European Journal of Mineralogy*, 25(5), 755–763. <https://doi.org/10.1127/0935-1221/2013/0025-2280>
- Caumon, M.-C., Tarantola, A., & Mosser-Ruck, R. (2015). Raman spectra of water in fluid inclusions: I. Effect of host mineral birefringence on salinity measurement: Effect of mineral birefringence on salinity measured by Raman spectroscopy. *Journal of Raman Spectroscopy*, 46(10), 969–976. <https://doi.org/10.1002/jrs.4708>
- Chan, L.-H., & Kastner, M. (2000). Lithium isotopic compositions of pore fluids and sediments in the Costa Rica subduction zone: implications for fluid processes and sediment contribution to the arc volcanoes. *Earth and Planetary Science Letters*, 183, 275–290.
- Chan, L.-H., Gieskes, J. M., Chen-Feng, Y., & Edmond, J. M. (1994). Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California. *Geochimica et Cosmochimica Acta*, 58(20), 4443–4454. [https://doi.org/10.1016/0016-7037\(94\)90346-8](https://doi.org/10.1016/0016-7037(94)90346-8)
- Clauer, N., Honty, M., Fallick, A. E., Šucha, V., & Aubert, A. (2014). Regional illitization in bentonite beds from the East Slovak Basin based on isotopic characteristics (K-Ar, $\delta^{18}\text{O}$ and δD) of illite-type nanoparticles. *Clay Minerals*, 49(2), 247–275. <https://doi.org/10.1180/claymin.2014.049.2.07>

- Clauer, Norbert, Williams, L. B., Lemarchand, D., Florian, P., & Honty, M. (2018). Illitization decrypted by B and Li isotope geochemistry of nanometer-sized illite crystals from bentonite beds, East Slovak Basin. *Chemical Geology*, 477, 177–194. <https://doi.org/10.1016/j.chemgeo.2017.10.027>
- Clendenen, W. S., Fisher, D., & Byrne, T. (2003). Cooling and exhumation history of the Kodiak accretionary prism, southwest Alaska. In V. B. Sisson, S. M. Roeske, & T. L. Pavlis, *Geology of a transpressional orogen developed during ridge-trench interaction along the North Pacific margin*. Geological Society of America. <https://doi.org/10.1130/0-8137-2371-X.71>
- Clift, P., & Vannucchi, P. (2004). Controls on tectonic accretion versus erosion in subduction zones: Implications for the origin and recycling of the continental crust. *Reviews of Geophysics*, 42(2), RG2001. <https://doi.org/10.1029/2003RG000127>
- Clift, P. D., Pavlis, T., DeBari, S. M., Draut, A. E., Rioux, M., & Kelemen, P. B. (2005). Subduction erosion of the Jurassic Talkeetna-Bonanza arc and the Mesozoic accretionary tectonics of western North America. *Geology*, 33(11), 881. <https://doi.org/10.1130/G21822.1>
- Colten-Bradley, V. A. (1987). Role of pressure in smectite dehydration; Effects on geopressure and smectite- to-illite transformation. *American Association of Petroleum Geologists Bulletin*, 71, 1414–1427.
- Connelly, W. (1978). Uyak Complex, Kodiak Islands, Alaska: A Cretaceous subduction complex. *Geological Society of America Bulletin*, 89, 755–769.
- Cox, S. F. (2010). The application of failure mode diagrams for exploring the roles of fluid pressure and stress states in controlling styles of fracture-controlled permeability enhancement in faults and shear zones. *Geofluids*, 10, 217–233. <https://doi.org/10.1111/j.1468-8123.2010.00281.x>
- Cox, Stephen F. (2002). Fluid flow in mid-to deep crustal shear systems: Experimental constraints, observations on exhumed high fluid flux shear systems, and implications for seismogenic processes. *Earth, Planets and Space*, 54(11), 1121–1125. <https://doi.org/10.1186/BF03353312>
- Dahlen, F. A. (1990). Critical Taper Model of Fold-And-Thrust Belts and Accretionary Wedges. *Annual Review of Earth and Planetary Sciences*, 18, 55–99. <https://doi.org/10.1146/annurev.ea.18.050190.000415>
- Dasgupta, T., & Mukherjee, S. (2020). Compaction of Sediments and Different Compaction Models. In T. Dasgupta & S. Mukherjee, *Sediment Compaction and Applications in Petroleum Geoscience* (pp. 1–8). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-13442-6_1
- Davis, D., Suppe, J., & Dahlen, F. A. (1983). Mechanics of fold-and-thrust belts and accretionary wedges. *Journal of Geophysical Research*, 88(B2), 1153. <https://doi.org/10.1029/JB088iB02p01153>
- Davis, D. W., Lowenstein, T. K., & Spencer, R. (1990). Melting behavior of fluid inclusions in laboratory-grown halite crystals in the systems NaCl-H₂O, NaCl-KCl-H₂O, NaCl-MgCl₂-H₂O, and NaCl-CaCl₂-H₂O. *Geochimica et Cosmochimica Acta*, 54, 591–601.
- De Parseval, P., Amouric, M., Baronnet, A., Fortune, J.-P., Moine, B., & Ferret, J. (1994). HRTEM study of the chloritization of micas in the talk-chlorite deposit at Trimouns (Pyrenees, France). *Eur. J. Mineral*, 6, 123–132.
- Delvaux, D., & Sperner, B. (2003). New aspects of tectonic stress inversion with reference to the TENSOR program. *Geological Society, London, Special Publications*, 212(1), 75–100. <https://doi.org/10.1144/GSL.SP.2003.212.01.06>
- Delvaux, Damien, Kipata, L., & Sintubin, M. (2013). Tectonic stress inversion of large multi-phase fracture data sets: application of Win-Tensor to reveal the brittle tectonic history of the Lufilan Arc, DRC. In *EGU General Assembly 2013* (Vol. 15, p. 1).
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., & Hattori, K. (2010). In situ characterization of serpentinites from forearc mantle wedges: Timing of serpentinitization and behavior of fluid-mobile elements in subduction zones. *Chemical Geology*, 269(3–4), 262–277. <https://doi.org/10.1016/j.chemgeo.2009.10.002>
- Deschamps, F., Guillot, S., Godard, M., Andreani, M., & Hattori, K. (2011). Serpentinites act as sponges for fluid-mobile elements in abyssal and subduction zone environments: Serpentinites act as

- p sponges for fluid-mobile elements.
- Terra Nova*
- , 23(3), 171–178.
- <https://doi.org/10.1111/j.1365-3121.2011.00995.x>
- Deschamps, F., Godard, M., Guillot, S., & Hattori, K. (2013). Geochemistry of subduction zone serpentinites: A review. *Lithos*, 178, 96–127. <https://doi.org/10.1016/j.lithos.2013.05.019>
- Di Toro, G., Han, R., Hirose, T., De Paola, N., Nielsen, S., Mizoguchi, K., et al. (2011). Fault lubrication during earthquakes. *Nature*, 471(7339), 494–498. <https://doi.org/10.1038/nature09838>
- Dia, A. N., Castrec-Rouelle, M., Boulègue, J., & Comeau, P. (1999). Trinidad mud volcanoes: where do the expelled fluids come from? *Geochimica et Cosmochimica Acta*, 63(7–8), 1023–1038. [https://doi.org/10.1016/S0016-7037\(98\)00309-3](https://doi.org/10.1016/S0016-7037(98)00309-3)
- Dimitrov, L. I. (2002). Mud volcanoes—the most important pathway for degassing deeply buried sediments. *Earth-Science Reviews*, 59(1–4), 49–76. [https://doi.org/10.1016/S0012-8252\(02\)00069-7](https://doi.org/10.1016/S0012-8252(02)00069-7)
- Ditullio, L., & Byrne, T. (1990). Deformation paths in the shallow levels of an accretionary prism: The Eocene Shimanto belt of southwest Japan. *Geological Society of America Bulletin*, 102(10), 1420–1438. [https://doi.org/10.1130/0016-7606\(1990\)102<1420:DPITSL>2.3.CO;2](https://doi.org/10.1130/0016-7606(1990)102<1420:DPITSL>2.3.CO;2)
- Drief, A., & Nieto, F. (2000). Chemical composition of smectites formed in clastic sediments. Implications for the smectite-illite transformation. *Clay Minerals*, 35(4), 665–678. <https://doi.org/10.1180/000985500547124>
- Dubacq, B., Vidal, O., & De Andrade, V. (2010). Dehydration of dioctahedral aluminous phyllosilicates: thermodynamic modelling and implications for thermobarometric estimates. *Contributions to Mineralogy and Petrology*, 159(2), 159–174. <https://doi.org/10.1007/s00410-009-0421-6>
- Dubessy, J., Geisler, D., Kosztolanyi, C., & Vernet, M. (1983). The determination of sulphate in fluid inclusions using the M.O.L.E. Raman microprobe. Application to a keuper halite and geochemical consequences. *Geochimica et Cosmochimica Acta*, 47(1), 1–10. [https://doi.org/10.1016/0016-7037\(83\)90086-8](https://doi.org/10.1016/0016-7037(83)90086-8)
- Elliott, T. (2003). Tracers of the slab. In J. Eiler (Ed.), *Geophysical Monograph Series* (Vol. 138, pp. 23–45). Washington, D. C.: American Geophysical Union. <https://doi.org/10.1029/138GM03>
- Epstein, G. S., Bebout, G. E., Angiboust, S., & Agard, P. (2020). Scales of fluid-rock interaction and carbon mobility in the deeply underplated and HP-Metamorphosed Schistes Lustrés, Western Alps. *Lithos*, 354–355, 105229. <https://doi.org/10.1016/j.lithos.2019.105229>
- Ernst, W. G., & McLaughlin, R. J. (2012). Mineral parageneses, regional architecture, and tectonic evolution of Franciscan metagraywackes, Cape Mendocino-Garberville-Covelo 30' × 60' quadrangles, northwest California: NW CALIFORNIAN FRANCISCAN METAGRAYWACKES. *Tectonics*, 31(1), n/a-n/a. <https://doi.org/10.1029/2011TC002987>
- Fagereng, Å., & Cooper, A. F. (2010). The metamorphic history of rocks buried, accreted and exhumed in an accretionary prism: an example from the Otago Schist, New Zealand. *Journal of Metamorphic Geology*, 28(9), 935–954. <https://doi.org/10.1111/j.1525-1314.2010.00900.x>
- Fagereng, A., & Sibson, R. H. (2010). Mélange rheology and seismic style. *Geology*, 38(8), 751–754. <https://doi.org/10.1130/G30868.1>
- Fagereng, Åke, Remitti, F., & Sibson, R. H. (2011). Incrementally developed slickenfibers — Geological record of repeating low stress-drop seismic events? *Tectonophysics*, 510(3–4), 381–386. <https://doi.org/10.1016/j.tecto.2011.08.015>
- Fagereng, Åke, Diener, J. F. A., Ellis, S., & Remitti, F. (2018). Fluid-related deformation processes at the up- and downdip limits of the subduction thrust seismogenic zone: What do the rocks tell us? In Timothy Byrne, M. B. Underwood, D. Fisher, L. McNeill, D. Saffer, K. Ujiie, & A. Yamaguchi, *Geology and Tectonics of Subduction Zones: A Tribute to Gaku Kimura*. Geological Society of America. [https://doi.org/10.1130/2018.2534\(12\)](https://doi.org/10.1130/2018.2534(12))
- Faghil, A., Kusky, T., & Samani, B. (2012). Kinematic analysis of deformed structures in a tectonic mélange: a key unit for the manifestation of transpression along the Zagros Suture Zone, Iran. *Geological Magazine*, 149(6), 1107–1117. <https://doi.org/10.1017/S0016756812000295>

- Farris, D. W. (2010). Tectonic and petrologic evolution of the Kodiak batholith and the trenchward belt, Kodiak Island, AK: Contact fault juxtaposition? *Journal of Geophysical Research*, 115(B7), B07208. <https://doi.org/10.1029/2009JB006434>
- Farris, D. W., & Paterson, S. R. (2009). Subduction of a segmented ridge along a curved continental margin: Variations between the western and eastern Sanak–Baranof belt, southern Alaska. *Tectonophysics*, 464(1–4), 100–117. <https://doi.org/10.1016/j.tecto.2007.10.008>
- Farris, D. W., Haeussler, P., Friedman, R., Paterson, S. R., Saltus, R. W., & Ayuso, R. (2006). Emplacement of the Kodiak batholith and slab-window migration. *Geological Society of America Bulletin*, 118(11–12), 1360–1376. <https://doi.org/10.1130/B25718.1>
- Farver, J. R., & Yund, R. A. (1991). Oxygen diffusion in quartz: Dependence on temperature and water fugacity. *Chemical Geology*, 90(1–2), 55–70. [https://doi.org/10.1016/0009-2541\(91\)90033-N](https://doi.org/10.1016/0009-2541(91)90033-N)
- Faulkner, D. R., Lewis, A. C., & Rutter, E. H. (2003). On the internal structure and mechanics of large strike-slip fault zones: field observations of the Carboneras fault in southeastern Spain. *Tectonophysics*, 367(3–4), 235–251. [https://doi.org/10.1016/S0040-1951\(03\)00134-3](https://doi.org/10.1016/S0040-1951(03)00134-3)
- Faulkner, D. R., Jackson, C. A. L., Lunn, R. J., Schlische, R. W., Shipton, Z. K., Wibberley, C. A. J., & Withjack, M. O. (2010). A review of recent developments concerning the structure, mechanics and fluid flow properties of fault zones. *Journal of Structural Geology*, 32(11), 1557–1575. <https://doi.org/10.1016/j.jsg.2010.06.009>
- Ferrill, D. A., Morris, A. P., Evans, M. A., Burkhard, M., Groshong, R. H., & Onasch, C. M. (2004). Calcite twin morphology: a low-temperature deformation geothermometer. *Journal of Structural Geology*, 26(8), 1521–1529. <https://doi.org/10.1016/j.jsg.2003.11.028>
- Ferry, J. M. (1981). Petrology of graphitic sulfide-rich schists from south-central Maine: an example of desulfidation during prograde regional metamorphism. *American Mineralogist*, 66, 908–930.
- Fisher, D., & Byrne, T. (1987a). Structural evolution of underthrust sediments, Kodiak Islands, Alaska. *Tectonics*, 6(6), 775–793. <https://doi.org/10.1029/TC006i006p00775>
- Fisher, D., & Byrne, T. (1987b). Structural evolution of underthrust sediments, Kodiak Islands, Alaska. *Tectonics*, 6(6), 775–793. <https://doi.org/10.1029/TC006i006p00775>
- Fisher, D., & Byrne, T. (1990). The character and distribution of mineralized fractures in the Kodiak Formation, Alaska: Implications for fluid flow in an underthrust sequence. *Journal of Geophysical Research*, 95(B6), 9069–9080. <https://doi.org/10.1029/JB095iB06p09069>
- Fisher, D. M., & Brantley, S. L. (1992). Models of quartz overgrowth and vein formation: Deformation and episodic fluid flow in an ancient subduction zone. *Journal of Geophysical Research*, 97(B13), 20043–20061. <https://doi.org/10.1029/92JB01582>
- Fisher, D. M., & Brantley, S. L. (2014). The role of silica redistribution in the evolution of slip instabilities along subduction interfaces: Constraints from the Kodiak accretionary complex, Alaska. *Journal of Structural Geology*, 69, 395–414. <https://doi.org/10.1016/j.jsg.2014.03.010>
- Fisher, D. M., & Byrne, T. (1992). Strain variations in an ancient accretionary complex: Implications for forearc evolution. *Tectonics*, 11(2), 330–347. <https://doi.org/10.1029/91TC01490>
- Fisher, D. M., Brantley, S. L., Everett, M., & Dzvonik, J. (1995). Cyclic fluid flow through a regionally extensive fracture network within the Kodiak accretionary prism. *Journal of Geophysical Research: Solid Earth*, 100(B7), 12881–12894. <https://doi.org/10.1029/94JB02816>
- Fisher, D. M., Hooker, J. N., Smye, A. J., & Chen, T.-W. (2021). Insights from the geological record of deformation along the subduction interface at depths of seismogenesis. *Geosphere*, 17, 18. <https://doi.org/10.1130/GES02389.1>
- Fisher, M. A. (1979). Structure and Tectonic Setting of Continental Shelf Southwest of Kodiak Island, Alaska. *AAPG Bulletin*, 63, 301–310. <https://doi.org/10.1306/C1EA55FD-16C9-11D7-8645000102C1865D>
- Fisher, M. A. (1980). Petroleum Geology of Kodiak Shelf, Alaska. *AAPG Bulletin*, 64(8), 1140–1157.

- Fisher, M. A., & Holmes, M. L. (1980). Large-scale structure of deep strata beneath Kodiak shelf, Alaska. *Geological Society of America Bulletin*, 91(4), 218–224. [https://doi.org/10.1130/0016-7606\(1980\)91<218:LSODSB>2.0.CO;2](https://doi.org/10.1130/0016-7606(1980)91<218:LSODSB>2.0.CO;2)
- Forster, M. A., & Lister, G. S. (2003). Cretaceous metamorphic core complexes in the Otago Schist, New Zealand. *Australian Journal of Earth Sciences*, 50(2), 181–198. <https://doi.org/10.1046/j.1440-0952.2003.00986.x>
- Foustoukos, D. I., James, R. H., Berndt, M. E., & Seyfried, W. E. (2004). Lithium isotopic systematics of hydrothermal vent fluids at the Main Endeavour Field, Northern Juan de Fuca Ridge. *Chemical Geology*, 212(1–2), 17–26. <https://doi.org/10.1016/j.chemgeo.2004.08.003>
- Frey, M. (1978). Progressive Low-Grade Metamorphism of a Black Shale Formation, Central Swiss Alps, with Special Reference to Pyrophyllite and Margarite Bearing Assemblages. *Journal of Petrology*, 19(1), 95–135. <https://doi.org/10.1093/petrology/19.1.95>
- Frey, Martin, Bucher, K., & Frank, E. (1980). Alpine metamorphism along the geotraverse Basel-Chiasso : a review. <https://doi.org/10.5169/SEALS-164971>
- Füger, A., Kuessner, M., Rollion-Bard, C., Leis, A., Magna, T., Dietzel, M., & Mavromatis, V. (2022). Effect of growth rate and pH on Li isotope fractionation during its incorporation in calcite. *Geochimica et Cosmochimica Acta*, 323, 276–290. <https://doi.org/10.1016/j.gca.2022.02.014>
- Giggenbach, W. F., Sano, Y., & Wakita, H. (1993). Isotopic composition of helium, and CO₂ and CH₄ contents in gases produced along the New Zealand part of a convergent plate boundary. *Geochimica et Cosmochimica Acta*, 57(14), 3427–3455. [https://doi.org/10.1016/0016-7037\(93\)90549-C](https://doi.org/10.1016/0016-7037(93)90549-C)
- Goffé, B., & Chopin, C. (1986). High-pressure metamorphism in the Western Alps : zoneography of metapelites, chronology and consequences. <https://doi.org/10.5169/SEALS-50880>
- Gudelius, D., Aulbach, S., Seitz, H.-M., & Braga, R. (2022). Crustal fluids cause strong Lu-Hf fractionation and Hf-Nd-Li isotopic provinciality in the mantle of continental subduction zones. *Geology*, 50(2), 163–168. <https://doi.org/10.1130/G49317.1>
- Guillot, S., Hattori, K., Agard, P., Schwartz, S., & Vidal, O. (2009). Exhumation Processes in Oceanic and Continental Subduction Contexts: A Review. In S. Lallemand & F. Funiciello (Eds.), *Subduction Zone Geodynamics* (pp. 175–205). Berlin, Heidelberg: Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-540-87974-9_10
- Hacker, B. R. (2008). H₂O subduction beyond arcs. *Geochemistry, Geophysics, Geosystems*, 9(3), n/a-n/a. <https://doi.org/10.1029/2007GC001707>
- Hacker, B. R., Abers, G. A., & Peacock, S. M. (2003). Subduction factory 1. Theoretical mineralogy, densities, seismic wave speeds, and H₂O contents. *Journal of Geophysical Research: Solid Earth*, 108(B1). <https://doi.org/10.1029/2001JB001127>
- Haeussler, P. J., & Bradley, D. C. (2003). Life and death of the Resurrection plate: Evidence for its existence and subduction in the northeastern Pacific in Paleocene–Eocene time. *Geological Society of America Bulletin*, 15.
- Haeussler, P. J., Bradley, D., Goldfarb, R., Snee, L., & Taylor, C. (1995). Link between ridge subduction and gold mineralization in southern Alaska. *Geology*, 23(11), 995–998.
- Hall, A. J. (1986). Pyrite-pyrrhotine redox reactions in nature. *Mineralogical Magazine*, 50(356), 223–229. <https://doi.org/10.1180/minmag.1986.050.356.05>
- Harris, R. A. (2003). “The Mechanics of Earthquakes and Faulting - Second Edition” by Christopher H. Scholz. *Seismological Research Letters*, 74(3), 333–333. <https://doi.org/10.1785/gssrl.74.3.333>
- Hattori, K. H., & Guillot, S. (2007). Geochemical character of serpentinites associated with high- to ultrahigh-pressure metamorphic rocks in the Alps, Cuba, and the Himalayas: Recycling of elements in subduction zones: GEOCHEMISTRY OF SERPENTINITES. *Geochemistry, Geophysics, Geosystems*, 8(9), n/a-n/a. <https://doi.org/10.1029/2007GC001594>

- Helper, J. P., Barnes, J. D., de Moor, J. M., Rodríguez, A., Barry, P. H., Ramos, E. J., & Lassiter, J. C. (2023). Li isotope ratios of spring fluids as an effective tracer of slab-derived subducted sources across the Costa Rica forearc. *Geology*, 51(9), 855–859. <https://doi.org/10.1130/G51277.1>
- Henry, C., Burkhard, M., & Goffé, B. (1996). Evolution of synmetamorphic veins and their wallrocks through a Western Alps transect: no evidence for large-scale fluid flow. Stable isotope, major- and trace-element systematics. *Chemical Geology*, 127(1–3), 81–109. [https://doi.org/10.1016/0009-2541\(95\)00106-9](https://doi.org/10.1016/0009-2541(95)00106-9)
- Hensen, C., Wallmann, K., Schmidt, M., Ranero, C. R., & Suess, E. (2004). Fluid expulsion related to mud extrusion off Costa Rica—A window to the subducting slab. *Geology*, 32(3), 201. <https://doi.org/10.1130/G20119.1>
- Herviou, Clément, & Bonnet, G. (2023). Paleocene-Eocene high-pressure carbonation of Western Alps serpentinites: positive feedback between deformation and CO₂-CH₄ fluid ingression responsible for slab slicing? *Geochemistry, Geophysics, Geosystems*.
- Herviou, Clément, Verlaquet, A., Agard, P., Locatelli, M., Raimbourg, H., Lefeuvre, B., & Dubacq, B. (2021). Along-dip variations of subduction fluids: The 30–80 km depth traverse of the Schistes Lustrés complex (Queyras-Monviso, W. Alps). *Lithos*, 394–395, 106168. <https://doi.org/10.1016/j.lithos.2021.106168>
- Herviou, Clément, Agard, P., Plunder, A., Mendes, K., Verlaquet, A., Deldicque, D., & Cubas, N. (2022). Subducted fragments of the Liguro-Piemont ocean, Western Alps: Spatial correlations and offscraping mechanisms during subduction. *Tectonophysics*, 827, 229267. <https://doi.org/10.1016/j.tecto.2022.229267>
- Heuret, A., Lallemand, S., Funicello, F., Piromallo, C., & Faccenna, C. (2011). Physical characteristics of subduction interface type seismogenic zones revisited: SUBDUCTION-TYPE SEISMOGENIC ZONES. *Geochemistry, Geophysics, Geosystems*, 12(1), n/a-n/a. <https://doi.org/10.1029/2010GC003230>
- Hoover, W. F., Penniston-Dorland, S., Baumgartner, L., Bouvier, A.-S., Dragovic, B., Locatelli, M., et al. (2022). Episodic fluid flow in an eclogite-facies shear zone: Insights from Li isotope zoning in garnet. *Geology*, 50(6), 746–750. <https://doi.org/10.1130/G49737.1>
- Hower, J., Eslinger, E. V., Hower, M. E., & Perry, E. A. (1976). Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geological Society of America Bulletin*, 87(5), 725. [https://doi.org/10.1130/0016-7606\(1976\)87<725:MOBMOA>2.0.CO;2](https://doi.org/10.1130/0016-7606(1976)87<725:MOBMOA>2.0.CO;2)
- von Huene, R., Miller, J. J., & Weinrebe, W. (2012). Subducting plate geology in three great earthquake ruptures of the western Alaska margin, Kodiak to Unimak. *Geosphere*, 8(3), 628–644. <https://doi.org/10.1130/GES00715.1>
- Hulme, S. M., Wheat, C. G., Fryer, P., & Mottl, M. J. (2010). Pore water chemistry of the Mariana serpentinite mud volcanoes: A window to the seismogenic zone. *Geochemistry, Geophysics, Geosystems*, 11(1). <https://doi.org/10.1029/2009GC002674>
- Hüpers, A., & Kopf, A. J. (2012). Effect of smectite dehydration on pore water geochemistry in the shallow subduction zone: An experimental approach. *Geochemistry, Geophysics, Geosystems*, 13(10). <https://doi.org/10.1029/2012GC004212>
- Hürzeler, J.-P., & Abart, R. (2008). Fluid flow and rock alteration along the Glarus thrust. *Swiss Journal of Geosciences*, 101(2), 251–268. <https://doi.org/10.1007/s00015-008-1265-1>
- Hyndman, R. D., & Wang, K. (1993). Thermal constraints on the zone of major thrust earthquake failure: The Cascadia Subduction Zone. *Journal of Geophysical Research: Solid Earth*, 98(B2), 2039–2060. <https://doi.org/10.1029/92JB02279>
- Hyndman, R. D., Yamano, M., & Oleskevich, D. A. (1997). The seismogenic zone of subduction thrust faults. *The Island Arc*, 6(3), 244–260. <https://doi.org/10.1111/j.1440-1738.1997.tb00175.x>
- James, R. H., Rudnicki, M. D., & Palmer, M. R. (1999). The alkali element and boron geochemistry of the Escanaba Trough sediment-hosted hydrothermal system. *Earth and Planetary Science Letters*, 171(1), 157–169. [https://doi.org/10.1016/S0012-821X\(99\)00140-5](https://doi.org/10.1016/S0012-821X(99)00140-5)

- Jarrard, R. D. (2003). Subduction fluxes of water, carbon dioxide, chlorine, and potassium: SUBDUCTION FLUXES OF WATER. *Geochemistry, Geophysics, Geosystems*, 4(5), n/a-n/a. <https://doi.org/10.1029/2002GC000392>
- John, T., Scambelluri, M., Frische, M., Barnes, J. D., & Bach, W. (2011). Dehydration of subducting serpentinite: Implications for halogen mobility in subduction zones and the deep halogen cycle. *Earth and Planetary Science Letters*, 308(1–2), 65–76. <https://doi.org/10.1016/j.epsl.2011.05.038>
- Jourdan, A.-L. V., Mullis, J., Ramseyer, K., & Spiers, C. J. (2009). Evidence of growth and sector zoning in hydrothermal quartz from Alpine veins. *European Journal of Mineralogy*, 21(1), 219–231. <https://doi.org/10.1127/0935-1221/2009/0021-1881>
- Kameda, J., Raimbourg, H., Kogure, T., & Kimura, G. (2011). Low-grade metamorphism around the down-dip limit of seismogenic subduction zones: Example from an ancient accretionary complex in the Shimanto Belt, Japan. *Tectonophysics*, 502(3–4), 383–392. <https://doi.org/10.1016/j.tecto.2011.02.010>
- Kastner, M., Elderfield, H., & Martin, J. B. (1991). Fluids in Convergent Margins: What do We Know about their Composition, Origin, Role in Diagenesis and Importance for Oceanic Chemical Fluxes? *Philosophical Transactions: Physical Sciences and Engineering*, 335(1638), 243–259.
- Kastner, Miriam. (1981). Authigenic silicates in deep-sea sediments: formation and diagenesis. In *The oceanic lithosphere The sea* (C. Emiliani, Vol. 7, pp. 915–980). Wiley.
- Kastner, Miriam, Solomon, E. A., Harris, R. N., & Torres, M. E. (2014). Fluid Origins, Thermal Regimes, and Fluid and Solute Fluxes in the Forearc of Subduction Zones. In *Developments in Marine Geology* (Vol. 7, pp. 671–733). Elsevier. <https://doi.org/10.1016/B978-0-444-62617-2.00022-0>
- Katagiri, G., Ishida, H., & Ishitani, A. (1988). Raman spectra of graphite edge planes. *Carbon*, 26(4), 565–571. [https://doi.org/10.1016/0008-6223\(88\)90157-1](https://doi.org/10.1016/0008-6223(88)90157-1)
- Kawabata, K., Tanaka, H., & Kimura, G. (2007). Mass transfer and pressure solution in deformed shale of accretionary complex: Examples from the Shimanto Belt, southwestern Japan. *Journal of Structural Geology*, 29(4), 697–711. <https://doi.org/10.1016/j.jsg.2006.11.009>
- van Keken, P. E., Kiefer, B., & Peacock, S. M. (2002). High-resolution models of subduction zones: Implications for mineral dehydration reactions and the transport of water into the deep mantle: HIGH-RESOLUTION MODELS OF SUBDUCTION ZONES. *Geochemistry, Geophysics, Geosystems*, 3(10), 1 of 20–20 20. <https://doi.org/10.1029/2001GC000256>
- van Keken, P. E., Hacker, B. R., Syracuse, E. M., & Abers, G. A. (2011). Subduction factory: 4. Depth-dependent flux of H₂O from subducting slabs worldwide. *Journal of Geophysical Research*, 116(B1), B01401. <https://doi.org/10.1029/2010JB007922>
- Kerckhove, C. (1963). Schéma structural de la nappe du Flysch à Helminthoïdes dans l’Embrunais-Ubaye: Grenoble. *Travaux Du Laboratoire de Géologie de Grenoble*, v. 39, 7–24.
- Kerrick, D. M., & Connolly, J. A. D. (2001). Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth’s mantle. *Nature*, 411(6835), 293–296. <https://doi.org/10.1038/35077056>
- Kominz, M. A., & Pekar, S. F. (2001). Oligocene eustasy from two-dimensional sequence stratigraphic backstripping. *Geological Society of America Bulletin*, 113(3), 291–304. [https://doi.org/10.1130/0016-7606\(2001\)113<0291:OEFTDS>2.0.CO;2](https://doi.org/10.1130/0016-7606(2001)113<0291:OEFTDS>2.0.CO;2)
- Komninou, A., & Sverjensky, D. A. (1995). Pre-ore hydrothermal alteration in an unconformity-type uranium deposit. *Contributions to Mineralogy and Petrology*, 121(1), 99–114. <https://doi.org/10.1007/s004100050092>
- Kondo, H., Kimura, G., Masago, H., Ohmori-Ikehara, K., Kitamura, Y., Ikesawa, E., et al. (2005). Deformation and fluid flow of a major out-of-sequence thrust located at seismogenic depth in an accretionary complex: Nobeoka Thrust in the Shimanto Belt, Kyushu, Japan: NOBEOKA THRUST, A SEISMOGENIC OST. *Tectonics*, 24(6), n/a-n/a. <https://doi.org/10.1029/2004TC001655>

- Kontak, D. J. (2004). Analysis of evaporate mounds as a complement to fluid-inclusion thermometric data: Case studies from granitic environments in Nova Scotia and Peru. *THE CANADIAN MINERALOGIST*, 16.
- Kopf, A. J. (2002). Significance of mud volcanism. *Reviews of Geophysics*, 40(2), 2-1-2–52. <https://doi.org/10.1029/2000RG000093>
- Kulm, L. D., von Huene, R., & et al. (1973). *Initial Reports of the Deep Sea Drilling Project*, 18 (Vol. 18). U.S. Government Printing Office. <https://doi.org/10.2973/dsdp.proc.18.1973>
- Kusky, T. M., Bradley, D. C., & Haeussler, P. (1997). Progressive deformation of the Chugach accretionary complex, Alaska, during a paleogene ridge-trench encounter. *Journal of Structural Geology*, 19(2), 139–157. [https://doi.org/10.1016/S0191-8141\(96\)00084-3](https://doi.org/10.1016/S0191-8141(96)00084-3)
- Lafay, R., Deschamps, F., Schwartz, S., Guillot, S., Godard, M., Debret, B., & Nicollet, C. (2013). High-pressure serpentinites, a trap-and-release system controlled by metamorphic conditions: Example from the Piedmont zone of the western Alps. *Chemical Geology*, 343, 38–54. <https://doi.org/10.1016/j.chemgeo.2013.02.008>
- Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., & Goffé, B. (2010). Evolution of the Raman spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland): RSCM in low-grade metasediments. *Terra Nova*, 22(5), 354–360. <https://doi.org/10.1111/j.1365-3121.2010.00956.x>
- Lambrecht, G., & Diamond, L. W. (2014). Morphological ripening of fluid inclusions and coupled zone-refining in quartz crystals revealed by cathodoluminescence imaging: Implications for CL-petrography, fluid inclusion analysis and trace-element geothermometry. *Geochimica et Cosmochimica Acta*, 141, 381–406. <https://doi.org/10.1016/j.gca.2014.06.036>
- Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E. G., & Schwartz, S. (2014). XMapTools: A MATLAB©-based program for electron microprobe X-ray image processing and geothermobarometry. *Computers & Geosciences*, 62, 227–240. <https://doi.org/10.1016/j.cageo.2013.08.010>
- Larsen, R. B., Henderson, I., Ihlen, P. M., & Jacamon, F. (2004). Distribution and petrogenetic behaviour of trace elements in granitic pegmatite quartz from South Norway. *Contributions to Mineralogy and Petrology*, 147(5), 615–628. <https://doi.org/10.1007/s00410-004-0580-4>
- Lauer, R. M., & Saffer, D. M. (2012). Fluid budgets of subduction zone forearcs: The contribution of splay faults: SPLAY FAULTS AND FOREARC HYDROGEOLOGY. *Geophysical Research Letters*, 39(13), n/a-n/a. <https://doi.org/10.1029/2012GL052182>
- Lauer, R. M., & Saffer, D. M. (2015). The impact of splay faults on fluid flow, solute transport, and pore pressure distribution in subduction zones: A case study offshore the Nicoya Peninsula, Costa Rica: Splay faults and forearc fluid flow. *Geochemistry, Geophysics, Geosystems*, 16(4), 1089–1104. <https://doi.org/10.1002/2014GC005638>
- Le Pichon, X., Bergerat, F., & Roulet, M.-J. (1988). Plate kinematics and tectonics leading to the Alpine belt formation; A new analysis. In *Geological Society of America Special Papers* (Vol. 218, pp. 111–132). Geological Society of America. <https://doi.org/10.1130/SPE218-p111>
- Lefeuvre, B., Agard, P., Verlaque, A., Dubacq, B., & Plunder, A. (2020). Massive formation of lawsonite in subducted sediments from the Schistes Lustrés (W. Alps): Implications for mass transfer and decarbonation in cold subduction zones. *Lithos*, 370–371, 105629. <https://doi.org/10.1016/j.lithos.2020.105629>
- Li, D., & Liu, Y. (2016). Spatiotemporal evolution of slow slip events in a nonplanar fault model for northern Cascadia subduction zone: NONPLANAR FAULT MODEL OF CASCADIA SSES. *Journal of Geophysical Research: Solid Earth*, 121(9), 6828–6845. <https://doi.org/10.1002/2016JB012857>
- Li, Z.-X. A., & Lee, C.-T. A. (2006). Geochemical investigation of serpentinitized oceanic lithospheric mantle in the Feather River Ophiolite, California: Implications for the recycling rate of water by

- subduction. *Chemical Geology*, 235(1–2), 161–185.
<https://doi.org/10.1016/j.chemgeo.2006.06.011>
- Lynton, S. J., Walker, R. J., & Candela, P. A. (2005). Lithium isotopes in the system Qz-Ms-fluid: An experimental study. *Geochimica et Cosmochimica Acta*, 69(13), 3337–3347.
<https://doi.org/10.1016/j.gca.2005.02.009>
- Magna, T., Wiechert, U. H., & Halliday, A. N. (2004). Low-blank isotope ratio measurement of small samples of lithium using multiple-collector ICPMS. *International Journal of Mass Spectrometry*, 239(1), 67–76. <https://doi.org/10.1016/j.ijms.2004.09.008>
- Magna, T., Wiechert, U., Grove, T. L., & Halliday, A. N. (2006). Lithium isotope fractionation in the southern Cascadia subduction zone. *Earth and Planetary Science Letters*, 250(3–4), 428–443.
<https://doi.org/10.1016/j.epsl.2006.08.019>
- Magna, T., Wiechert, U., & Halliday, A. N. (2006). New constraints on the lithium isotope compositions of the Moon and terrestrial planets. *Earth and Planetary Science Letters*, 243(3–4), 336–353.
<https://doi.org/10.1016/j.epsl.2006.01.005>
- Magna, T., Novák, M., Cempírek, J., Janoušek, V., Ullmann, C. V., & Wiechert, U. (2016). Crystallographic control on lithium isotope fractionation in Archean to Cenozoic lithium-cesium-tantalum pegmatites. *Geology*, 44(8), 655–658. <https://doi.org/10.1130/G37712.1>
- Majzlan, J., Grevel, K.-D., & Navrotsky, A. (2003). Thermodynamics of Fe oxides: Part II. Enthalpies of formation and relative stability of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and maghemite (γ-Fe₂O₃). *American Mineralogist*, 88(5–6), 855–859. <https://doi.org/10.2138/am-2003-5-614>
- Makvandi, S., Huang, X., Beaudoin, G., Quirt, D., Ledru, P., & Fayek, M. (2021). Trace element signatures in hematite and goethite associated with the Kiggavik–Andrew Lake structural trend U deposits (Nunavut, Canada). *Mineralium Deposita*, 56(3), 509–535.
<https://doi.org/10.1007/s00126-020-00980-y>
- Marriott, C. S., Henderson, G. M., Crompton, R., Staubwasser, M., & Shaw, S. (2004). Effect of mineralogy, salinity, and temperature on Li/Ca and Li isotope composition of calcium carbonate. *Chemical Geology*, 212(1–2), 5–15. <https://doi.org/10.1016/j.chemgeo.2004.08.002>
- Marschall, H. R., Altherr, R., Ludwig, T., Kalt, A., Gmeling, K., & Kasztovszky, Z. (2006). Partitioning and budget of Li, Be and B in high-pressure metamorphic rocks. *Geochimica et Cosmochimica Acta*, 70(18), 4750–4769. <https://doi.org/10.1016/j.gca.2006.07.006>
- Marschall, H. R., Pogge von Strandmann, P. A. E., Seitz, H.-M., Elliott, T., & Niu, Y. (2007). The lithium isotopic composition of orogenic eclogites and deep subducted slabs. *Earth and Planetary Science Letters*, 262(3–4), 563–580. <https://doi.org/10.1016/j.epsl.2007.08.005>
- Martin, J. B., Kastner, M., Henry, P., Le Pichon, X., & Lallement, S. (1996). Chemical and isotopic evidence for sources of fluids in a mud volcano field seaward of the Barbados accretionary wedge. *Journal of Geophysical Research: Solid Earth*, 101(B9), 20325–20345.
<https://doi.org/10.1029/96JB00140>
- Masci, L., Dubacq, B., Verlaquet, A., Chopin, C., De Andrade, V., & Herviou, C. (2019). A XANES and EPMA study of Fe³⁺ in chlorite: Importance of oxychlorite and implications for cation site distribution and thermobarometry. *American Mineralogist*, 104(3), 403–417.
<https://doi.org/10.2138/am-2019-6766>
- Menant, A., Angiboust, S., Gerya, T., Lacassin, R., Simoes, M., & Grandin, R. (2020). Transient stripping of subducting slabs controls periodic forearc uplift. *Nature Communications*, 11(1), 1823.
<https://doi.org/10.1038/s41467-020-15580-7>
- Meneghini, F., Marroni, M., Moore, J. C., Pandolfi, L., & Rowe, C. D. (2009). The processes of underthrusting and underplating in the geologic record: structural diversity between the Franciscan Complex (California), the Kodiak Complex (Alaska) and the Internal Ligurian Units (Italy). *Geological Journal*, 44(2), 126–152. <https://doi.org/10.1002/gj.1144>
- Merle, O. (1982). Mise en place séquentielle de la Nappe du Parpaillon en Embrunais-Ubaye (Flysch à Helminthoïdes, Alpes occidentales). *Comptes Rendus de l'Académie Des Sciences*, 603–606.

- Millot, R., Guerrot, C., & Vigier, N. (2004). Accurate and High-Precision Measurement of Lithium Isotopes in Two Reference Materials by MC-ICP-MS. *Geostandards and Geoanalytical Research*, 28(1), 153–159. <https://doi.org/10.1111/j.1751-908X.2004.tb01052.x>
- Misra, S., & Froelich, P. N. (2012). Lithium Isotope History of Cenozoic Seawater: Changes in Silicate Weathering and Reverse Weathering. *Science*, 335, 818–823. <https://doi.org/DOL:10.1126/science.1214697>
- Mochizuki, K., Henrys, S., Haijima, D., Warren-Smith, E., & Fry, B. (2021). Seismicity and velocity structure in the vicinity of repeating slow slip earthquakes, northern Hikurangi subduction zone, New Zealand. *Earth and Planetary Science Letters*, 563, 116887. <https://doi.org/10.1016/j.epsl.2021.116887>
- Molnar, P., & Stock, J. (1987). Relative motions of hotspots in the Pacific, Atlantic and Indian Oceans since late Cretaceous time. *Nature*, 327(6123), 587–591. <https://doi.org/10.1038/327587a0>
- Moore, G. F., Taira, A., Klaus, A., Becker, L., Boeckel, B., Cragg, B. A., et al. (2001). New insights into deformation and fluid flow processes in the Nankai Trough accretionary prism: Results of Ocean Drilling Program Leg 190: DEFORMATION AND FLUID FLOW PROCESSES. *Geochemistry, Geophysics, Geosystems*, 2(10), n/a-n/a. <https://doi.org/10.1029/2001GC000166>
- Moore, J. C. (1989). Tectonics and hydrogeology of accretionary prisms: role of the décollement zone. *Journal of Structural Geology*, 11, 95–106.
- Moore, J. Casey. (1978). Orientation of underthrusting during latest Cretaceous and earliest Tertiary time, Kodiak 258 Islands, Alaska. *Geology*, 6, 209–213.
- Moore, J. Casey, & Vrolijk, P. (1992). Fluids in accretionary prisms. *Reviews of Geophysics*, 30(2), 113–135. <https://doi.org/10.1029/92RG00201>
- Moore, J. Casey, Byrne, T., Plumley, P. W., Reid, M., Gibbons, H., & Coe, R. S. (1983). Paleogene evolution of the Kodiak 266 Islands, Alaska: Consequences of ridge-trench interaction in a more southerly latitude. *Tectonics*, 2, 265–293.
- Moore, J.C., & Allwardt, A. (1980). Progressive deformation of a Tertiary Trench Slope, Kodiak Islands, Alaska. *Journal of Geophysical Research: Solid Earth*, 85, 4741–4756.
- Moore, J.C., Mascle, A., & et al. (Eds.). (1990). *Proceedings of the Ocean Drilling Program, 110 Scientific Results* (Vol. 110). Ocean Drilling Program. <https://doi.org/10.2973/odp.proc.sr.110.1990>
- Moran, A. E., Sisson, V. B., & Leeman, W. P. (1992). Boron depletion during progressive metamorphism: Implications for subduction processes. *Earth and Planetary Science Letters*, 111(2–4), 331–349. [https://doi.org/10.1016/0012-821X\(92\)90188-2](https://doi.org/10.1016/0012-821X(92)90188-2)
- Morgan, W. J. (1971). Convection plumes in the lower mantle. *Nature*, 230, 42–43.
- Mortimer, N. (2000). Metamorphic discontinuities in orogenic belts: example of the garnet-biotite-albite zone in the Otago Schist, New Zealand. *International Journal of Earth Sciences*, 89(2), 295–306. <https://doi.org/10.1007/s005310000086>
- Mottl, M. J., Komor, S. C., Fryer, P., & Moyer, C. L. (2003). Deep-slab fluids fuel extremophilic Archaea on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. *Geochem. Geophys. Geosyst.*, 4(9009). <https://doi.org/doi:10.1029/2003GC000588>
- Mottl, M. J., Wheat, C. G., Fryer, P., Gharib, J., & Martin, J. B. (2004). Chemistry of springs across the Mariana forearc shows progressive devolatilization of the subducting plate. *Geochimica et Cosmochimica Acta*, 68(23), 4915–4933. <https://doi.org/10.1016/j.gca.2004.05.037>
- Mourgues, R., & Cobbold, P. R. (2006). Thrust wedges and fluid overpressures: Sandbox models involving pore fluids: THRUST WEDGES AND FLUID OVERPRESSURES. *Journal of Geophysical Research: Solid Earth*, 111(B5), n/a-n/a. <https://doi.org/10.1029/2004JB003441>
- Muffler, L. J. P., & White, D. F. (1969). Active Metamorphism of Upper Cenozoic Sediments in the Salton Sea Geothermal Field and the Salton Trough, Southeastern California. *Geological Society of America Bulletin*, 80, 157–182.

- Müller, A., & Koch-Müller, M. (2009). Hydrogen speciation and trace element contents of igneous, hydrothermal and metamorphic quartz from Norway. *Mineralogical Magazine*, 73(4), 569–583. <https://doi.org/10.1180/minmag.2009.073.4.569>
- Müller, Axel, Wiedenbeck, M., van den Kerkhof, A. M., Kronz, A., & Simon, K. (2003). Trace elements in quartz - a combined electron microprobe, secondary ion mass spectrometry, laser-ablation ICP-MS, and cathodoluminescence study. *European Journal of Mineralogy*, 15(4), 747–763. <https://doi.org/10.1127/0935-1221/2003/0015-0747>
- Mullis, J., Dubessy, J., Poty, B., & O’Neil, J. (1994). Fluid regimes during late stages of a continental collision: Physical, chemical, and stable isotope measurements of fluid inclusions in fissure quartz from a geotraverse through the Central Alps, Switzerland. *Geochimica et Cosmochimica Acta*, 58(10), 2239–2267. [https://doi.org/10.1016/0016-7037\(94\)90008-6](https://doi.org/10.1016/0016-7037(94)90008-6)
- Muñoz-Montecinos, J., Angiboust, S., & Garcia-Casco, A. (2021). Blueschist-facies paleo-earthquakes in a serpentinite channel (Zagros suture, Iran) enlighten seismogenesis in Mariana-type subduction margins. *Earth and Planetary Science Letters*, 573, 117135. <https://doi.org/10.1016/j.epsl.2021.117135>
- Muñoz-Montecinos, J., Angiboust, S., Garcia-Casco, A., Glodny, J., & Bebout, G. (2021). Episodic hydrofracturing and large-scale flushing along deep subduction interfaces: Implications for fluid transfer and carbon recycling (Zagros Orogen, southeastern Iran). *Chemical Geology*, 571, 120173. <https://doi.org/10.1016/j.chemgeo.2021.120173>
- Myers, G., & Vrolijk, P. (1986). Fluid evolution associated with the accretion of the Kodiak Formation, Kodiak Island, 269 Alaska. (Vol. 67, p. 1219). Presented at the AGU.
- Neukampf, J., Laurent, O., Tollan, P., Bouvier, A.-S., Magna, T., Ulmer, P., et al. (2022). inclusions and host quartz in a Yellowstone rhyolite. *Geochimica et Cosmochimica Acta*, 326, 56–76. <https://doi.org/10.1016/j.gca.2022.03.037>
- Neuzil, C. E. (1994). How permeable are clays and shales? *Water Resources Research*, 30(2), 145–150.
- Nishi, H. (1988). Structural analysis of the Shimanto Accretionary Complex, Kyushu, Japan, based on foraminiferal biostratigraphy. *Tectonics*, 7(3), 641–652. <https://doi.org/10.1029/TC007i003p00641>
- Nishiyama, N., Ujiie, K., & Kano, M. (2021). Spatial changes in inclusion band spacing as an indicator of temporal changes in slow slip and tremor recurrence intervals. *Earth, Planets and Space*, 73(1), 126. <https://doi.org/10.1186/s40623-021-01448-7>
- Noda, A., & Miyakawa, A. (2017). Deposition and Deformation of Modern Accretionary-Type Forearc Basins: Linking Basin Formation and Accretionary Wedge Growth. In Y. Itoh (Ed.), *Evolutionary Models of Convergent Margins - Origin of Their Diversity*. InTech. <https://doi.org/10.5772/67559>
- Oleskevich, D. A., Hyndman, R. D., & Wang, K. (1999). The updip and downdip limits to great subduction earthquakes: Thermal and structural models of Cascadia, south Alaska, SW Japan, and Chile. *Journal of Geophysical Research: Solid Earth*, 104(B7), 14965–14991. <https://doi.org/10.1029/1999JB900060>
- Osozawa, S., & Wakabayashi, J. (2015). Late stage exhumation of HP metamorphic rocks, progressive localization of strain, and changes in transport direction, Sambagawa belt, Japan. *Journal of Structural Geology*, 75, 1–16. <https://doi.org/10.1016/j.jsg.2015.03.006>
- Pajang, S., Cubas, N., Letouzey, J., Le Pourhiet, L., Seyedali, S., Fournier, M., et al. (2021). Seismic hazard of the western Makran subduction zone: Insight from mechanical modelling and inferred frictional properties. *Earth and Planetary Science Letters*, 562, 116789. <https://doi.org/10.1016/j.epsl.2021.116789>
- Palazzin, G., Raimbourg, H., Famin, V., Jolivet, L., Kusaba, Y., & Yamaguchi, A. (2016). Deformation processes at the down-dip limit of the seismogenic zone: The example of Shimanto accretionary complex. *Tectonophysics*, 687, 28–43. <https://doi.org/10.1016/j.tecto.2016.08.013>

- Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., & Expedition 320/321 Scientists (Eds.). (2010). *Proceedings of the IODP, 320/321* (Vol. 320/321). Integrated Ocean Drilling Program. <https://doi.org/10.2204/iodp.proc.320321.2010>
- Pašava, J., Ackerman, L., Žák, J., Svojtka, M., Magna, T., Pour, O., et al. (2023). Multi-stage metal enrichment and formation of gold mineralization in black shales: the role of high heat flow in a rift setting. *Mineralium Deposita*, 58(6), 1051–1073. <https://doi.org/10.1007/s00126-023-01169-9>
- Pasteris, J. D. (1989). In Situ Analysis in Geological Thin-Sections by Laser Raman Microprobe Spectroscopy: A Cautionary Note. *Applied Spectroscopy*, 43(3), 567–570. <https://doi.org/10.1366/0003702894202878>
- Pavlis, T. L., Monteverde, D. H., Bowman, J. R., Rubenstone, J. L., & Reason, M. D. (1988). Early Cretaceous near-trench plutonism in southern Alaska: Atonalite-Trondhjemite Intrusive Complex injected during ductile thrusting along the Border Ranges Fault System. *Tectonics*, 7(6), 1179–1199. <https://doi.org/10.1029/TC007i006p01179>
- Peacock, S. M. (1993). The importance of blueschist → eclogite dehydration reactions in subducting oceanic crust. *Geological Society of America Bulletin*, 105(5), 684–694. [https://doi.org/10.1130/0016-7606\(1993\)105<0684:TIOBED>2.3.CO;2](https://doi.org/10.1130/0016-7606(1993)105<0684:TIOBED>2.3.CO;2)
- Penniston-Dorland, S. C., Sorensen, S. S., Ash, R. D., & Khadke, S. V. (2010). Lithium isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA. *Earth and Planetary Science Letters*, 292(1–2), 181–190. <https://doi.org/10.1016/j.epsl.2010.01.034>
- Penniston-Dorland, S. C., Bebout, G. E., Pogge von Strandmann, P. A. E., Elliott, T., & Sorensen, S. S. (2012). Lithium and its isotopes as tracers of subduction zone fluids and metasomatic processes: Evidence from the Catalina Schist, California, USA. *Geochimica et Cosmochimica Acta*, 77, 530–545. <https://doi.org/10.1016/j.gca.2011.10.038>
- Perny, B., Eberhardt, P., Ramseier, K., Mullis, J., & Pankrath, R. (1992). Microdistribution of Al, Li, and Na in α quartz: Possible causes and correlation with short-lived cathodoluminescence. *American Mineralogist*, 77, 534–544.
- Perry, E. A., & Hower, J. (1970). Burial diagenesis in Gulf Coast pelitic sediments. *Clays Clay Minerals*, 18, 165–177.
- Peterková, T., & Dolejš, D. (2019). Magmatic-hydrothermal transition of Mo-W-mineralized granite-pegmatite greisen system recorded by trace elements in quartz: Krupka district, Eastern Krušné hory/Erzgebirge. *Chemical Geology*, 523, 179–202. <https://doi.org/10.1016/j.chemgeo.2019.04.009>
- Peters, D., Bretscher, A., John, T., Scambelluri, M., & Pettke, T. (2017). Fluid-mobile elements in serpentinites: Constraints on serpentinisation environments and element cycling in subduction zones. *Chemical Geology*, 466, 654–666. <https://doi.org/10.1016/j.chemgeo.2017.07.017>
- Plafker, G., Moore, J. C., Winkler, G. R., & Berg, H. (1994). Geology of the southern Alaska margin. *The Geology of 249 Alaska: Boulder, Colorado, Geological Society of America, Geology of North America*, 1, 389–449.
- Plank, T. (2014). The Chemical Composition of Subducting Sediments. In *Treatise on Geochemistry* (pp. 607–629). Elsevier. <https://doi.org/10.1016/B978-0-08-095975-7.00319-3>
- Plank, Terry, & Langmuir, C. H. (1998). The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chemical Geology*, 145(3–4), 325–394. [https://doi.org/10.1016/S0009-2541\(97\)00150-2](https://doi.org/10.1016/S0009-2541(97)00150-2)
- Platt, J. P. (1986). Dynamics of orogenic wedges and the uplift of high-pressure metamorphic rocks. *Geological Society of America Bulletin*, 97, 1037–1093.
- Plunder, A., Agard, P., Dubacq, B., Chopin, C., & Bellanger, M. (2012). How continuous and precise is the record of P-T paths? Insights from combined thermobarometry and thermodynamic modelling into subduction dynamics (Schistes Lustrés, W. Alps): TOWARDS Continuous P-T PATHS? *Journal of Metamorphic Geology*, 30(3), 323–346. <https://doi.org/10.1111/j.1525-1314.2011.00969.x>

- Qiu, L., Rudnick, R. L., Ague, J. J., & McDonough, W. F. (2011). A lithium isotopic study of sub-greenschist to greenschist facies metamorphism in an accretionary prism, New Zealand. *Earth and Planetary Science Letters*, 301(1–2), 213–221. <https://doi.org/10.1016/j.epsl.2010.11.001>
- Rahn, M., Mullis, J., Erdelbrock, K., & Frey, M. (1994). Very low-grade metamorphism of the Taveyanne greywacke, Glarus Alps, Switzerland. *Journal of Metamorphic Geology*, 12(5), 625–641. <https://doi.org/10.1111/j.1525-1314.1994.tb00047.x>
- Raimbourg, H. (2015). Fluid circulation in the depths of accretionary prisms: an example of the Shimanto Belt, Kyushu, Japan, 16.
- Raimbourg, H., Tadahiro, S., Asuka, Y., Haruka, Y., & Kimura, G. (2009). Horizontal shortening versus vertical loading in accretionary prisms. *Geochemistry, Geophysics, Geosystems*, 10(4), n/a-n/a. <https://doi.org/10.1029/2008GC002279>
- Raimbourg, H., Augier, R., Famin, V., Gadenne, L., Palazzin, G., Yamaguchi, A., & Kimura, G. (2014). Long-term evolution of an accretionary prism: The case study of the Shimanto Belt, Kyushu, Japan: Long-term evolution of the Shimanto Belt. *Tectonics*, 33(6), 936–959. <https://doi.org/10.1002/2013TC003412>
- Raimbourg, H., Thiéry, R., Vacelet, M., Famin, V., Ramboz, C., Boussafir, M., et al. (2017). Organic matter cracking: A source of fluid overpressure in subducting sediments. *Tectonophysics*, 721, 254–274. <https://doi.org/10.1016/j.tecto.2017.08.005>
- Raimbourg, H., Famin, V., Palazzin, G., Yamaguchi, A., & Augier, R. (2017). Tertiary evolution of the Shimanto belt (Japan): A large-scale collision in Early Miocene: Early Miocene Collision in Shimanto Belt. *Tectonics*, 36(7), 1317–1337. <https://doi.org/10.1002/2017TC004529>
- Raimbourg, H., Famin, V., Palazzin, G., Mayoux, M., Jolivet, L., Ramboz, C., & Yamaguchi, A. (2018). Fluid properties and dynamics along the seismogenic plate interface. *Geosphere*, 14(2), 469–491. <https://doi.org/10.1130/GES01504.1>
- Raimbourg, H., Famin, V., Palazzin, G., Yamaguchi, A., Augier, R., Kitamura, Y., & Sakaguchi, A. (2019). Distributed deformation along the subduction plate interface: The role of tectonic mélanges. *Lithos*, 334, 69–87. <https://doi.org/10.1016/j.lithos.2019.01.033>
- Raimbourg, H., Rajič, K., Moris-Muttoni, B., Famin, V., Palazzin, G., Fisher, D. M., et al. (2021). Quartz vein geochemistry records deformation processes in convergent zones. *Geochemistry, Geophysics, Geosystems*, 22. <https://doi.org/10.1029/2020GC009201>
- Raimbourg, H., Famin, V., Canizarès, A., & Le Trong, E. (2022). Fluid Pressure Changes Recorded by Trace Elements in Quartz. *Geochemistry, Geophysics, Geosystems*, 23(10). <https://doi.org/10.1029/2022GC010346>
- Rajič, K., Raimbourg, H., Lerouge, C., Famin, V., Dubacq, B., Canizarès, A., et al. (2023). Metamorphic reactions and their implication for the fluid budget in metapelites at seismogenic depths in subduction zones. *Tectonophysics*, 857.
- Ramirez, G., Smye, A., Fisher, D. M., Hashimoto, Y., & Yamaguchi, A. (2021). Constraints on Element Mobility During Deformation Within the Seismogenic Zone, Shimanto Belt, Japan. *Geochemistry, Geophysics, Geosystems*, 22(8). <https://doi.org/10.1029/2020GC009594>
- Ranero, C. R., Grevemeyer, I., Sahling, H., Barckhausen, U., Hensen, C., Wallmann, K., et al. (2008). Hydrogeological system of erosional convergent margins and its influence on tectonics and interplate seismogenesis: CONVERGENT MARGINS AND TECTONICS. *Geochemistry, Geophysics, Geosystems*, 9(3), n/a-n/a. <https://doi.org/10.1029/2007GC001679>
- Rauchenstein-Martinek, K., Wagner, T., Wälle, M., Heinrich, C. A., & Arlt, T. (2016). Chemical evolution of metamorphic fluids in the Central Alps, Switzerland: insight from LA-ICPMS analysis of fluid inclusions. *Geofluids*, 16(5), 877–908. <https://doi.org/10.1111/gfl.12194>
- Rea, D. K., & Ruff, L. J. (1996). Composition and mass flux of sediment entering the world's subduction zones: Implications for global sediment budgets, great earthquakes, and volcanism. *Earth and Planetary Science Letters*, 140(1–4), 1–12. [https://doi.org/10.1016/0012-821X\(96\)00036-2](https://doi.org/10.1016/0012-821X(96)00036-2)

- Reyes, A. G., Christenson, B. W., & Faure, K. (2010). Sources of solutes and heat in low-enthalpy mineral waters and their relation to tectonic setting, New Zealand. *Journal of Volcanology and Geothermal Research*, 192(3–4), 117–141. <https://doi.org/10.1016/j.jvolgeores.2010.02.015>
- Reynard, B. (2013). Serpentine in active subduction zones. *Lithos*, 178, 171–185. <https://doi.org/10.1016/j.lithos.2012.10.012>
- Rice, J. R. (2006). Heating and weakening of faults during earthquake slip: HEATING AND WEAKENING OF FAULTS. *Journal of Geophysical Research: Solid Earth*, 111(B5), n/a-n/a. <https://doi.org/10.1029/2005JB004006>
- Richard, A., Banks, D. A., Hendriksson, N., & Lahaye, Y. (2018). Lithium isotopes in fluid inclusions as tracers of crustal fluids: An exploratory study. *Journal of Geochemical Exploration*, 184, 158–166. <https://doi.org/10.1016/j.gexplo.2017.10.017>
- Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2(2), 65–71. <https://doi.org/10.1107/S0021889869006558>
- Ring, U., Brandon, M. T., Willett, S. D., & Lister, G. S. (1999). Exhumation processes. *Geological Society, London, Special Publications*, 154(1), 1–27. <https://doi.org/10.1144/GSL.SP.1999.154.01.01>
- Roeske, S. M., Mattinson, J. M., & Armstrong, R. L. (1989). Isotopic ages of glaucophane schists on the Kodiak Islands, 251 southern Alaska, and their implications for the Mesozoic tectonic history of the Border Ranges fault system. *Geological Society of America Bulletin*, 101, 1021–1037.
- Rossetti, F., Tecce, F., Aldega, L., Brilli, M., & Faccenna, C. (2006). Deformation and fluid flow during orogeny at the palaeo-Pacific active margin of Gondwana: the Early Palaeozoic Robertson Bay accretionary complex (north Victoria Land, Antarctica). *J. Metamorphic Geol.*, 24, 33–53. <https://doi.org/doi:10.1111/j.1525-1314.2005.00620.x>
- Rowe, C. D., Meneghini, F., & Moore, J. C. (2009). Fluid-rich damage zone of an ancient out-of-sequence thrust, Kodiak Islands, Alaska. *Tectonics*, 28(1), n/a-n/a. <https://doi.org/10.1029/2007TC002126>
- Rubatto, D., & Hermann, J. (2001). Exhumation as fast as subduction? *Geology*, 29(1), 3. [https://doi.org/10.1130/0091-7613\(2001\)029<0003:EAFAS>2.0.CO;2](https://doi.org/10.1130/0091-7613(2001)029<0003:EAFAS>2.0.CO;2)
- Rupke, L. (2004). Serpentine and the subduction zone water cycle. *Earth and Planetary Science Letters*, 223(1–2), 17–34. <https://doi.org/10.1016/j.epsl.2004.04.018>
- Saffer, D. M. (2003). Pore pressure development and progressive dewatering in underthrust sediments at the Costa Rican subduction margin: Comparison with northern Barbados and Nankai: PORE PRESSURE AND DEWATERING. *Journal of Geophysical Research: Solid Earth*, 108(B5). <https://doi.org/10.1029/2002JB001787>
- Saffer, D. M., & Tobin, H. J. (2011). Hydrogeology and Mechanics of Subduction Zone Forearcs: Fluid Flow and Pore Pressure. *Annual Review of Earth and Planetary Sciences*, 39(1), 157–186. <https://doi.org/10.1146/annurev-earth-040610-133408>
- Saffer, D. M., Lockner, D. A., & McKiernan, A. (2012). Effects of smectite to illite transformation on the frictional strength and sliding stability of intact marine mudstones: FRICTION AND SMECTITE TRANSFORMATION. *Geophysical Research Letters*, 39(11), n/a-n/a. <https://doi.org/10.1029/2012GL051761>
- Sahling, H., Masson, D. G., Ranero, C. R., Hühnerbach, V., Weinrebe, W., Klauke, I., et al. (2008). Fluid seepage at the continental margin offshore Costa Rica and southern Nicaragua: CONTINENTAL MARGIN FLUID SEEPAGE. *Geochemistry, Geophysics, Geosystems*, 9(5), n/a-n/a. <https://doi.org/10.1029/2008GC001978>
- Saito, M. (1996). Geological Map of Japan, 1:50,000. Geol. Surv. Jpn., Shiibamura.
- Sakaguchi, A. (1999). Thermal maturity in the Shimanto accretionary prism, southwest Japan, with the thermal change of the subducting slab: fluid inclusion and vitrinite reflectance study. *Earth and Planetary Science Letters*, 173(1–2), 61–74. [https://doi.org/10.1016/S0012-821X\(99\)00219-8](https://doi.org/10.1016/S0012-821X(99)00219-8)

- Sakai et al., T. (1984). Microfossil stratigraphy of the Paleogene System in Kyushu Shimanto Belt. *Biostratigraphy and International Correlation of the Paleogene System in Japan*, 95–112.
- Sample, J. C., & Fisher, D. M. (1986). Duplex accretion and underplating in an ancient accretionary prism, Kodiak Islands, Alaska. *Geology*, 14, 160–163.
- Sample, J. C., & Moore, J. C. (1987). Structural style and kinematics of an underplated slate belt, Kodiak and adjacent 260 islands, Alaska. *Geological Society of America Bulletin*, 99, 7–20.
- Scambelluri, M., Fiebig, J., Malaspina, N., Müntener, O., & Pettke, T. (2004). Serpentine Subduction: Implications for Fluid Processes and Trace-Element Recycling. *International Geology Review*, 46(7), 595–613. <https://doi.org/10.2747/0020-6814.46.7.595>
- Scambelluri, M., Müntener, O., Ottolini, L., Pettke, T. T., & Vannucci, R. (2004). The fate of B, Cl and Li in the subducted oceanic mantle and in the antigorite breakdown fluids. *Earth and Planetary Science Letters*, 222(1), 217–234. <https://doi.org/10.1016/j.epsl.2004.02.012>
- Scambelluri, M., Pettke, T., & Cannaò, E. (2015). Fluid-related inclusions in Alpine high-pressure peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps). *Earth and Planetary Science Letters*, 429, 45–59. <https://doi.org/10.1016/j.epsl.2015.07.060>
- Scambelluri, M., Cannaò, E., & Gilio, M. (2019). The water and fluid-mobile element cycles during serpentine subduction. A review. *European Journal of Mineralogy*, 31(3), 405–428. <https://doi.org/10.1127/ejm/2019/0031-2842>
- Schauble, E. A. (2004). Applying Stable Isotope Fractionation Theory to New Systems. *Reviews in Mineralogy & Geochemistry*, 55, 65–111. <https://doi.org/10.2138/gsrmg.55.1.65>
- Schito, A., Corrado, S., Aldega, L., & Grigo, D. (2016). Overcoming pitfalls of vitrinite reflectance measurements in the assessment of thermal maturity: the case history of the lower Congo basin. *Marine and Petroleum Geology*, 74, 59–70. <https://doi.org/10.1016/j.marpetgeo.2016.04.002>
- Schito, A., Romano, C., Corrado, S., Grigo, D., & Poe, B. (2017). Diagenetic thermal evolution of organic matter by Raman spectroscopy. *Organic Geochemistry*, 106, 57–67. <https://doi.org/10.1016/j.orggeochem.2016.12.006>
- Schmid, S. M., Kissling, E., Diehl, T., van Hinsbergen, D. J. J., & Molli, G. (2017). Ivrea mantle wedge, arc of the Western Alps, and kinematic evolution of the Alps–Apennines orogenic system. *Swiss Journal of Geosciences*, 110(2), 581–612. <https://doi.org/10.1007/s00015-016-0237-0>
- Schmidt, D., Schmidt, S. T., Mullis, J., Ferreiro Mählmann, R., & Frey, M. (1997). Very low grade metamorphism of the Tavéyanne formation of western Switzerland. *Contributions to Mineralogy and Petrology*, 129(4), 385–403. <https://doi.org/10.1007/s004100050344>
- Schmidt, D. A., & Gao, H. (2010). Source parameters and time-dependent slip distributions of slow slip events on the Cascadia subduction zone from 1998 to 2008. *Journal of Geophysical Research*, 115(B00A18). <https://doi.org/doi:10.1029/2008JB006045>
- Schmidt, M., Hensen, C., Mörz, T., Müller, C., Grevemeyer, I., Wallmann, K., et al. (2005). Methane hydrate accumulation in “Mound 11” mud volcano, Costa Rica forearc. *Marine Geology*, 216(1–2), 83–100. <https://doi.org/10.1016/j.margeo.2005.01.001>
- Schmidt, M. W., & Poli, S. (2014). Devolatilization During Subduction. In *Treatise on Geochemistry* (pp. 669–701). Elsevier. <https://doi.org/10.1016/B978-0-08-095975-7.00321-1>
- Schneider, C. A., Rasband, W. S., & Eliceiri, K. W. (2012). NIH Image to ImageJ: 25 years of image analysis. *Nature Methods*, 9(7), 671–675. <https://doi.org/10.1038/nmeth.2089>
- Scholl, D. W., & von Huene, R. (2010). Subduction zone recycling processes and the rock record of crustal suture zonesThis article is one of a series of papers published in this Special Issue on the theme *Lithoprobe — parameters, processes, and the evolution of a continent* . *Canadian Journal of Earth Sciences*, 47(5), 633–654. <https://doi.org/10.1139/E09-061>
- Scholz, F., Hensen, C., De Lange, G. J., Haeckel, M., Liebetrau, V., Meixner, A., et al. (2010). Lithium isotope geochemistry of marine pore waters – Insights from cold seep fluids. *Geochimica et Cosmochimica Acta*, 74(12), 3459–3475. <https://doi.org/10.1016/j.gca.2010.03.026>

- Seyfried, W. E., Chen, X., & Chan, L. H. (1998). Trace element mobility and lithium exchange during hydrothermal alteration of seafloor weathered basalt; an experimental study at 350 degrees C, 500 bars. *Ceochim. Cosmochim. Acta*, 62, 949–960.
- Shervais, J. W., & Jean, M. M. (2012). Inside the subduction factory: Modeling fluid mobile element enrichment in the mantle wedge above a subduction zone. *Geochimica et Cosmochimica Acta*, 95, 270–285. <https://doi.org/10.1016/j.gca.2012.07.006>
- Sibson, R. H., Moore, J. Mc. M., & Rankin, A. H. (1975). Seismic pumping—a hydrothermal fluid transport mechanism. *Journal of the Geological Society*, 131(6), 653–659. <https://doi.org/10.1144/gsjgs.131.6.0653>
- Sibson, Richard H. (1994). Crustal stress, faulting and fluid flow. *Geological Society, London, Special Publications*, 78(1), 69–84. <https://doi.org/10.1144/GSL.SP.1994.078.01.07>
- Simon-Labric, T., Rolland, Y., Dumont, T., Heymes, T., Authemayou, C., Corsini, M., & Fornari, M. (2009). ⁴⁰Ar/ ³⁹Ar dating of Penninic Front tectonic displacement (W Alps) during the Lower Oligocene (31–34 Ma). *Terra Nova*, 21(2), 127–136. <https://doi.org/10.1111/j.1365-3121.2009.00865.x>
- Simons, K. K., Harlow, G. E., Brueckner, H. K., Goldstein, S. L., Sorensen, S. S., Hemming, N. G., & Langmuir, C. H. (2010). Lithium isotopes in Guatemalan and Franciscan HP–LT rocks: Insights into the role of sediment-derived fluids during subduction. *Geochimica et Cosmochimica Acta*, 74(12), 3621–3641. <https://doi.org/10.1016/j.gca.2010.02.033>
- Smeraglia, L., Aldega, L., Billi, A., Carminati, E., Di Fiore, F., Gerdes, A., et al. (2019). Development of an intrawedge tectonic mélange by out-of-sequence thrusting, buttressing, and intraformational rheological contrast, Mt. Massico ridge, Apennines, Italy. *Tectonics*, 38, 1233–1249. <https://doi.org/10.1029/2018TC005243>
- Spandler, C., & Pirard, C. (2013). Element recycling from subducting slabs to arc crust: A review. *Lithos*, 170–171, 208–223. <https://doi.org/10.1016/j.lithos.2013.02.016>
- Spandler, C., Hermann, J., Arculus, R., & Mavrogenes, J. (2003). Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contributions to Mineralogy and Petrology*, 146(2), 205–222. <https://doi.org/10.1007/s00410-003-0495-5>
- Sperner, B., & Zweigel, P. (2010). A plea for more caution in fault–slip analysis. *Tectonophysics*, 482(1–4), 29–41. <https://doi.org/10.1016/j.tecto.2009.07.019>
- Spinelli, G. A. (2004). Along-strike variations in underthrust sediment dewatering on the Nicoya margin, Costa Rica related to the updip limit of seismicity. *Geophysical Research Letters*, 31(4), L04613. <https://doi.org/10.1029/2003GL018863>
- Stampfli, G. M., Mosar, J., Marquer, D., Marchant, R., Baudin, T., & Borel, G. (1998). Subduction and obduction processes in the Swiss Alps. *Tectonophysics*, 296(1–2), 159–204. [https://doi.org/10.1016/S0040-1951\(98\)00142-5](https://doi.org/10.1016/S0040-1951(98)00142-5)
- Steel-MacInnis, M., Bodnar, R. J., & Naden, J. (2011). Numerical model to determine the composition of H₂O–NaCl–CaCl₂ fluid inclusions based on microthermometric and microanalytical data. *Geochimica et Cosmochimica Acta*, 75(1), 21–40. <https://doi.org/10.1016/j.gca.2010.10.002>
- Stern, C. R. (2011). Subduction erosion: Rates, mechanisms, and its role in arc magmatism and the evolution of the continental crust and mantle. *Gondwana Research*, 20(2–3), 284–308. <https://doi.org/10.1016/j.gr.2011.03.006>
- Stern, R. J. (2002). SUBDUCTION ZONES: SUBDUCTION ZONES. *Reviews of Geophysics*, 40(4), 3-1-3–38. <https://doi.org/10.1029/2001RG000108>
- Sterner, M. S., Hall, D. L., & Keppler, H. (1995). Compositional re-equilibration of fluid inclusions in quartz. *Contributions to Mineralogy and Petrology*, 119(1), 1–15. <https://doi.org/10.1007/BF00310713>

References

- Sun, Q., Zhao, L., Li, N., & Liu, J. (2010). Raman spectroscopic study for the determination of Cl⁻ concentration (molarity scale) in aqueous solutions: Application to fluid inclusions. *Chemical Geology*, 272(1–4), 55–61. <https://doi.org/10.1016/j.chemgeo.2010.02.004>
- Szeliga, W., Melbourne, T., Santillan, M., & Miller, M. (2008). GPS constraints on 34 slow slip events within the Cascadia subduction zone, 1997–2005. *Journal of Geophysical Research*, 113(B4), B04404. <https://doi.org/10.1029/2007JB004948>
- Taetz, S., John, T., Bröcker, M., & Spandler, C. (2016). Fluid–rock interaction and evolution of a high-pressure/low-temperature vein system in eclogite from New Caledonia: insights into intraslab fluid flow processes. *Contributions to Mineralogy and Petrology*, 171(11), 90. <https://doi.org/10.1007/s00410-016-1295-z>
- Tagami, T., & Dumitru, T. A. (1996). Provenance and thermal history of the Franciscan accretionary complex: Constraints from zircon fission track thermochronology. *Journal of Geophysical Research: Solid Earth*, 101(B5), 11353–11364. <https://doi.org/10.1029/96JB00407>
- Taira, A., Okada, H., Whitaker, J. H., & Smith, A. J. (1982). The Shimanto Belt of Japan: Cretaceous–lower Miocene active-margin sedimentation. *Geological Society, London, Special Publications*, 10(1), 5–26. <https://doi.org/10.1144/GSL.SP.1982.010.01.01>
- Tarantola, A., Mullis, J., Vennemann, T., Dubessy, J., & de Capitani, C. (2007). Oxidation of methane at the CH₄/H₂O–(CO₂) transition zone in the external part of the Central Alps, Switzerland: Evidence from stable isotope investigations. *Chemical Geology*, 237(3–4), 329–357. <https://doi.org/10.1016/j.chemgeo.2006.07.007>
- Tarantola, A., Mullis, J., Guillaume, D., Dubessy, J., de Capitani, C., & Abdelmoula, M. (2009). Oxidation of CH₄ to CO₂ and H₂O by chloritization of detrital biotite at 270±5 °C in the external part of the Central Alps, Switzerland. *Lithos*, 112(3–4), 497–510. <https://doi.org/10.1016/j.lithos.2009.04.008>
- Tatsumi, Y., & Kogiso, T. (2003). The subduction factory: its role in the evolution of the Earth's crust and mantle. *Geological Society, London, Special Publications*, 219(1), 55–80. <https://doi.org/10.1144/GSL.SP.2003.219.01.03>
- Taylor, J., & Clapp, R. (1991). New Features and Advanced Applications of Siroquant: A Personal Computer XRD Full Profile Quantitative Analysis Software Package. *Advances in X-Ray Analysis*, 35(A), 49–55. <https://doi.org/doi:10.1154/S037603080000865X>
- Tenthorey, E., & Hermann, J. (2004). Composition of fluids during serpentinite breakdown in subduction zones: Evidence for limited boron mobility. *Geology*, 32(10), 865. <https://doi.org/10.1130/G20610.1>
- Teraoka, Y., & Okumura, K. (1992). Tectonic division and Cretaceous sandstone compositions of the Northern Belt of the Shimanto Terrane, southwest Japan. *Mem. Geol. Soc. Jpn.*, 38, 261–270.
- Tobin, H., Vannucchi, P., & Meschede, M. (2001). Structure, inferred mechanical properties, and implications for fluid transport in the décollement zone, Costa Rica convergent margin. *Geology*, 29(10), 907. [https://doi.org/10.1130/0091-7613\(2001\)029<0907:SIMPAI>2.0.CO;2](https://doi.org/10.1130/0091-7613(2001)029<0907:SIMPAI>2.0.CO;2)
- Toriumi, M., & Teruya, J. (1988). Tectono-metamorphism of the Shimanto Belt. *Modern Geology*, 12, 303–324.
- Torsvik, T. H., Doubrovine, P. V., Steinberger, B., Gaina, C., Spakman, W., & Domeier, M. (2017). Pacific plate motion change caused the Hawaiian-Emperor Bend. *NATURE COMMUNICATIONS*, (30), 12. <https://doi.org/10.1038/ncomms15660>
- Tréhu, A. M., Bohrmann, G., Rack, F. R., Torres, M. E., Bangs, N. L., Barr, S. R., & Borowski, W. S. (2003). Shipboard Scientific Party. In Tréhu, A.M, Bohrmann, G., Rack, F.R., Torres, M.E., et al., *Proc. ODP, Init. Repts.*, 204 (pp. 1–131). College Station, TX: Ocean Drilling Program. Retrieved from doi:10.2973/odp.proc.ir.204.104.2003
- Tsuji, T., Kimura, G., Okamoto, S., Kono, F., Mochinaga, H., Saeki, T., & Tokuyama, H. (2006). Modern and ancient seismogenic out-of-sequence thrusts in the Nankai accretionary prism: Comparison of laboratory-derived physical properties and seismic reflection data: MODERN AND ANCIENT

- SEISMOGENIC THRUSTS. *Geophysical Research Letters*, 33(18), n/a-n/a.
<https://doi.org/10.1029/2006GL027025>
- Tuba, G., Kontak, D. J., Zajacz, Z., & Petrus, J. A. (2019). Bulk microanalysis of assemblages of small fluid inclusions by LA-ICP-MS: Methodology and application to orogenic gold systems. *Chemical Geology*, 529, 119326. <https://doi.org/10.1016/j.chemgeo.2019.119326>
- Ujiie, K. (1997). Off-scraping accretionary process under the subduction of young oceanic crust: The Shimanto Belt of Okinawa, Ryukyu Arc. *Tectonics*, 16, 305–322.
<https://doi.org/doi:10.1029/96TC03367>
- Ujiie, K. (2003). Deformation and fluid pressure variation during initiation and evolution of the plate boundary décollement zone in the Nankai accretionary prism. *Journal of Geophysical Research*, 108(B8), 2398. <https://doi.org/10.1029/2002JB002314>
- Ujiie, K., Saishu, H., Fagereng, Å., Nishiyama, N., Otsubo, M., Masuyama, H., & Kagi, H. (2018). An Explanation of Episodic Tremor and Slow Slip Constrained by Crack-Seal Veins and Viscous Shear in Subduction Mélange. *Geophysical Research Letters*, 45(11), 5371–5379.
<https://doi.org/10.1029/2018GL078374>
- Urey, H. C. (1947). The thermodynamic properties of isotopic substances. *J Chem Soc*, (0), 562–581.
- Vannucchi, P. (2019). Scaly fabric and slip within fault zones. *Geosphere*, 15(2), 342–356.
<https://doi.org/10.1130/GES01651.1>
- Velde, B. (1985). *Clay Minerals: a Physico-chemical Explanation of their Occurrence*. Elsevier.
- Velde, B. (1996). Compaction trends of clay-rich deep sea sediments. *Marine Geology*, 133(3–4), 193–201. [https://doi.org/10.1016/0025-3227\(96\)00020-5](https://doi.org/10.1016/0025-3227(96)00020-5)
- Vidal, O., & Parra, T. (2000). Exhumation paths of high-pressure metapelites obtained from local equilibria for chlorite-phengite assemblages. *Geological Journal*, 35(3–4), 139–161.
<https://doi.org/10.1002/gj.856>
- Vidal, O., De Andrade, V., Lewin, E., Munoz, M., Parra, T., & Pascarelli, S. (2006). P-T-deformation-Fe³⁺/Fe²⁺ mapping at the thin section scale and comparison with XANES mapping: application to a garnet-bearing metapelite from the Sambagawa metamorphic belt (Japan): P-T-DEFORMATION-FE³⁺/FE²⁺ MAPPING. *Journal of Metamorphic Geology*, 24(7), 669–683.
<https://doi.org/10.1111/j.1525-1314.2006.00661.x>
- Vityk, M. O., Bodnar, R. J., & Doukhan, J.-C. (2000). Synthetic fluid inclusions. XV. TEM investigation of plastic flow associated with reequilibration of fluid inclusions in natural quartz. *Contributions to Mineralogy and Petrology*, 139(3), 285–297. <https://doi.org/10.1007/s004100000142>
- Vrolijk, P., Myers, G., & Moore, J. C. (1988). Warm fluid migration along tectonic melanges in the Kodiak Accretionary Complex, Alaska. *Journal of Geophysical Research: Solid Earth*, 93(B9), 10313–10324. <https://doi.org/10.1029/JB093iB09p10313>
- Vrolijk, P., Fisher, A., & Gieskes, J. (1991). Geochemical and geothermal evidence for fluid migration in the Barbados accretionary prism, 18(5), 947–950.
- Wakabayashi, J. (2015). Anatomy of a subduction complex: architecture of the Franciscan Complex, California, at multiple length and time scales. *International Geology Review*, 57(5–8), 669–746.
<https://doi.org/10.1080/00206814.2014.998728>
- Wallace, Laura M., Reyners, M., Cochran, U., Bannister, S., Barnes, P. M., Berryman, K., et al. (2009). Characterizing the seismogenic zone of a major plate boundary subduction thrust: Hikurangi Margin, New Zealand: HIKURANGI MARGIN SEISMOGENIC ZONE. *Geochemistry, Geophysics, Geosystems*, 10(10), n/a-n/a. <https://doi.org/10.1029/2009GC002610>
- Wallace, L.M., Saffer, D. M., Barnes, P. M., Pecher, I. A., Petronotis, K. E., LeVay, L. J., & Expedition 372/375 Scientists (Eds.). (2019). *Proceedings of the International Ocean Discovery Program Volume 372B/375*. International Ocean Discovery Program.
<https://doi.org/10.14379/iodp.proc.372B375.2019>

- Wang, H. (1996). Diagenesis and Metamorphism of Clay Minerals in the Helvetic Alps of Eastern Switzerland. *Clays and Clay Minerals*, 44(1), 96–112. <https://doi.org/10.1346/CCMN.1996.0440109>
- Westbrook, G. K., & Smith, M. J. (1983). Long decollements and mud volcanoes: Evidence from the Barbados Ridge Complex for the role of high pore-fluid pressure in the development of an accretionary complex. *Geology*, 11(5), 279. [https://doi.org/10.1130/0091-7613\(1983\)11<279:LDAMVE>2.0.CO;2](https://doi.org/10.1130/0091-7613(1983)11<279:LDAMVE>2.0.CO;2)
- Wheat, C. G., Seewald, J. S., & Takai, K. (2020). Fluid transport and reaction processes within a serpentinite mud volcano: South Chamorro Seamount. *Geochimica et Cosmochimica Acta*, 269, 413–428. <https://doi.org/10.1016/j.gca.2019.10.037>
- Wibberley, C. A. J., & Shimamoto, T. (2003). Internal structure and permeability of major strike-slip fault zones: the Median Tectonic Line in Mie Prefecture, Southwest Japan. *Journal of Structural Geology*, 25(1), 59–78. [https://doi.org/10.1016/S0191-8141\(02\)00014-7](https://doi.org/10.1016/S0191-8141(02)00014-7)
- Williams, L. B., Hervig, R. L., Holloway, J. R., & Hutcheon, I. (2001). Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illitization of smectite. *Geochimica et Cosmochimica Acta*, 65(11), 1769–1782. [https://doi.org/10.1016/S0016-7037\(01\)00557-9](https://doi.org/10.1016/S0016-7037(01)00557-9)
- Williams, L. B., Hervig, R. L., Wieser, M. E., & Hutcheon, I. (2001). The influence of organic matter on the boron isotope geochemistry of the gulf coast sedimentary basin, USA. *Chemical Geology*, 174(4), 445–461. [https://doi.org/10.1016/S0009-2541\(00\)00289-8](https://doi.org/10.1016/S0009-2541(00)00289-8)
- Wilson, J. T. (1963). A possible origin of the Hawaiian Islands. *Can. J. Phys.*, 41, 863–870.
- Yamaji, K., Makita, Y., Watanabe, H., Sonoda, A., Kanoh, H., Hirotsu, T., & Ooi, K. (2001). Theoretical Estimation of Lithium Isotopic Reduced Partition Function Ratio for Lithium Ions in Aqueous Solution. *The Journal of Physical Chemistry A*, 105(3), 602–613. <https://doi.org/10.1021/jp001303i>
- Yamato, P., Burov, E., Agard, P., Le Pourhiet, L., & Jolivet, L. (2008). HP-UHP exhumation during slow continental subduction: Self-consistent thermodynamically and thermomechanically coupled model with application to the Western Alps. *Earth and Planetary Science Letters*, 271(1–4), 63–74. <https://doi.org/10.1016/j.epsl.2008.03.049>
- Yang, D., Hou, Z., Zhao, Y., Hou, K., Yang, Z., Tian, S., & Fu, Q. (2015). Lithium isotope traces magmatic fluid in a seafloor hydrothermal system. *Scientific Reports*, 5(1), 13812. <https://doi.org/10.1038/srep13812>
- Yoshida, K., Hirajima, T., Ohsawa, S., Kobayashi, T., Mishima, T., & Sengen, Y. (2015). Geochemical features and relative B–Li–Cl compositions of deep-origin fluids trapped in high-pressure metamorphic rocks. *Lithos*, 226, 50–64. <https://doi.org/10.1016/j.lithos.2015.03.002>
- You, C.-F., Spivack, A. J., Gieskes, J. M., & Rosenbauer, R. (1995). Experimental study of boron geochemistry: Implications for fluid processes in subduction zones. *Geochimica et Cosmochimica Acta*, 59, 2435–2442.
- You, C.-F., Chan, L. H., Spivack, A. J., & Gieskes, J. M. (1995). Lithium, boron, and their isotopes in sediments and pore waters of Ocean Drilling Program Site 808, Nankai Trough: Implications for fluid expulsion in accretionary prisms. *Geology*, 23(1), 37. [https://doi.org/10.1130/0091-7613\(1995\)023<0037:LBATII>2.3.CO;2](https://doi.org/10.1130/0091-7613(1995)023<0037:LBATII>2.3.CO;2)
- You, Chen-Feng, & Gieskes, J. M. (2001). Hydrothermal alteration of hemi-pelagic sediments: experimental evaluation of geochemical processes in shallow subduction zones. *Applied Geochemistry*, 16(9–10), 1055–1066. [https://doi.org/10.1016/S0883-2927\(01\)00024-5](https://doi.org/10.1016/S0883-2927(01)00024-5)
- Zajacz, Z., Hanley, J. J., Heinrich, C. A., Halter, W. E., & Guillong, M. (2009). Diffusive reequilibration of quartz-hosted silicate melt and fluid inclusions: Are all metal concentrations unmodified? *Geochimica et Cosmochimica Acta*, 73(10), 3013–3027. <https://doi.org/10.1016/j.gca.2009.02.023>

References

- Zane, A., Sassi, A., & Guidotti, C. V. (1998). New Data On Metamorphic Chlorite As A Petrogenetic Indicator Mineral, With Special Regard To Greenschist-Facies Rocks. *THE CANADIAN MINERALOGIST*, 36, 713–726.
- Zhang, L., Chan, L.-H., & Gieskes, J. M. (1998). Lithium isotope geochemistry of pore waters from ocean drilling program Sites 918 and 919, Irminger Basin. *Geochimica et Cosmochimica Acta*, 62(14), 2437–2450. [https://doi.org/10.1016/S0016-7037\(98\)00178-1](https://doi.org/10.1016/S0016-7037(98)00178-1)

Tectonique, métamorphisme et circulation des fluids dans les complexes d'accrétion

Les fluides jouent un rôle important dans les zones de subduction. Dans cette étude, nous avons appliqué un large éventail de méthodes analytiques dans les roches métapélitiques et les inclusions fluides de trois complexes (Kodiak, Alaska ; Shimanto, Japon ; les Alpes occidentales ; 220-380°C). A Kodiak, nous avons pu distinguer la déformation à l'interface des plaques (cisaillement non coaxial) et la déformation intra-prisme (raccourcissement coaxial horizontal). La transformation de l'illite en chlorite est la principale réaction minérale entre 250°C et 330°C à Shimanto et Kodiak. Une telle réaction consomme des fluides interstitiels, comme en témoigne l'augmentation de la salinité dans les inclusions fluides. Les éléments majeurs, les éléments fluides mobiles (FME) et $\delta^7\text{Li}$ dans Kodiak indiquent un système fermé. Au contraire, Shimanto se comporte comme un système ouvert, mis en évidence par le lessivage de FME de la roche hôte à mesure que la température augmente. Les concentrations de lithium et le $\delta^7\text{Li}$ des IF suggèrent une interaction constante entre fluide et sédiments, car le $\delta^7\text{Li}$ des fluides est déplacé vers la signature du protolith.

Mots clés : Subduction; Prisme d'accrétion ; Inclusions fluides ; Interactions roche/fluide ; Eléments mobiles ; Isotopes du lithium

Tectonics, metamorphism, and fluid circulation in accretionary complexes

Fluids play an important role in subduction zones. In this study, we applied a wide range of analytical methods in metapelitic rocks and fluid inclusions from three complexes (the Kodiak complex, the Shimanto belt, Japan, and Western Alps; T range 220-380°C). In Kodiak, we discriminate between deformation that occurred at the plate-boundary interface (non-coaxial shear) and as intra-wedge deformation (horizontal coaxial shortening). Illite-to-chlorite transformation is the main mineral reaction between 250°C and 330°C in Shimanto and Kodiak. Such reaction consumes pore fluids, evidenced by salinity increase in FI. Major elements, fluid-mobile elements (FME) and $\delta^7\text{Li}$ in Kodiak point to the closed system. Contrary, Shimanto behave as an open system, evidenced by leaching of FME from the host rock as temperature rises. Li concentrations in FI and low $\delta^7\text{Li}$ suggests constant interaction between fluid and sediments, changing $\delta^7\text{Li}$ of fluids towards the signature of protolith.

Keywords: Subduction; Accretionary prisms; Fluid inclusions; Fluid-rock interactions; Fluid-mobile elements; Lithium isotopes