

The behaviour of halogens (F, Cl, Br, I) and other fluid-mobile elements in subduction zones

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Abstract

The high abundance of fluid-mobile elements (FMEs) in arc magmas relative to the mantle attests to their recycling in subduction zones. Aqueous fluids released from the subducting slab transport these elements to the overlying mantle wedge for arc magma generation. However, some FME may be retained in the slab to the deeper mantle, incorporating into melts that form back-arc basalts, intraplate ocean island basalts (OIBs), carbonatites and kimberlites. This thesis reports the abundance and distribution of halogens (F, Cl, Br, I) and other FME (e.g., B, N) in various subducted lithologies to evaluate the behaviour of these elements during subduction, their partitioning among coexisting high pressure (HP) minerals and the role of these rocks and minerals in transporting these elements to the deeper mantle.

Abyssal lizardite-serpentinites, such as those from the Dominican Republic Tertiary subduction complex, are enriched in halogens and B from hydration by seawater and sediment-modified fluids. During the subduction and subsequent lizardite-antigorite transition of serpentinites, F and B are retained or replenished, while Cl, Br and I are expelled. Halogen compositions of shallow (<25 km) forearc mantle lizardite-serpentinites from the Dominican Republic suggest their hydration by fluids released from subducting altered oceanic crust, with only minor sediment contribution. This is in contrast with deep mantle wedge antigorite-serpentinites associated with the Tso Moriri UHP unit, NW Himalaya where elevated F (avg. 185 ppm), Br (avg. 0.13 ppm), I (avg. 0.16 ppm), B (avg. 51 ppm) and N (avg. 23 ppm) contents and their ratios demonstrate significant contributions from subducted shallow water sediments. The latter results are significant because they demonstrate serpentinites can host FME to depths of at least 100 km in the mantle wedge, and possibly to 200 km (limit of antigorite stability) in the slab of cold subduction zones or to 300 km in phase A after antigorite decomposition.

A similar decoupling of F from Cl during subduction is also observed in the metamorphosed crust. Blueschists from the Tavsanlı zone, NW Turkey and eclogites from the Tso Moriri UHP unit and the Sulu UHP belt, China contain low bulk Cl and Br contents relative to their presumed protoliths, whereas their F contents are similar or elevated. Iodine is also enriched in the blueschists and Tso Moriri eclogites, but depleted in the Sulu eclogites relative to their protolith rocks. Enrichments of F and I in the metamorphosed crust are attributed to fluids released from subducting marine sediments, suggesting geochemical exchange among subducting lithologies. Shallow water trench sediments would be especially enriched in these elements given the close proximity of continents to these subduction zones. Apatite and phengite are the major host of halogens in these rocks as demonstrated by high F in these minerals; blueschists contain up to 3.5 wt% and 500 ppm F, respectively, and eclogites contain up to 2.3 wt% and 1600 ppm F, respectively. Other halogen-bearing minerals include lawsonite, Na-amphibole +/- chlorite in the blueschists and possibly titanite +/- Na-amphibole in the eclogites. Liberated F may be subsequently incorporated into antigorite-serpentinites of the overlying mantle wedge. Bulk B contents are generally low in the subducted crust, however phengite can host up to 100 ppm B to at least blueschists facies conditions.

Overall, Cl, Br and I are lost from the altered oceanic crust and lizardite-serpentinites during shallow (< 50 km) subduction, while F and some B are retained. Given the stability of minerals such as antigorite, phase A (after antigorite decomposition), apatite, lawsonite and phengite to depths of 200-300 km in cold subduction zones and their accommodation of FME, they may transport significant F, some B and N and minor Cl, Br and I beyond subarc depths (~ 100 km) and contribute to their abundances in magmas derived from the deeper mantle.

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Chapter 1.

Global Introduction

1.1 Pre-ambles

Subduction of the Earth's lithosphere provides a mechanism for recycling fluids and fluid-mobile elements (FME) from the surface to the mantle. As the slab is subducted, rocks are progressively dehydrated to release fluids. Upward migration of the released fluids leads to partial melting of the overlying mantle wedge for arc magma generation. The contribution of a subduction component in arc magmas is evidenced by their enrichment in certain incompatible trace elements such as large ion lithophile elements (LILE; K, Rb, Cs, Ba), light rare earth elements (LREE), U, Pb, As, Sb, B and volatiles (H₂O, S, Cl, N) relative to mantle-derived melts from other tectonic settings, such as mid-oceanic ridge basalts (MORBs) and ocean-island basalts (OIBs) (Wallace et al., 2005; Pearce & Stern, 2006; Mitchell et al., 2010; Spandler and Pirard, 2013). Most volatiles are considered to have shallow cycling through subduction zones, however, there is growing evidence for their partial retention to the deeper mantle. For example, the recent discovery of ringwoodite (high pressure hydrous Mg-silicate) inclusions in kimberlitic diamonds (Pearson et al., 2014) provides direct evidence that the transition zone (~ 410-660 km depth) contains significant water.

Water and other volatiles may have become concentrated in the Earth's deep mantle during accretion (e.g., Albarede, 2009). Alternatively, or perhaps, additionally, volatiles may have been transported to the deep mantle by subduction very early in the Earth's history (>2.5 billion years ago; Sobolev et al., 2016). This is supported by high ¹⁵N of OIBs and carbonatites characteristic of subducting sediments (Marty and Dauphas, 2003). Fluorine and chlorine are also abundant in some deep-seated magmas, such as certain OIBs (e.g., Kendrick et al., 2017) and kimberlites (e.g., Kjarsgaard et al., 2009). Recently, elevated Br/Cl and I/Cl ratios akin to seafloor serpentinites were reported in Hawaiian OIB melt inclusions (Broadley et al., 2019). These ratios are also positively correlated with Ni/(Mg/Fe) – a proxy for the incorporation of

recycled oceanic crust in the form of pyroxenite into the Hawaiian mantle plume source (Broadley et al., 2019). Halogen abundances in back-arc basalts (BAB) and OIBs compared to MORB glasses also suggests up to 10% of subducted Cl, Br and I may be retained beyond the depth of slab for volcanic arc fronts (Kendrick et al., 2012b, 2014a,b). Finally, the correlation of F/Cl with K/Cl (considered a proxy for contribution from subducted material) in some EM1 end-member OIBs (e.g., Pitcairn seamounts in the South Pacific) also suggests F may be sourced from the subducting lithosphere and possibly preferentially subducted relative to Cl (Kendrick et al., 2014b). Despite growing evidence for the transport of volatiles to the deeper mantle by subduction, details of this mechanism, including what minerals may be involved, are not fully understood. This thesis addresses this question.

1.2 Composition of the subducting slab

Oceanic lithosphere is comprised of varying proportions of mafic crust, mantle peridotites and marine sediments. Its structure is primarily determined by the spreading rate of the oceanic ridge from which it originates. At fast-spreading ridges (>5 cm/yr; Dick et al., 2006), large quantities of mafic magmas are generated, yielding the classic ‘Penrose’ style of oceanic lithosphere (Penrose Conference Participants, 1972). The crust is composed of layers of pillow basalts, sheeted dykes and layered gabbros (~ 6 km thick) underlain by mantle peridotite (

Figure 1-1A; Dick et al., 2006). Fractures and faults expose deep sections of oceanic lithosphere to seawater or submarine hydrothermal fluids, resulting in hydration of these peridotites to form serpentinites. In contrast, the oceanic lithosphere produced at slow- (2-5 cm/yr) and ultraslow- (<2 cm/yr; Dick et al., 2003) spreading ridges is much more heterogeneous, typically consisting of a thin or intermittent covering of basalt along with abundant hydrated mantle peridotites and variable sediment cover (

Figure 1-1B; Cannat et al., 1997; Muller et al., 1997). In these environments abyssal serpentinites may comprise up to 25% of the oceanic lithosphere (Cannat et al., 2010).

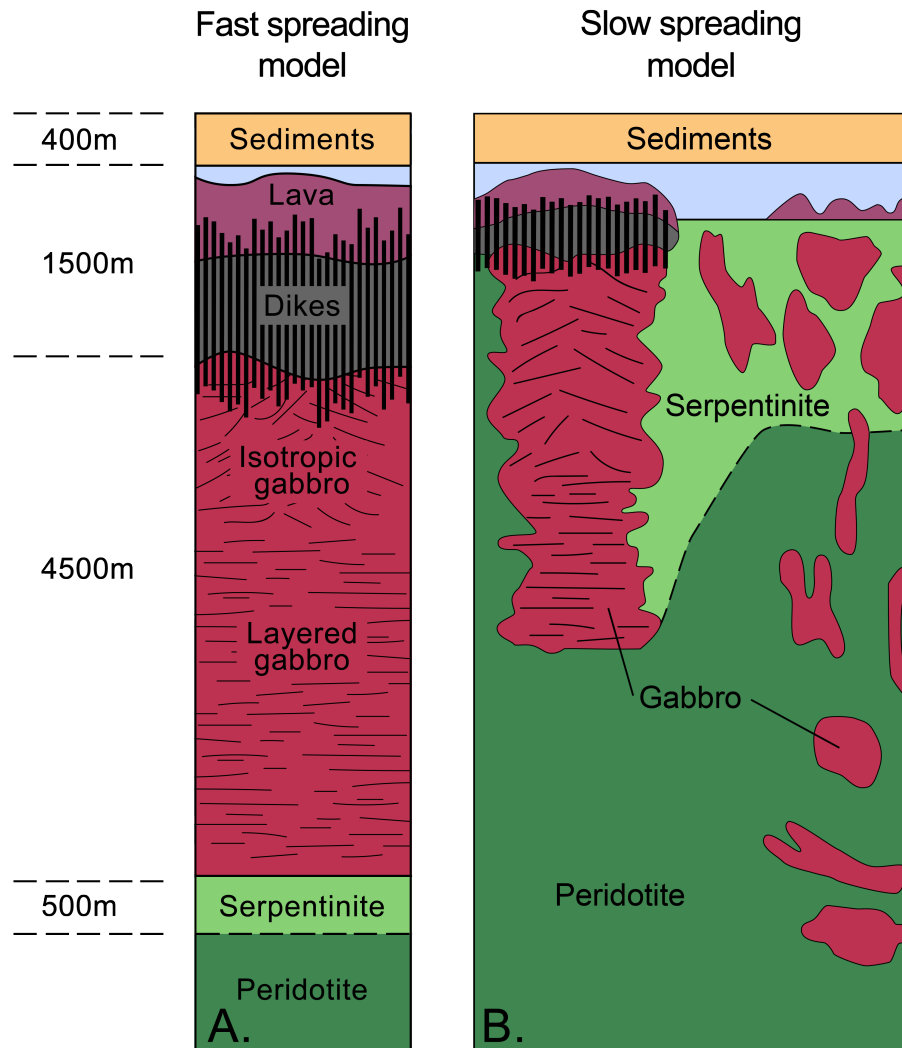


Figure 1-1: Simplified schematic diagram of representative cross sections of oceanic lithosphere produced at (A) fast- and (B) slow-spreading ridges. Based on models proposed by Penrose Conference Participants (1972) for fast-spreading crust and Cannat et al. (1997) and Muller et al. (1997) for slow-spreading crust. Serpentine in the diagram represents either concentrated zones of serpentinization or diffuse serpentinization throughout the upper lithospheric mantle (Kendrick, 2018). Figure modified from Kendrick, 2018.

Serpentinites are composed of serpentine, a hydrous phyllosilicate mineral with the chemical formula $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$. Lizardite and chrysotile are low-temperature phases that form below 400°C (Figure 1-2; Schwartz et al., 2013). Upon subduction, they transition to the high-temperature phase, antigorite (Figure 1-2). The varieties of serpentine phases are due to the different ways for the mineral to adjust to geometric strain between the tetrahedral and octahedral sheets (Evans et al., 2013). In addition to oceanic ridges, abyssal peridotites are also hydrated at the outer rise near trenches by fluid infiltration along extensional faults of the bending slab prior to subduction (Kerrick, 2002; Ranero et al., 2003). The estimated volume of abyssal serpentinites entering subduction zones range from a conservative 1-2% of the upper 10 km of lithospheric mantle (Kendrick et al., 2017) to 15% of the upper 30 km (Ranero et al., 2003). Serpentinization can also occur in mantle wedges by fluids released from subducting slabs (Hattori and Guillot, 2003).

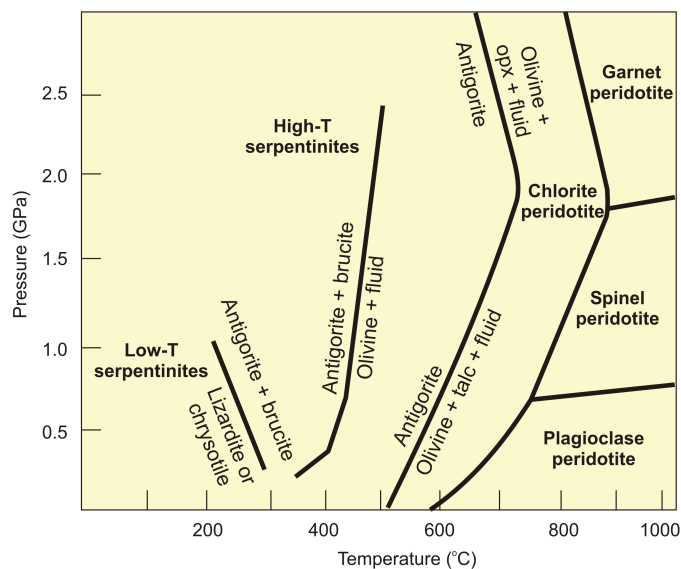


Figure 1-2: Pressure-temperature diagram for hydrated peridotitic rocks. Modified from Scambelluri et al. (2004).

The altered oceanic crust has typically undergone variable degrees of alteration to produce hydrated minerals such as amphibole, smectite and chlorite (Alt et al., 1986). Upon subduction, the crust is metamorphosed through a low temperature-high pressure path including prehnite-pumpellyite, greenschist, blueschist and eclogite facies (Figure 1-3). Each facies is characterized by a stable mineral assemblage that is specific to a given range of P-T conditions and starting bulk composition. Blueschist facies rocks are characterized by the formation of blue sodic amphibole and lawsonite (colder conditions) or epidote (warmer conditions) at the expense of tremolite, chlorite and albite. Other minor phases may include paragonite, phengite, chlorite, rutile, titanite, quartz, albite, pumpellyite and apatite. The blueschist-eclogite transition occurs at ~500-600°C and 1.2-1.6 GPa (Peacock, 1993), which corresponds to a depth of ~80-100 km in most subduction zones. It is characterized by the loss of most hydrous minerals, the formation of green omphacitic pyroxene and red Mg-rich garnet and the liberation of water.

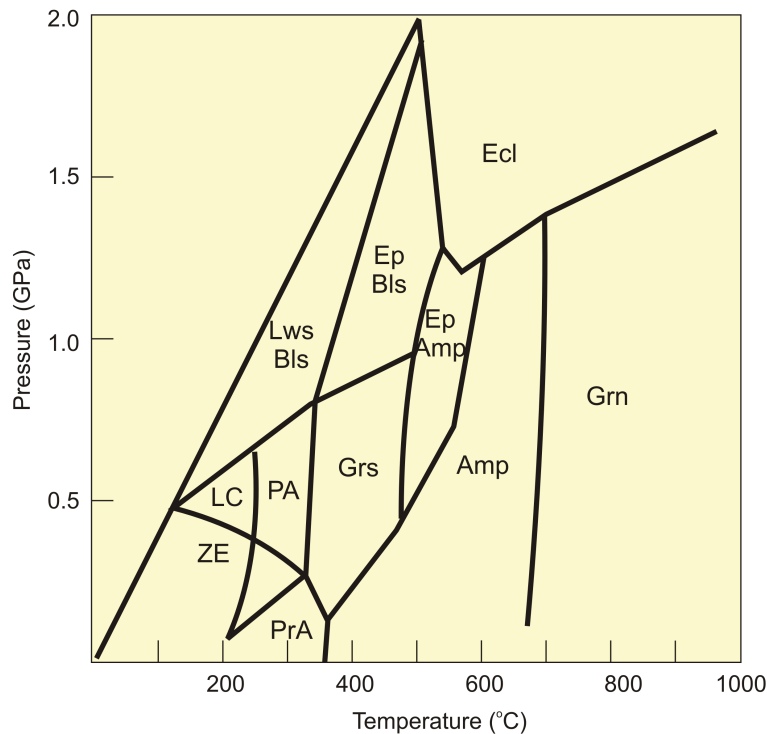


Figure 1-3: Pressure-temperature diagram for metamorphic facies of basaltic rocks. Metamorphic facies abbreviations: Modified from Peacock (1993).

When analyzing a petrogenetic grid, such as Figure 1-2 and Figure 1-3, it is important to consider certain caveats including, variations in the activity of water due to the presence of other volatiles (e.g., CO_2 , halogens), mineral solid solutions (i.e., substitution of elements that change the mineral's thermodynamic properties) and disequilibrium mineral assemblages (Philpotts & Ague, 2009). In terms of halogens, the substitution of F in certain minerals, such as amphibole and mica, may widen their stability to higher pressures and temperatures (Foley, 1991), thus changing the position of key reactions on the relevant petrogenetic grid.

Sediments in the subducting slab are typically 50-500 m thick (Plank and Langmuir, 1998) and are an accumulation of materials from continental erosion, marine life productivity and inorganic precipitation from seawater (Li and Schoonmaker, 2003). The global average

composition of incoming plate sediments (GLOSS and GLOSS-II) is similar to the composition of the upper continental crust except for the enrichment of Ba, Mn and heavy REE and dilution of detrital elements such as alkalis, Th, Zr and Hf (Plank and Langmuir, 1998; Plank, 2014). During subduction, seafloor sediments are either scraped off the incoming plate and accreted, or they accompany the slab into the mantle (Plank and Langmuir, 1993).

1.3 Global distribution and geochemical importance of the halogens

The halogens (F, Cl, Br, I) are highly volatile, lithophile elements primarily concentrating in the Earth's surface reservoirs, with much lower concentrations in the mantle due their removal by partial melting (Figure 1-4). Recently, Kendrick et al. (2017) presented updated halogen values and abundance ratios for the primitive and processed (or depleted) mantles based on the analysis of ~400 MORB and OIB glasses from a variety of settings.

Chlorine is highly abundant in seawater, evaporites and other marine sediments. Bromine is also abundant in the oceans, and along with I, it concentrates in organic matter and sedimentary rocks. Fluorine also accumulates in marine sediments and, along with Cl, is relatively abundant in crustal rocks (a few hundred ppm). In silicates, halogens are considered to be incorporated into the hydroxyl (OH^-) sites of minerals. Additionally, the small F ion (1.33 Å) may replace O^{2-} (1.21 Å) via a coupled substitution reaction with Al^{3+} replacing Si^{4+} in hydrous or nominally anhydrous minerals (e.g., Beyer et al., 2012; Dalou et al., 2012; Bernini et al., 2013). Chlorine and F are essential constituents of non-silicate minerals, such as chlor- and fluorapatite and evaporite minerals. Given the prevalence of amphiboles, micas and apatites in a variety of lithologies, these minerals play significant roles in halogen geochemical cycles (Mi and Pan, 2018).

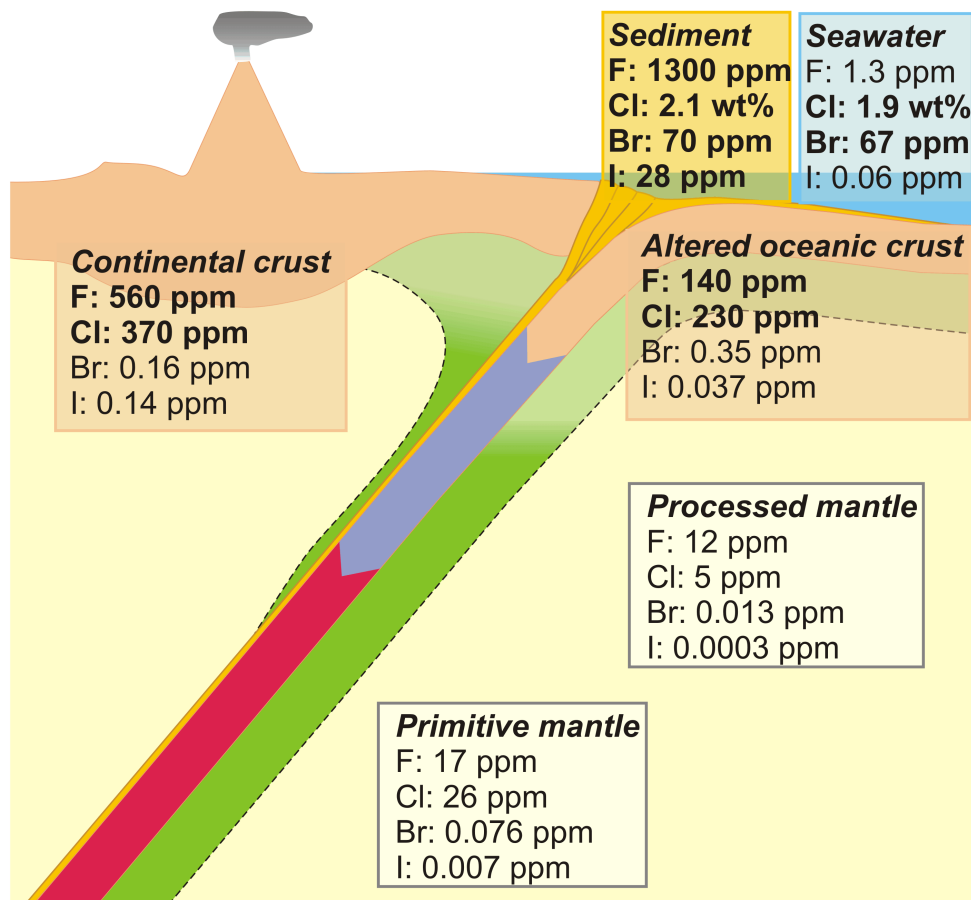


Figure 1-4: Average halogen contents of reservoirs relevant to subduction zones, including primitive mantle (Kendrick et al., 2017), processed or depleted mantle (Kendrick et al., 2017), seawater (Li, 1982), pelagic sediments (Li & Schoonmaker, 2003), altered oceanic crust (Magenheim et al., 1995; Straub and Layne, 2003; Sano et al., 2008; Barnes and Cisneros, 2012; Chavrit et al., 2016) and continental crust (Rudnick & Gao, 2003).

Fluorine and Cl can strongly influence the composition of hydrothermal fluids and behaviour of magmas (see Dolejš and Zajacz, 2018; Pirajno, 2018 and Webster et al., 2018 for reviews), and they serve as ligands for soluble metal complexes that contribute to metal transport in aqueous fluids and the formation of metal deposits (see Seward et al., 2014 for review). Chlorine and F are also abundant constituents of gases released from active volcanoes after H₂O,

CO₂ and S species (Symonds et al., 1994). As such, the degassing of HCl and HF have important atmospheric (e.g. stratospheric ozone losses; Millard et al., 2006) and biological implications (e.g. fluorosis in grazing animals; Cronin et al., 2003). Although the abundances of Br and I are orders of magnitude lower than those of F and Cl, their prevalence in biochemical reactions and resulting affinity of organic material strongly influences their distribution in geochemical systems and provides a tool for tracing sedimentary signatures (e.g., Fuge and Johnson 1986, Muramatsu and Wedepohl, 1998; Leri et al., 2010; Worden, 2018).

Due to its smaller size and higher electronegativity, F has a greater compatibility in many hydrous and nominally anhydrous minerals relative to the heavier halogens (e.g., Mathez and Webster, 2005; Dalou et al. 2012; Bernini et al. 2013; Joachim et al., 2015; Bénard et al., 2017), and is preferentially enriched in silicate melt during the immiscible separation of aqueous fluid (Seyfried and Ding, 1995; Kohler et al., 2009) while Cl, Br and I preferentially partition into the fluid phase (Bureau et al., 2000). Bromine and I are even less compatible than Cl given their larger ionic radii. The contrasting solubilities, compatibilities and elemental abundances of the halogens means their relative abundance ratios – i.e., F/Cl, Br/Cl, I/Cl – in combination with other data, such as noble gas chemistry, Pb and Sr isotopes and additional volatiles, are particularly useful for tracing fluid sources and migration during processes such as hydrothermal alteration, dehydration, partial melting and degassing (Hanley and Koga, 2018 and references therein). In a given reservoir, absolute halogen abundances may vary significantly, but their halogen ratios are often distinct.

1.4 Halogen quantification in geologic materials

The relatively low abundance of Br and I in igneous and metamorphic rocks (<1 ppm) and absence of suitable international rock references with known concentrations makes it difficult to quantify these elements using in situ techniques such as electron microprobe analysis (EPMA),

secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Even F concentrations upwards of 1000 ppm are difficult to analyze using an electron microprobe because of overlap of X-rays from F with that of Fe (e.g., Witter and Kuehner, 2004) and escape of F from solids during the analysis. Fluorine and Cl analyses with SIMS have lower detection limits, but are hampered by matrix effects and absence of calibration standards (e.g., Ottolini et al., 2000). Bulk halogen extraction methods, such as pyrohydrolysis or alkali fusion digestion (e.g., Hall et al. 1986; Schnetger and Muramatsu, 1996; Blackwell et al., 1997; Michel and Villemant, 2003; Wang et al., 2010) allow for the determination of all four halogens in solution to ppb levels. The most common analysis techniques are ion chromatography (IC; F, Cl and Br), ICP-MS (Cl, Br and I), ion selective electrode (ISE; F), and neutron activation analysis (NAA; Cl, Br and I). In the recently developed method the heavy halogens are converted to noble gases by neutron irradiation and their abundances are measured using a noble gas mass spectrometer (Kendrick, 2012a), however, since F is not converted to Ne through irradiation, it cannot be analyzed using this method.

1.5 Halogen in subduction zones

1.5.1 Inputs

Halogen contents in the basaltic-gabbroic rocks of the oceanic crust are primarily controlled by the presence of amphibole and clay minerals and vary depending on the degree of hydrothermal alteration and the temperature of the alteration. Given the high degree of composition variability, few studies have reported bulk halogen contents of the altered oceanic crust. Estimates for bulk Cl content range from 152 to 334 ppm (Sano et al., 2008; Barnes and Cisneros, 2012; Chavrit et al., 2016), and F ranges from 136 ppm to 216 ppm (Magenheim et al, 1995; Straub and Layne, 2003). Bromine and I data are even more scarce, but a recent study by

Chavrit et al. (2016) report average bulk contents of 351 ppb Br and 37 ppb I with average Br/Cl and I/Cl ratios of 0.0021 and 0.0025, respectively (Chavrit et al., 2016).

Serpentinites are major hosts of Cl, Br and I in the subducting slab (Scambelluri et al., 1997; 2004; Sharp and Barnes, 2004; Barnes and Sharp, 2006; John et al., 2011; Kodolányi et al., 2012; Kendrick et al., 2011; 2013; Debret et al., 2014). Abyssal serpentinites have average bulk Cl concentrations of ~1500 ppm (Sharp and Barnes, 2004; Barnes and Sharp, 2006; Kodolanyi et al., 2012; Kendrick et al., 2013) structurally bound in the serpentine mineral. Data for Br and I contents in serpentinites have been limited due to their much lower concentrations compared to Cl. Bulk analyses reveal concentrations of 0.16-6.8 ppm Br (avg. 2.4 ppm) and 0.016-2.6 ppm I (avg. 0.65 ppm) in seafloor and obducted abyssal serpentinites (John et al., 2011; Kendrick et al., 2013). Average Br/Cl ratios of these abyssal serpentinites (0.0043) are similar to that of seawater (0.0036; Li, 1982), but I/Cl ratios extend to much higher values (avg. 0.0026 cf. 0.0000032 for seawater; Li, 1982) and overlap with those of sedimentary pore fluids (0.000025-0.015; see Kendrick, 2018 for review), suggesting a strong sedimentary contribution to serpentinizing fluids on the seafloor or near convergent margins.

Fluorine concentrations in abyssal serpentinites show considerable variation based on few available reports, with bulk rock concentrations ranging from 1 to 204 ppm (Mével, 2003; John et al., 2011) and in situ analyses of serpentine grains documenting concentrations up to 470 ppm (Orberger et al., 1999; Debret et al., 2014). Variable enrichment is likely related to the nature of the serpentinizing fluid. Abyssal peridotites at slow and ultra-slow spreading ridges are primarily hydrated by F-poor seawater, whereas seafloor serpentinites formed near volcanic centres may have elevated F due to a contribution of magmatic fluids.

1.5.2 Behaviour of halogens during subduction

Preliminary studies of halogens in subducted oceanic crust reveal Cl contents positively correlate with water, and their concentrations decrease with increasing metamorphic grade (Marschall et al., 2009). This suggests Cl is lost from the slab along with fluids during subduction. *In situ* analyses of metamorphic amphiboles also reveal a loss of Cl under greenschist to eclogites facies conditions (Debret et al., 2016). Bromine and I may be even more readily lost to fluids, as indicated by Br/Cl and I/Cl ratios in fluid inclusions of Norwegian eclogites that are up to an order of magnitude greater than modern seawater (Svenson et al., 2001). These eclogites also have high F/Cl mineral-fluid partitioning coefficients, particularly for the metamorphic minerals, apatite and phengite (cf. amphibole). In warmer slabs, F may be mobilized by slab melting (Van den Bleeken and Koga, 2015), but in cold subduction zones, the stability of apatite and phengite to 200 km (Konzett and Frost, 2009) and 300 km (Schmidt and Poli, 1998) depth, respectively, may allow them to host F to the deeper mantle.

During subduction, lizardite changes to antigorite, a high-temperature form of serpentine. This lizardite-antigorite transition is considered to be accompanied by the release of water (Evans, 2004) and certain FME (Barnes et al., 2008). This is supported by higher concentrations of Cl, Br and I in seafloor and obducted abyssal lizardite-serpentinites than subducted abyssal antigorite-serpentinites (Scambelluri et al., 2004; John et al., 2011; Kendrick et al., 2018). Chlorine, Br and I released from slabs are incorporated into newly hydrated forearc mantle peridotites at the base of mantle wedges, as evidenced by the halogen signatures of forearc mantle serpentinites (e.g., Snyder et al., 2005; Wei et al., 2005; Kodolányi and Pettke, 2011; Kendrick et al., 2013) and fluid inclusions of mantle peridotites beneath volcanic fronts (e.g., Snyder et al., 2005; Wei et al., 2005; Kobayashi, et al., 2016). However, the contributions of

different slab components –serpentinites, altered oceanic crust and sediments – to the hydration of the forearc mantle, is not fully understood.

The behaviour of F during serpentinite subduction is not as well constrained as the other halogens (John et al., 2011; Debret et al., 2014). Abundance of F in forearc serpentinites is limited (Wei et al., 2005), however there is evidence that F may be retained during serpentinite subduction and dehydration based on high F in metamorphic olivine after antigorite dehydration (De Hoog et al., 2014). Preliminary mass balance calculations for fluxes of all four halogens through subduction zones (John et al., 2011; Barnes et al., 2018) indicate a portion of the subducted halogens may be transferred to the deeper mantle, however, given the uncertainties in the halogen content of the deeply subducted slab, these fluxes and the contributions of each slab component to halogen abundances are poorly constrained.

1.6 Boron in subduction zones

Similar to the halogens, B is useful for tracing volatile recycling in subduction zones. Boron enrichment in arc lavas (10s of ppm; e.g., Ryan and Langmuir, 1993; Straub and Layne 2003; Bouvier et al., 2008; Sadofsky et al., 2008) and continental crust (17 ppm ; Rudnick and Gao, 2003) relative to the mantle (<0.3 ppm; Palme and O'Neil, 2003) is considered to suggest a slab component in arc magmas. Boron is abundant in seawater (4.4 ppm; Li, 1982) and marine sediments (10s to 100s ppm; Li and Schoonmaker, 2003; Plank, 2014), but low in unaltered MORB (~1 ppm; White and Klein, 2014). Boron contents of the altered oceanic crust are highly variable due to varying degrees of seawater alteration, with an average estimate of ~5 ppm (Smith et al., 1995). Boron is also variably abundant in abyssal serpentinites (10-100 ppm; Scambelluri et al., 2004; Vils et al., 2008; Kodolanyi et al., 2012).

During shallow subduction, a significant amount of B is lost from sediments (Moran et al., 1992; Bebout et al., 1999, 2007) and presumed to migrate to the overlying mantle wedge where

it is incorporated into forearc serpentinites (Snyder et al., 2005; Wei et al., 2005; Kodolanyi et al., 2012; Pabst et al., 2011). The behaviour of B in subducting serpentinites is not as well understood. Some studies show a loss of B during the serpentine phase change from low-temperature lizardite and/or chrysotile to high-temperature antigorite (Scambelluri et al., 2004; Kodolanyi and Pettke, 2011), while others report its retention during the phase transition (Scambelluri and Tonarini, 2012). There is also evidence for B incorporation into secondary olivine after antigorite dehydration (De Hoog et al., 2014).

Preliminary mass balance calculations for B recycling through subduction zones suggest up to 62% of subducted B is returned to the surface via arc magmatism (Moran et al., 1992). However, this calculation does not consider B input from subducting serpentinites and therefore, may overestimate the fraction of subducted B recycled through arc magmatism.

1.7 Nitrogen in subduction zones

Nitrogen in the lithosphere is largely controlled by organics in sediments, making it a useful tracer of sediment-derived fluids (Bebout, 1997). Nitrogen is lost from sediments during high-temperature prograde metamorphism (e.g., Bebout and Fogel, 1992; Mingram and Braüer, 2001; Jia, 2006), but appears to be retained along low-temperature prograde pathways akin to modern subduction zones (e.g., Busigny et al., 2003). Recently, the efficiency of recycling of N through arc volcanism is in discussion. Some studies conclude that nearly 100% of subducted N is returned to the surface via arc magmas (e.g., Fischer et al., 2002). However, if incoming N in altered oceanic crust is also considered (e.g., Li et al., 2007; Halama et al., 2010), this amount is reduced to 15-40% (e.g., Sadofsky and Bebout, 2004). This could be reduced even further if N in abyssal serpentinites is also considered, however the abundance of N in serpentinites and their contribution to recycling is not well established (e.g., Philippot et al., 2007; Halama et al., 2014).

1.8 Research objectives

The primary objectives of this project are i) to assess the abundance of halogens (F, Cl, Br, I) and other FME (B, N) in subduction-related rocks to constrain the behaviour of these elements during subduction and the implications for their global geochemical cycling, and ii) to evaluate the partitioning of halogens among coexisting high pressure (HP) mineral phases to determine how these minerals may contribute to the replenishing of FME outgassed from volcanoes or their transport to the deeper mantle. Samples studied include metasediments, blueschists, eclogites, (subducted) abyssal serpentinites and mantle wedge serpentinites.

1.9 Thesis organization

This thesis comprises eight chapters and seven appendices. It begins with a global introduction that includes a preamble, relevant previous work, a description of thesis objectives and organization and an outline and statement of contribution. Chapter 2 describes the analytical methods developed and used for this project. The subsequent four chapters are published manuscripts including appendices written by the author. Chapter 3 documents the halogen and B contents of obducted abyssal, subducted abyssal and shallow (<35 km) forearc mantle serpentinites from the Dominican Republic. Chapter 4 examines the halogen, B and N abundances of deep (>100 km) mantle wedge serpentinites from the Tso Moriri UHP unit in northwestern Himalaya. Chapter 5 discusses the halogen abundances of lawsonite blueschists from northwestern Turkey and their distribution among coexisting HP minerals. Chapter 6 reviews the incorporation of halogens in abyssal serpentinites and their behaviour during subduction. Chapter 7 is a manuscript in preparation to be submitted after significant improvement to a refereed journal. It documents the halogen content of eclogite rocks and minerals from the Tso Moriri unit and Sulu UHP belt, China and discusses the behaviour of these elements during the blueschist-eclogite facies transition. The final chapter provides a

summary of the thesis work. Appendices include supplementary material for prepared manuscripts (Appendices I to V), additional halogen data sets (Appendix VI) and conference abstracts (Appendix VII).

1.10 Statement of contribution

This thesis encompasses original research conducted by Lilianne Pagé under the supervision of Professor Keiko Hattori at the University of Ottawa. This section outlines the contribution of the author and collaborators to each manuscript.

Chapter 3. Tracing halogen and B cycling in subduction zones based on obducted, subducted and forearc serpentinites of the Dominican Republic

L. Pagé and K. Hattori

Contributions:

- Samples were collected by K. Hattori and Benoit Simard during his MSc field work.
- L. Pagé wrote the chapter and produced all figures and tables.
- L. Pagé established halogen extraction protocols with assistance of the late Jack Cornett, conducted bulk halogen extractions and carried out ICP-MS and IC analyses with the assistance of Nimal De Silva (lab manager) and Ping Zhang (lab technician) at the University of Ottawa.
- L. Pagé prepared samples for B analysis by Prompt Gamma Neutron Activation Analysis (PGNAA) at Activation Laboratories (Ancaster, Canada).
- K. Hattori gave advices and edited the manuscript.
- L. Pagé acted as corresponding author during the submission and review process.

This manuscript was peer reviewed by Dr. Dorrit Jacob (Associate Editor) and two anonymous reviewers. It was published by Nature Scientific Reports in 2017:

Pagé, L., and Hattori, K. (2017). Tracing halogen and B cycling in subduction zones based on obducted, subducted and forearc serpentinites of the Dominican Republic. *Scientific reports*, 7(1), 1-9, doi:10.1038/s41598-017-18139-7.

Chapter 4. Mantle wedge serpentinites: A transient reservoir of halogens, boron, and nitrogen for the deeper mantle

L. Pagé, K. Hattori and S. Guillot

Contributions:

- Samples were collected by K. Hattori and S. Guillot.
- L. Pagé wrote the chapter and produced all figures and tables.
- L. Pagé established halogen extraction protocols with assistance of the late Jack Cornett, conducted bulk halogen extractions and carried out ICP-MS and IC analyses with the assistance of Nimal De Silva (lab manager) and Ping Zhang (lab technician) at the University of Ottawa.
- L. Pagé established protocol for low-level N analysis with the assistance of Paul Middlestead (lab manager) and conducted analyses at the University of Ottawa.
- L. Pagé prepared samples for B analysis by Prompt Gamma Neutron Activation Analysis (PGNAA) at Activation Laboratories (Ancaster, Canada).
- K. Hattori and S. Guillot gave advices and edited the manuscript.
- L. Pagé acted as corresponding author during the submission and review process.

This manuscript was peer reviewed by Dr. Dennis Brown (Associate Editor), Mark Kendrick, Horst Marschall and an anonymous reviewer. It was published by *Geology* in 2018:

Pagé, L., Hattori, K., and Guillot, S. (2018). Mantle wedge serpentinites: A transient reservoir of halogens, boron, and nitrogen for the deeper mantle. *Geology*, 46(10), 883-886, doi:10.1130/G45204.1.

Chapter 5. Halogen (F, Cl, Br, I) behaviour in subducting slabs: A study of lawsonite blueschists in western Turkey

L. Pagé, K. Hattori, J.C.M de Hoog and A. Okay

Contributions:

- Samples were collected by K. Hattori and A. Okay.
- L. Pagé wrote the chapter and produced all figures and tables.
- L. Pagé conducted petrography and separation of mineral fractions at the University of Ottawa.
- L. Pagé established halogen extraction protocols with assistance of the late Jack Cornett, conducted bulk halogen extractions and carried out ICP-MS and IC analyses with the assistance of Nimal De Silva (lab manager) and Ping Zhang (lab technician) at the University of Ottawa.
- L Pagé conducted scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) work with the assistance of Glenn Poirier (lab manager) at the University of Ottawa. Reduction of EPMA data was conducted by Glenn Poirier.
- L. Pagé prepared samples for secondary ion mass spectrometry (SIMS) work with the assistance of Tom Pestaj and Bill Davis of the Geological Survey of Canada. C.J.M de Hoog collected and reduced SIMS data at the University of Edinburgh.
- L . Pagé prepared samples for bulk rock major and trace element analysis by X- ray fluorescence and four acid digestion with ICP-MS, respectively, at ALS Global (North Vancouver, Canada).
- K. Hattori, J.C.M de Hoog and A. Okay gave advices and edited the manuscript.
- L Pagé acted as corresponding author during the submission and review process.

This manuscript was peer reviewed by Dr. Bernard Marty (Associate Editor), Mark Kendrick and an anonymous reviewer. It was published by Earth and Planetary Science Letters in 2016:

Pagé, L., Hattori, K., de Hoog, J. C., and Okay, A. I. (2016). Halogen (F, Cl, Br, I) behaviour in subducting slabs: A study of lawsonite blueschists in western Turkey. *Earth and Planetary Science Letters*, 442, 133-142, doi: 10.1016/j.epsl.2016.02.054.

Chapter 6. Abyssal Serpentinites: Transporting Halogens from Earth's Surface to the Deep Mantle

L. Pagé and K. Hattori

Contributions:

- L. Pagé wrote the chapter and produced all figures and tables.
- L. Pagé reviewed current literature, compiled relevant data and completed mass balance calculations.
- K. Hattori gave advices and edited the manuscript.
- L Pagé acted as corresponding author during the submission and review process.

This manuscript was peer reviewed by Dr. Agnes Elmaleh, (Guest Editor) and two anonymous reviewers. It was published by Minerals in 2019:

Pagé, L., and Hattori, K. (2019). Abyssal Serpentinites: Transporting Halogens from Earth's Surface to the Deep Mantle. *Minerals*, 9(1), 61-74, doi: 10.3390/min9010061.

Chapter 7. Halogens in eclogites of the Tso Moriri UHP unit and Sulu UHP belt: Implications for the recycling of F to the deeper mantle

Contributions:

- Himalayan samples were collected by K. Hattori, S. Guillot and Julia de Sigoyer. Sulu samples were collected by K. Hattori and Jian Wing.

- L. Pagé wrote the manuscript and produced all tables and figures 3 to 11. Paul Dagenais prepared figures 1 and 2.
- L. Pagé conducted X-ray fluorescence (XRF) work for major and trace elements of Sulu bulk rocks at the University of Ottawa.
- Paul Capiez conducted XRF work for major and trace elements of Tso Moriri bulk rocks at the Université de Lyon (data originally published in Dr. Julia de Sigoyer's PhD thesis).
- L. Pagé conducted petrography, established halogen extraction protocols with assistance of the late Jack Cornett, conducted bulk halogen extractions and carried out ICP-MS and IC analyses with the assistance of Nimal De Silva (lab manager) and Ping Zhang (lab technician) at the University of Ottawa.
- L. Pagé conducted scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) work with the assistance of Glenn Poirier (lab manager) at the University of Ottawa. Reduction of EPMA data was conducted by Glenn Poirier.
- K. Hattori provided advice and comments on the manuscript.

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Chapter 2.

Methodology

2.1 Bulk rock methods

All hand samples were washed prior to grinding to remove surface salts and soluble organics. Bulk samples (200-1000 g) were crushed by a TM Engineering Rhino Jaw Crusher and milled using a ceramic grinding dish in a TM/S Series Vibratory Ring Pulveriser to a finely (<75 μm particle size) ground powder.

2.1.1 Halogen extraction by pyrohydrolysis

The modified pyrohydrolysis method at the University of Ottawa was developed after Schnetger and Muramatsu (1996) and Michel & Villemant (2003). The initial set-up of the pyrohydrolysis method consisted of a CuO catalyst, dry oxygen gas flow of <0.1 Lmin^{-1} rate, a closed silica boat and no mechanism to prevent condensation in the output glassware. This set-up gave chemical yields of <60%, as monitored by a I-125 tracer (Cornett et al., 1997). Changes were made to the set-up systematically and monitored with I-125 tracer until yields exceeded >85%. The resulting method and set-up (Figure 2-1) is outlined below.

A 0.5 g weight of powdered sample was combined in a silica boat with an equal weight of Elemental Microanalysis Ltd reagent grade V_2O_5 (0.39 ppm F, 48 ppb Br and 3.9 ppb I; Cl is below detection limit) previously heated to 325°C for 24 hours. A wet oxygen gas flow of 0.8 Lmin^{-1} was created using an Erlenmeyer flask of water on low heat connected to a tank of ultrapure oxygen gas. The main silica tube was housed in a Lindberg Blue M tube furnace set to an initial temperature of 500°C. A glass rod was used to insert a silica wool plug into the main tube and position it just beyond the wall of the furnace. The purpose of plug was to prevent solid material from entering the trap and clogging the frit. The sample was slowly introduced to the main tube and positioned directly in the middle of the furnace. Once the system was reconnected, the furnace temperature was increased to 1100°C for 15 minutes. The temperature on the output end of the main tube beyond the furnace was maintained at 120°C+ with heating tape to prevent

condensation. The evolved gas was passed through a frit inside the trap to maximize surface area contact with the 7 mL of 25 mM NaOH trap solution (prepared from extra pure N₂-flushed NaOH pellets from Acros Organics). The collection vessel was submerged in an ice bath during collection to promote condensation of the halogens in solution. After 15 minutes the furnace temperature was reduced to 500°C before expelling the sample and quartz wool from the main tube. The system was purged with oxygen for 10-15 minutes, fresh quartz wool and the next sample were inserted, and a clean collection vessel was connected to the trap. All glassware was cleaned with deionized water after every two to three runs (i.e. duplicates or triplicates of one sample). This included back flushing the fritted tip to remove build-up of silica fibers. Typical daily throughput is 6-8 samples.

Possible improvements to the method could include an improved method of weighing and transferring sample and catalyst to the silica boat to minimize sample loss and using a catalyst with a higher melting point than V₂O₅ (690°C), such as WO₂ (>1400°C).

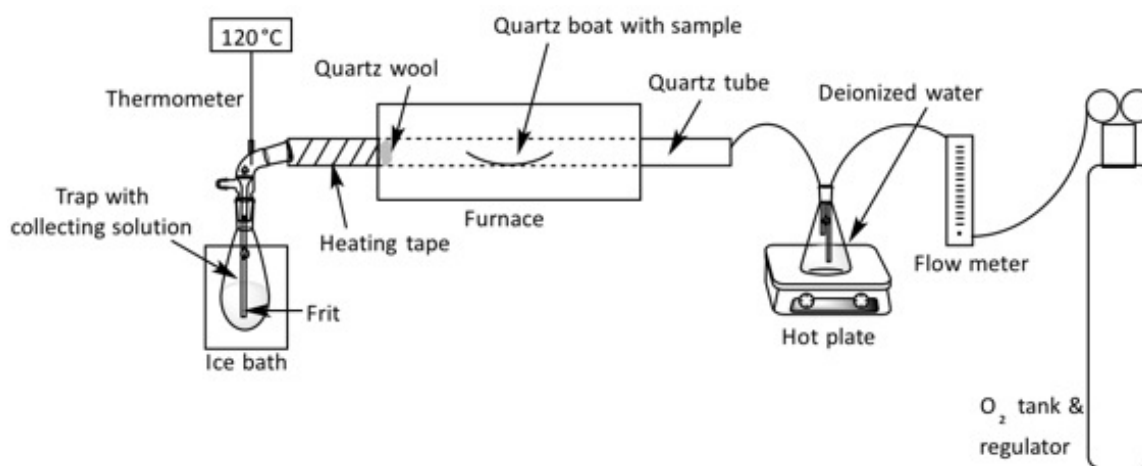


Figure 2-1: Schematic of pyrohydrolysis set-up.

2.1.2 Halogen analysis by IC and ICP-MS

Solutions collected by pyrohydrolysis extraction were diluted 5x for inductively coupled plasma – mass spectrometry (ICP-MS) analysis, and NH_3 (~1% of total solution) was added to stabilize anions in solution. Dilution was not necessary for ion chromatography (IC) analysis. Fluorine and Cl analyses were carried out at the University of Ottawa using a Dionex Model 2100 Ion Chromatograph equipped with KOH eluent generator. Certified chloride and fluoride standard solutions from Ultra Scientific Analytical Solution were used to create calibration solutions ranging from 0.078 to 10 ppm F and Cl by a series of dilutions with Milli-Q water. Instrumental detection limits (3σ) for F and Cl were 0.017 ppm and 0.034 ppm in solution, respectively. Bromine (^{79}Br), I (^{127}I) and Cl (^{35}Cl) analyses were carried out at the University of Ottawa using an Agilent 7700 ICP mass spectrometer. Certified chloride, bromide and iodide standard solutions from Ultra Scientific Analytical Solution were used to create calibration solutions ranging from 2.5 to 10 ppm Cl and 12.5 to 50 ppb Br and I by serial dilution with distilled deionized water. Instrumental detection limits (3σ) for Cl, Br and I were 6.5 ppb, 0.022 ppb and 0.041 ppb, respectively. The method blank, as determined by repeat extractions without sample or catalyst, is 0.019 ppm F, 0.12 ppm Cl, 4.1 ppb Br and 2.9 ppb I (Table 2-1).

Accuracy of the pyrohydrolysis technique is based on the analysis of five international reference materials – BCR-2 (basalt), JB-1 (basalt), JB-3 (basalt), MRG-1 (gabbro) and UB-N (serpentine). Percent yields (i.e., extraction efficiencies) range from 72 to 93% for F, 85 to 106% for Cl by IC, 96 to 124% for Cl by ICP-MS, 49 to 88% for Br and 55 to 151% for I (Table 2-1). Relative standard deviations (RSD) of triplicate analyses of these standards range from 4.1 to 7.0% for F, 1.7 to 5.8% for Cl by IC, 0.6 to 5.6% for Cl by ICP-MS, 4.1 to 22% for Br and 9.0 to 31% for I. Based on the slopes and r^2 values (coefficients of determination) of measured-reference concentration plots (Figure 2-2), the IC method yields marginally better results for Cl

determination than ICP-MS. Therefore, all published articles comprising this thesis present IC-determined Cl data.

The relatively large spread in yields (Table 2-1) is likely the result of uncertainty in reference values, particularly for Br and I, given their low concentrations in these rock types. The consistently slightly lower F values obtained for the standards may indicate some structural F (perhaps F^- replacing O^{2-}) is not completely extracted. In the future, this may be overcome by increased extraction time or the use of a different, more effective catalyst.

Table 2-1: Halogen content of five international reference materials.

	n	Dionex IC				ICP-MS						Reference Values				Yield (%)					Refs.
		F	rsd	Cl	rsd	Cl	rsd	Br	rsd	I	rsd	F	Cl	Br	I	F	Cl*	Cl†	Br	I	
BCR-2	3	410	4.2	85.3	5.4	97.8	5.6	bdl	bdl	0.026	25	440 [3]	89-98 [4][5]	0.157-0.175 [5]	0.017 [5]	93	96	110	bdl	151	[1][2]
JB-1	3	351	4.2	157	5.8	173	4.8	0.28	22	0.016	27	385	176	0.58	0.03	91	89	98	49	55	[3]
JB-3	3	216	4.4	276	1.7	322	0.066	0.44	19	0.027	9.0	253 [1]	259 [1]	0.5 [6]	0.028 [1]	86	106	124	88	97	[3][4]
MRG-1	3	184	7.0	145	3.6	164	3.5	0.083	14	0.0083	31	240 ± 40	170 ± 30			77	85	96			[5]
UB-N	3	68.3	4.1	775	4.4	873	4.2	4.2	4.1	0.016	25	95	800 ± 301			72	97	109			[6]
Method blank	5	0.019	56	0.12	39	0.35	4.6	0.0041	19	0.0029	5.8										

[1] Wang et al. 2009, [2] Michel & Villemant 2003, [3] Imai et al. 1995, [4] Schmetger et al. 1998, [5] Gladiney & Roelands 1990, [6] Govindaraju, 1995

*Cl by IC; †Cl by ICP-MS

Note: IC - ion chromatography; ICP-MS - inductively coupled plasma-mass spectrometry; bdl - below detection limit; RSD - relative standard deviation

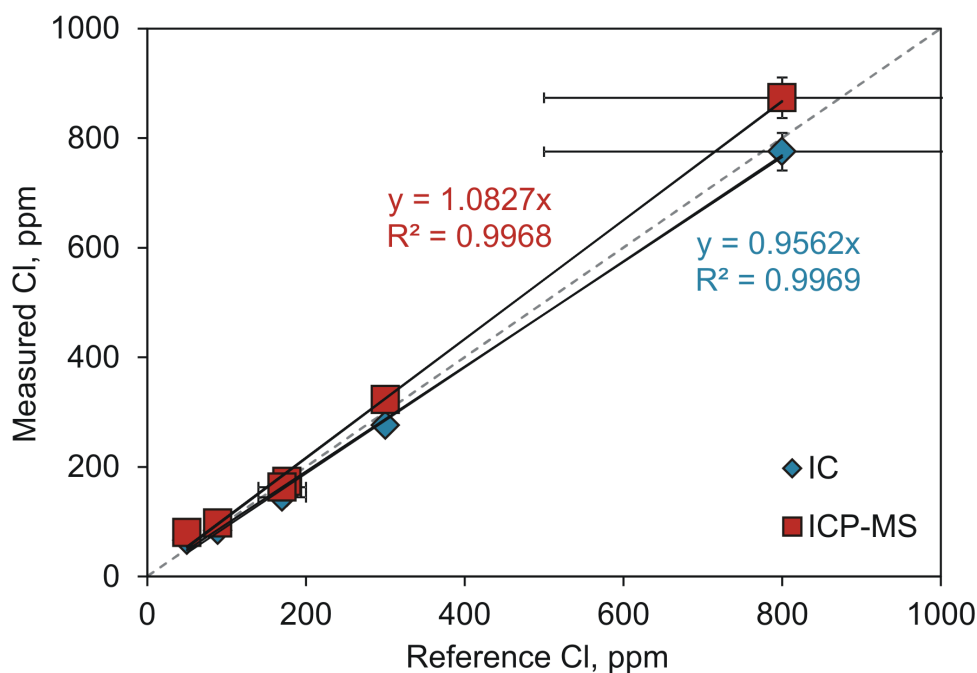


Figure 2-2: Comparison of measured Cl content in reference materials by ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS).

2.1.3 Nitrogen

Nitrogen contents are determined using an Elementar vario EL cube elemental analyzer (EA) in C-N-S simultaneous analysis mode (CNS mode). The analyzer consists of a large capacity (38 mm diameter) combustion tube operating at 1150°C, a reduction tube at 850°C with copper wire to reduce evolved NO_x and SO_x gases to N₂ and SO₂, a series of chemical traps to remove SO₂, H₂O and CO₂ and a thermal conductivity detector (TCD). Samples (~200 mg) are weighed to the nearest 0.001 mg and mixed with WO₂ (dried at 890°C for 24h) and Sn powder (Elemental Microanalysis Ltd; ~100 mg each) in large (20x10x8 mm) Sn capsules. Tin and WO₂ are used to catalyze sample combustion and control the reaction of alkali and alkaline earth metals, respectively. Low- (B-2152; 0.13 wt% N) and high- (B-2150; 0.52 wt% N) organic soil

reference materials (Elemental Microanalysis Ltd) are used to create a calibration curve ranging from 0.001 mg to 1.0 mg N against recorded integration values (N peak areas).

To analyze low-N samples, larger sample sizes (and thus larger amounts of the WO₂ catalyst) are required. However, increasing sample size also increases the volume of air-filled interstitial space between grains, resulting in higher N blanks (reported as integration values; Figure 2-3). To improve the N detection limit, atmospheric N is removed prior to sample combustion by He flushing or evacuation with vacuum. Helium flushing involves displacing air by He and sealing the boat with a liquid sealing device. Helium flushing at a high (~1000 mL/min) flow rate can reduce atmospheric N (Figure 2-4). However, powder dispersed from the high flow may adhere to the inner walls of the boat preventing an effective seal or be lost from the boat completely, yielding unreliable results. Alternatively, air can be removed from samples by vacuum. During normal operation of the EA, He gas is used to flush air from the ball valve as it rotates to drop the sample from the auto-sampler into the combustion tube. During vacuum-modified operation, atmospheric N is removed from samples by placing them under vacuum in the ball valve for 20 seconds before combustion. Vacuum is achieved by replacing one of two He inlets with a vacuum pump and blocking the output tap of the ball valve. Vacuum draw is controlled by tube diameter (0.2 mm) and length (300 mm). The second inlet provides He to flood the combustion chamber and carry evolved gases to the detector. On average, using a vacuum pump compared to He flushing reduces the N blank of 200 mg WO₂ from 482 ± 254 (n=15) to 28 ± 10 (n=8) (Figure 2-5), and is the preferred method for removal of atmospheric N from low-N samples.

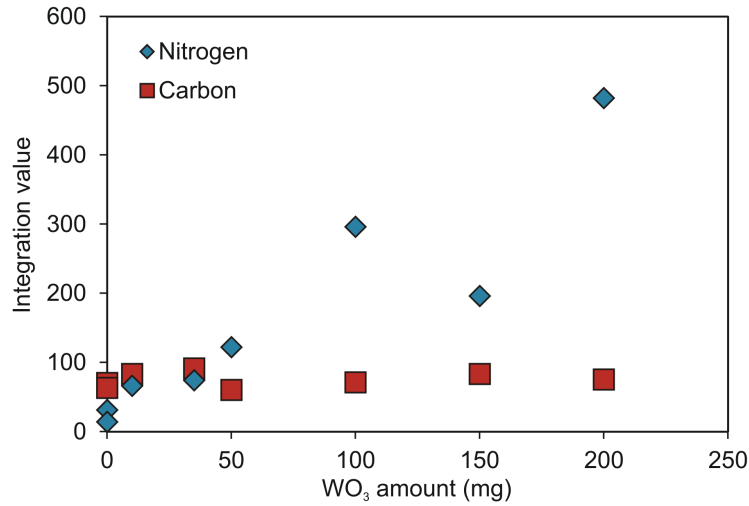


Figure 2-3: Nitrogen and C integration values versus WO_2 sample size. Nitrogen integration values (area under N peak of raw time-count graphs) increase with increasing amount of WO_3 , where as C integration values remains constant, indicating a higher N blank is the result of increasing atmospheric N within interstitial space.

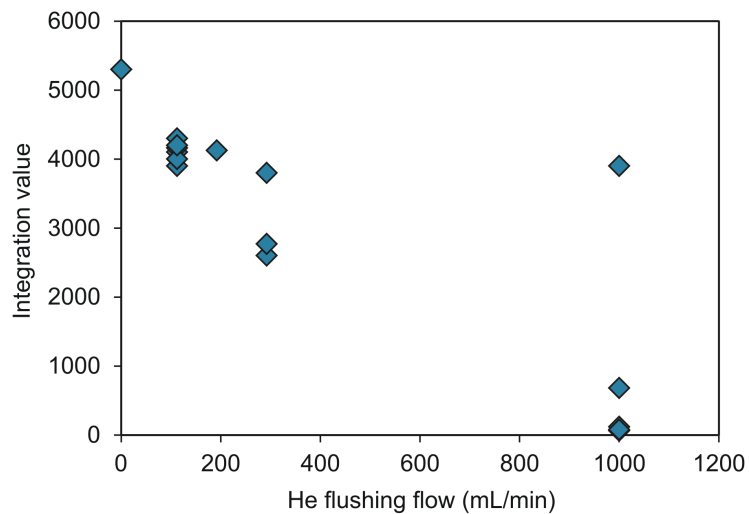


Figure 2-4: Nitrogen integration values versus He flushing rates. Higher flushing rates yield reduced atmospheric N in 200 mg WO_2 samples, but is unreliable at high rates due to powder dispersion and adhesion to the boat walls preventing an effective seal.

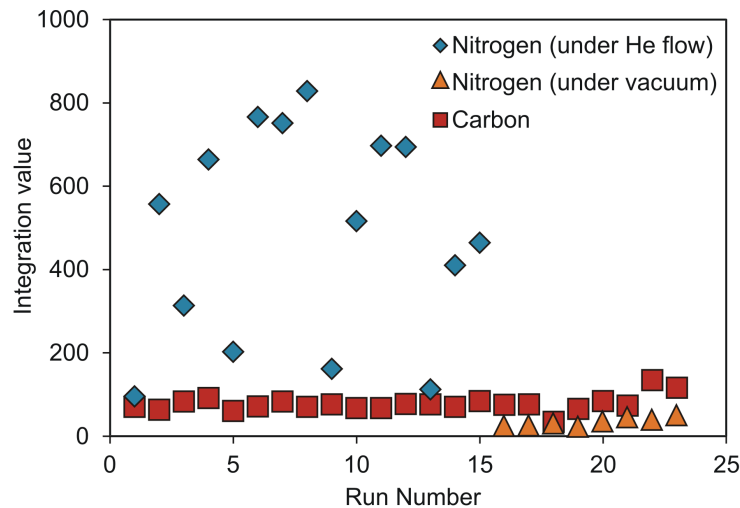


Figure 2-5: Comparison of He flushing versus vacuum methods for removal of atmospheric N from 200 mg WO₂ blank samples. The N blank is dramatically and consistently reduced with the vacuum method. Carbon integration values are shown for reference.

Method blanks and detection limit are reported as integration values (area under N peak of raw time-count graphs) and compared to that of a typical sample (Table 2-2; Figure 2-6). Accuracy of the method is based on the analysis of four international reference materials BHVO-2 (basalt), SCo-1 (shale) and MAG-1 (marine mud) and SO-3 (soil). Percent yields range from 42-65% for the lowest N standard (BHVO-2) to 104-105% for the highest N standard (MAG-1; Table 2-3). The RSD of quadruplicate analyses is 15% for BHVO-2 and <3% for the other standards.

Table 2-2: Background, blanks and limit of detection of N determination.

Integration value*	
Background (n=5)	3±4
Sn capsule only (n=6)	7±4
Capsule + 100 mg Sn + 100 mg WO ₂ (n=7) [†]	18±9
LOD [§]	27
Sample CH146 (n=3)	296±4
*Nitrogen peak area on time-count graph (Figure A1-7)	
[†] Standard deviation used to calculate LOD	
[§] LOD – limit of detection (3σ)	

Table 2-3: Nitrogen content of four international reference materials.

Standard n=4	N ppm	SD ppm	RSD %	Yield %	Published data
BHVO-2	15	2.8	19	42-65	36±5*; 23 [†]
SO-3	119	6.9	5.8	70-85	171±18*; 140±50 [†] ; 152±9 [§]
SCo-1	572	5.0	0.87	89-99	644±42*; 580±30 [§]
MAG-1	2971	35	1.2	104-105	2863±78*; 2840±55 [§]
<i>Note:</i> SD – standard deviation; RSD – relative SD					
*Kubota, 2009; [†] Govindaraju, 1994					

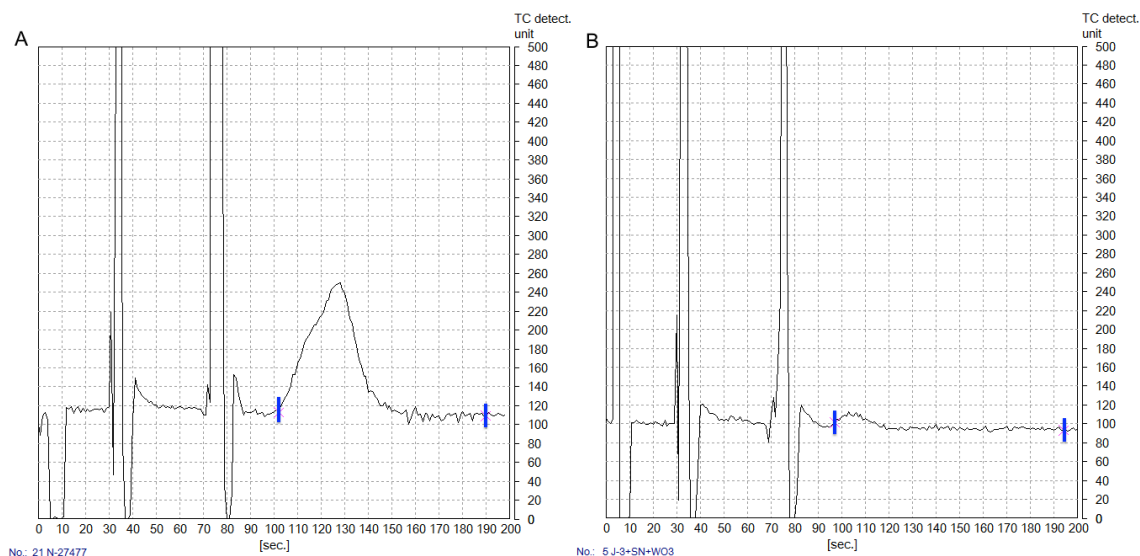


Figure 2-6: Time versus counts received at detector for N determination by elemental analyzer.

A) N peak observed for typical sample (CH146 shown here). B) N peak observed for blank (i.e., Sn capsule with Sn and WO₂ powders). Blue lines designate portion of curve integrated to determine N area.

2.1.4 Boron

Bulk B concentrations were determined on 1.0 g of finely ground sample material by Activation Laboratories (Ancaster, Ontario, Canada) by prompt gamma neutron activation analysis (PGNAA) with a 2 ppm or 0.5 ppm detection limit. Samples are encapsulated in a polyethylene vial and placed in a thermalized beam of neutrons produced from a nuclear reactor. Samples are measured for the doppler broadened prompt gamma ray at 478 KeV using a high purity GE detector. Accuracy of the technique was verified by analysis of two geologic reference materials (SY-2 and SY-3).

2.1.5 Major and trace elements

Bulk rock major and minor element compositions of samples from Turkey were determined by ALS Global (North Vancouver, Canada) using X-ray fluorescence (XRF) after fusion of rock powder with 50/50 $\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$, and trace element composition was determined at the same facility by ICP-MS following digestion of rock powder by concentrated $\text{HF-HNO}_3\text{-HClO}_4\text{-HCl}$.

Bulk rock major and trace element compositions of samples from Sulu and metabasites from the Dominican Republic were determined by XRF at the University of Ottawa. Powdered samples weighing 0.8 ± 0.0002 g were combined with 7.2 ± 0.0002 g of in-house 79/21 $\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2 + 1\%$ LiBr non-wetting agent. A Claisse M4 fluxer was used to fuse samples for XRF analysis. Samples were analyzed for all major rock-forming elements and select traces using a Rigaku Supermini 200 benchtop wavelength dispersive XRF under vacuum equipped with a 50 kV, 200 W Pd-anode X-ray tube, Zr primary beam filter and a flow-proportional counter (F-PC) and scintillation detector. International reference materials used for calibration curves include UB-N, UM-2, MRG-1, PM-S, BCR-2, WS-E, SY-3 BHVO-2, BM, AN-G, BCR-032 and PC-1016. Standards SY-3, MRG-1 and BCR-032 were used for drift correction, and GSP-2 and BHVO-1 were used as checks. Method precision and accuracy is verified by the analysis of SY-3 and MRG-1, yielding average relative variation over six analytical runs of 1.9%, and average relative variation over published values of 2.7%.

2.2 In situ analyses

2.2.1 Electron probe microanalysis (EPMA)

Thin sections of 30- μm were prepared and carbon-coated. Silicates were analyzed for Si, Ti, Al, Mg, Fe, Ca, Na, K and Mn ($\pm$ Cr, Ni, F and Cl) at the University of Ottawa with a JEOL 8230 electron microprobe using a wavelength dispersive spectrometer. A 5 μm diameter 20 nA

beam accelerated to 20 kV was used. Peak counting times were 10 s per element for the $K\alpha$ lines of Fe, Mn, Cr and Si, 20 s for K, Ca, P, Al, Ti, Na and Mg, 50 s for Ni and Cl and 150 s for F. The high beam current and longer counting time for F were used to overcome low count rates for light element X-rays associated with the conventional TAP diffraction crystal.

Instrument calibration used sanidine (Si, Al, K), diopside (Ca, Mg), albite (Na), hematite (Fe), tephroite (Mn), San Carlos olivine (Ni), rutile (Ti), chromite (Cr), apatite (P), Mg-mica or fluorite (F) and tugtupite (Cl). Mineral formulae of Na-amphibole grains were calculated using 23(O), and ferric and ferrous iron contents were determined on the basis of stoichiometric composition after normalizing to 8 Si atoms. For lawsonite, all iron was assumed to be Fe^{3+} , and mineral formulae were determined using 8(O). Mineral formulae of phengite and the amount of Fe^{3+} were calculated based on stoichiometric composition and charge balance using 11(O).

The analytical conditions for apatite were 10 kV accelerating voltage, 4 nA beam current, and 10 μm diameter beam size as recommended by Goldoff et al. (2012) for optimal analysis of fluorchlorapatites. Each grain was analyzed in 1–3 spot(s), depending on grain size. Peak counting times were 10 s per element for Si ($K\alpha$), Fe ($K\alpha$), Mg ($K\alpha$), K ($K\alpha$), S ($K\alpha$), Ce ($L\alpha$), La ($L\alpha$) and As ($L\alpha$), 20 s for Al ($K\alpha$), Ca ($K\alpha$), Na ($K\alpha$), P ($K\alpha$), Sr ($L\alpha$) and Cl ($K\alpha$), and 50 s for F ($L\alpha$). Instrument calibration used sanidine (Si, Al, K), hematite (Fe), diopside (Mg), apatite (Ca, P, F), albite (Na), celestine (S, Sr), CePO_4 (Ce), LaPO_4 (La), GaAs (As) and tugtupite (Cl). A synthetic multi-layered diffraction crystal, LDE1, was used to enhance the count rate for F. Apatite mineral formulae were calculated based on normalizing to 13 (O, OH, F, Cl).

Detection limits (DL) for F and Cl in silicates are calculated using the following equation:

$$DL = \frac{mass(\%)_{STD}}{I_{NetSTD}} \sqrt{\frac{2I_{BKD}}{t_{BKD}}}$$

where $mass(\%)_{STD}$ is the mass % of the given element in the standard, I_{NetSTD} is the net intensity of a given X-ray in the standard, I_{BKD} is the average intensity of the lower and higher backgrounds and t_{BKD} is the total counting time of the lower and higher backgrounds. Detection limits were ~50 ppm for Cl, and either ~150 ppm F using the TAP crystal for silicates or ~440 ppm F using the LDE1 crystal for apatite. The precision of F and Cl analyses are evaluated by plotting counting errors (relative standard deviation [RSD] of measured X-ray intensities) against measured concentrations (Figure 2-7). As F or Cl concentrations decrease, the associated counting errors increase according to a power regression model. Average counting errors for F analyses are 31% at 500 ppm and 9% at 2000 ppm. Average counting errors for Cl analyses are 27% at 30 ppm and 9% at 100 ppm.

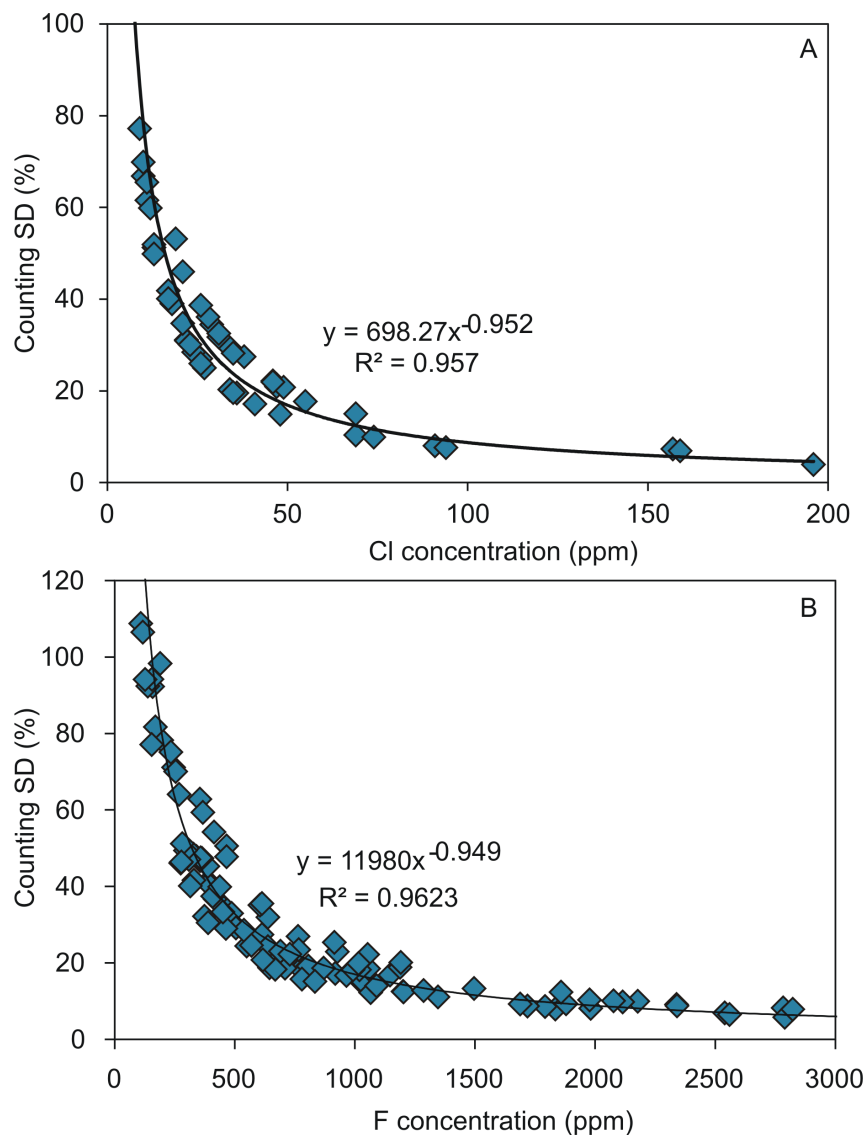


Figure 2-7: Counting errors (%) of A) F and B) Cl concentration measurements.

2.2.2 Secondary ion mass spectrometry (SIMS)

Grains for *in situ* analyses were selected from EPMA-analyzed samples. Grains were cored from polished thin sections using a diamond-tipped drill bit, mounted in indium-filled Al holders and gold-coated. Fluorine, Cl and H₂O were measured by SIMS using a Cameca 4f instrument at the Edinburgh Ion Microprobe Facility (EIMF), University of Edinburgh. A 5-nA primary beam of negative ¹⁶O ions accelerated to 14.5 kV was used. Pit diameter was *ca.* 15 μm,

depth of the analysis pits was $<2\ \mu\text{m}$. Total counting times were 30 s per isotope per analysis. Chlorine and H_2O were calibrated using an in-house basaltic glass standard (St81-A9; Lesne et al., 2011). Fluorine was calibrated using T1-G glass (Guggino and Hervig, 2010).

Reproducibility for all elements, as determined by repeat measurements of glass standards, is better than 10% for all elements. The use of glass standards may introduce a bias due to matrix effects. Therefore, amphibole standards of known H_2O , F and Cl contents were used to calibrate the matrix effects associated with Fe–Mg hydrous silicates. Correction factors of 1.4 for F and 1.9 for Cl were ascertained and applied to the analysis of Na-amphibole and phengite (Figure 2-8). No matrix-induced fractionation was observed for H_2O . Due to a lack of suitable standards for lawsonite, F and Cl contents of this mineral were calibrated using basaltic glass standards (Figure 2-8).

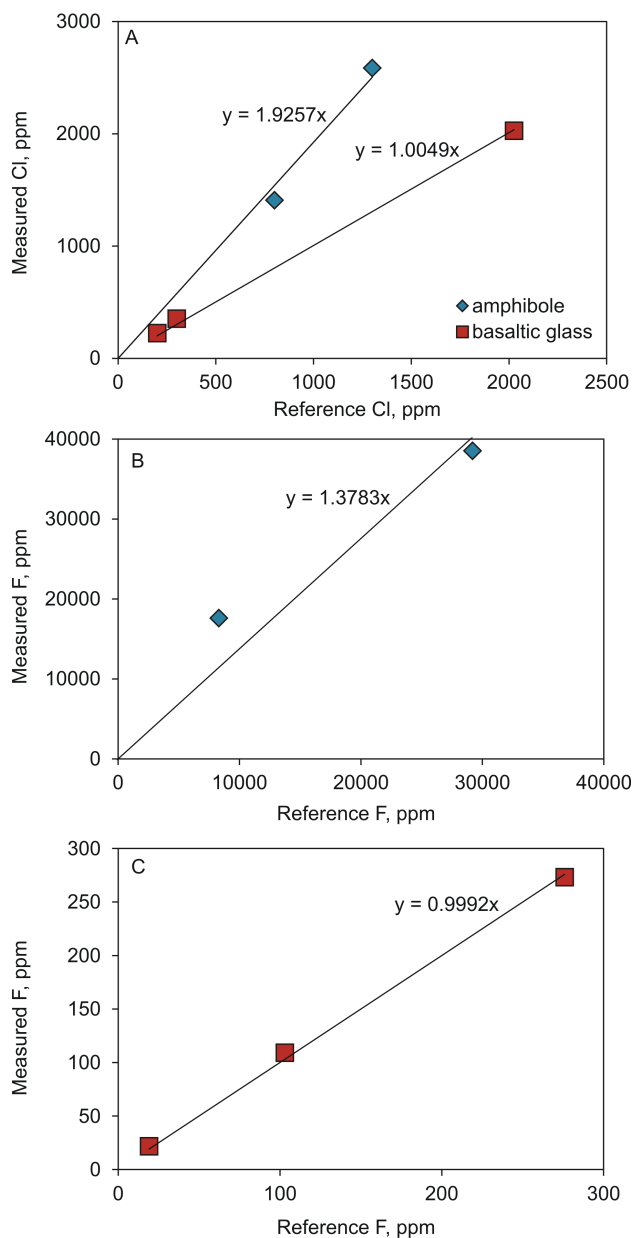


Figure 2-8: Measured halogen concentrations of standards using SIMS, relative to literature values. Slopes of best fit lines are taken as correction factors and applied to analyzed samples. Amphibole standards used for amphibole and phengite correction, and basaltic glass standards used for lawsonite correction. A) Cl in amphibole and basaltic glass standards, B) F in amphibole standards, C) F in basaltic glass standards.

Overall, F data obtained by SIMS and EPMA for silicate minerals are in good agreement ($R^2 = 0.813$) and show a linear trend near the 1:1 ratio line (Figure 2-9). Phengite Cl contents correlate well ($R^2 = 0.998$), but SIMS results are up to 2.6x higher than those determined by EPMA (Figure 2-9). Systematically higher Cl concentrations determined by SIMS are also observed for Na-amphibole and lawsonite. These differing results may reflect micro-scale heterogeneities in the samples, volatile migration away from the beam during electron probe analyses, contamination/alteration of sample surfaces during their preparation for SIMS following EPMA, matrix effects associated with SIMS or uncertainty associated with reference sample concentrations.

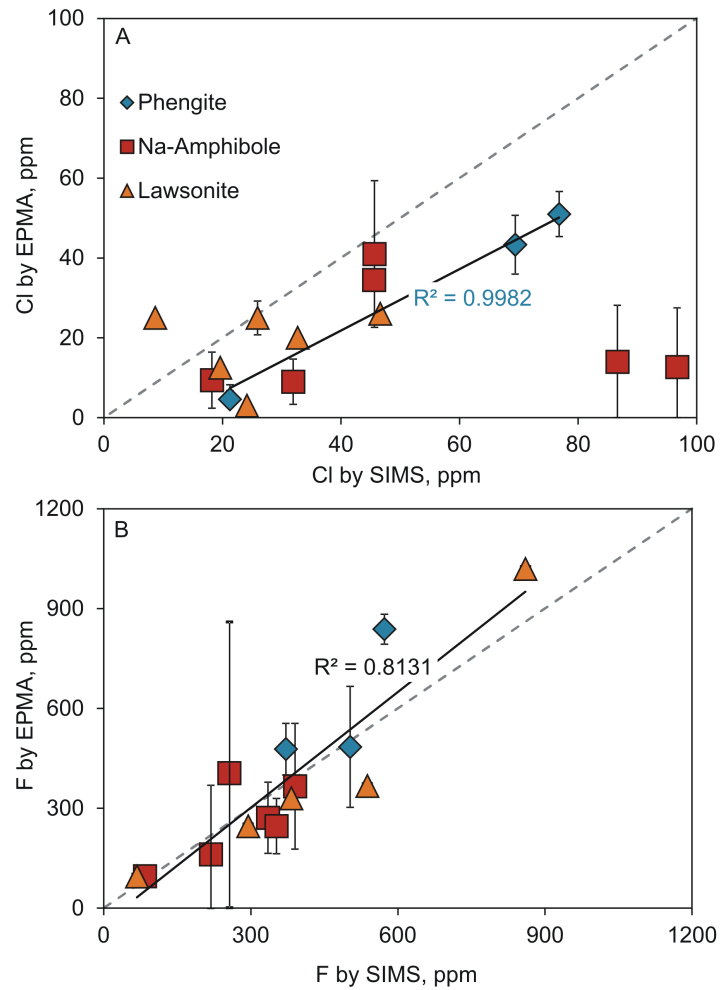


Figure 2-9: Comparison of F (A) and Cl (B) concentrations in blueschists minerals determined by electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS).

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Chapter 3.

Tracing halogen and B cycling in subduction zones based on obducted, subducted and forearc serpentinites of the Dominican Republic

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Abstract

Serpentinites are important reservoirs of fluid-mobile elements in subduction zones, contributing to volatiles in arc magmas and their transport into the Earth's mantle. This paper reports halogen (F, Cl, Br, I) and B abundances of serpentinites from the Dominican Republic, including obducted and subducted abyssal serpentinites and forearc mantle serpentinites. Abyssal serpentinite compositions indicate the incorporation of these elements from seawater and sediments during serpentinization on the seafloor and at slab bending. During their subduction and subsequent lizardite-antigorite transition, F and B are retained in serpentinites, whilst Cl, Br and I are expelled. Forearc mantle serpentinite compositions suggest their hydration by fluids released from subducting altered oceanic crust and abyssal serpentinites, with only minor sediment contribution. This finding is consistent with the minimal subduction of sediments in the Dominican Republic. Forearc mantle serpentinites have F/Cl and B/Cl ratios similar to arc magmas, suggesting the importance of serpentinite dehydration in the generation of arc magmatism in the mantle wedge.

3.1 Introduction

Subduction of hydrated lithologies provides a mechanism for recycling fluid-mobile elements (FME) from surface reservoirs, such as the hydrosphere, atmosphere and sediments, into the Earth's mantle. The high abundance of volatiles, such as halogens and B, in arc magmas (refs. 1, 2), attest to their recycling at convergent plate boundaries. Serpentinites, primarily composed of the mineral serpentine, are an important component of the volatile budget in subduction zones because they contain up to 13 wt% H₂O and are stable to >100 km depth (ref. 3), making them effective vehicles for the transport of FME into the mantle. Recent studies of abyssal and forearc mantle serpentinites have demonstrated their importance as reservoirs for halogens and B in subduction zones (refs. 4, 5, 6, 7, 8, 9, 10, 11, 12). However, the role of

serpentinites in the recycling of these elements is not fully understood. Halogen concentrations and ratios can offer a tool for tracking fluids through subduction zones. For example, the halogen ratios of forearc mantle serpentinites may provide insight into the make-up of the slab in a given subduction complex, and help elucidate the extent to which abyssal serpentinites, altered oceanic crust, and sediments contribute to slab-derived fluids. The first study of all four halogens in abyssal serpentinites and their subducted counterparts was conducted on the serpentinitized Erro-Tobbio peridotites of the Ligurian Alps (ref. 13). Our paper expands on this work by presenting the halogen and B contents of Dominican Republic (DR) serpentinites, including those of abyssal origin and of the forearc mantle, with the purpose of evaluating the behaviour and fractionation of these elements in subduction zones.

3.2 Samples

Serpentinite samples were collected from the Tertiary subduction complex in northern Dominican Republic on the island of Hispaniola. This complex was formed by the subduction of the Proto-Caribbean oceanic lithosphere beneath the NE-migrating Caribbean plate. The former was produced at an ultra-slow spreading ridge (ref. 21), and, as such, it was primarily composed of abyssal peridotites with minor cover of basaltic rocks and sediments. During subduction, the upper part of this young oceanic lithosphere was scraped off to form an accretionary prism on the northern part of the island, while the remaining slab was subducted (Figure 3-1). The subduction complex includes the Puerto Plata Complex (PPC) and the Rio San Juan Complex (RSJC) (ref. 14).

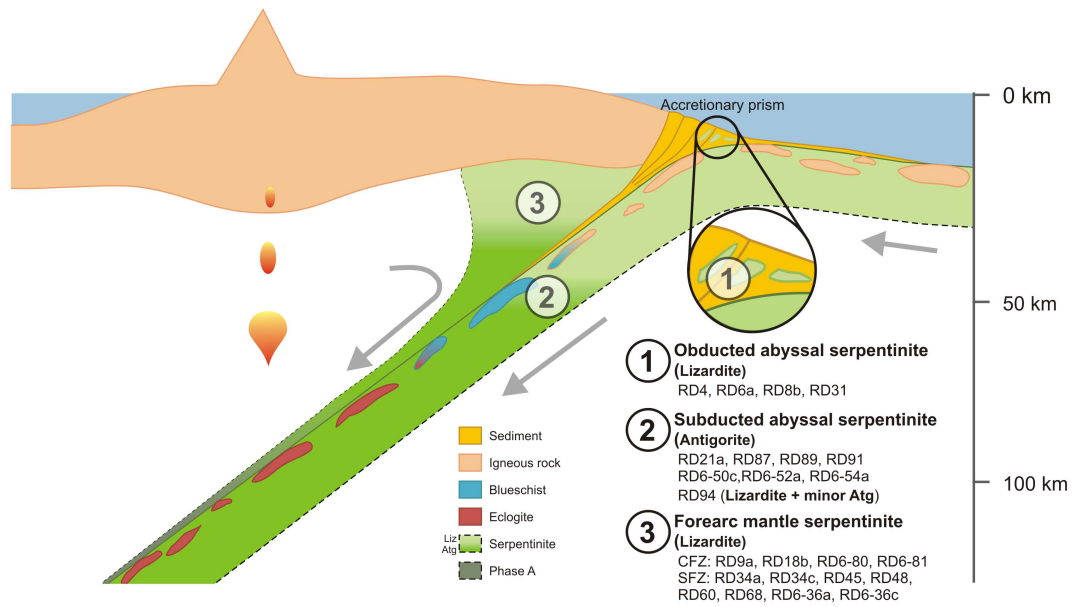


Figure 3-1: Schematic cross-section of a subduction complex showing position of serpentinite samples from the Dominican Republic: (1) obducted abyssal lizardite, (2) subducted abyssal antigorite (~ 50 km depth), and (3) forearc mantle lizardite (< 35 km depth). The incoming plate formed at an ultra-slow spreading ridge was composed of abyssal peridotites with minor oceanic basalts and overlying sediments. The upper portion of the slab was obducted forming an accretionary prism. Fluids released from the slab hydrated the overlying peridotites to form forearc mantle serpentinites. Liz – lizardite, Atg – antigorite.

The DR serpentinite samples were previously characterized on the basis of their occurrences and petrographical and geochemical data (ref. 15). They are classified into three types: i) obducted abyssal ii) subducted abyssal, and iii) forearc mantle serpentinites (Figure 3-1). Abyssal serpentinites are formed by the hydration of abyssal peridotites near oceanic ridges and on the seafloor (ref. 16), or at the outer rise by fluid infiltration along extensional faults in the bending slab (ref. 17). Obducted abyssal serpentinites are in the accretionary prism (Figure

3-1), and have not been subducted. Forearc mantle serpentinites are hydrated by fluids released from the subducting slab (ref. 16). Detailed descriptions of samples and their protoliths are given in Supplementary Information [Appendix I].

Samples representing obducted abyssal serpentinites were collected from the PPC and the northern RSJC (RD31, RD4, RD6a, RD8b). They are comprised of lizardite (low temperature serpentine phase) pseudomorphically replacing olivine and orthopyroxene. Samples representing subducted abyssal serpentinites were collected from the mélanges of Arroyo Sabana (RD87, RD89) and Jagua Clara (RD21a, RD91, RD94, RD650c, RD6-52a, RD6-54a) of the RSJC. They are composed of antigorite (high temperature phase), with minor chlorite, talc and tremolite, except for RD94 that is predominantly lizardite with minor antigorite blades. Lizardite changes to antigorite between 320 and 390 °C (ref 18). Using the geothermal gradient of this subduction zone (8°C/km) (ref 19), the depth of lizardite-bearing sample RD94 is estimated to be ~40-50 km, whereas, the remaining antigorite-only serpentinites come from depths >50 km. A lack of metamorphic olivine in these samples further constrains their depth to <80 km, given its crystallization from antigorite at 650 °C (ref 20).

Samples representing shallow forearc mantle lizardite-serpentinites were collected from boulders along the stream of Rio Cuevas (RD45, RD48, RD60) and from the serpentinite lenses along two major strike-slip fault zones: the Septentrional fault zone (RD34a, RD34c, RD68, RD6-36a, RD6-36c) and the Camú fault zones (RD9a, RD18b, RD6-80, RD6-81). The lack of antigorite in these samples constrains their depth to <40 km. A forearc mantle origin of these samples is indicated by low Al and high Ir-type platinum group element concentrations in the bulk rocks and high Cr in relict spinel (ref. 15).

3.3 Results

3.3.1 Halogens

For each sample, bulk halogen data are obtained using pyrohydrolysis extraction with ion chromatography (F, Cl) and ICP-MS (Br, I), and bulk B data are obtained by prompt gamma neutron activation analysis (Table 3-1; Figure 3-2). The obducted abyssal lizardite-serpentinites display two different halogen signatures (Table 3-1; Figure 3-2). Samples RD4 and RD6a contain higher concentrations of Cl (480-580 ppm), Br (1.3-1.4 ppm) and I (0.24-0.44 ppm) compared to RD31 and RD8b (78-100 ppm Cl, 0.40-0.42 ppm Br, 0.025-0.059 ppm I). Fluorine contents are relatively low in all obducted abyssal serpentinites (6.1-31 ppm). Ratios of F/Cl, Br/Cl and I/Cl for these samples range from 0.014 to 0.089, 0.0024 to 0.0051 and 0.00032 to 0.00091, respectively (Figure 3-3).

Table 3-1. Bulk halogen and B contents (ppm) of serpentinites from the northern Dominican Republic, as determined by ICP-MS (Br, I) and IC (F, Cl) following pyrohydrolysis extractions and PGNAA (B).

Sample n=2 or 3	Serpentine phase	F pp	Cl pp	Br ppm	I ppm	B pp	F/Cl	Br/Cl	I/Cl	B/
Obducted										
RD4	lizardite	31	57	1.4	0.24	30.	0.05	0.002	0.000	0.0
RD6a	lizardite	6.8	48	1.3	0.44	48.	0.01	0.002	0.000	0.1
RD8b	lizardite	7.0	78	0.40	0.025	9.8	0.08	0.005	0.000	0.1
RD31	lizardite	6.1	10	0.42	0.059	9.4	0.05	0.004	0.000	0.0
<i>Average</i>		<i>13</i>	<i>31</i>	<i>0.89</i>	<i>0.19</i>	<i>24.</i>	<i>0.05</i>	<i>0.003</i>	<i>0.000</i>	<i>0.0</i>
Subducted										
<i>RD6-50c</i>	antigorite	76	7	0.24	0.040	7.1	10.7	0.034	0.005	1.0

Sample n=2 or 3	Serpentine phase	F pp	Cl pp	Br ppm	I ppm	B pp	F/Cl	Br/Cl	I/Cl	B/ I
RD6-52a	antigorite	64	34	0.32	bdl	26.	1.9	0.010	bdl	0.7
RD6-54a	antigorite	37	25	0.14	0.038	51.	1.5	0.005	0.001	2.0
RD21a	antigorite	3	33	0.13	0.142	32.	0.1	0.003	0.004	0.9
RD87	antigorite	81	13	0.30	bdl	45.	0.6	0.002	bdl	0.3
RD89	antigorite	14	12	0.27	bdl	10.	1.2	0.002	bdl	0.0
RD91	antigorite	15	16	0.08	bdl	5.0	9	0.005	bdl	0.3
RD94	lizardite	34	42	0.52	0.078	13.	0	0.001	0.000	0.0
<i>Average*</i>		<i>80</i>	<i>54</i>	<i>0.21</i>	<i>0.074</i>	<i>25.</i>	<i>3.63</i>	<i>0.008</i>	<i>0.003</i>	<i>0.7</i>
Forearc mantle										
Septentrional Fault Zone										
RD34a	lizardite	10	61	1.3	0.20	7.0	0.17	0.002	0.000	0.0
RD34c	lizardite	60	66	0.97	0.08	16.	0.09	0.001	0.000	0.0
RD45	lizardite	72	72	1.1	0.058	2.0	0.09	0.001	0.000	0.0
RD48	lizardite	51	78	1.1	0.116	13.	0.06	0.001	0.000	0.0
RD60	lizardite	52	87	1.3	0.11	16.	0.05	0.001	0.000	0.0
RD68	lizardite	10	52	0.6	0.13	11.	0.19	0.001	0.000	0.0
RD6-36a	lizardite	36	85	1.4	0.18	13.	0.04	0.001	0.000	0.0
RD6-36c	lizardite	65	73	1.3	0.14	16.	0.08	0.001	0.000	0.0
Camú Fault Zone										
RD9A	lizardite	96	36	0.79	0.07	32.	0.26	0.002	0.000	0.0
RD18B	lizardite	66	48	1.5	0.17	61.	0.14	0.003	0.000	0.1
RD6-80	lizardite	59	36	0.6	0.08	48.	0.16	0.001	0.000	0.1
RD6-81	lizardite	13	36	0.67	0.12	11.	0.03	0.001	0.000	0.0
<i>Average</i>		<i>64</i>	<i>61</i>	<i>1.1</i>	<i>0.12</i>	<i>21</i>	<i>0.15</i>	<i>0.002</i>	<i>0.000</i>	<i>0.0</i>
*Average excludes lizardite-bearing RD94										
bdl - below detection limit										

The subducted antigorite-serpentinites have much lower Cl (7.1-140 ppm) and Br (0.088-0.32 ppm) concentrations than their obducted lizardite-bearing counterparts. The one exception is RD94, a subducted lizardite-bearing sample that contains similarly high concentrations of Cl (430 ppm) and Br (0.52 ppm) (Figure 3-2). Iodine concentrations are only reported for four of the eight subducted serpentinites due to the higher I blank of the pyrohydrolysis extraction method (see Methods for details). These concentrations (0.038-0.14 ppm) are similar to those of the obducted samples. Fluorine contents of most of the subducted serpentinites are elevated (up to 150 ppm) relative to the obducted samples. The Br/Cl and I/Cl ratios of lizardite-bearing RD94 (0.0012 and 0.00019, respectively) are lower than those of the obducted lizardite-serpentinites, whereas the Br/Cl and I/Cl ratios of the remaining subducted antigorite-serpentinites are higher and cover a larger range (0.0016-0.0057 and 0.0022-0.034, respectively; Figure 3-3b). The F/Cl ratio of RD94 (0.080) is also similar to those of the obducted serpentinites, while the ratios of other subducted serpentinites are up to two orders of magnitude greater, and they cover a wide range (0.10-11; Figure 3-3c).

The lizardite-serpentinites from the shallow forearc mantle have high heavy halogen concentrations (360-880 ppm Cl, 0.63-1.5 ppm Br, 0.058-0.20 ppm I), similar to those of the obducted abyssal lizardite-serpentinites (Figure 3-2a, b), but their Br/Cl and I/Cl ratios (0.0012-0.0031 and 0.00008-0.00035, respectively) trend towards lower values (Figure 3-3b). Their Br/Cl and I/Cl ratios are also much lower than those of the antigorite-serpentinites of the slab, but are similar to those of the subducted lizardite-bearing sample. Fluorine concentrations are also high in the forearc mantle lizardite-serpentinites (13-100 ppm) and similar to those of the subducted antigorite-serpentinites (Figure 3-2c). Yet, their F/Cl ratios (0.035-0.26) are much lower due to elevated Cl contents in the serpentinized mantle. The F/Cl ratios of the forearc mantle serpentinites are similar to those of the obducted abyssal lizardite-serpentinites (Figure 3-3c).

3.3.2 *Boron*

The B/Cl ratios of the obducted abyssal lizardite-serpentinites cover a narrow range (0.053-0.13; Figure 3-4). Chlorine-rich samples (RD4 and RD6A) contain high B (31-49 ppm) and Cl-poor samples (RD31 and RD8b) have low B (9-10 ppm) (Table 3-1). Boron concentrations of the subducted (5-51 ppm B) and shallow forearc mantle (2-62 ppm B) serpentinites cover a large, yet comparable range. Their B/Cl ratios (0.03-1.0 and 0.0027-0.13, respectively) also cover large ranges, but they differ by up to an order of magnitude, reflecting the differing Cl concentrations of the two sample sets.

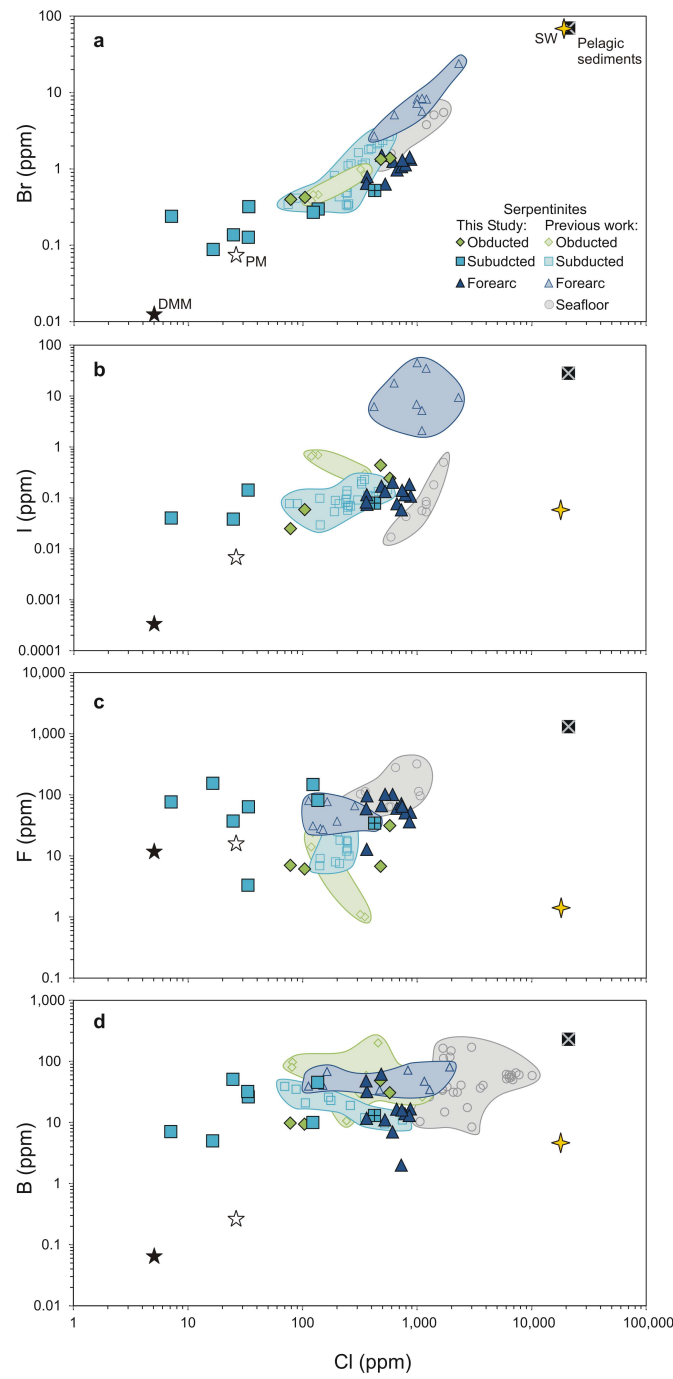


Figure 3-2: Halogen and B concentrations of abyssal and forearc serpentinites from the Dominican Republic. (a) Bromine and Chlorine show a broad positive correlation along a linear trend with the depleted MORB mantle (DMM) (ref. 22) , primitive mantle (PM) (ref. 22) and

seawater (SW) (ref. 25). Data for the DR obducted abyssal lizardite-serpentinites overlap with those of other pre-subduction serpentinites elsewhere (ref. 13), and Cl contents of the DR forearc lizardite-serpentinites are similar to those of other forearcs, such as Mariana and Guatemala (ref. 8). The subducted serpentinites show wide ranges in Cl and Br contents, with the antigorite-bearing samples displaying lower concentrations than lizardite-bearing sample RD94. (b) The I and Cl values of all samples lie along the linear trend defined by DMM, PM and average pelagic sediment (ref. 30) values, except for the antigorite-samples. (c) Fluorine and Chlorine do not appear to correlate across the three sample sets. Data for all DR serpentinites, except the antigorite-bearing samples, plot within the triangle defined by seawater, the DMM, and pelagic sediment. (d) Boron concentrations are similar among all samples and literature data.

3.4 Discussion

3.4.1 *Halogen and B uptake by abyssal serpentinites*

The protoliths of the DR abyssal serpentinites are formed at an ultra slow spreading ridge (ref. 21) with compositions between those of the primitive mantle (PM) and the depleted MORB mantle (DMM). The Cl, Br and I contents of the obducted abyssal lizardite-serpentinites are up to one order of magnitude greater than those of the PM (26 ± 8 ppm Cl; 76 ± 25 ppb Br; 7 ± 4 ppb I) (ref. 22) and two orders of magnitude greater than those of the DMM (5 ± 2 ppm Cl, 13 ± 6 ppb Br, 0.3 ± 0.1 ppb I) (ref. 22) (Figure 3-2a, b). Their B concentrations are also elevated, exceeding those of the PM (0.30 ppm) (ref. 23) by two orders of magnitude and the DMM (0.06 ppm) (ref. 24) by up to three (Figure 3-2d). Seawater provides Cl and Br to account for the observed enrichment, as supported by Br/Cl ratios (avg. 0.0029) similar to that of seawater (0.0037) (ref. 25) (Figure 3-3a). In contrast, I/Cl ratios are up to 270 times greater than that of seawater,

overlapping with pore fluids in marine sediments (Figure 3-3a), and B/Cl ratios are up to 510 times greater than seawater. Given the high I (1.6-20 ppm) (ref. 26) and B (96-490 ppm) (ref. 27) contents of pelagic sediments, the I- and B-enrichment of abyssal serpentinites is attributed to a contribution of sediment-modified seawater for serpentinization. Similar halogen and B contents have been obtained for other obducted abyssal serpentinites, such as those of the Northern Apennines and the Ligurian Alps, Italy (refs. 5, 8, 13) (Figure 3-2).

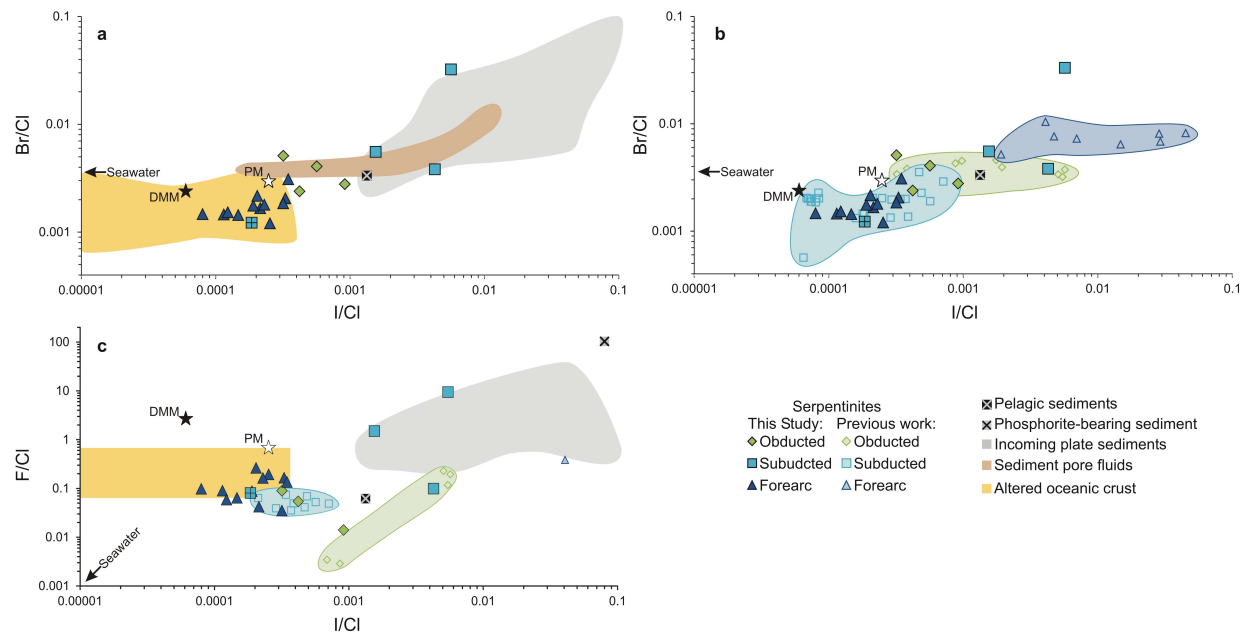


Figure 3-3: Halogen ratios of abyssal and forearc serpentinites from the Dominican Republic are compared to other rock types and serpentinite data from elsewhere. (a) There is a broad correlation between Br/Cl and I/Cl ratios among all samples and lithologies. The DR obducted abyssal lizardite-serpentinites have Br/Cl and I/Cl ratios that overlap with the lower end of sedimentary marine pore fluids (refs. 55, 56), while their subducted antigorite-bearing counterparts have ratios that extend to higher values (except for lizardite-bearing RD94). The forearc lizardite-serpentinites have the lowest Br/Cl and I/Cl ratios and overlap with values for

altered oceanic crust (ref. 39). (b) The DR obducted lizardite-serpentinites are similar to other pre-subduction serpentinites, whereas the DR forearc samples have lower ratios than other forearc serpentinites, such as those from Mariana and Guatemala. (c) The F/Cl ratios of the DR obducted abyssal and forearc mantle serpentinites are similar to those of other lizardite-bearing serpentinites, and the forearc samples overlap with altered oceanic crust values (ref. 57). The DR subducted antigorite-serpentinites have higher F/Cl ratios (Table 1) than other antigorite-bearing samples and overlap with incoming sediments. References for SW, DMM, PM and plate sediments are the same as in Fig. 2.

Chlorine and Br concentrations of the obducted abyssal lizardite-serpentinites from the Dominican Republic and elsewhere (e.g., Ligurian Alps) are lower than present-day seafloor serpentinites, such as those from mid-oceanic ridges and passive continental margins (460-1700 ppm Cl and 1.3-6.8 ppm Br) (ref. 8) (Figure 3-2a), but their Br/Cl ratios are very similar (Figure 3-3b). This may suggest a minor loss of Cl and Br during accretion. On the other hand, I and B concentrations of the obducted lizardite-serpentinites are very similar to those of the present-day abyssal serpentinites (refs. 8, 10) (Figure 3-2b, d).

Bulk F contents in the DR obducted serpentinites are similar to those of the PM (17 ± 6 ppm) and the DMM (12 ± 2 ppm) (ref. 22) (Figure 3-2c). These low concentrations and associated low F/Cl ratios (<0.1) are similar to other pre-subduction lizardite-serpentinites, such as those from the Erro-Tobbio peridotite, Ligurian Alps (ref. 13) (Figure 3-3c). Abyssal peridotites at slow and ultra-slow spreading ridges are primarily hydrated by seawater, which contains very low F (<2 ppm) (ref. 25). Therefore, such abyssal serpentinites are expected to be low in F. On the contrary, seafloor serpentinites formed near volcanic centres, such as the Logatchev

hydrothermal field (ref. 28) and the MARK area (ref. 12) (Figure 3-2c), have elevated F contents due to a contribution of magmatic fluids.

Fluorine contents of the DR subducted antigorite-serpentinites are variable (3-150 ppm F; Table 3-1), but overall values are greater than the DMM and elevated compared to their obducted lizardite-bearing counterparts (Figure 3-2c). They also have elevated F/Cl ratios, which overlap with incoming plate sediments (ref. 13) (Figure 3-3c). The variably high F contents of the subducted serpentinites are attributed to sediments. Fluorine contents can vary widely among sediments, but they are particularly high in shallow water marine sediments, such as carbonates (up to 1700 ppm F) (ref. 29) and phosphorites (up to 3.1 wt% F) (ref. 30). Subduction zone trenches are filled with such shallow water sediments along with terrigenous material from volcanic arcs and pelagic sediments on the incoming plate. The pore fluids of trench sediments are likely F-rich since some minerals, such as carbonates, dissolve in deep water. We suggest the F-enrichment in subducting serpentinites is attributed to the interaction of abyssal serpentinites with these fluids.

3.4.2 *Halogen and B behaviour during shallow subduction*

Except for the lizardite-bearing sample RD94, the Cl and Br concentrations of the subducted serpentinites are up to one order of magnitude lower than those of the obducted abyssal serpentinites, and they are among the lowest concentrations reported for subducted serpentinites in previous studies (refs. 7, 13) (Figure 3-2a). These results suggest a loss of these elements during subduction and are consistent with previous reports of up to a 90% loss of Cl during the shallow (<30 km) subduction of abyssal serpentinites (refs. 5, 9). Iodine contents of the DR subducted serpentinites are similar to those of the obducted samples and to other subducted samples in the literature (Figure 3-2b). Yet, considering four of the eight samples contain I concentrations below method detection limit (Table 3-1), the average I content of the

subducted serpentinites is most likely below those of the DR obducted samples and subducted serpentinites of other studies. In all studies of paleo-subduction zone serpentinites, including this one, there is some uncertainty regarding the composition of abyssal serpentinites prior to their subduction. In this study, although we consider the obducted abyssal serpentinites to represent the composition of abyssal serpentinites prior to their subduction, the former may have been modified during obduction and therefore, may not be a true representation of the composition of incoming abyssal serpentinites. Also, variability may exist in the timing and sources of hydration. Some serpentinites may have been hydrated at the ridge or on the seafloor, whereas, some may have been hydrated by fluids dominated by sedimentary pore fluids along bend faults of the outer rise or within the trench. Varying hydration processes before subduction may explain a wide range of compositions in serpentinites from different subduction zones.

In contrast to the heavy halogens, F contents are high in subducted abyssal serpentinites. This is attributed, in part, to an input of F from F-rich sediments in the trench. The fractionation of F from the heavier halogens during subduction is also likely related to the serpentine phase change from lizardite to antigorite. This phase change at 300-350°C is considered to be accompanied by the release of water (ref. 31) and is conducive to the liberation of FME. In lizardite, the Si-O tetrahedra are distorted to match the octahedral sheet resulting in a flat layer structure. In antigorite, Si-O tetrahedral sheets are connected to the concave side of the continuous octahedral sheet but display periodic reversals in orientation resulting in a more wavy structure (ref. 31). Consequently, layers in antigorite are bound through stronger, primarily covalent Si-O bonds. Antigorite's tighter structure may not as readily accommodate larger halogens in its hydroxyl site, thus resulting in the expulsion of these larger anions during the phase transition (ref. 6). The smaller F ion (1.33 Å), on the other hand, has a similar ionic radius to OH⁻ (1.35 Å) and is more likely to remain in the serpentine structure during the phase

transition. Furthermore, F may be incorporated into the O site of serpentine by the coupled substitution of Al^{3+} and F^- with Si^{4+} and O^{2-} (1.21 Å), as previously suggested for F in pyroxenes (ref. 32). This mechanism is supported by the high Al content of the antigorite-serpentinites of our study (ref. 15).

The subducted antigorite-serpentinites of this study contain similar B contents to the obducted lizardite-bearing samples (Figure 3-2d), but they have higher B/Cl ratios (Figure 3-4). This indicates B is likely retained during subduction and the serpentine phase change. These results are in contrast with B loss during this transition reported by some studies (refs. 5, 9), but they are consistent with the retention of B with increasing metamorphic grade reported by others (ref. 11). Since B is incorporated into sheet silicates by replacing tetrahedral Si or Al, it is likely retained in the mineral structure during the lizardite-antigorite phase transition. The high B concentration in the DR antigorite-serpentinites may also be the result of additional input by FME-rich fluids from trench sediments (Figure 3-1), as previously suggested to account for enrichment of other FME, such as As and Sb, in these samples (ref. 33)

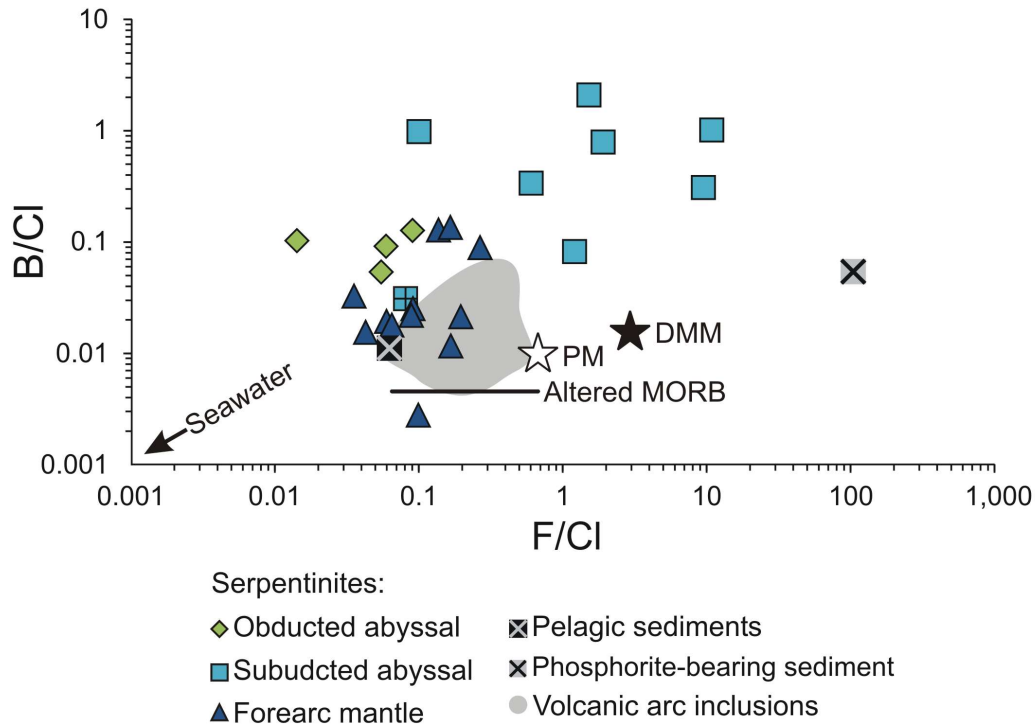


Figure 3-4: B/Cl and F/Cl ratios of serpentinites from the Dominican Republic are shown along with altered oceanic crust (refs. 57, 58), average pelagic sediment (ref. 30) and volcanic melt inclusions (refs. 1, 2). The B/Cl and F/Cl ratios of the forearc lizardite-serpentinites overlap with those of the melt inclusions, while those of the subducted antigorite-serpentinites extend to much higher values. References for DMM and PM are the same as Fig. 2.

3.4.3 Halogen and B uptake by forearc mantle serpentinites

Aqueous fluids are released from the slab during shallow subduction (<50 km) through compaction and dehydration of sediments and hydrous phases of the altered oceanic crust (ref. 34). Additionally, fluids and FME may be released from underlying abyssal serpentinites during the transition from lizardite to antigorite (refs. 32, 35). A fraction of these slab-derived fluids are refluxed back to the surface along the subduction interface (ref. 36) and some are transferred to

the overlying forearc mantle to form lizardite-serpentinites at the base of the wedge (ref. 37). Eventually, the forearc mantle serpentinites are dragged downwards by mantle corner flow and dehydrate when temperatures reach $\sim 600\text{--}700^\circ\text{C}$ (ref. 3). In the mantle wedge, this corresponds to depths ranging from 80 to 130 km (ref. 37) and leads to the release of abundant fluids and FME for partial melting in the mantle wedge (Figure 3-1) (refs. 37, 38). This model is supported by F/Cl and B/Cl ratios of the DR forearc mantle lizardite-serpentinites that overlap with those of magmas of the Izu (ref. 1) and Lesser Antilles (ref. 2) arcs (Figure 3-3a, c & Figure 3-4).

Forearc mantle serpentinite compositions reflect those of fluids derived from sediments, oceanic crust and abyssal lizardite-serpentinites in the slab. These three lithologies have distinct Br/Cl and I/Cl ratios (Figure 3-3a). Typically, incoming plate sediments have very high Br/Cl and I/Cl ratios (up to 0.1), whereas abyssal lizardite-serpentinites have Br/Cl ratios similar to those of seawater and the primitive mantle (~ 0.003) and I/Cl ratios between those of the primitive mantle (0.0002) and pelagic sediments (0.001). The Br/Cl and I/Cl ratios of altered MORB cover relatively large ranges (0.0007 to 0.004 and 0.000003 to 0.0004, respectively) (ref. 39), extending to values much lower than those of incoming sediments and abyssal serpentinites (Figure 3-3a). The Br/Cl and I/Cl ratios of the forearc DR serpentinites overlap with those of altered MORB, and they are lower than those of incoming plate sediments (Figure 3-3a), suggesting a more important contribution from dehydrating oceanic crust than from sediments. Halogen loss from the dehydrating crust is consistent with previous reports of lower Br and Cl concentrations in blueschist-facies metabasites from Turkey relative to pre-subducted altered oceanic crust (ref. 40). Our interpretation is also consistent with the tectonic setting of the Dominican Republic in which the majority of sediments overlying the young oceanic lithosphere are accreted instead of subducted. Indeed, geophysical modeling confirms minimal metasediments in the subduction channel of the Dominican Republic (ref. 41). On the contrary,

lizardite-serpentinites from other forearc mantle wedges, such as Mariana and Guatemala, have Br/Cl and I/Cl ratios that are elevated with respect to abyssal lizardite-serpentinites (Figure 3-3b), reflecting significant contribution from incoming plate sediments. This suggests dehydrating sediments make a considerable contribution to the composition of slab fluids in these particular subduction zones. Indeed, Mariana and Guatemala witness the subduction of old oceanic plates in which all incoming sediments are subducted instead of accreted (ref. 42).

Fluorine contents of the DR forearc mantle lizardite-serpentinites are slightly elevated relative to the PM and DMM and are similar to those of Mariana forearc mantle serpentinites (ref. 6) (Figure 3-2c). We consider the most likely source of F in these forearc mantle serpentinites to be F expelled from sediment pore fluids during their early (<15 km) subduction. Structurally-bound F, on the other hand, likely remains in sediments during early subduction due to the high thermal stability of F-bearing amphibole and mica (ref. 43) and the ability of F^- to substitute for O^{2-} in nominally anhydrous minerals (ref. 32). It also seems unlikely that F is sourced from abyssal serpentinites since the average F content of the subducted serpentinites is actually higher than that of the obducted samples. The retention of structurally-bound F during subduction is supported by low (0.02-0.42) partitioning coefficients of F between water and hydrous minerals (ref. 44) and mass balance calculations that predict ~95% of subducted F is not recycled to volcanic arcs (ref. 1).

Elevated B concentrations in the DR forearc lizardite-serpentinites are likely sourced from dehydrating sedimentary and mafic rocks of the subducting slab during progressive metamorphism (refs. 45, 46). Perhaps, some B may be derived from subducting serpentinites during lizardite-antigorite transition (refs. 5, 9). However, the high B concentrations in the DR antigorite-serpentinites and in HP serpentinites of the Ligurian Alps, Italy (ref. 11), suggest the retention of significant B in the slab during its subduction.

3.4.4 *Deep volatile cycling*

Slabs are much cooler than the mantle wedge at a given depth, and as such, serpentinites in the slab are stable to greater depths than serpentinites in the mantle wedge. Thermal models have shown that abyssal antigorite-serpentinites dehydrate at depths of 80 to 150 km in warm subduction zones (ref. 47) but may be stable to depths greater than 200 km in cool subduction zones (ref. 34). Therefore, they may have the capacity to transport fluids and FME beyond slab depths associated with most volcanic arcs.

The high F and B contents and F/Cl and B/Cl ratios of the antigorite-serpentinites suggest F and B are, at least partially, retained in the slab during subduction. These findings support previous estimates of low fractions of these elements returning to the surface through volcanic front magmas. For example, Straub & Layne (2003a) (ref. 1) calculate ~4-5% F and ~77-100% Cl entering subduction zones are discharged through volcanic front magmas at the Izu arc, and Moran et al. (1992) (ref. 48) suggest a maximum of 62% of subducted B is returned to the surface via arc magmatism. However, neither of these calculations consider the significant input of volatiles from subducting abyssal serpentinites, nor do they account for volatile reflux back to the surface along the subduction interface. Therefore, these estimates may overstate the true fraction of FME incorporated into arc magmatism from the subducting slab.

In addition to antigorite, significant F and B may also be retained in the slab in minerals such as apatite (F) and phengite (F, B) that are stable to depths of 200 and 300 km, respectively (refs., 34, 49). Indeed high F contents have been reported in apatite (up to 3.5 wt%) and phengite (up to 570 ppm) of lawsonite blueschists (ref. 40), and high B (~100 ppm) has been documented in phengite of blueschist facies metasedimentary rocks (ref. 50). Fluids and FME may also be retained to depths of 300 km in hydrous phase-A after antigorite breakdown (ref. 34). Even after the complete decomposition of the aforementioned minerals, a significant portion of FME may

be retained in the slab by nominally anhydrous phases. Experimental studies have shown the accommodation of F and B in olivine, pyroxenes and garnet under high pressures and temperatures (refs. 32, 51, 52, 53), and high F (up to 130 ppm) and B (up to 20 ppm) have been reported in secondary olivine after serpentine (ref. 54). The retention of F in slabs may contribute to its high concentration in deep-seated magmas, such as ocean island basalts (ref. 22).

Compositions of the DR antigorite-serpentinites, and compositions of metabasites and metasedimentary rocks in slabs from elsewhere, suggest F and B are likely retained in the slab to great depths, while others, such as Cl, Br and I, have much shallower cycling in subduction zones.

3.5 Methods

Halogens are extracted from 0.5 g of finely ground sample material using a pyrohydrolysis technique with the accuracy of the technique verified by the analysis of four reference standards (BCR-2, JB-1, JB-3 and MRG-1) (ref. 40). Analyses of F and Cl are carried out using a Dionex ICS-2100 ion chromatography system equipped with KOH eluent generator at the University of Ottawa. Instrumental detection limits (3σ) for F and Cl are 0.053 ppm and 0.042 ppm, respectively. Analyses of Br (^{79}Br) and I (^{127}I) are carried out using an Agilent Technologies 7700 series inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Ottawa. Samples are diluted 5x to minimize the effects of Na precipitate, and 1% NH_3 is added to stabilize the anions in solution. Instrumental detection limits (3σ) for Br and I are 0.028 and 0.14 ppb, respectively. The reagent grade V_2O_5 (Elemental Microanalysis Ltd.) used as a catalyst for the extractions contains 0.36 ppm F, 0.004 ppm Cl, 32 ppb Br and 2.7 ppb I after drying at 325°C for 24h. The method blank, as determined by repeat extractions without sample or catalyst, is 0.011 ppm F, 0.108 ppm Cl, 4.1 ppb Br and 2.7 ppb I. Average standard deviations (1σ) of repeat halogen extractions ($n=2$ or 3) are 8.93 % for F, 14.9 % for Cl, 30.6 % for Br and

12.4 % for I. Bulk B concentrations were determined on 1.0 g of finely ground sample material by Activation Laboratories (Ancaster, Ontario, Canada) by prompt gamma neutron activation analysis (PGNAA) with a 2 ppm detection limit. Accuracy of the technique was verified by analysis of two geologic reference materials (SY-2 and SY-3).

Acknowledgments

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Chapter 4.

Mantle wedge serpentinites: A transient reservoir of halogens, boron, and nitrogen for the deeper mantle

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Abstract

Fluorine (50–650 ppm), bromine (0.03–0.3 ppm), iodine (0.03–0.4 ppm), boron (20–100 ppm) and nitrogen (5–45 ppm) concentrations are elevated in antigorite-serpentinites associated with the Tso Moriri ultrahigh-pressure unit (Himalayas) exhumed from >100 km depth in the mantle wedge. These fluid-mobile elements are likely released with fluids from subducted marine sediments on the Indian continental margin to hydrate overlying forearc serpentinites at shallow depths. Of these, F and B appear to remain in serpentinites during the lizardite-antigorite transition. Our results demonstrate serpentinites as transient reservoirs of halogens, B, and N to at least 100 km depth in the mantle wedge, and likely deeper in colder slabs, providing a mechanism for their transport to the deeper mantle.

4.1 Introduction

Subduction is the mechanism for transferring fluids and fluid-mobile elements (FMEs) from surface reservoirs to Earth's mantle. Serpentinites facilitate this process due to their high water content (≤ 16 wt%) and wide stability. Abyssal serpentinites are hydrated by seawater, and mantle wedge serpentinites by fluids from the subducting slab. During subduction of the former and dragging down of the latter by mantle flow, serpentine changes from lizardite to antigorite at 300–350 °C (Evans et al., 2013) and dehydrates at 600–700 °C (70–200 km depth; Schmidt and Poli, 1998).

Recent studies of serpentinites highlight their importance for hosting chlorine, bromine, iodine, and boron in the mantle (e.g., Snyder et al., 2005; Kodolányi et al., 2011; Kendrick et al., 2011, 2013; Debret et al., 2014), but reports including fluorine, particularly in antigorite (atg)-serpentinites, are limited (John et al., 2011; Pagé and Hattori, 2017; Kendrick et al., 2018). Furthermore, the abundance of nitrogen in serpentinites is not well known (Philippot et al., 2007; Halama et al., 2014), despite evidence for the subduction of N to the deep mantle (e.g., Marty

and Dauphas, 2003). We report halogen, B, and N abundances in deep (>100 km) mantle wedge antig-serpentinites and discuss the role of serpentinites in their transport to the deeper mantle.

4.2 Geological setting and samples

The Ladakh area of the northwestern Himalaya represents a terrane formed during subduction of the Neotethys, and subsequent collision of the Indian continent with Eurasia (Guillot et al., 2001). The Tso Moriri ultra-high pressure (UHP) unit—composed of metasedimentary rocks and eclogite lenses—represents this subducted margin, which reached 3.9 GPa and 750 °C (Mukherjee et al., 2003). The unit is bounded to the north by the Zildat fault, which contains lenses of massive serpentinite (100 × 500 m; Figure 4-1) with no reaction zones with adjacent rocks. The close association of the serpentinites with the UHP unit, and similar deformation, suggest their exhumation from >100 km depth (Guillot et al., 2001), consistent with the presence of secondary olivine replacing serpentine (Figure AII-1 [in Appendix II]).

The serpentinites, collected from the interior of lenses, are composed of antigorite (> 90%) with minor secondary olivine, magnetite, relic chromite, talc, chlorite, and rare chrysotile veinlets (Table AII-1 [in Appendix II]). High concentrations of bulk Cr (~2000 ppm), Ni (>2000 ppm), and Ir-type platinum group elements, and high Cr# in chromite, confirm their protolith as highly depleted mantle (DM) peridotites (Guillot et al., 2001; Hattori and Guillot, 2007). Sample descriptions are in the data repository [Appendix II].

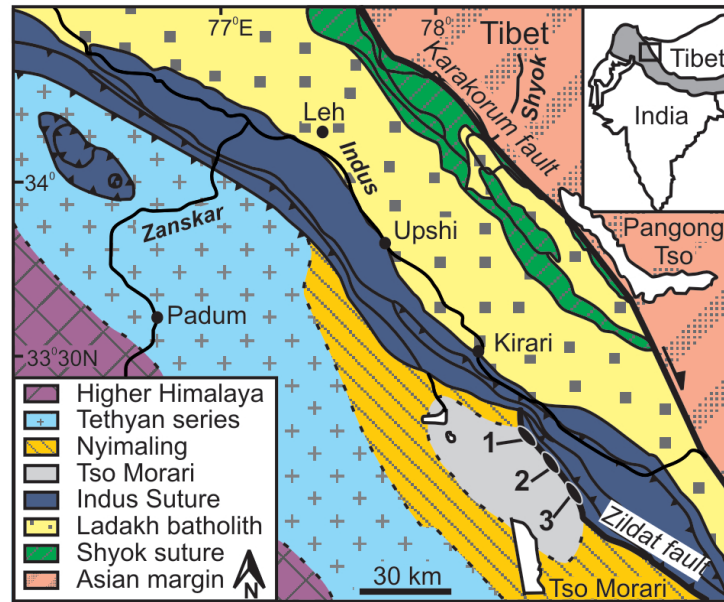


Figure 4-1: Geological map of the Ladakh area, northwestern Himalaya. Samples from serpentinite lenses (labeled 1 [samples CH187, CH422, CH423], 2 [CH98A,B, CH430, CH433], and 3 [CH146]) along the northern edge of the Tso Morari ultrahigh-pressure massif. Solid circles are villages and towns. Map modified after Guillot et al. (2001) and Hattori and Guillot (2007).

4.3 Halogen, boron, and nitrogen abundances

Bulk halogen, B, and N data were obtained by pyrohydrolysis with ion chromatography (F, Cl) and inductively coupled plasma–mass spectrometry (Br, I), prompt gamma neutron activation analysis (B), and combustion with an elemental analyzer (N). Methods are in the Data Repository [Appendix II].

The Himalayan serpentinites are slightly enriched in Cl (8.8–35 ppm) and especially enriched in Br (0.027–0.25 ppm), I (0.029–0.42 ppm), F (50–650 ppm), B (20–100 ppm; Figure 4-2), and N (4.9–46 ppm; Figure 4-3A) relative to the DM protolith (Salters and Stracke, 2004;

Marty, 2012; Kendrick et al., 2017). High I, F, and B lead to I/Cl (0.0032–0.0207), F/Cl (1.4–73), and B/Cl (1.6–7.8) ratios higher than DM values, whereas Br/Cl ratios (0.0031–0.020) overlap with the DM (Figure 4-2).

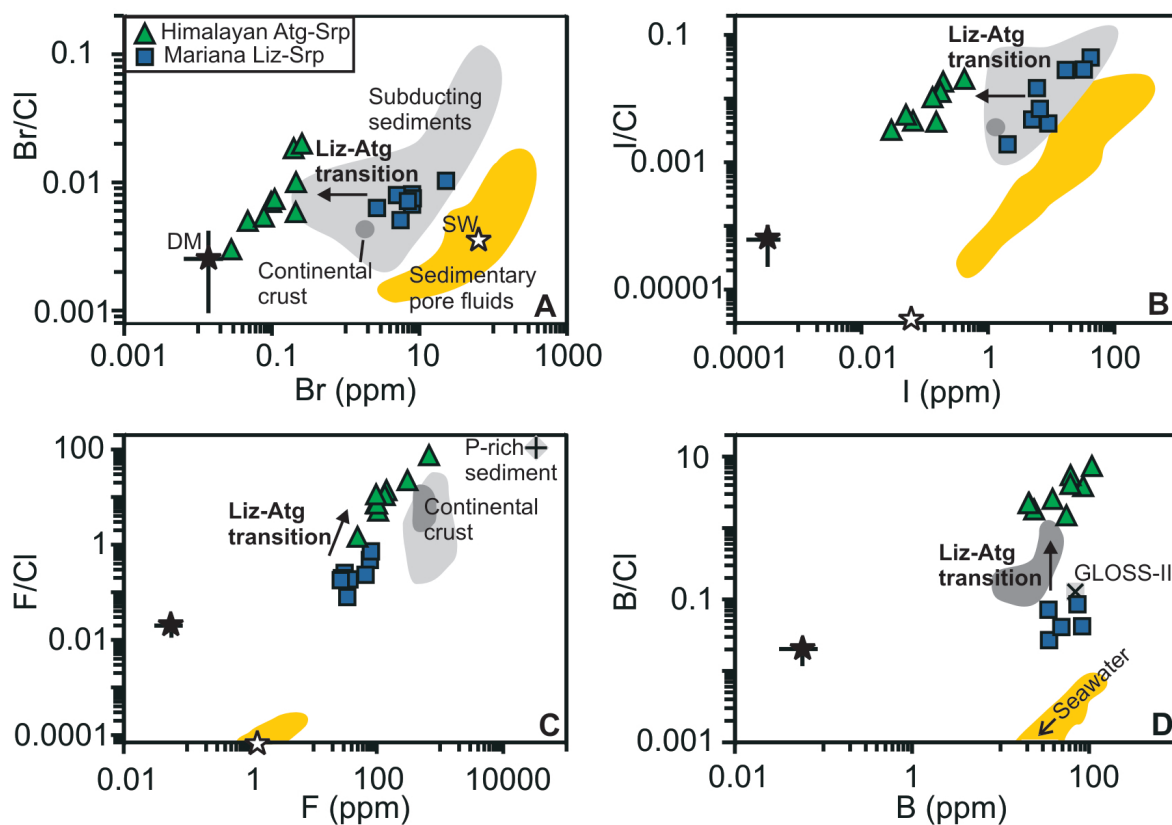


Figure 4-2: Halogen and boron systematics of the Himalayan antigorite-serpentinites (Atg-Srp). A,B: Bromine and iodine are enriched relative to the depleted mantle (DM; black star), and Br/Cl and I/Cl signatures are similar to subducting marine sediments (John et al., 2011) and sedimentary pore fluids (see Kendrick et al. [2018] for a review). Bromine and I contents are lower than lizardite-serpentinites (Liz-Srp) from the Mariana forearc (Pacific Ocean) (Kendrick et al., 2013), but similar Br/Cl and I/Cl signatures indicate a coherent loss of these halogens from serpentinites as they are dragged into the mantle wedge. SW—seawater (white star). C: F/Cl ratios and F concentrations are similar to the upper continental crust (Rudnick and Gao, 2003,

and references therein) and subducting marine sediments, but extend to higher values than Mariana serpentinites (Wei et al., 2005), suggesting retention of F during the lizardite-antigorite transition and/or an influx of F from the deeper slab. D: Boron contents are similar to Mariana serpentinites (Kodolányi et al., 2011) and global subducting sediment (GLOSS-II; Plank, 2014), but higher B/Cl ratios indicate B is preferentially retained over Cl by antigorite. Seawater values are from Li (1982). Values of DM are cited in the text.

4.4 Sources of fluid-mobile elements in serpentinites

The Himalayan serpentinites are hydrated by fluids released from marine sediments on the Neotethys and Indian continent margin (Guillot et al., 2001; Hattori and Guillot, 2007). This is consistent with their Br/Cl and I/Cl ratios that are similar to those of sedimentary pore fluids (Kendrick, 2018, and references therein) and continental crust (Rudnick and Gao, 2003; Figure 4-2A and 2B). High B and N contents are also consistent with high contents in marine sediments (230 ppm B, 600 ppm N; Li and Schoonmaker, 2003). Previous studies suggest serpentinization at shallow (<25 km) depths based on the occurrence of arsenate (As^{5+} ; Hattori et al., 2005). Boron and N are also likely released from sediments at low temperatures (<350 °C; Bebout et al., 1999), as are the heavy halogens, given their affinity with aqueous fluids and a positive correlation between I and As (Figure 4-3C). Fluorine is high in shallow marine sediments (up to 3.1 wt% F in phosphorites; Li and Schoonmaker, 2003; Figure 4-2C) and in crust (560 ppm, F; Rudnick and Gao, 2003) but is retained in the slab at shallow (<80 km) depth (Pagé et al., 2016). Fluorine does not correlate with As in our samples (Figure 4-3D), suggesting the release of F from the slab at greater depths (e.g., Debret et al., 2016). The possible enrichment of FMEs during or after exhumation is rejected based on different compositional patterns of FMEs in the

serpentinites and continental crust, and the occurrence of secondary olivine after antigorite (Hattori and Guillot, 2007).

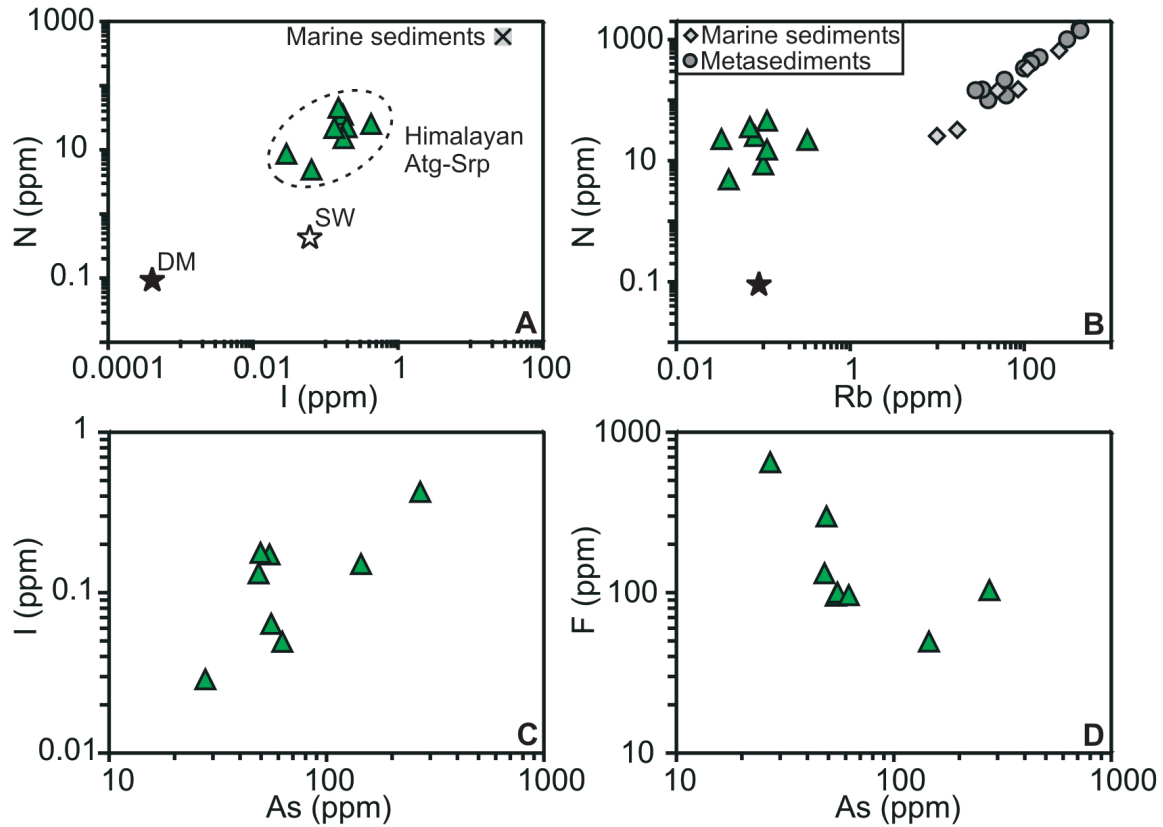


Figure 4-3: Concentrations of select fluid-mobile elements (FMEs) in Himalayan antigorite-serpentinites (Atg-Srp). A: Nitrogen and iodine contents broadly correlate along a linear trend with depleted mantle (DM; black star) and marine sediments. SW—seawater (white star). B: Nitrogen correlates with alkalis (Rb) in metasediments (Busigny et al., 2003), but not in the serpentinites. Alkalis are represented by Rb because its concentration is accurately determined by isotopic dilution. C: The heavy halogens (I) positively correlate with As, suggesting derivation from subducting sediments at shallow depth. D: Fluorine does not correlate with As, indicating it may be sourced from the deeper slab. References in text.

4.5 Accommodation of fluid-mobile elements in serpentinites

4.5.1 Chlorine, Bromine, and Iodine

The Himalayan serpentinites are enriched in Cl, Br, and I relative to DM, but concentrations are lower than those of shallow (<35 km) forearc serpentinites, such as Mariana (Pacific Ocean) (Figure 4-2A,B; Kendrick et al., 2013). In the Himalaya and Mariana sites, all incoming sediments are subducted to contribute to mantle wedge serpentinization. Therefore, the Mariana lizardite (liz)-serpentinites provide a reasonable shallow level analog of the Himalayan samples. The low Cl, Br, and I contents of the Himalayan atg-serpentinites relative to shallower forearc serpentinites (Figure 4-2A,B) suggest these elements are partially lost during the serpentine phase transition. In serpentine, most halogens reside in the OH^- site. Compared to lizardite, antigorite has a tighter crystal structure (Evans et al., 2013), which inhibits accommodation of larger halogens. This explains the overall low Cl, Br, and I contents in atg-serpentinites of the slab compared to their lizardite counterparts (John et al., 2011; Pagé and Hattori, 2017; Kendrick et al., 2018).

4.5.2 Fluorine

Fluorine contents in the Himalayan atg-serpentinites are up to an order of magnitude greater, and F/Cl ratios are up to two orders of magnitude greater, than those of shallow forearc liz-serpentinites (Figure 4-2C). This is consistent with a late influx of F from the slab and a preferential accommodation of F relative to Cl in antigorite. Indeed, F is likely more compatible with minerals than the heavier halogens given its high electronegativity and similar ionic radius (1.33 Å) to OH^- (1.35 Å). Fluorine may also replace O^{2-} (1.38 Å) coupled with the substitution of Si^{4+} by Al^{3+} (Beyer et al., 2012). Chlorite (12 wt% H_2O) may host F, as reported in the Cerro del Almirez (Spain) harzburgites (Kendrick et al., 2018), but chlorite (<1 vol%) has little contribution to the F budget in our samples.

4.5.3 Boron

Previous *in situ* analyses of the Himalayan serpentinites confirm FMEs, including B, are in serpentine (Deschamps et al., 2010) and indicate that the bulk rock values reported here are slightly diluted by B-poor minerals. Since B likely replaces tetrahedral Si, it is likely to be retained during the phase change. This is supported by similar B contents in our atg-serpentinites and Mariana liz-serpentinites (Figure 4-2D) and consistent B contents in subducted serpentinites with increasing depth (Scambelluri and Tonarini, 2012).

4.5.4 Nitrogen

Possible occurrence of N in silicates includes (1) NH_4^+ replacing K^+ (Busigny et al., 2003), (2) N_2 in fluid inclusions or on crystal lattice defects (Li et al., 2013), and (3) N^{3-} (1.46 Å) replacing O^{2-} (1.38 Å), such as $\text{Si}_2\text{N}_2\text{O}$ in meteorites (Andersen et al., 1964). Our samples contain low K (<0.005 wt% K_2O ; Hattori and Guillot, 2007) and no correlation with N (Figure 4-3B), and the large effective size of NH_4^+ (1.48 Å) precludes its accommodation in the serpentine lattice. The serpentinites do not contain observable fluid inclusions, but the presence of N_2 between grains cannot be ruled out. Replacement of O^{2-} by N^{3-} appears possible, with coupled substitution of Mg^{2+} by Al^{3+} or Si^{4+} by As^{5+} , as supported by high Al (<2.5 wt%) and As (<275 ppm) in our samples (Hattori and Guillot, 2007). Furthermore, the reduction of N_2 to N^{3-} is feasible under the low oxygen fugacity associated with serpentinization (e.g., Evans et al., 2013).

4.6 Implications for deep cycling of FMEs

The elevated FMEs in our serpentinite samples demonstrate their transport to >100 km depths in the mantle wedge, and possibly deeper (>200 km; Schmidt and Poli, 1998) in the cooler slab. The retention of F in serpentinites is consistent with its low fractions (~2–5%; Barnes et al., 2018, and references therein) returned to Earth's surface by arc magmas. Mass

balance calculations also indicate partial return of B and N (<60%; Bebout, 1996) through arc magmatism. Previously, all subducted Cl is considered to return to the surface (e.g., Straub and Layne, 2003), but recent work including input of abyssal serpentinites suggest up to 10% of subducted Cl, Br, and I may also be retained (Barnes et al., 2018). A simple calculation suggests the importance of serpentinites for hosting FMEs in the slab. Serpentinites of 450 m thickness constitute 8% of residual Cl, 28% B, and 7% N in the metamorphosed slab (Figure 4-4). If serpentinite thickness is increased to 4500 m (Ranero et al., 2003), their contribution increases to 45% for Cl, 80% for B, and 41% for N.

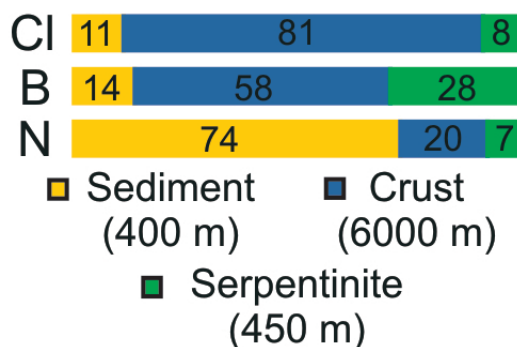


Figure 4-4: Summary of Cl, B and N budget calculations for a metamorphosed slab composed of sediment (25 ppm Cl, 28 ppm B, 287 ppm N; Bebout et al., 1999; Halama et al., 2014; Selverstone and Sharp, 2015), igneous crust (12 ppm Cl, 7.8 ppm B, 5.1 ppm N; Marschall et al., 2009; Halama et al., 2014; Pagé et al., 2016) and antigorite-serpentinites. Thicknesses of each lithological unit are reported in brackets. Numbers in bars denote the % contributions of each unit to the total residual FMEs in the slab.

After serpentine dehydration, FMEs may be incorporated in other hydrous phases, including chlorite (Kendrick et al., 2018) and hydrous phase-A (e.g., Schmidt and Poli, 1998), or

in nominally anhydrous minerals. Indeed, olivine and pyroxene can accommodate F, B, and N (Hålenius et al., 2010; Beyer et al., 2012; Li et al., 2013), and high F (<130 ppm) and B (<20 ppm) are documented in secondary olivine (De Hoog et al., 2014), and high N (<20 ppm) in chlorite harzburgites (Halama et al., 2014). These minerals may transfer FMEs to deep-seated magmas, such as the high F in ocean island basalts (OIBs; Kendrick et al., 2017) and kimberlites (Paul et al., 1976) and high ^{15}N in OIBs and carbonatites (Marty and Dauphas, 2003). Our study shows that serpentinites retain significant quantities of halogens, B, and N, to at least 100 km depth in the mantle wedge, and as such, they may assist in transporting these elements to the deep upper mantle.

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Chapter 5.

Halogen (F, Cl, Br, I) behaviour in subducting slabs: A study of lawsonite blueschists in western Turkey

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Abstract

We examined the F, Cl, Br and I abundance of minimally retrogressed lawsonite blueschists from the Tavsanlı Zone in northwest Turkey to evaluate the behaviour of halogens in subduction zones, and to determine the role coexisting high pressure minerals may play in transporting the halogens to the Earth's mantle. The blueschists contain sodic amphibole and lawsonite, with variable amounts of phengite and chlorite, and minor apatite. A positive correlation between Cl, Br and I contents in bulk rocks suggests their overall coherent behaviour in subduction zones, although high ratios of I/Cl and Br/Cl compared to altered oceanic crust indicate that Cl is preferentially lost relative to Br and I before or during blueschist metamorphism. Iodine and F are enriched relative to altered oceanic crust, suggesting incorporation from marine sediments. *In situ* analyses of minerals in thin sections reveal F preferentially concentrates in apatite (avg. 3.13 wt%), over phengite (482 ppm), lawsonite (avg. 413 ppm) and Na-amphibole (257 ppm). Chlorine also preferentially resides in apatite (138 ppm), followed by equal partitioning between phengite (59 ppm) and Na-amphibole (56 ppm), and lower concentrations in lawsonite (27 ppm). Upon apatite decomposition at a depth of ~200 km, F may redistribute into lawsonite and phengite in slabs, whilst Cl is likely expelled to the overlying mantle wedge. Given the stability of lawsonite and phengite to a depth of 280-300 km in cold subduction zones, they may transport F beyond subarc depths, contributing to the high F in magmas derived from the deep mantle.

5.1 Introduction

Halogens are predominantly concentrated in the Earth's surface reservoirs, including seawater and sediments. Their concentrations are low in the primitive mantle, with current estimates of 18 ppm F, 1.4 ppm Cl, 0.0036 ppm Br and 0.001 ppm I (Lyubetskaya & Korenaga 2007). As halogens are not compatible with mantle minerals, they are preferentially removed

from the mantle during partial melting, and as such their concentrations are even lower in the depleted MORB mantle (DMM). Despite having low concentrations in the mantle, halogens are abundant in mantle-derived magmas, and are continuously discharged from volcanoes of a variety of settings. For example, F and Cl are the most abundant constituents of volcanic gases discharged from arc volcanoes after H₂O, CO₂ and S species (Symonds et al. 1994). The key mechanism responsible for volcanic outputs is the recycling of elements from surface reservoirs to the mantle through subduction. Many studies have primarily focused on Cl in subduction zones, using it as a proxy for the other halogens (e.g. Scambelluri et al. 2004; Marschall et al. 2009).

During subduction, aqueous fluids released from the slab move upward to the overlying mantle wedge, which leads to partial melting of the interior of the hot mantle wedge for arc magmatism. The depth of fluid release is related to the geothermal gradient of the subduction zone and the stability of hydrous minerals. As halogens are soluble in aqueous fluids, their behaviour is expected to follow that of water, but the stability of hydrous minerals differs widely, and hydrous minerals have varying ability to accommodate fluid-mobile elements, including halogens. Therefore, the composition of fluids released from slabs is likely to change with increasing depth. Furthermore, some hydrous minerals, such as serpentine (~13wt% H₂O), lawsonite (~11wt% H₂O) and phengite (~4wt% H₂O), are stable to depths of 200-300 km in cold subduction zones (Schmidt & Poli 1998), far beyond the depths beneath arcs. This suggests that these minerals are able to transport not only water, but also fluid-mobile elements, to the deeper mantle.

Recent work has documented the importance of serpentinite in the transport and fractionation of the halogens in subduction zones (e.g. John et al. 2011; Kendrick et al. 2013), with their findings suggesting Br and I are preferentially released relative to Cl and F during

serpentine phase transition and decomposition. However, there are few studies documenting the abundance of halogens in other hydrous minerals. This paper reports the abundance of halogens in lawsonite-bearing blueschists from the Tavsanlı Zone in northwestern Turkey using a variety of analytical techniques, and discusses the behaviour of halogens, particularly F, in subduction zones and the implications for global halogen recycling.

5.2 Geological setting

Turkey is comprised of several continental fragments that assembled during the Tertiary collision of Laurasia and Gondwana. In western Turkey, the Izmir-Ankara-Erzincan suture marks the collision of the southern and northern terranes. Prior to the collision, the margin of the southern continent, the Anatolide-Tauride Block, was subducted to a depth of 80 km by 80 Ma in an intra-oceanic subduction zone and was metamorphosed in blueschist facies (Sherlock et al. 1999; Okay & Whitney 2010). The resulting blueschist belt, known as the Tavsanlı Zone, is exposed immediately south of the suture (Figure 5-1). It is primarily comprised of Paleozoic-Mesozoic metabasites and metasedimentary rocks representing the subducted continental margin, in addition to tectonically overlying oceanic accretionary complex and peridotite. The east-west trending Tavsanlı Zone is 50-60 km wide and approximately 250 km long (Okay & Whitney 2010). It is one of the most extensive and well-preserved blueschist belts in the world with little retrogression (Okay 1980).

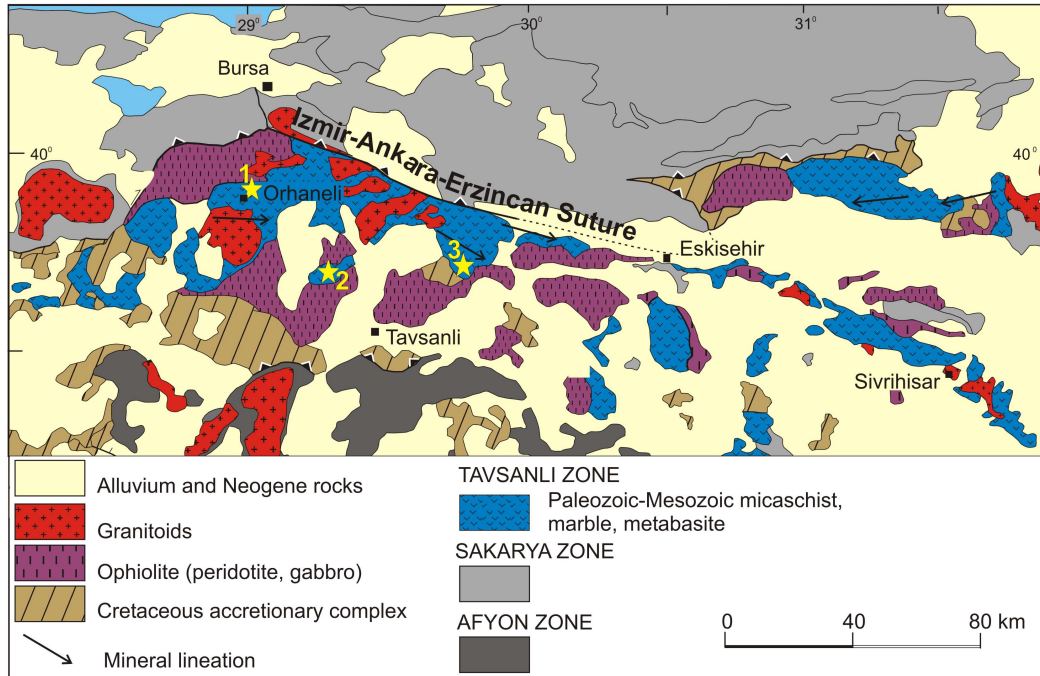


Figure 5-1: Simplified geological map of the Tavsanlı Zone in northwestern Turkey (modified from Okay & Whitney 2010). Sample outcrop locations are numbered and marked with stars.

In the western part of the Tavsanlı Zone, the Orhaneli Group blueschists are divided into three units. The base is the quartz-mica-pelitic schists of the Kocasu Formation (Okay 2002), which gradually changes to the overlying İnönü Marble. The mica schist consists of quartz, phengite, jadeite, chloritoid, Na-amphibole, lawsonite, and chlorite. The assemblage constrains the peak metamorphic conditions to 24 ± 3 kbar and $430 \pm 30^\circ\text{C}$, corresponding to a low geotherm of $5^\circ\text{C}/\text{km}$ (Okay 2002). The uppermost unit, the Devlez Formation, is composed of metabasite (>80 vol%) with minor metasedimentary rocks metamorphosed under similar blueschist facies conditions (Okay 1980). The metabasites contain euhedral lawsonite laths in a matrix of foliated sodic amphibole with variable amounts of phengite and chlorite. Rb-Sr

phengite ages of $78.5 - 79.7 \pm 1.6$ Ma likely reflect the age of metamorphism in the region (Sherlock et al. 1999). These metabasites are the focus of this study.

5.3 Samples

Lawsonite-rich metabasites were collected from three outcrops of the western Tavsanlı Zone (Figure 5-1). All samples contain idioblastic lawsonite laths (< few mm in length) with varying abundance of blue amphibole (Table 5-1). Samples are characterized by prograde mineral assemblages with very little retrograde products (e.g. no secondary calcic amphibole, and only minor epidote and albite).

Table 5-1: Summary of sample mineralogy of Tavsanlı Zone blueschists in northwest Turkey.

Outcrop No. in Figure 1	Sample ID	Mineralogy	
		Major	Minor
1	TUR12	Lws, Na-Amp, Chl, Jd, Ttn	Qtz, Ap, Ep
	TUR14	Lws, Na-Amp, Ph, Chl	Qtz, Ttn, Rt, Ap
2	TUR23	Lws, Chl, Ph, Ttn	Na-Amp, Ap, Py
3	TUR30	Lws, Na-Amp, Ph, Qtz, Chl	Ap, Ttn, Rt
	TUR31	Lws, Chl, Ph, Qtz	Ap, Ttn, Ab
	TUR32	Lws, Na-Amp, Qtz, Ab	Chl, Ttn, Ap
	TUR33	Lws, Na-Amp, Ph, Ap, Ttn	Fe-oxides, Chl

Samples TUR12 and TUR14 are blueschists collected in the Orhaneli region, near the town of Deliballar (Okay & Whitney 2010). TUR12 contains an intergrowth of prismatic lawsonite (< 0.5 mm) and Na-amphibole grains (< 0.5 mm), with minor chlorite (Figure 5-2A). Lawsonite contains inclusions of quartz, Na-amphibole and titanite. There are interstitial quartz, apatite, Na-Ca pyroxene and minor epidote throughout the sample. Large (up to 4 mm) euhedral lawsonite of TUR14 are highly fractured and contain inclusions of Na-amphibole and minor

quartz. They are set in a matrix of fibrous Na-amphibole prisms (and some larger grains up to 0.5 mm), in addition to fibrous chlorite and minor rutile. Phengite grains are larger than in other samples (up to 0.3 mm), and are often found in clusters (Figure 5-2B). Blueschists from this region have been previously described by Okay (2002).

One sample (TUR23) was collected from a blueschist outcrop near Harmancik (southeast of Orhaneli). It contains clusters of idioblastic lawsonite laths (~ 1 mm length) along with minor Na-amphibole needles (<0.2 mm) and minor titanite set in fine-grained aggregates of phengite and chlorite (Figure 5-2C). The surrounding dark matrix is composed of fine-grained actinolite, chlorite, titanite, apatite and pyrite.

The remaining samples (TUR30, 31, 32, 33) were collected from the Devlez Formation near the village of Ketenlik, farther east along the Tavsanlı Zone (Figure 5-1). Sample TUR30 is characterized by elongated lawsonite laths surrounded by Na-amphibole, phengite, quartz, minor apatite and minor titanite (Figure 5-2D). The lawsonite laths of TUR31 vary in size (up to 1 mm) and contain inclusions of quartz and titanite. They are surrounded by green Na-amphibole, chlorite, interstitial quartz and disseminated albite and phengite (Figure 5-2E). Wide (up to 5 mm) quartz veins are also present in the sample. TUR32 shows foliation defined by fibrous Na-amphibole and lawsonite laths (Figure 5-2F). Na-amphibole is compositionally zoned with Al-rich cores and Fe-rich rims. There is also minor chlorite, quartz and titanite throughout the sample. Generally, TUR32 is more fine-grained than the other three samples from this area. TUR33 contains veins composed of large lawsonite laths (up to 5 mm), which are fractured and contain inclusions of Na-amphibole, apatite and magnetite, similar to those of TUR14.

Lawsonite is surrounded by a matrix of fine-grained fibrous Na-amphibole, iron oxides, apatite, titanite, phengite and minor chlorite (Figure 5-2G). Some phengite forms aggregates up to 0.5

mm. Blueschists from this outcrop have been previously described by Okay (1980) and sampling locations are described in the field trip guidebook by Okay & Whitney (2010).

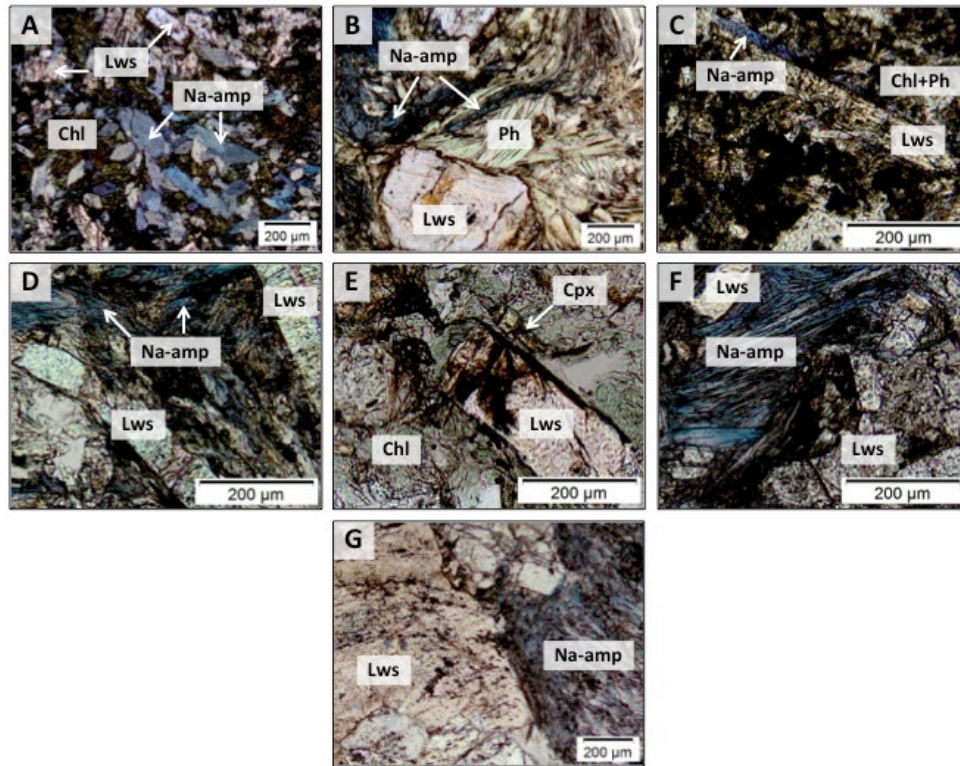


Figure 5-2: Photomicrographs of lawsonite blueschist samples from the Tavsanlı Zone, northwest Turkey. (a) TUR12, (b) TUR14, (c) TUR23, (d) TUR30, (e) TUR31, (f) TUR32 and (g) TUR33. Chl: chlorite, Cpx: clinopyroxene, Lws: lawsonite, Na-amp: Na-amphibole, Ph: phengite.

5.4 Analytical Methods

5.4.1 Bulk-rock chemistry

Bulk rock major and minor element composition was determined by ALS Global (North Vancouver, Canada) using X-ray fluorescence (XRF) after fusion of rock powder with 50/50

$\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$, and trace element composition was determined at the same facility by ICP-MS following digestion of rock powder by concentrated $\text{HF-HNO}_3\text{-HClO}_4\text{-HCl}$.

Halogen extraction: pyrohydrolysis + IC/ICP-MS

Amphibole-rich and lawsonite-rich fractions were separated from four samples (TUR14, 30, 32, 33) by hand under a binocular microscope. A phengite-rich fraction was also collected from TUR14. The remaining samples were too fine-grained for separation. Halogens were extracted from the mineral-rich fractions and bulk rock samples using a modified pyrohydrolysis technique after Muramatsu et al. (2007) and references therein. Method details are in Appendix A. Analysis for F and Cl was carried out at the University of Ottawa using a Dionex Model 2100 Ion Chromatograph equipped with KOH eluent generator. Instrumental detection limits (3σ) for F and Cl were 0.017 ppm and 0.034 ppm in solution, respectively. Analysis for Br (^{79}Br) and I (^{127}I) was carried out at the University of Ottawa using an Agilent 7700 ICP mass spectrometer. Instrumental detection limits (3σ) for Br and I were 0.022 and 0.041 ppb, respectively. Standard deviations (1σ) for duplicate or triplicate analyses of samples are in the range 0.3-15 % for F, 1.7-36 % for Cl, 2.3-25% for Br, and 2.0-29% for I. Accuracy of the pyrohydrolysis technique is based on the analysis of four international reference materials (BCR-2, JB-1, JB-3 and MRG-1). Percent yield ranges from 76-93 % for F, 85-106 % for Cl, 66-111 % for Br, and 110-156 % for I (refer to Table A I-1 in supplementary files [of Appendix IV] for details).

5.4.2 Mineral chemistry

5.4.2.1 Electron microprobe analysis (EPMA)

Na-amphibole, lawsonite and phengite were analyzed for Si, Ti, Al, Mg, Fe, Ca, Na, K, Mn, Cr and Ni at the University of Ottawa with a JEOL 8230 electron microprobe using a wavelength dispersive spectrometer. A 5 μm diameter 20 nA beam accelerated to 20 kV was used. Peak counting times were 10s per element for the $K\alpha$ lines of Fe, Mn, Cr and Si, 20s for K,

Ca, P, Al, Ti, Na and Mg, and 50s for Ni. Instrument calibration used sanidine (Si, Al, K), diopside (Ca, Mg), albite (Na), hematite (Fe), tephroite (Mn), San Carlos olivine (Ni), rutile (Ti), chromite (Cr) and apatite (P).

Mineral formulae of Na-amphibole grains were calculated using 23(O), and ferric and ferrous iron contents were determined on the basis of stoichiometric composition after normalizing to 8 Si atoms. For lawsonite, all iron was assumed to be Fe^{3+} , and mineral formulae were determined using 8(O). Mineral formulae of phengite and the amount of Fe^{3+} were calculated based on stoichiometric composition and charge balance using 11(O).

The analytical conditions for apatite were 10 kV accelerating voltage, 4 nA beam current, and 10 μm diameter beam size as recommended by Goldoff et al. (2012) for optimal analysis of fluor-chlorapatites. Each grain was analyzed in 1-3 spot(s), depending on grain size. Peak counting times were 10s per element for Si (Ka), Fe (Ka), Mg (Ka), K (Ka), S (Ka), Ce (La), La (La) and As (La), 20s for Al (Ka), Ca (Ka), Na (Ka), P (Ka), Sr (La) and Cl (Ka), and 50s for F (La). Instrument calibration used sanidine (Si, Al, K), hematite (Fe), diopside (Mg), apatite (Ca, P, F), albite (Na), celestine (S, Sr), CePO_4 (Ce), LaPO_4 (La), and GaAs (As). The apatite standard contains 3.53 wt% F. An LDE1 diffraction crystal was used to enhance the count of F. Apatite mineral formulae were calculated based on normalizing to 13 (O, OH, F, Cl).

5.4.2.2 Ion microprobe analyses by secondary ion mass spectrometer (SIMS)

Grains for *in situ* analyses were selected from EPMA-analyzed samples. Grains were cored from polished thin sections using a diamond-tipped drill bit, mounted in indium-filled Al holders, and gold-coated. Fluorine, Cl and H_2O were measured by SIMS using a Cameca 4f instrument at the Edinburgh Ion Microprobe Facility (EIMF), University of Edinburgh. A 5-nA primary beam of negative ^{16}O ions accelerated to 14.5 kV was used. Pit diameter was *ca.* 15 μm , depth of the analysis pits was <2 μm . Total counting times were 30s per isotope per analysis.

Water and Cl were calibrated using an in-house basaltic glass standard (St81-A9; Lesne et al. 2011). Fluorine was calibrated using T1-G glass (Guggino and Hervig, 2010). Reproducibility for all elements, as determined by repeat measurements of glass standards, is better than 10% for all elements.

The use of glass standards may introduce a bias due to matrix effects. Therefore, amphibole standards of known H₂O, F and Cl contents were used to calibrate the matrix effects associated with Fe-Mg hydrous silicates. Correction factors of 1.4 for F and 1.9 for Cl were ascertained and applied to the analysis of Na-amphibole and phengite. No matrix-induced fractionation was observed for H₂O. Due to a lack of suitable standards for lawsonite, F and Cl contents of this mineral were calibrated using basaltic glass standards. Calibration curves can be found in supplementary material (Figure A III-1) [Appendix III].

5.5 Results

5.5.1 Bulk rock chemistry

All samples have a basaltic chemical composition (44.4-52.1 wt% SiO₂; Table A III-1) that is slightly more alkaline (3.2-4.3 wt% Na₂O + K₂O; Table A III-1) than typical N-MORB values. Samples have moderate bulk-rock Mg# (0.47-0.62). TiO₂ content of most samples (0.98-2.8 wt%) is consistent with a ridge basalt protolith rather than an arc basalt (White & Klein 2014), and the presence of phengite in most samples corresponds to elevated K₂O (0.33-1.2 wt%) relative to typical N-MORB values. High P₂O₅ (up to 0.34 wt%) in most samples is consistent with the presence of apatite. Overall, major element data of the Tvasanli Zone blueschists are consistent with their origin as basaltic rocks of the Neo Tethys.

5.5.2 Mineral chemistry

5.5.2.1 Na-Amphibole

All amphiboles are sodic following the classification of Leake et al. (2003), with Na dominating the B-site (≥ 1.50 pfu; Table A III-2; Figure 5-3). Other than minor K (<0.01 pfu), the A-site is vacant in all samples except for TUR31 which has high Na (<1.92 pfu). Most samples are characterized by high Fe^{3+} (0.242 - 1.80 pfu) in the C-site. Amphibole composition is similar to previous reports of blueschist amphiboles in this region (e.g. Okay 2002, Davis & Whitney 2006) and other HP belts (e.g. Schliestedt 1986, Spandler et al. 2003; Figure 5-3).

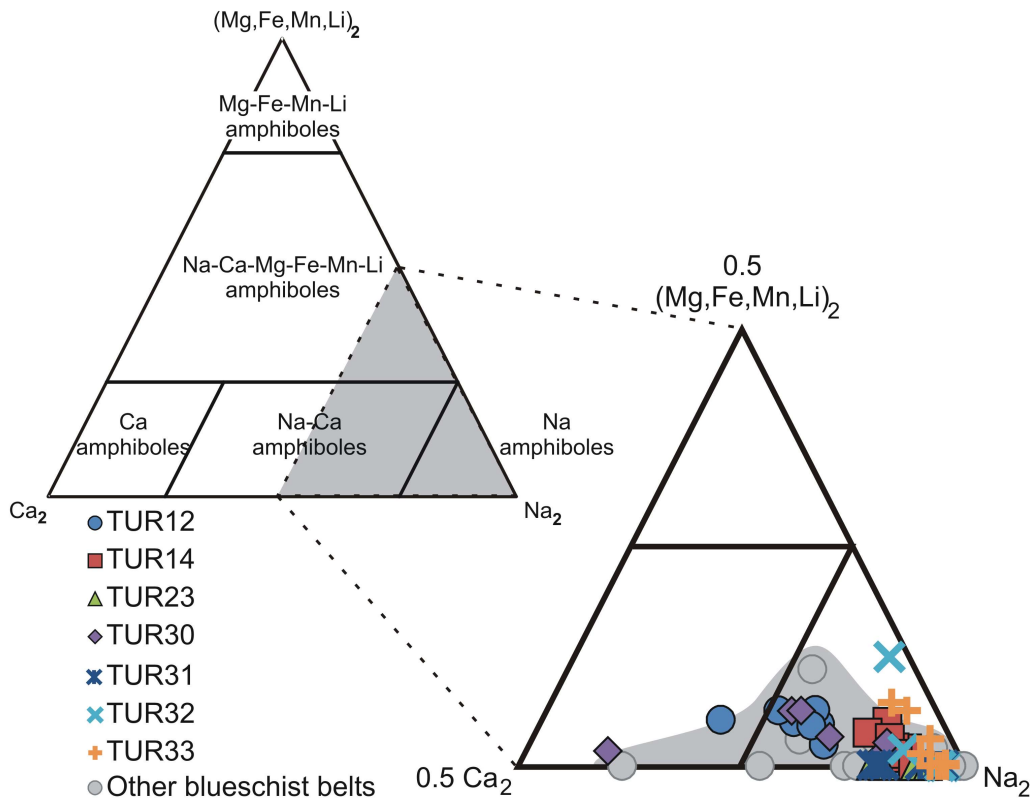


Figure 5-3: Composition of amphiboles from lawsonite blueschists of the Tavsanlı Zone, northwestern Turkey. Classification based on B-site (B_2) occupancy according to Leake et al. (2003). Modified from Hawthorne & Oberti (2006). For comparison, the composition of other blueschists in Turkey (e.g. Okay 2002, Davis & Whitney 2006), Greece (Schliestedt 1986) and New Caledonia (Spandler et al. 2003) are plotted.

5.5.2.2 Lawsonite

The lawsonite grains have near-ideal chemical composition with minimal variation among different grains, and among different samples (Table A III-3). Total Fe content is elevated, up to 2.3 wt%, compared to other lawsonites in blueschists worldwide (e.g. Spandler et al. 2003), but the values are similar to those of lawsonite of the Sivrihisar Massif in the eastern part of the Tavsanlı Zone (Davis & Whitney 2006).

5.5.2.3 Phengite

Phengite is common in TUR14, TUR30 and TUR33, and is a minor constituent of TUR23 and TUR31. In the latter, grains are small (< 100 μm) and often intergrown with chlorite, making precise composition analysis difficult. Phengite composition in the Deliballar outcrop sample (TUR14) covers a narrow range (Si = 3.4-3.5 pfu; Table A III-4), similar to previous reports for white mica in other lawsonite blueschists in the world (e.g. Spandler et al. 2003; Davis & Whitney 2006; Bebout et al. 2007). A wider spread in Si content (3.4-3.9 pfu) is observed for two samples from the Ketenlik outcrop (TUR30, TUR33). From the same outcrop, phengite in TUR31 has low Si (3.2-3.4 pfu) and K/Na (< 30; Figure 5-4), suggesting this sample may have re-equilibrated at low temperatures.

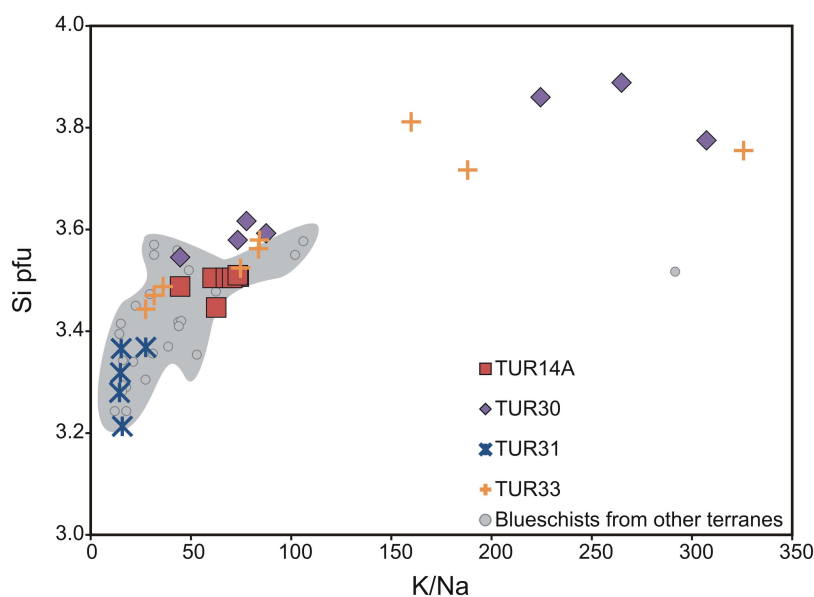


Figure 5-4: Composition of phengite from lawsonite blueschists of the Tavsanlı Zone, northwestern Turkey. Atomic ratios of K/Na increases with increasing Si atoms per formula unit (pfu). The compositions are similar to phengite in blueschists from other terranes, including New

Caledonia (Spandler et al. 2003), the Catalina Schist, California (Bebout et al. 2007), Mariana forearc (Pabst et al. 2012), and the Sivrihisar Massif of the eastern Tavsanlı Zone (Davis & Whitney 2006).

5.5.2.4 Apatite

Apatite in all samples contain high F (2.64-3.75 wt%), but low Cl (<0.06 wt%), classifying them as fluorapatites (Table A III-5; Figure 5-5). In addition to CaO and P₂O₅, most samples contain minor amounts of MgO (<0.07 wt%), Na₂O (<0.09 wt%), K₂O (<0.15 wt%), SrO (<0.41 wt%), Ce₂O₃ (<0.64 wt%), La₂O₃ (<0.63 wt%), Al₂O₃ (<0.1 wt%), SO₃ (<0.55 wt%), and As₂O₅ (<0.17 wt%), along with variable FeO (<1.4 wt%) and SiO₂ (<2.3 wt%).

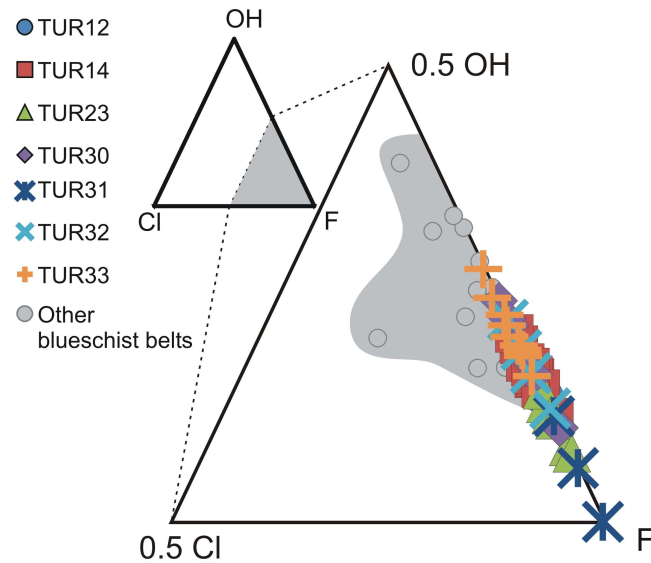


Figure 5-5: Volatile contents (atomic proportion) in apatite from lawsonite blueschists of the Tavsanlı Zone, northwestern Turkey. Hydroxyl component calculated by difference ($X_{OH} = 1 - X_F - X_{Cl}$). There is overlap with apatites from other HP belts (e.g. Svensen et al. 2001, John et al. 2008), however in general the Tavsanlı blueschists have higher F.

5.5.3 Halogens

5.5.3.1 Mineral fractions and bulk rock by pyrohydrolysis

Bulk rock Cl concentrations (8-22 ppm) are two orders of magnitude greater than those for Br (0.07-0.24 ppm) and I (0.13-0.52 ppm), with Br/Cl and I/Cl ratios covering a narrow range (0.006-0.019 and 0.011-0.024, respectively; Table A III-6; Figure 5-6; Figure 5-7). Fluorine is the most abundant halogen in all bulk samples, with concentrations ranging from 222 to 616 ppm and corresponding F/Cl ratios of 25.3 to 74.1.

Mineral-rich fractions have a larger spread in halogen concentrations, particularly for F and Cl. Sodic amphibole-rich fractions show high F (198-608 ppm) compared to the heavier halogens (10-40 ppm Cl, 0.16-0.26 ppm Br, and 0.12-1.01 ppm I). Despite the wider spread in heavy halogen concentrations, their ratios fall within narrow ranges (0.005-0.016 Br/Cl, 0.011-0.025 I/Cl), but F/Cl ratios (7.9-38.4) do not. An even larger spread is observed for the halogen concentrations of lawsonite-rich fractions (120-955 ppm F, 8-56 ppm Cl, 0.14-0.47 ppm Br, and 0.14-1.37 ppm I), but the spread in Br/Cl and I/Cl ratios is narrow (0.008-0.021 and 0.018-0.024, respectively) compared to the spread in F/Cl ratios (8.8-37.2). The phengite-rich fraction has F/Cl, Br/Cl and I/Cl ratios of 34, 0.013 and 0.016, respectively.

Fluorine and Cl contents of bulk samples are broadly correlated with bulk K_2O and P_2O_5 (Figure A III-2), providing evidence that phengite and apatite may influence the bulk halogen content of these blueschists.

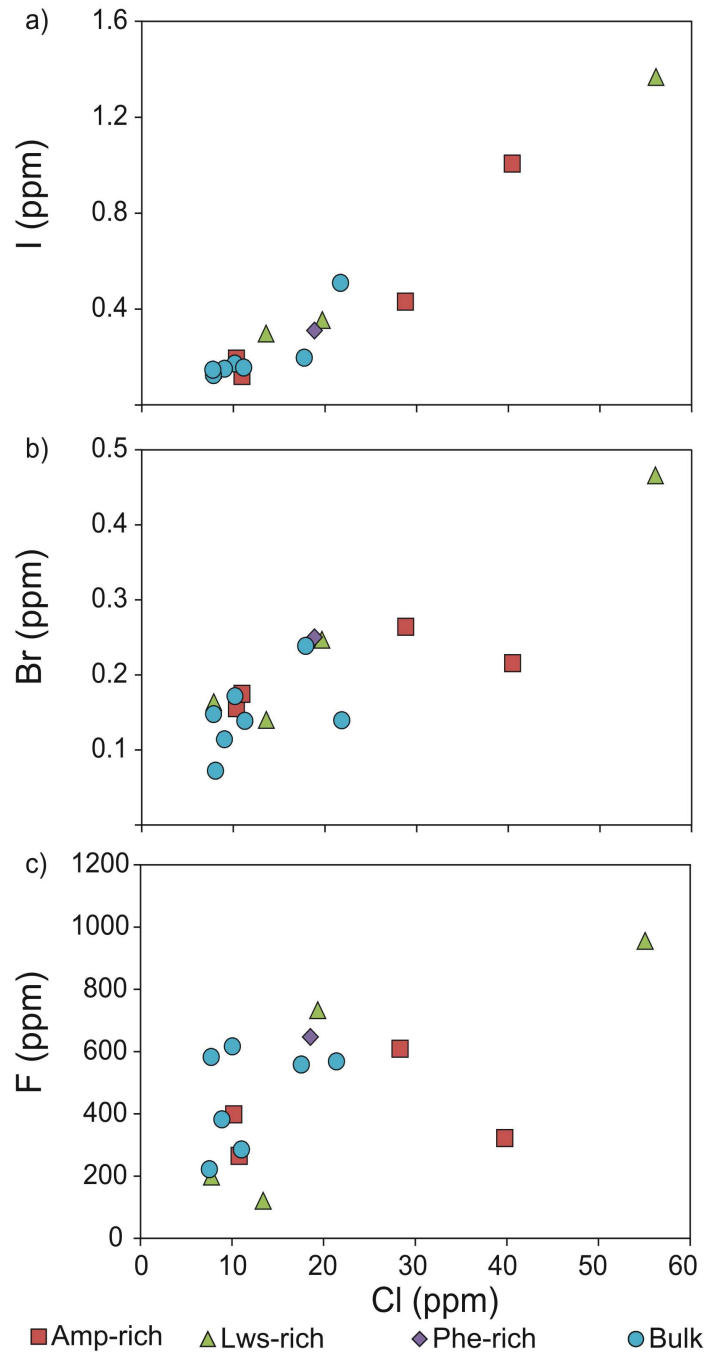


Figure 5-6: Halogen content of bulk samples and mineral separates for lawsonite blueschists of the Tavsanlı Zone, northwestern Turkey. Chlorine is plotted against (a) I, (b) Br and (c) F. There is a positive correlation between Cl, Br and I, but not F.

5.5.3.2 *Hydrous mineral concentrations by SIMS*

Phengite and lawsonite contain higher F (372-572 ppm and 295-861 ppm, respectively) than Na-amphibole (84-390 ppm) (Table 5-2). Chlorine concentrations are lower than those of F for all three minerals and in all samples by an order of magnitude or more, agreeing with the results from bulk pyrohydrolysis extractions in this study. Phengite (21-77 ppm) and Na-amphibole (18-97 ppm) have similar concentrations, while lawsonite has lower Cl concentrations spanning a narrow range (20-46 ppm). Na-amphibole and lawsonite F/Cl ratios (0.97-21 and 11-36, respectively) cover a range of two orders of magnitude, similar to those of the corresponding extracted mineral fractions. Phengite F/Cl ratios also cover a range of two orders of magnitude (5-27), slightly lower than the ratio reported for the only phengite-rich mineral fraction.

5.5.3.3 *Apatite concentrations by EMPA*

Apatite contains higher F concentrations (up to 3.51 wt%; Table 5-2) than Na-amphibole, lawsonite and phengite, contributing up to 51% of total F in bulk samples. Chlorine concentrations in apatite are also elevated (up to 253 ppm) with respect to the other minerals, but to a lesser extent than F concentrations, as evidenced by apatite's higher F/Cl ratios (114-493).

Table 5-2: Halogen concentrations in blueschist facies minerals from the Tavsanlı Zone, northwestern Turkey. Na-amphibole, lawsonite and phengite results were determined by SIMS, and apatite by EMPA. Apatite concentrations are an average of 1-3 analyses/grain for 1-4 grains/sample, depending on grain size and abundance.

	H ₂ O wt%	F ppm	Cl ppm	F/Cl
Phengite				
TUR14A	5.75	503	77	6.54
TUR30	5.77	572	21	26.9
TUR33	6.07	372	69	5.35
<i>Average</i>	<i>5.87</i>	<i>482</i>	<i>56</i>	<i>12.9</i>
Na-amphibole				
TUR12	2.15	218	46	4.79
TUR14A	2.17	335	97	3.47
TUR30	2.02	390	18	21.4
TUR32	2.09	256	46	5.60
TUR33	2.19	84	87	0.967
<i>Average</i>	<i>2.12</i>	<i>257</i>	<i>59</i>	<i>7.25</i>
Lawsonite				
TUR23	10.5	334	20	16.9
TUR30	10.1	383	33	11.8
TUR31	10.7	861	24	35.9
TUR32	10.4	295	27	10.8
TUR33	10.0	538	46	11.6
<i>Average</i>	<i>10.3</i>	<i>482</i>	<i>30</i>	<i>17.4</i>
Apatite				
TUR12		30600	nd	nd
TUR14A		30590	130	235
TUR23		32790	163	201
TUR30		29560	60	493
TUR31		35070	108	325
TUR32		31800	113	281
TUR33		28770	253	114
<i>Average</i>		<i>31310</i>	<i>138</i>	<i>275</i>
nd - not detected				

5.5.3.4 Mineral partitioning

The distribution of halogens among Na-amphibole, phengite and lawsonite is varied across samples. In TUR30, F distributes evenly between amphibole and lawsonite (distribution coefficient, $D_{\text{Amp-Lws}}^{\text{F}}=1.0$), and Cl concentrates in lawsonite ($D_{\text{Amp-Lws}}^{\text{Cl}}=0.56$). However, in TUR32 and TUR33, F partitions into lawsonite ($D_{\text{Amp-Lws}}^{\text{F}}=0.16-0.87$) and Cl into amphibole ($D_{\text{Amp-Lws}}^{\text{Cl}}=1.67-1.87$). Phengite/lawsonite distribution coefficients reveal F preferentially partitions into phengite ($D_{\text{Ph-Lws}}^{\text{F}}=1.5$) and Cl into lawsonite ($D_{\text{Ph-Lws}}^{\text{Cl}}=0.65$) for sample TUR30, but the reverse is observed ($D_{\text{Ph-Lws}}^{\text{F}}=0.69$, $D_{\text{Ph-Lws}}^{\text{Cl}}=1.5$) for TUR33. The phengite/amphibole distribution coefficients for Cl cover a small range around ~1 (0.79-1.2, avg. 0.92), indicating equal partitioning in both minerals, whereas F preferentially concentrates in phengite ($D_{\text{Ph-Amp}}^{\text{F}}=1.5-4.4$, avg. 2.5) for all samples.

Fluorine concentrations in apatite are two to three orders of magnitude greater than in the hydrous minerals (Table 5-2). The partitioning of F between apatite and Na-amphibole is varied across all samples ($D_{\text{Ap-Amp}}^{\text{F}}=76-343$), more so than the distribution between apatite and lawsonite ($D_{\text{Ap-Lws}}^{\text{F}}=41-108$) or phengite ($D_{\text{Ap-Ph}}^{\text{F}}=52-77$). The distribution of Cl between apatite and Na-amphibole ($D_{\text{Ap-Amp}}^{\text{Cl}}=1.3-3.3$), lawsonite ($D_{\text{Ap-Lws}}^{\text{Cl}}=1.8-8.2$), and phengite ($D_{\text{Ap-Ph}}^{\text{Cl}}=1.7-3.6$) is similar for all three mineral pairings.

5.6 Discussion

5.6.1 Halogen concentrations in blueschists

Bulk rock halogen abundances were calculated based on the measured halogen concentrations of Na-amphibole, lawsonite, phengite and apatite along with their modal abundances in each sample. Calculated F and Cl values in bulk rock are generally in good

agreement with the measured bulk rock concentrations (Table A III-6; Table A III-7). This verifies that there are no other major halogen-rich phases in the blueschist samples.

5.6.1.1 Halogen uptake

Since the Tavsanlı zone blueschists are characterized by prograde mineral assemblages with very little retrogression (Table 5-1), halogens in these samples represent those deep in the subduction zone, as opposed to acquired during retrogression at shallow depths.

The presence of hydrous minerals and high Na in our samples are consistent with seafloor alteration prior to subduction, which should enrich Cl in basaltic rocks. However, the Cl content of these blueschists is much lower than that of the altered oceanic crust (e.g. 334 ppm; Sano et al. 2008), indicating that Cl may have been expelled before or during blueschist metamorphism. Very few studies have been carried out on the abundance of Br and I in oceanic crust. Since amphibole is considered to be the major host of halogens in altered mafic rocks, the halogen concentrations of secondary amphibole from oceanic metagabbros (Kendrick et al. 2015) are used to approximate altered oceanic crust. The Br content of the metagabbros (0.46-1.98 ppm) is comparable to the range of Br in unaltered MORB (0.26-3.12 ppm; Kendrick et al. 2012), and up to an order of magnitude higher than Br concentrations in the Tavsanlı Zone blueschists. This may suggest that like Cl, Br is lost from the slab during subduction, however, elevated Br/Cl ratios with respect to unaltered and altered MORB (Figure 5-7) may indicate preferential retention of Br in the down-going slab relative to Cl.

This study shows elevated abundances of I and F in bulk rock and mineral-rich fractions compared to the values in unaltered MORB (avg. 0.046 ppm I, Kendrick et al. 2012; avg. 147 ppm F, Le Roux et al. 2006) and altered oceanic crust (avg. 0.023 ppm I, Kendrick et al. 2015; avg. 216 ppm F, Straub & Layne 2003). Seawater concentrations of F and I are too low to explain this enrichment. A plausible source of F and I are sediments on the sea floor or near

subduction zones (e.g. John et al. 2011). High F values are reported in pelagic clays (up to 1300 ppm; Li 1982) and organic-rich sediments, in particular, contain high concentrations of I (e.g. Muramatsu et al. 2007). Following fluid circulation through overlying sediments near subduction zones, it is likely that the oceanic crust becomes enriched in F and I on the sea floor prior to subduction, or along bending-related extensional faults at the outer rise. In addition, a large supply of I-rich shallow water sediments would have been available given the close proximity of continents to this particular subduction zone.

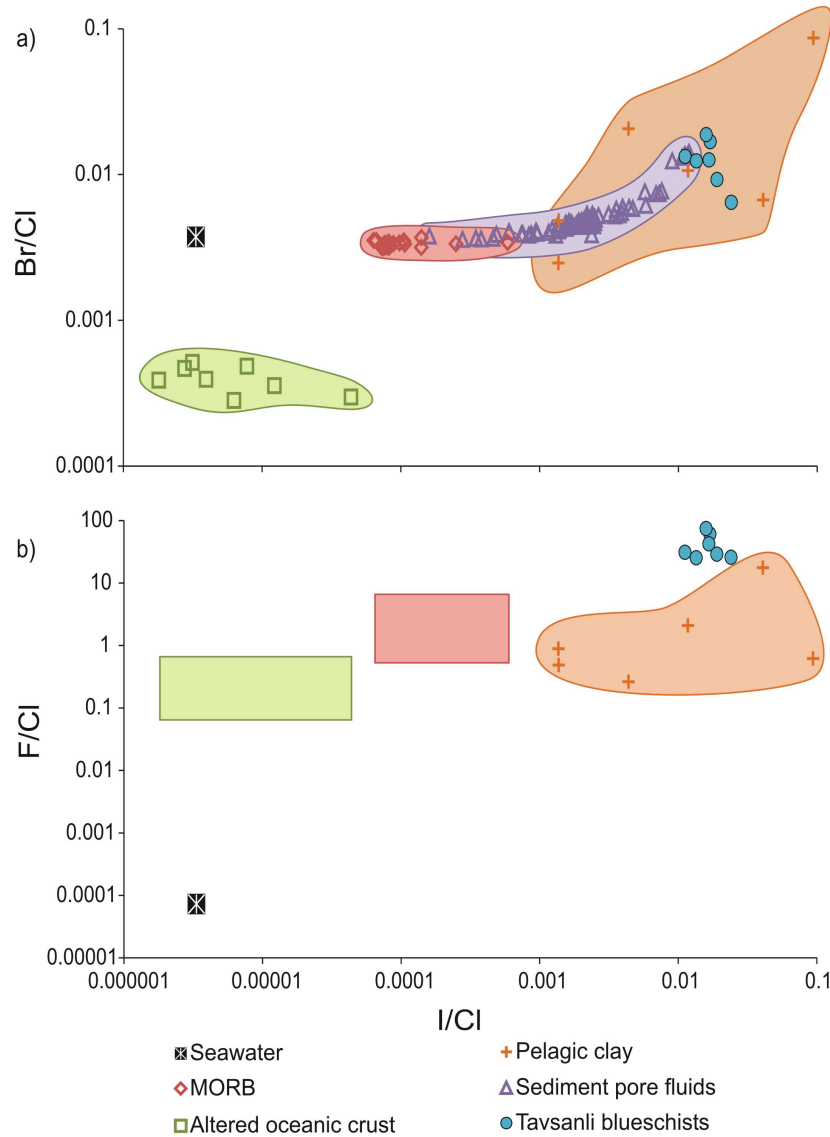


Figure 5-7: Compilation of halogen ratios in unaltered and altered oceanic crust, sedimentary marine reservoirs and Tavsanlı Zone blueschist bulk rocks. (a) Given the scarcity of bulk rock data for Br and I in altered oceanic crust, Br/Cl and I/Cl of secondary amphiboles in oceanic metagabbros (Kendrick et al. 2015) are used as a proxy for altered oceanic crust. The low Br/Cl ratios of the altered oceanic crust relative to unaltered MORB and seawater (Li 1982) suggest Cl is preferentially incorporated into amphibole over Br during hydrothermal alteration. Br/Cl and I/Cl ranges for MORB (Kendrick et al. 2012) overlap with the lower range of pore fluids of

marine sediments (Muramatsu et al. 2007). Pore fluid data extends to higher values, overlapping with incoming plate sediments (John et al. 2011), and the Tavsanlı zone blueschists analyzed in this study. (b) The F/Cl range for altered oceanic crust (Magenheim et al. 1995) is lower than that of unaltered MORB (Le Roux et al. 2006), but significantly elevated relative to seawater (Li 1982). F/Cl values of the Tavsanlı blueschists are higher than MORB values, and overlap with the upper range of incoming plate sediments.

5.6.1.2 Halogen fractionation

A positive correlation between Cl, Br and I in mineral fractions suggests an overall similar behaviour in subduction zones (Figure 5-6A,B). Conversely, F concentrations do not correlate well with the heavier halogens (Figure 5-6C). This difference in behaviour of halogens is attributed to the enhanced reactivity of F due to its smaller size and higher electronegativity. Of the four halogens, the ionic radius (1.33 Å) of F is most similar to that of OH⁻ (1.35 Å), making it most compatible for substitution in hydrous minerals. An additional mechanism for the incorporation of F into silicate minerals is the coupled substitution of Al³⁺ and F⁻ with Si⁴⁺ and O²⁻ (1.21 Å), as previously suggested to explain F uptake in pyroxenes (Mosenfelder & Rossman 2013). The elevated I/Cl, Br/Cl and F/Cl ratios of our samples relative to altered oceanic crust (Figure 5-7), suggest either I, Br and F are enriched in the crust prior to subduction, or these halogens are preferentially retained relative to Cl during subduction-related metamorphism.

5.6.2 Halogen partitioning between hydrous minerals

5.6.2.1 Chlorine

Chlorine preferentially partitions into phengite and Na-amphibole, with average concentrations for each mineral in all samples of 59 ppm for Na-amphibole, 56 ppm for phengite

and 27 ppm for lawsonite (Table 5-2). The low Cl content of lawsonite may be related to structural differences among the three minerals. Micas and amphiboles have appreciably more M^{2+} cations in their octahedral sites than lawsonite, which minimizes distortion of their hydroxyl sites and allows for greater substitution of Cl^- in the OH^- site (Volfinger et al. 1985). Furthermore, hydrogen bonding may also affect halogen uptake. Amphibole and phengitic muscovite have weak hydrogen bonding (Catlow & Wright 1999; Gatta et al. 2011), but lawsonite contains multiple hydrogen bonds (Libowitzky & Rossman 1996). Therefore, hydroxyl substitution may be less energetically favourable in lawsonite given the additional energy requirements to overcome these bonds.

5.6.2.2 Fluorine

In situ measurements reveal F preferentially concentrates in phengite (avg. 482 ppm) and lawsonite (avg. 482 ppm) over Na-amphibole (257 ppm). Fluorine may be more readily retained by phengite and lawsonite due an increase in the electrostatic attraction between F and interlayer K^+ in phengite and A-site Ca^{2+} in lawsonite. When F^- substitutes for OH^- , the reduced distance between the halogen and interlayer/cavity cations allows for a greater attraction between them. The Na-amphiboles, on the other hand, have vacancy in the A-site, and thus may not as readily retain F. Our results are in agreement with data from other eclogites showing higher F in phengite over co-existing amphiboles (e.g. Svensen et al. 2001).

5.6.2.3 Bromine and iodine

Partitioning of Br and I between co-existing minerals is evaluated from pyrohydrolysis extractions of amphibole- and lawsonite-rich fractions. Bromine concentrations appear uniform between both mineral phases in all samples, except for TUR33 in which the lawsonite concentrate has two times more Br. Iodine seems to preferentially partition into lawsonite, as observed by elevated concentrations in the lawsonite-rich fractions of TUR 30, 32 and 33. In

addition to substitution for OH⁻ groups, large cavities containing H₂O and Ca⁺ in lawsonite's structure may accommodate I ions.

5.6.3 *Halogens in apatite*

Apatite preferentially incorporates F from fluids (Spear & Pyle 2002), and the small F ion can easily fit in the columnar anion site, coplanar with the M2 cations. In contrast, Cl and OH ions are too large, and are displaced above or below the cation plane. With increasing pressure, the incorporation of small F is favoured. Since F is an essential component of fluorapatites, it is preferentially concentrated in apatite over other minerals, such as amphibole, lawsonite and phengite. The halogen abundance of apatite in our samples is similar to metamorphic apatite from Norwegian eclogites (Svensen et al. 2001). Measured F contents in phengite in our samples are similar, but those in Na-amphibole and lawsonite are higher than those in blueschist facies metagabbros reported by Debret et al (2016). Furthermore, their estimated bulk F contents based on concentrations in these minerals and their modal abundances are much lower than our measured values. The difference may be related to apatite since it is the major mineral phase hosting F in our samples, but is not considered in their calculations as their samples may contain low P.

5.6.4 *Implications for halogen recycling*

Low Cl concentrations recorded for all hydrous minerals in these samples imply that Cl is expelled at much shallower depths in the subduction zone. This is in good agreement with previous estimates that as much as 75% of the subducted Cl in rocks and pore fluids may be released from the accretionary prism at slab depth <15 km (Jarrard 2003). Metamorphism before or during the blueschist facies may also contribute to Cl loss from the subducting slab before 80 km depth. This proposed interpretation is supported by the broad correlation between bulk rock

Cl and As concentrations (0.5-2.2 ppm) (Figure A III-3). Since As is lost early from subducting slabs (< 35 km depth; Hattori et al. 2005), the evidence supports Cl loss in addition to other fluid-mobile elements during shallow subduction. Similarly low concentrations of Cl have been reported for bulk rock blueschists (60-300 ppm) and eclogites (30-60 ppm) from the island of Syros, Greece (Marschall et al. 2009).

In contrast, elevated F concentrations in these blueschists suggest F is retained during subduction to at least 80 km depth. A positive correlation between F and Be in our bulk rocks (Figure A III-3) supports this interpretation, since Be exhibits conservative behaviour during subduction-related dehydration reactions (Marschall et al. 2007).

Na-amphibole decomposition at < 90 km depth (associated with the blueschist-eclogite transition) has been proposed to contribute to partial melting for arc magmatism (Peacock 1993). However, the F/Cl ratios for Na-amphibole in these blueschists are higher than those reported for volcanic arc outputs and back-arc basin basalts (Figure 5-8), suggesting amphibole dehydration may not be the dominant source for these halogen signatures. Given the relatively shallow depth of dehydration, Na-amphibole is likely not relevant for the transfer of halogens to the deeper mantle. However, F in the amphibole structure may widen its stability to higher pressures and temperatures, allowing F-rich Na-amphibole to remain stable under eclogite facies conditions (Holloway & Ford 1975), and carry F to greater depths.

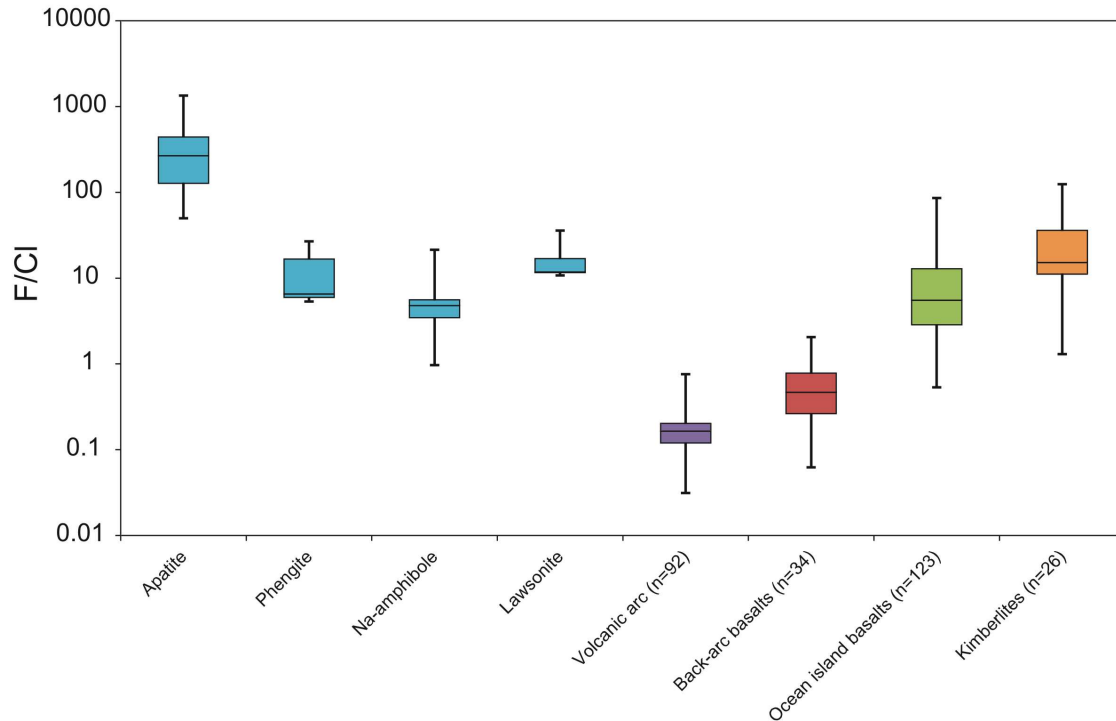


Figure 5-8: Box-and-whisker plot displaying the F/Cl ratios of apatite, Na-amphibole, lawsonite and phengite from the Tavsanlı Zone blueschists, northwestern Turkey. For comparison, F/Cl ratios for various magmas have been added. High F/Cl ratios of lawsonite and phengite suggest these minerals may provide a means for transporting F to the deep upper mantle, supplying magmas of deeper origin such as ocean island basalts (e.g. Hawaiian melt inclusions, Hauri 2002; Samoa glasses, Kendrick et al. 2015) and kimberlites (e.g. bulk rock from Greenland, South Africa and India, Paul et al. 1976). Volcanic arc data are from Lesser Antilles melt inclusions (Heath et al. 1998), Central American Arc pyroclastic rocks (John et al. 2011), and Izu Arc glasses and fallout tephra (Straub & Layne 2003). Back-arc basalt data are bulk rock data from the Lau Basin (Bezous et al. 2009).

The high F contents of lawsonite and phengite in this study are of particular interest given the wide stability of these minerals in cool subduction zones. Lawsonite is stable to 80-90 kbar,

and phengite to 100 kbar, at 900°C (Schmidt & Poli 1998). Once they decompose, the resulting fluids would have high F/Cl ratios. It is interesting to note that these ratios are comparable to melt formed at deep levels, including ocean island basalts (e.g. Hauri 2002, Kendrick et al. 2015), and kimberlites (e.g. Paul et al. 1976) (Figure 5-8), suggesting the importance of these minerals for the transfer of F to the deep mantle.

Despite not contributing to the water budget of subducting slabs, apatite is likely an important repository of halogens during HP metamorphism, transporting F (and some Cl) beyond subarc depths. Upon apatite breakdown at ~200 km, halogens in apatite may be released to the overlying mantle, or possibly incorporated into stable hydrous silicates such as phengite and lawsonite (Konzett & Frost 2009).

Chlorite (12 wt% H₂O) is present in variable abundance in all samples, and the texture and occurrence suggest it is a prograde product. Chlorite stability is primarily temperature dependent, and in cold subduction zones it may remain stable to 40+ kbar (~100+ km; Mookherjee & Mainprice 2014). Although we did not determine halogen contents in chlorite due to its intergrowth with other minerals, the bulk rock data for chlorite-rich TUR31 (582 ppm F, 8 ppm Cl) suggest chlorite likely contains F and Cl concentrations similar to the other hydrous minerals, and there is little partitioning of F and Cl between chlorite and other minerals.

Low Cl and high F content in the Tavsanlı Zone blueschists support previously proposed interpretation based on the halogen content of arc magmas that Cl is effectively liberated during subduction at shallow depths, whereas F is largely retained in the down-going slab beyond arc front depths (Straub & Layne 2003). Liberation of Cl during early subduction is also documented by expulsion of saline fluids from accretionary prisms (e.g. Godon et al. 2004). High I/Cl ratios of bulk samples and mineral separates suggest I may be fractionated from Cl during subduction, and like F, incorporated into hydrous minerals. Bromine may also be fractionated from Cl based

on slightly elevated Br/Cl ratios, but to a much lesser extent than F or I. Chlorine, and most Br, is likely released before or during blueschist metamorphism, whereas F is retained in phengite, lawsonite and apatite at blueschist depth. When apatite eventually breaks down at ~200 km, F may be redistributed to phengite and lawsonite, whereas minor Cl in apatite is most likely released to the overlying mantle wedge. Finally, at ~280-300 km in cold subduction zones, lawsonite and phengite decompose, releasing F to the deeper upper mantle.

5.6.5 *Conclusions*

Hydrous blueschist minerals of the Tavsanlı Zone contain high F and low Cl concentrations, suggesting F is preferentially retained, whereas Cl is lost at shallow depths (< 80 km) in subduction zones. A positive correlation between Cl, Br and I contents of the pyrohydrolysis extracts suggests Br and I may behave similarly to Cl in subduction zones, although high I/Cl and slightly high Br/Cl ratios relative to MORB indicate some fractionation of I and Br from Cl during subduction and blueschist facies metamorphism.

Chlorine partitioning among the four analysed minerals follows apatite>phengite≈Na-amphibole>lawsonite, and F partitioning follows apatite>>>phengite≈lawsonite>Na-amphibole. The halogens preferentially reside in apatite because they are accommodated in the M2 site. The eventual decomposition of apatite at ~200 km may lead to a redistribution of F into lawsonite and phengite. The accommodation of F in lawsonite and phengite suggests F may be transported by these minerals to a depth of 280-300 km in cold subduction zones, and may contribute to the high F content observed in deep mantle magmas, such as ocean island basalts and kimberlites.

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Chapter 6.

Abyssal Serpentinites: Transporting Halogens from Earth's Surface to the Deep Mantle

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Abstract

Serpentinized oceanic mantle lithosphere is considered an important carrier of water and fluid-mobile elements, including halogens, into subduction zones. Seafloor serpentinite compositions indicate Cl, Br and I are sourced from seawater and sedimentary pore fluids, while F may be derived from hydrothermal fluids. Overall, the heavy halogens are expelled from serpentinites during the lizardite–antigorite transition. Fluorine, on the other hand, appears to be retained or may be introduced from dehydrating sediments and/or igneous rocks during early subduction. Mass balance calculations indicate nearly all subducted F is kept in the subducting slab to ultrahigh-pressure conditions. Despite a loss of Cl, Br and I from serpentinites (and other lithologies) during early subduction, up to 15% of these elements are also retained in the deep slab. Based on a conservative estimate for serpentinite thickness of the metamorphosed slab (500 m), antigorite serpentinites comprise 37% of this residual Cl, 56% of Br and 50% of I, therefore making an important contribution to the transport of these elements to the deep mantle.

6.1 Introduction

The high water content and enrichment of fluid-mobile elements (FME) in arc magmas attest to their recycling from Earth's surface to the mantle. The subduction of hydrated rocks, including sediments, altered oceanic crust (AOC) and abyssal serpentinites, at convergent plate boundaries provides a mechanism for this recycling. Abyssal serpentinites, primarily composed of the hydrous phyllosilicate mineral serpentine, are formed by the hydration of mantle peridotites on or near the seafloor. Recent geophysical and geochemical data have emphasized their importance for a variety of subduction-zone-related phenomena, including seismic activity and the exhumation of ultrahigh-pressure (UHP) rocks [1]. Furthermore, the high water content (up to 13 wt%) and wide stability (>100 km) [2] of serpentinites make them effective vehicles for the transport of FME, including halogens, into the mantle. This article reviews the

incorporation of F, Cl, Br and I by the oceanic lithosphere during seafloor alteration and discusses the importance of abyssal serpentinites for halogen transfer from the Earth's surface to the deeper mantle.

6.2 Halogens as tracers of geological processes

The halogens (F, Cl, Br, I) are highly reactive, volatile elements primarily concentrating in Earth's surface reservoirs, such as seawater (Cl, Br) and sediments (F, Br, I). They are also abundant in arc magmas compared to oceanic ridge magmas [3–5]. In addition, high F contents have been reported in magmas originating from the deeper mantle, such as ocean island basalts (OIBs) [6] and kimberlites [7].

The halogens are relatively abundant in crustal rocks compared to mantle peridotites [8] because they are preferentially partitioned into the silicate melt during partial melting due to their incompatibility with mantle minerals. Chlorine, Br and I are also highly soluble in aqueous fluids, while the solubility of F is low [9]. Owing to its smaller size and higher electronegativity, F is far more compatible in hydrous and nominally anhydrous minerals than the other halogens [10–12]. As a consequence of their variable abundances and compatibilities, the halogens and their ratios (i.e., Br/Cl, I/Cl and F/Cl) are useful for tracing fluid sources and their migration in a variety of geological settings [13]. The halogens, particularly Cl, are also important ligands to form soluble metal complexes that contribute to metal transport and formation of metal deposits [14].

6.3 Abyssal serpentinite formation

The composition and structure of the oceanic lithosphere is primarily controlled by the spreading rate along the Earth's >67,000 km [15] of oceanic ridges. At fast-spreading ridges (>5 cm/yr) [16], the rate of magma supply exceeds that of plate divergence, and large quantities of

mafic magmas are generated. This produces the classic “Penrose” style of oceanic lithosphere [17] where layers of pillow basalts, sheeted dykes and layered gabbros are overlain by variable sediment cover and underlain by mantle peridotite [18] (Figure 6-1A). This transition from gabbro to peridotite at ~6–7 km depth represents the seismic Mohorovicic discontinuity (Moho) [18]. Hydrated mantle peridotites are observed along fractures and faults, which expose deep sections of oceanic lithosphere, such as Siqueiros Fracture Zone [19].

In contrast, the oceanic lithosphere produced in slow- (2–5 cm/yr) and ultraslow- (<2 cm/yr) [16] spreading ridges, such as the Mid-Atlantic Ridge (MAR) and South West Indian Ridge (SWIR), is much more heterogeneous [18]. It is characterized by sea floor exposure of variably serpentinized mantle peridotite overlain by a thin layer of pillow basalt and sheeted dykes, as described for the MAR [20], or a tectonically thinned out layer of volcanic rocks underlain by up to 3 km of extensively serpentinized peridotite, as described for the SWIR [21] (Figure 6-1B). The rifting of plates at the ridges exposes mantle peridotites to hydration by seawater or submarine hydrothermal fluids yielding abyssal serpentinites, which may comprise up to 25% of the oceanic lithosphere formed at slow-spreading ridges [22]. In these cases, the seismic Moho at shallower depths (1–4 km) may represent the serpentinization front [23].

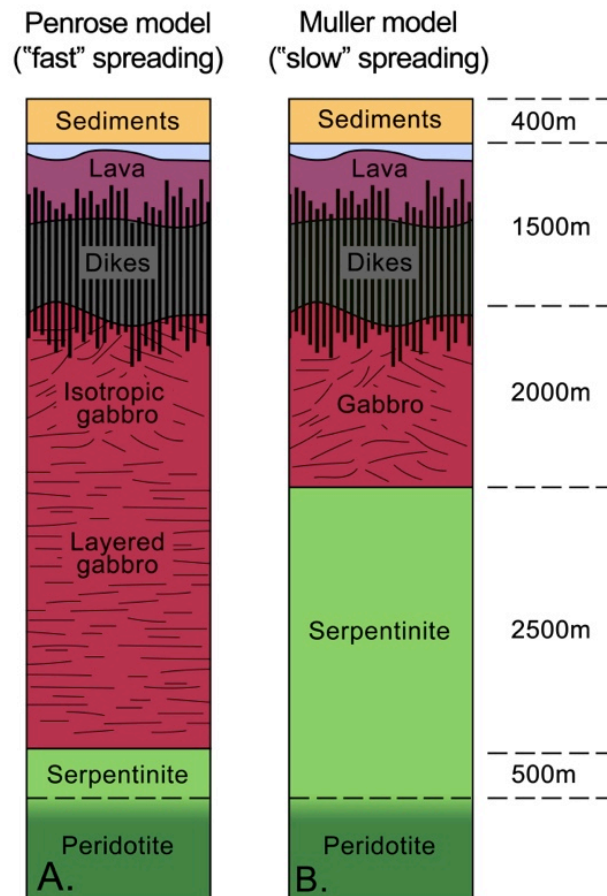


Figure 6-1: Simplified schematic diagram of representative cross sections of oceanic lithosphere produced at (A) fast- [17] and (B) slow- [21] spreading ridges. Serpentinite in the diagram represents either concentrated zones of serpentinization or diffuse serpentinization throughout the upper lithospheric mantle [24]. Oceanic lithosphere produced at slow- and ultraslow-spreading ridges is particularly heterogeneous, with serpentinites commonly outcropping on the ocean floor [20,22].

In addition to ridges, abyssal peridotites are hydrated at the outer rise near trenches by fluid infiltration along faults in the bending slab [25,26] (Figure 6-2). Estimates for the volume of abyssal serpentinites entering subduction zones range from a conservative 1–2% of the upper

10 km of lithospheric mantle [6] to 15% of the upper 30 km [26]. Serpentinization can also occur in mantle wedges by fluids released from subducting slabs [27] (Figure 6-2).

The formation of low-temperature (LT) serpentine phases, chrysotile and lizardite, occurs at temperatures below 400 °C [32]. The varieties of serpentine phases are due to the different ways for the mineral to adjust geometric strain between the tetrahedral and octahedral sheets [33]. Conditions that favour chrysotile formation over lizardite include a high water/rock ratio, isotopic shear stress and the hydration of microenvironments, such as veins and pores [32]. In close proximity of oceanic ridges, the fluid is dominated by seawater, as evidenced by serpentine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to that of present-day seawater [34]. Oxygen isotope compositions are also used to evaluate the nature of the hydrating fluid. For example, most serpentinites have $\delta^{18}\text{O}$ signatures between that of seawater (0‰_{SMOW}) and anhydrous peridotites ($\sim +5\text{--}6\text{‰}_{\text{SMOW}}$) [35]. However, some serpentinites formed at fast-spreading ridges, such as Hess Deep, have higher $\delta^{18}\text{O}$ values ($\sim 7\text{‰}$), interpreted as evidence for hydration by evolved seawater, with possible contribution of magmatic fluids [36]. The existence of magmatic fluids at Hess Deep is also suggested by low $\delta^{13}\text{C}$ (-7.8‰ to -4.5‰) compared to 0‰ for dissolved carbonate in sea water and consistent with magmatic values [36]. During its transport from ridges to subduction zones, abyssal sediments deposit on the oceanic lithosphere. These abyssal sediments, and those derived from the overlying plate through erosion near trenches, can also influence the composition of serpentinization fluids along bend-related faults of the outer rise or within the subduction channel at shallow depths [37].

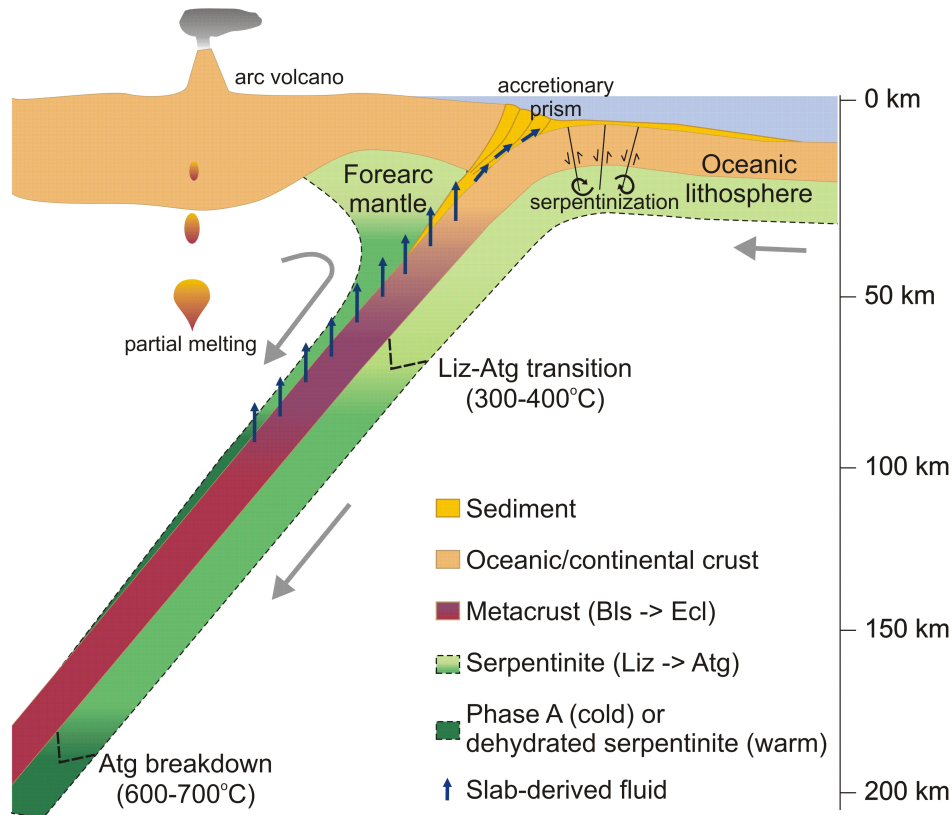


Figure 6-2: Schematic cross section of a cold subduction zone. Serpentinization of abyssal peridotite occurs on or near the seafloor and along fractures of the bending slab at the outer rise [25,26]. The approximate depths of the lizardite (Liz)–antigorite (Atg) transition [28] and antigorite decomposition [2] are based on a geothermal gradient of $\sim 5^\circ\text{C}/\text{km}$ [29]. In cold subduction zones, fluids and fluid-mobile elements may persist in hydrous phase A after antigorite breakdown [30,31]. Bls: blueschist; Ecl: eclogite.

6.4 Incorporation of halogens by abyssal serpentinites

Serpentinization of abyssal peridotites is characterized by moderate to strong enrichment of many FME, including halogens [38-48]. In situ analyses of serpentine grains from modern seafloor and obducted abyssal serpentinites show that concentrations of structurally bound Cl cover a large range (80 to 6000 ppm) [38,39,41,47], with an average of ~ 1500 ppm. This

structurally bound Cl is considered to reside in the OH⁻ site of serpentine minerals [39]. Bulk rock analyses of abyssal serpentinites average slightly higher at ~2500 ppm Cl (Figure 6-3A) [40,42,44,46,49]. This extra Cl in the bulk rock data is likely in the form of Cl along grain boundaries [40].

The variable uptake of Cl by serpentinites has been attributed to several factors, including water/rock ratio, fluid salinity, primary minerals (i.e., olivine versus pyroxene) and temperature. Preliminary studies suggested different Cl contents of bulk serpentinites were the result of different water/rock ratios [42]; however, this is debated because of comparable Cl contents among serpentine grains from partially (20%) and fully serpentinized abyssal peridotites [47]. Furthermore, experimental serpentine products show similar Cl concentrations regardless of the water/rock ratio during the hydration of peridotites [50]. Fluid salinity also appears to have a negligible impact on the uptake of structurally bound Cl [50]; however, when Cl-poor serpentinites are equilibrated with saline fluids at ambient temperature and pressure, the uptake of structurally bound Cl in the serpentinites is proportional to the fluid salinity [51]. Chlorine contents have been shown to be higher in serpentine after orthopyroxene (bastite textures) compared to serpentine after olivine (mesh textures) in natural and experimental samples [39,49,51]. Compared to olivine, orthopyroxene contains significant Al replacing Si in the tetrahedral site [52]. Since Al has a larger ionic radius than Si, the substitution of Al for tetrahedral Si in lizardite reduces the distortion between the smaller tetrahedral and larger octahedral layers, which may allow the accommodation of the larger Cl ion (1.82 Å) in the OH⁻ site. The influence of temperature on Cl uptake is illustrated by an increase in the Cl content in serpentinite with increasing temperature up to a maximum of 200 °C and then a decrease in Cl contents at higher temperatures (300–500 °C) [50].

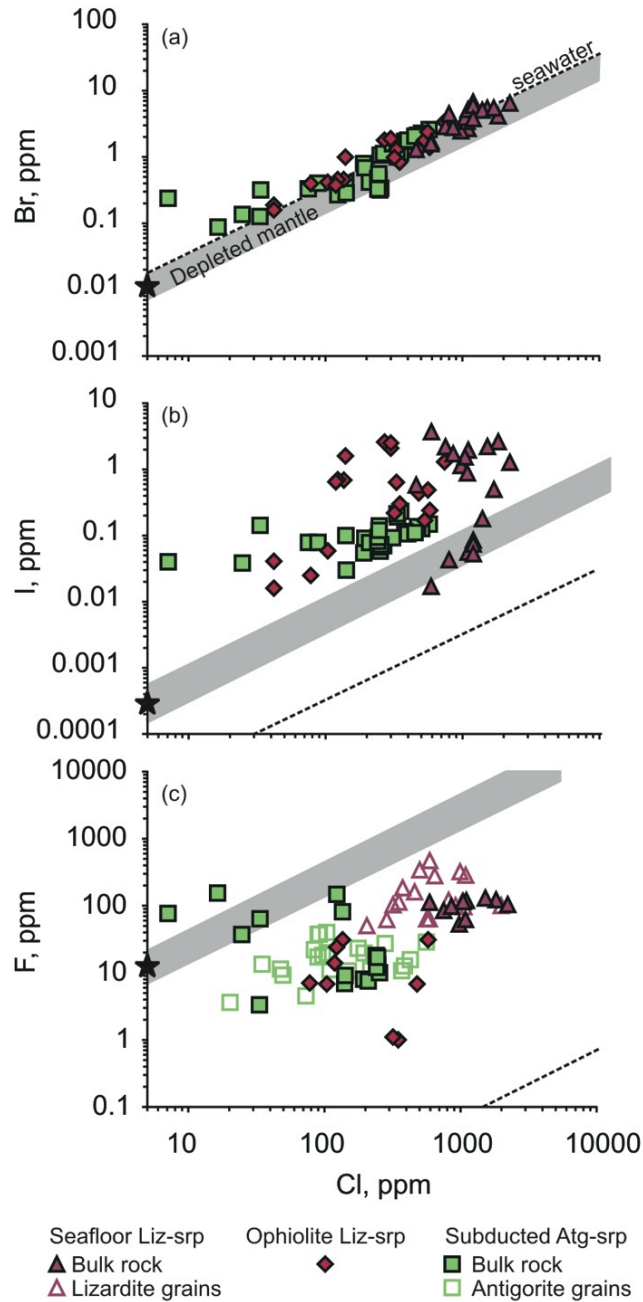


Figure 6-3: Halogen concentrations of seafloor and obducted abyssal lizardite serpentinites (Liz srp) and subducted antigorite serpentinites (Atg srp). Bulk serpentinite data are from [43,44,49,53]. In situ data of serpentine grains are from [34,43]. The F/Cl, Br/Cl and I/Cl ratios of the depleted mantle (grey fields) [6] and seawater (dashed lines) [54] are shown, along with the average concentrations of F, Cl, Br and I in the depleted mantle (black stars) [6]. Figures

modified after [55]. (a) Bromine and Cl concentrations in all serpentinites are elevated with respect to the average depleted mantle but are strongly correlated along a linear trend defined by the Br/Cl ratio of the mantle and seawater, suggesting their coherent behaviour during serpentinization (hydration) and subduction (dehydration). On average, the obducted abyssal serpentinites having lower Br and Cl concentrations than the seafloor samples, and the subducted serpentinites have lower concentrations than the obducted samples. (b) All samples have elevated I concentrations with respect to the depleted mantle, and most samples also have I/Cl ratios greater than the mantle. Iodine and Cl broadly correlate among the seafloor and obducted abyssal serpentinites. The seafloor and obducted abyssal serpentinites have similar I concentrations, while their subducted counterparts extend to lower values. (c) Individual lizardite grains have higher F content than antigorite, but bulk rock values for lizardite- and antigorite serpentinites are similar. The higher F content of some subducted serpentinites may indicate an influx of F during antigorization from other dehydrating lithologies.

In contrast to Cl, there are fewer data available for Br and I in serpentinites due to their much lower concentrations. Electron microprobe analyses can determine the Cl content of most serpentine grains but not Br and I; therefore, data of these elements is mostly limited to bulk rock compositions. Recent bulk rock analyses suggest concentrations of 0.16–6.8 ppm Br (avg. 1.2 ppm; Figure 6-3A) and 0.016–2.6 ppm I (avg. 0.78 ppm; Figure 6-3B) in seafloor and obducted abyssal serpentinites [44,48,53]. Abyssal serpentinites have similar Br/Cl ratios to that of seawater, but their I/Cl ratios are much higher and overlap with those of sedimentary pore fluids (Figure 6-4A), suggesting a considerable contribution of sediments to serpentinizing fluids of abyssal serpentinites.

Few reports document the bulk F content in modern seafloor and obducted abyssal serpentinites. Obducted abyssal serpentinites in Tertiary subduction complexes in Dominican Republic and the Alps have concentrations (7–31 ppm F) [48,53] similar to those of the depleted mantle (12 ± 2 ppm) [6], whereas seafloor serpentinites from the Logatchev Hydrothermal Field along the Mid-Atlantic Ridge are enriched in F (50–130 ppm; Figure 6-3C). A similar enrichment is also observed for individual serpentine minerals from Logatchev and the Mid-Atlantic Ridge Kane (MARK) fracture zone (50 to 470 ppm; Figure 6-3C) [38,47]. The variable enrichment of F in abyssal serpentinites likely reflects the composition of the serpentinizing fluid. Seawater is generally low in F (<2 ppm) [54]; therefore, abyssal peridotites primarily hydrated by seawater are also expected to be low in F relative to the other halogens. On the contrary, abyssal serpentinites formed near volcanic centres, such as Logatchev and the MARK area, may have elevated F contents and F/Cl ratios due to a contribution of hydrothermal fluids from volcanic rocks, which have been shown to have higher F/Cl ratios than seawater (Figure 6-4B) [56].

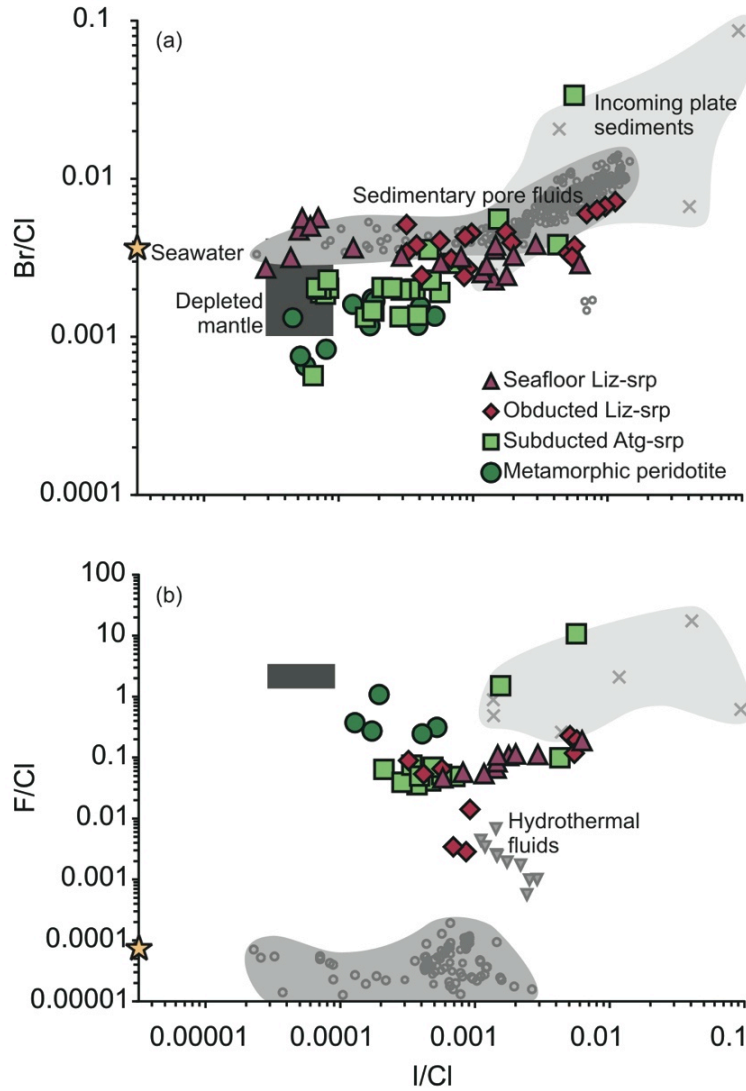


Figure 6-4: Halogen ratios of seafloor and obducted abyssal lizardite serpentinites (Liz srp), subducted antigorite serpentinites (Atg srp) and metamorphic peridotites after serpentinite dehydration. Bulk serpentinite data are from [43,44,48,53]. (a) Br/Cl and I/Cl ratios of the seafloor and obducted abyssal serpentinites overlap with those of sedimentary pore fluids (see [24] for review), while the Br/Cl ratios of the subducted serpentinites and metamorphic peridotites extend to lower values, similar to the depleted mantle [6]. (b) F/Cl ratios of all serpentinites are much higher than seawater [54], suggesting input from F-rich hydrothermal fluids (e.g., Escanaba Trough high $^3\text{He}/^4\text{He}$ pore fluids) [56] on the seafloor, or F mobilized from

incoming plate sediments [53] and igneous lithologies during shallow subduction. On average, the subducted antigorite serpentinites and metamorphic peridotites have higher F/Cl ratios relative to their lizardite-bearing counterparts.

Additional F enrichment may occur during serpentinization at the outer rise or within the shallow subduction channel by F mobilized from overlying sediments or igneous lithologies. In general, F content and F/Cl ratios of sediment pore fluids are low (similar to seawater) due to the low solubility of F in aqueous fluids [9]. However, enrichment of F in water is expected during the dissolution of marine carbonates in water below the carbonate compensation depth, which contain up to 1700 ppm F [57] and high F/Cl ratios (~4–8) [58].

Similar to the heavy halogens, F is considered to reside in the serpentine OH^- site, but it may also be incorporated into the O^{2-} site due to their similar ionic radii. Charge imbalance is compensated for by the coupled substitution of Al^{3+} and F^- (1.33 Å) with Si^{4+} and O^{2-} (1.21 Å), as suggested for F in pyroxenes [10].

Recently published halogen budget calculations for a representative section of the oceanic lithosphere are based on a Penrose-type oceanic lithosphere typically produced at fast-spreading ridges [24]. It comprises 400 m of mature or lithified marine sediment, 1500 m of pillow basalts and sheeted dykes, 4500 m of gabbros and 500 m of serpentinites. In this model, serpentinites contribute 31% of the total I in the lithosphere, 23% Br, 26% Cl and 2% F (Table 6-1; Figure 6-5). However, the degree of serpentinization is still poorly constrained, and this is considered a conservative lower limit for the contribution of serpentinites to the overall halogen budget of the oceanic lithosphere. Oceanic lithosphere produced at slow-spreading ridges likely contains a much larger volume of abyssal serpentinites. If we apply the Muller model [21] for oceanic lithosphere produced at slow-spreading ridges, which comprises up to 3000 m of

serpentinized mantle peridotites, the contribution of serpentinites increases to 73% for I, 69% for Br, 78% for Cl and 14% for F (). Mass balance calculations for a convergence rate of 5 cm/yr, bulk plate density of 2.8 g/cm³ and global trench length of 44,000 km [3] yield a global F influx of 6.41×10^{12} g/yr regardless of the model used (Table 6-1). On the contrary, the total global influx of Cl, Br and I entering subduction zones with the Muller model (3.55×10^{13} g/yr) doubles in comparison to that with the Penrose model (1.79×10^{13} g/yr; Table 6-1), illustrating the importance for constraining the volume of serpentinites entering subduction zones.

Table 6-1: Summary of global mass balance calculations.

	Thickness	Average Concentration (μg/g)				Global Flux (g/yr)			
	(m)	F	Cl	Br	I	F(×10 ¹²)	Cl(×10 ¹²)	Br(×10 ⁹)	I(×10 ⁹)
Penrose model ¹									
Incoming slab ²									
Sediment	400	1000	700	12	4.0	2.5	1.7	30	9.9
AOC, layer 2	1500	260	160	0.3	0.02	2.4	1.5	2.8	0.2
AOC, layer 3	4500	50	360	0.7	0.01	1.4	10	19	0.3
Liz serpentinite	500	50	1500	5.0	1.5	0.2	4.6	15	4.6
Bulk lithosphere	6900	151	419	1.6	0.4	6.4	18	67	15
% in sediment						38	10	44	66
% in AOC						59	64	33	3
% in serpentinite						2	26	23	31
Metamorphosed slab									
Metasediment ³	400	289	22	0.07	0.1	0.7	0.1	0.2	0.2
Eclogitic basalt ⁴	1500	341	18	0.006	0.0005	3.2	0.2	0.1	0.004
Eclogitic gabbro ⁴	4500	90	37	0.06	0.0007	2.5	1.0	1.8	0.02
A serpentinite ⁵	500	42	235	0.8	0.09	0.1	0.7	2.6	0.3
Bulk lithosphere	6900	153	46	0.1	0.01	6.5	2.0	4.6	0.5
% in sediment						11	3	4	45
% in AOC						87	60	40	4
% in serpentinite						2	37	56	50
% retained in slab						101	11	7	4
Muller slow-spreading model ⁶									
Incoming slab									
Sediment	400	1000	700	12	4.0	2.5	1.7	30	9.9
AOC, layer 2	1500	260	160	0.3	0.02	2.4	1.5	2.8	0.2
AOC, layer 3	2000	50	360	0.7	0.01	0.6	4.4	8.6	0.1

	Thickness (m)	Average Concentration ($\mu\text{g/g}$)				Global Flux (g/yr)			
		F	Cl	Br	I	F($\times 10^{12}$)	Cl($\times 10^{12}$)	Br($\times 10^9$)	I($\times 10^9$)
Liz serpentinite	3000	50	1500	5.0	1.5	0.9	28	92	28
Bulk lithosphere	6900	151	832	3.1	0.9	6.4	35	133	38
% in sediment						38	5	22	26
% in AOC						47	17	9	1
% in serpentinite						14	78	69	73
Metamorphosed slab									
Metasediment	400	289	22	0.07	0.1	0.7	0.1	0.2	0.2
Eclogitic basalt	1500	341	18	0.006	0.0005	3.2	0.2	0.1	0.004
Eclogitic gabbro	2000	90	37	0.06	0.0007	1.1	0.5	0.8	0.01
Atg serpentinite	3000	42	235	0.8	0.09	0.8	4.3	16	1.6
Bulk lithosphere	6900	135	118	0.4	0.04	5.7	5.0	17	1.8
% in sediment						12	1	1	13
% in AOC						74	12	5	1
% in serpentinite						13	87	94	86
% retained in slab						90	14	12	5

¹ Thicknesses of lithological units from [24]; ² Compilation of halogen concentrations of sediments, AOC and lizardite serpentinites of incoming slab from [24] and references therein; ³ Himalayan Tso Moriri UHP sediments (unpublished data of Page, Hattori and Guillot, 2019 [Appendix IV]); sampling and bulk chemistry described in [59]; halogen contents determined using methodology described in [48,60]; ⁴ Halogen data for eclogitic basalt and gabbro from Western Alps [61]; ⁵ Halogen data for antigorite serpentinites from Dominican Republic and Western Alps [48,53]; ⁶ Thicknesses of lithological units from [21]; AOC: altered oceanic crust; Liz: lizardite; Atg: antigorite.

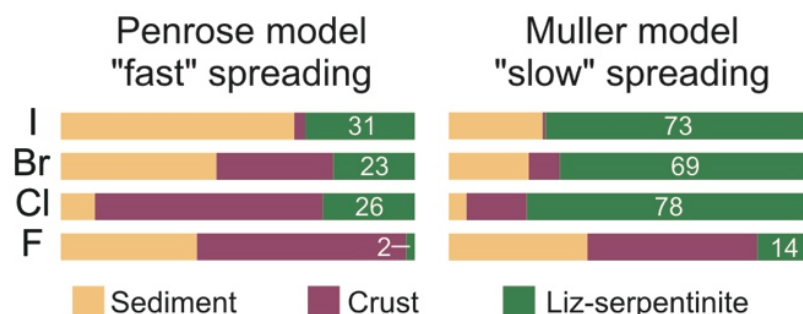


Figure 6-5: Summary of F, Cl, Br and I budget calculations for an incoming slab according to Penrose-type and Muller-type models of oceanic lithosphere produced at fast- and slow-spreading centers, respectively. The Penrose model consists of 400 m sediment, 6000 m igneous crust and 500 m lizardite serpentinites. The Muller model consists of 400 m sediment, 3500 m igneous crust and 300 m lizardite serpentinites. Average halogen concentrations for each unit are reported in Table 1. Numbers in bars denote the percent contribution of serpentine to the total budget for each element.

6.5 Halogen behaviour during serpentinite subduction

Available data of FME for subducted abyssal serpentinites are mostly from oceanic lithosphere produced at slow-spreading ridges, such as serpentinites of the Greater Antilles extinct arc in Dominican Republic [48], ophiolitic massifs of the Western Alpine–Northern Apennine chain in Italy [41,43,44,47,53] and the Cerro del Almirez massif in Spain [55]. Buoyant oceanic lithosphere formed at such slow-spreading ridges subducts at shallow angles and forms accretionary prisms, where the upper portion of the incoming oceanic lithosphere with sediments is scraped off and obducted [62]. The remaining serpentinites (and oceanic crust) are subducted to form subducted abyssal serpentinites. The FME data of abyssal serpentinites from fast-spreading ridges are virtually nonexistent, with the exception of those from Hess Deep of the Pacific plate [36]. To date, there is no data for their subducted equivalents; however,

serpentinization of oceanic lithosphere from fast-spreading ridges is suggested along deep fracture zones and during infiltration of fluids along extensional faults at the outer rise [26]. These serpentinites likely reside much deeper in the oceanic lithosphere, stay cooler for much longer than those near the top of the slab and as a consequence may transport FME even deeper in the mantle than summarized in this section.

6.5.1 *Lizardite–Antigorite Transition*

During shallow (<15 km) subduction, abundant water is expelled from sediments during their compaction and refluxed back to the Earth's surface (Figure 6-2) [63,64], but water structurally bound in hydrous minerals remains in subducting metasediments, altered oceanic crust and serpentinites. As the slab descends, the lizardite +/- chrysotile transition to antigorite occurs at ~300–400 °C [28] and is considered to be accompanied by the release of additional water [32] and certain FME [65]. This is supported by much higher concentrations of Cl, Br and I in seafloor and obducted abyssal lizardite serpentinites than subducted abyssal antigorite serpentinites [41,48,53,55]. This is also in agreement with lower Cl contents in other subducted lithologies (i.e., metasediments and metabasites) compared to their pre-subduction equivalents [60,66–68]. The transition is temperature-dependent. Therefore, it may occur at relatively shallow depths, 20–30 km, in warm subduction zones (~15 °C/km), or much deeper (60–80 km) in cold subduction zones (~5 °C/km; Figure 6-2).

Some antigorite serpentinites display lower Br/Cl and I/Cl ratios compared to their lizardite-bearing counterparts (Figure 6-4A), suggesting a preferential loss of Br and I relative to Cl during the serpentine phase transition [44,53,55], whereas others have slightly higher ratios (Figure 6-4A) [48]. Given the limited data available for HP serpentinites and the uncertainty regarding the exact composition of their protoliths, it is difficult to fully assess these subtle differences in halogen behaviour. The wide range of serpentinite compositions likely reflects

variations in the timing and sources of serpentinization. Differences in halogen behaviour may also be attributed to different geothermal gradients and, consequently, varying depth of stability of host minerals among subduction zones. Regardless of these differences, overall, all studies indicate a loss of the heavy halogens during the transformation to antigorite. The halogens released from the slab during shallow subduction may be refluxed back to the ocean or transferred to the overlying mantle wedge where they are incorporated into forearc mantle serpentinites. Shallow (<25 km) forearc serpentinites have elevated halogen concentrations relative to the depleted mantle [44,48,69,70]. These serpentinites are considered an important transient reservoir for the halogens and other FME in the mantle wedge [71], and their dehydration in the deeper mantle may influence partial melting and volcanic front formation, as indicated by their similar FME enrichment patterns to those of arc magmas [27].

In contrast to the heavy halogens, bulk F contents of subducted abyssal antigorite serpentinites are similar to, if not higher than, those of obducted abyssal lizardite serpentinites (Figure 6-3C) [48,53]. Antigorite serpentinites also have consistently higher F/Cl ratios (Figure 6-4B), indicating a preferential retention of F and/or an additional influx during antigorite formation. During subduction, additional F may be mobilized from metasedimentary or crustal rocks. The improved accommodation of F relative to the heavier halogens is attributed to its smaller size and the crystallographic differences of lizardite and antigorite. In lizardite, the entire Si–O tetrahedral sheet is distorted to match the Mg–O octahedral sheet, resulting in a flat crystal structure, but in antigorite, individual Si–O tetrahedra are periodically reversed, yielding a more wavy structure with stronger bonds between layers and a tighter crystal structure overall [33]. As a result, the larger halogens may be more readily expelled from the hydroxyl sites during the phase transition [69], while the smaller F ion (1.33 Å), which has a similar ionic radius to OH[−] (1.35 Å), is more likely to remain in the antigorite crystal structure. The retention of F in

serpentine minerals during this transition is supported by in situ analyses of coexisting lizardite and antigorite grains from Western Alps that show similar F content in both serpentine phases [47].

6.5.2 *Antigorite Dehydration*

As the slab subducts farther into the mantle, antigorite eventually dehydrates to metamorphic peridotite at ~600–700 °C [2]. In warm subduction zones, this corresponds to a slab depth of ~80 km [30], but in cold subduction zones, the geothermal gradient is much smaller (~5 °C/km) [29], and abyssal serpentinites are thermodynamically stable to depths >150 km (Figure 6-2) [30,31]. Cold subduction zones are also characterized by much thicker oceanic lithosphere, resulting in a larger temperature difference (~200 °C) between the top and bottom of the slab [29]. Consequently, serpentinites of the lower section of the slab may remain stable to depths >200 km.

The dehydration of antigorite is accompanied by the release of fluids that become progressively depleted in Br and I relative to Cl [43,53], suggesting Br and I are preferentially lost during the early stages of antigorite breakdown. These fluids may be incorporated into the overlying mantle wedge, as evidenced by similar Br/Cl and I/Cl ratios to fluids in deep mantle wedge peridotites [72]. Yet, some Cl (<160 ppm), Br (<0.2 ppm) and I (<0.07 ppm) are retained in the dehydrated peridotite residues of subducting slabs and likely contained in desiccated fluid inclusions of olivine and pyroxene [55].

Fluorine residing in the antigorite OH⁻ site is also expected to be released during serpentinite dehydration, but F in the O²⁻ sites may be retained in nominally anhydrous minerals after antigorite decomposition. Indeed, high F (up to 130 ppm) has been reported in secondary olivine after antigorite decomposition [73]. The higher F in bulk HP serpentinites may also be attributed to the occurrence of Ti-clinohumite [53], a F-bearing accessory mineral of HP

ultramafic rocks [74], or contained in chlorite as observed for the Cerro del Almirez (Spain) metamorphic peridotites [55].

6.6 Halogen transfer to the deeper mantle

Preliminary mass balance calculations suggest nearly all subducted Cl is returned to surface reservoirs through arc volcanism [3,63]; however, these studies do not account for the significant Cl in abyssal serpentinites. More recent calculations that include abyssal serpentinites suggest inputs of Cl (and Br and I) in subduction zones may exceed volcanic outputs [53,75], and they also support the retention of nearly all subducted F (up to 95%) beyond subarc depths. Here we show that subducted serpentinites are an important reservoir for halogens in the metamorphosed slab and a vehicle for their transport to the deeper mantle. Considering a model for oceanic lithosphere produced at fast-spreading ridges [24], serpentinites of 500 m thickness constitute 50% of residual I, 56% of Br, 37% of Cl and 2% of F in the eclogitized slab (Table 6-1; Figure 6-6). Yet, as previously mentioned, the volume of serpentinitized peridotites entering subduction zones is not well defined. If serpentinite thickness is considered to be 3000 m, which is more representative of oceanic lithosphere produced at slow-spreading ridges [21], the serpentinite contribution increases to 86% for I, 94% for Br, 87% for Cl and 13% for F (Table 6-1; Figure 6-6).

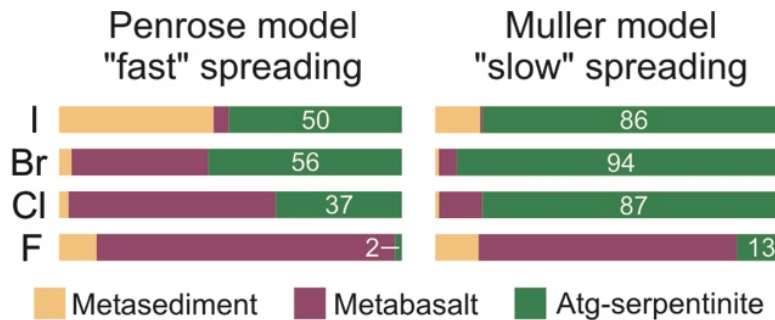


Figure 6-6: Summary of F, Cl, Br and I budget calculations for a metamorphosed slab according to Penrose-type and Muller-type models of oceanic lithosphere. See Figure 6-1 for descriptions of unit thicknesses. Average halogen concentrations for each unit are reported in Table 1. Numbers in bars denote the percent contribution of serpentinite to the total residual halogens in the slab.

Mass balance calculations confirm nearly all F is retained to HP-UHP conditions and suggest up to 14% Cl, 12% Br and 5% I may also be retained to such depths in the mantle, presumably beyond subarc depths (Table 6-1). These findings are in agreement with previous evidence for halogen retention beyond the depth of arc fronts based on their concentrations and ratios in magmas from the deeper mantle, including back-arc basin basalts (BABB) and ocean island basalts (OIB) [76–78]. Despite a loss of Cl, Br and I during early subduction, HP antigorite serpentinites can still retain appreciable amounts of these elements, along with significant F, compared to their peridotite protoliths [43,48,49,55,71]. Given its stability to ~200 km in cold subduction zones, antigorite may provide a reservoir for these elements to depths beyond those associated with most volcanic arcs (~100 km) [79], and some water and FME may be transported even deeper (up to 300 km) by hydrous phase A after antigorite decomposition (Figure 6-2) [31].

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Chapter 7.

Halogens in eclogites of the Tso Moriri UHP unit and Sulu UHP belt: Implications for the recycling of F to the deep mantle

Lilianne Pagé, Keiko Hattori, Stéphane Guillot and Jian Wing

Abstract

We examined halogen (F, Cl, Br, I) abundances of eclogitic rocks from the Tso Morari ultra-high pressure (UHP) unit in eastern Ladakh, NW Himalaya and the Sulu UHP belt in NE China to evaluate their behaviour in subduction zones and identify minerals that may contribute to their transport to the deeper mantle. Bulk samples contain variably low Cl (<100 ppm) and Br (<0.3 ppm) compared to their presumed protoliths of plume-related and arc basalts, respectively, but they have similar Br/Cl ratios, suggesting coherent loss of Cl and Br from the subducting slab prior to or during eclogite facies metamorphism. Iodine contents of the Tso Morari eclogites (<0.3 ppm) are slightly elevated relative to plume-related basalts, while I contents of the Sulu eclogites (<0.004 ppm) are lower than those of arc rocks. Fluorine contents of the eclogites (<400 ppm) are similar to their presumed protoliths, but lower than blueschists rocks, likely reflecting the dehydration of halogen-bearing amphibole during eclogitization. Broad positive correlations between bulk F and P_2O_5 and K_2O suggest apatite and phengite likely control the bulk halogen concentrations in these rocks. *In situ* analyses support this interpretation with high F in apatite (up to 2.3 wt%) and phengite (1600 ppm). Combined, apatite and phengite constitute up to 97% of the total bulk F. These results show that Cl and Br are expelled from subducting slabs at shallow depths, whereas F and some I are retained or added during shallow subduction. Given the stability of apatite and phengite to depths of 200 and 300 km, respectively, they may transport F beyond subarc depths and contribute to magmas formed in the deeper mantle.

7.1 Introduction

Volcanoes and associated processes are responsible for the continual flux of volatiles out of the Earth's mantle. Subduction at convergent plate boundaries provides a mechanism for recycling volatiles from the hydrosphere into the mantle where dehydration of the subducting slab supplies fluids to the overlying mantle wedge for arc magma generation. However, some

volatiles may be retained to much deeper in the mantle. For example, the recent discovery of hydrous inclusions in kimberlitic diamonds provides direct evidence that the transition zone of the deep mantle contains significant water (Pearson et al., 2014). The transition zone may also accommodate halogens (Roberge et al., 2015). The halogens have also been detected in deep-seated magmas, such as ocean island basalts (Kendrick et al., 2017), kimberlites (Kjarsgaard et al., 2009) and komatiites (Sobolev et al., 2016). Water and other volatiles may have become concentrated in the Earth's deep mantle during accretion (e.g., Albarede, 2009). Alternatively, or perhaps, additionally, volatiles may have been transported to the deep mantle by subduction very early in the Earth's history (>2.5 billion years ago; Sobolev et al., 2016). This agrees with mass balance calculations that indicate nearly all subducted F (up to 95%) is retained beyond subarc depths (Straub & Layne, 2003; John et al., 2011; Barnes et al., 2018); however the details of this mechanism are not well understood, particularly what minerals may be involved.

The halogens are non-metallic, highly volatile elements characterized by a single electron deficiency in their outermost orbital. As such, they readily react with other elements to form halide anions. In general, halogen contents are low in the Earth's mantle (Kendrick et al., 2017) and high in surface reservoirs, such as seawater (Li, 1982), sediments (Li & Schoonmaker, 2003) and crustal rocks (e.g., Rudnick & Gao, 2003). Bromine and I are particularly enriched in organic-rich sediments and sediment-modified fluids (see Kendrick, 2018 for review). Iodine and F are also enriched in carbonate minerals (Rude & Aller, 1991; Claret et al., 2010; Kendrick et al., 2019). Their increased compatibilities relative to Cl and Br ions (e.g., Kitano et al. 1975; Okumura et al. 1986) are attributed to $2F^-$ and IO_3^- readily substituting for CO_3^{2-} in these minerals (Ohde & Kitano, 1980; Lu et al., 2010). All halogens are considered incompatible with minerals during dehydration reactions and partial melting, but due to its smaller size and higher electronegativity F is less incompatible and less soluble in aqueous fluids than Cl, Br and I.

These differences in and their contrasting abundances in various reservoirs, the absolute and relative abundances of the halogens are useful for tracing fluid sources and migration as well as global volatile cycling. The halogens, particularly Cl, also readily complex with metals, influencing metal transport within subduction zones and contributing to metal deposit formation (Seward et al., 2014). Chlorine is typically considered to have shallow cycling in subduction zones based on its preferential partitioning into aqueous fluids compared to minerals (e.g., Fabbrizio et al., 2013a,b; Chevychelov et al. 2008c), and preliminary mass balance calculations suggest nearly all subducted Cl is returned to the surface through arc volcanism (e.g., Straub & Layne 2003; Jarrard, 2003). However, more recent calculations (John et al., 2011; Barnes et al., 2018; Pagé & Hattori, 2019) and halogen compositions of back-arc basalts and ocean island basalts compared to MORB glasses (Kendrick et al., 2012b, 2014a,b) suggest some Cl (and Br and I) may be retained in subducting slabs beyond subarc depths.

The subducting slab is comprised of oceanic crust overlain by sediments and underlain by variably serpentized lithospheric mantle. The water budget and maximum depth of stability of these lithologies and their minerals have important implications for volatile transport. Minerals of interest for halogen transport in the subducting oceanic crust include amphibole, lawsonite, phengite and chlorite (Pagé et al., 2016; Debret et al., 2016; Hughes et al., 2018). Although often an accessory mineral, apatite may also be an important contributor to the transport of halogens given significant Cl and F are common in its crystal structure (Pagé et al., 2016). Lawsonite, phengite and apatite are of particular importance given their stabilities to depths of 200-300 km in cold subduction zones (Schmidt & Poli, 1998; Konzett & Frost, 2009), well below the depth associated with most volcanic arcs (~100 km; Syracuse & Abers, 2006). Therefore, these minerals could be effective vehicles for the transport of volatiles to the much deeper mantle. This paper reports halogen abundances in eclogitic rocks and minerals from the Tso Moriri UHP unit,

NW Himalaya and the Sulu UHP belt, China and discusses their behaviour in the deeply subducted slab and implications for their global geochemical cycling.

7.2 Geological setting and samples

7.2.1 Tso Morari

The Tso Morari UHP unit is part of the Ladakh (India) subduction complex in northwestern Himalaya formed during the closure of the Neo-Tethys and subsequent subduction of the Indian continental margin below Eurasia (Guillot et al., 2001). It is bound by the Indus Suture Zone to the north and the Zaskar sedimentary unit to the south. The Tso Morari unit is a large (100×50 km) suite of metasedimentary rocks intercalated with granitic gneisses and metabasites (Figure 7-1). The unit is considered to be a block of Indian continental margin subducted to peak metamorphic conditions of 3.9 Gpa and 750 °C based on the occurrence of coesite-bearing eclogite in the northern part of the unit (Mukherjee et al., 2003), which, given the geothermal gradient of this subduction zone (~6-7°C/km), corresponds to a depth >100 km. Additional evidence for deep subduction is provided by secondary olivine in serpentinite lenses of the Zildat fault along the northern edge of the dome (Pagé et al., 2018). The close association and similar thermal relaxation-related deformation of these serpentinites and the Tso Morari UHP rocks suggest they were exhumed together (Guillot et al., 2000; 2001). Peak metamorphism is dated at 55 ± 6 Ma by Lu-Hf, Sm-Nd and U-Pb geochronology on garnet-omphacite-whole rock, garnet-glaucophane-whole rock, and allanite, respectively (de Sigoyer et al., 2000).

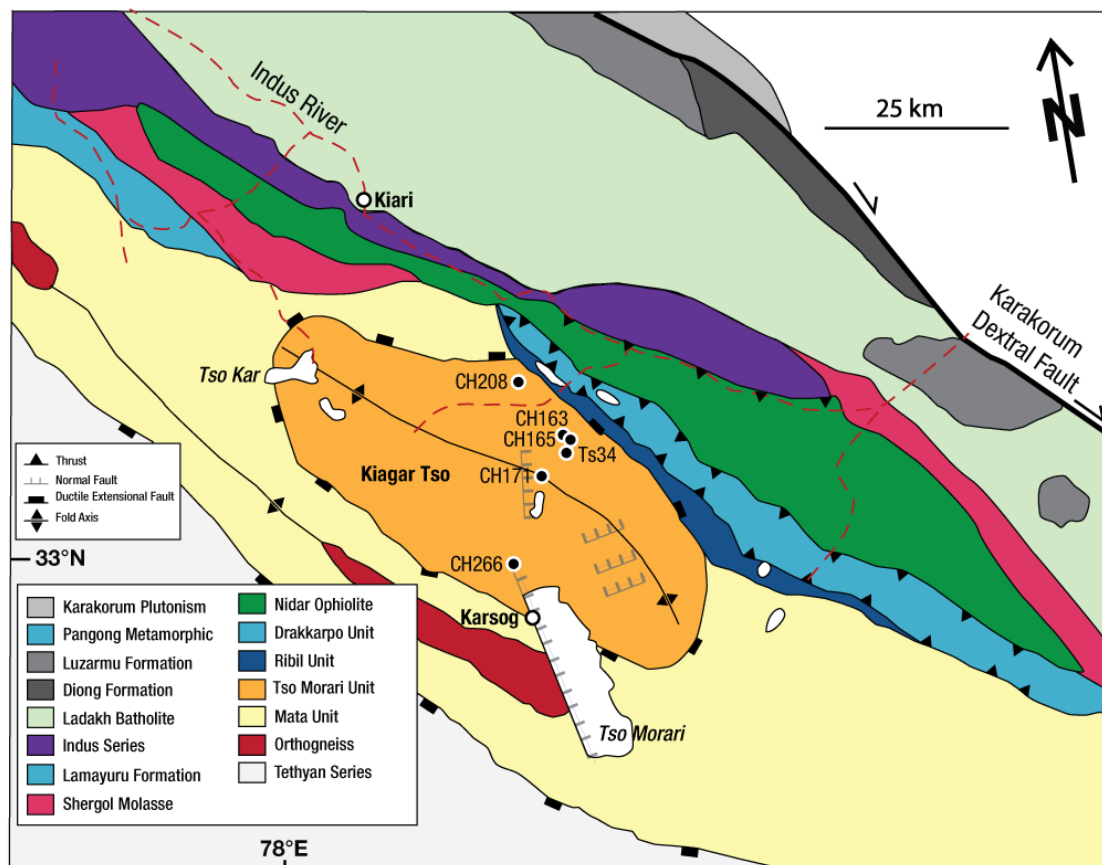


Figure 7-1: Simplified geologic map of the Tso Morari area in northwestern Himalaya. Sample locations are marked with black-filled circles with white outline. Modified after de Sigoyer et al. (2004).

All eclogite samples contain abundant euhedral garnet (<2 mm) and omphacite (<1 mm) with variable amounts of phengite (< 1 mm) and quartz (<0.5 mm) and minor rutile and apatite (Table 7-1; Figure 7-3). Some samples also contain variable zoisite $\pm$ jadeite $\pm$ paragonite $\pm$ biotite $\pm$ carbonates. Sample CH266 contains minor symplectitic intergrowths of plagioclase and Na-augite between omphacite grains. Garnets contain inclusions of quartz, glaucophane, omphacite, apatite and rutile.

7.2.2 *Sulu*

The Sulu UHP belt is the eastern portion of the ~2000 km long Qinling–Dabie–Sulu orogenic belt formed by the subduction of the margin of the Yangtze Craton beneath the North China Craton during the early Mesozoic. The Sulu belt is offset northward from the remainder of the belt by the NE-trending Tan-Lu fault, and it is bounded by the Wulian–Qingdao–Yantai Fault (WQYF) to the northwest and by the Jiashan–Xiangshui Fault (JXF) to the southeast (Figure 7-2). The UHP metamorphic zone of the Sulu belt is characterized by layers of coesite-bearing eclogites and serpentized peridotites in granitic gneisses, marbles and schists (e.g., Zhang et al., 1995; Kato et al., 1997; Xie et al., 2013). The petrology, mineralogy and geochronology of the Dabie–Sulu eclogites have been extensively studied in previous publications, with a review in Zheng et al. (2003). Pressure-temperature estimates using equilibrium mineral assemblages of garnet and omphacite suggest the eclogites of the UHP belt reached peak metamorphic conditions of 650–890 °C and 25–44 kbars (e.g., Zhang et al., 1995; Banno et al., 2000; Zhang and Liou, 2003) at 210–240 Ma based on whole rock and garnet–omphacite Sm–Nd ages, garnet–omphacite–phengite Rb–Sr ages and zircon U–Pb ages (e.g., Chavagnac & Jahn, 1996; Zhao et al., 2006; Liu et al., 2015). The presence of exsolved clinopyroxene and coesite inclusions in garnet suggest these rocks were subducted to a depth >200 km (Zhang et al., 1995; Zhang & Liou, 2003).

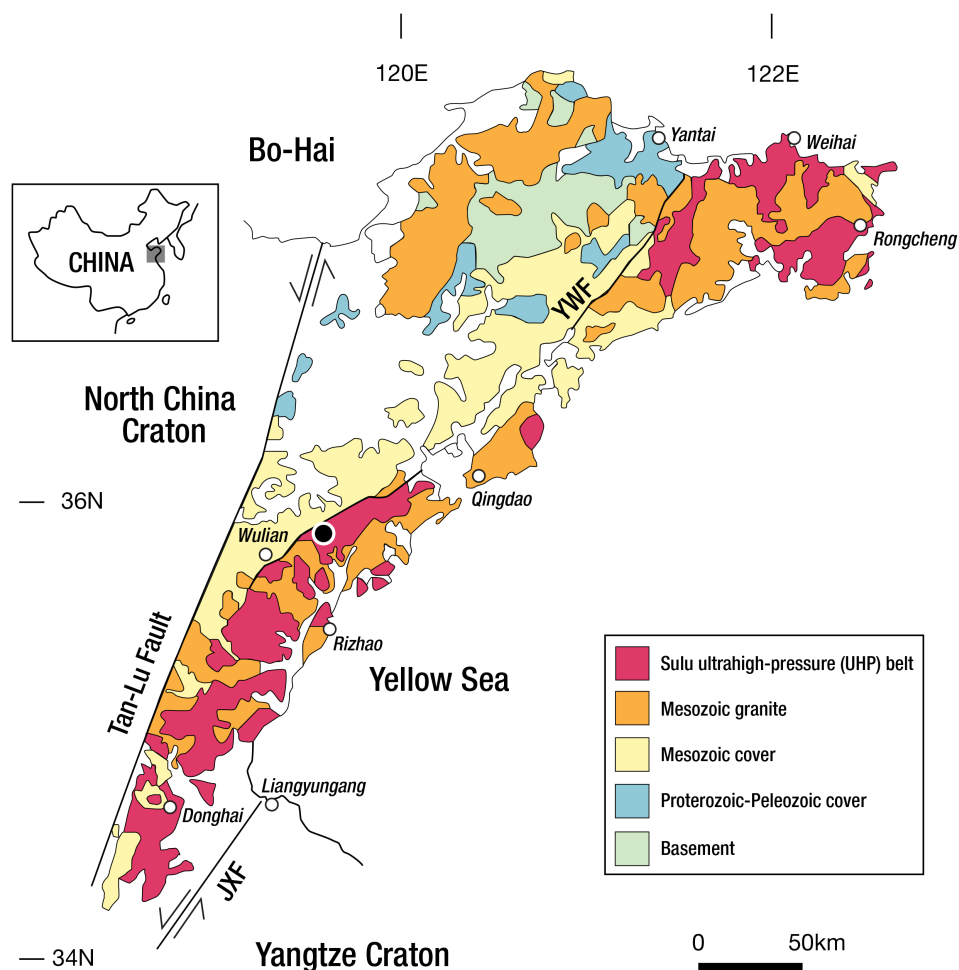


Figure 7-2: Simplified geologic map of the Sulu study area in northeastern China. Sampling location marked with black-filled circles with white outline. Modified after Xie et al. (2013).

Eclogites were collected from a quarry ($35^{\circ}51'18.0''\text{N}$, $119^{\circ}32'38.0''\text{E}$) near the city of Zhucheng in Shandong, China. Samples are characterized by UHP metamorphic mineral assemblages with minimal retrogression products (Table 7-1; Figure 7-3). All samples contain abundant garnet (<2 mm) and omphacite (<2 mm), with variable phengite and minor rutile and apatite. Some samples also contain variable zoisite $\pm$ Na-amphibole $\pm$ kyanite $\pm$ quartz. Metamorphic foliation is defined by the preferred orientation of omphacite grains.

Table 7-1: Observed mineralogy of eclogite samples from Sulu UHP belt and Tso Morari UHP unit. All values in percent.

Locality	Sulu UHP Belt				Tso Morari UHP unit, Himalaya					
Sample ID	SL41	SL45	SL47	SL48	CH163	CH165	CH171	CH208	CH266	TS34
Garnet	40	55	45	45	45	40	60	30	50	55
Omphacite	25	30	25	50	35	30	20	45	20	20
Phengite*	1	2	4	1	8	10	3	11	11	9
Na-amphibole	-	5	21	2	2	3	5	2	5	5
Jadeite					4	6	-	-	-	-
Zoisite	20	2	<1	<1	2	2	3	1	-	3
Kyanite	13	5	<1	-	-	-	-	-	-	-
Rutile	<1	<1	1	1	3	3	1	1	3	3
Apatite [†]	<1	<1	1	<1	1	1	<1	<1	1	1
Quartz	-	-	1	<1	<1	2	8	8	1	3
Zircon	-	<1	<1	-	-	-	-	-	-	-
Paragonite	-	-	-	-	-	2	-	2	-	<1
Biotite	-	-	-	-	-	-	-	-	3	<1
Carbonates	-		-	-	-	<1	-	-	<1	<1
Symplectite [§]	-		-	-	-	-	-	-	5	-

*calculated from bulk K₂O assuming stoichiometric composition of phengite

[†]calculated from bulk P₂O₅ assuming stoichiometric composition of apatite

[§]Ca-clinopyroxene + plagioclase after omphacite

-Not observed

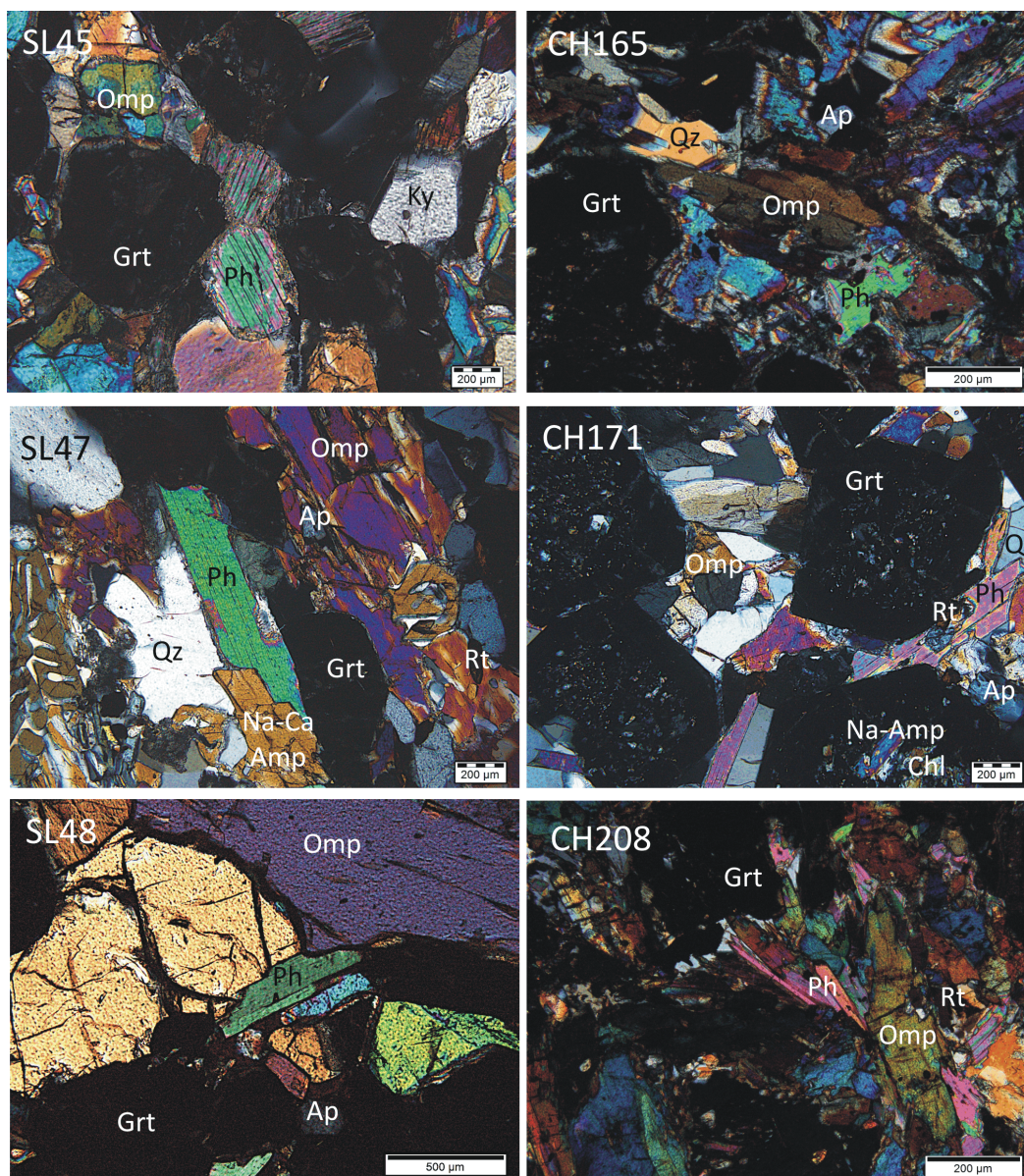


Figure 7-3: Photomicrographs of eclogites from the Sulu UHP belt (SL45, SL47, SL48) and the Tso Moriri UHP unit, NW Himalaya (CH165, CH171, CH208). Ap: apatite, Chl: chlorite, Grt: garnet; ; Ky: kyanite; Na-(Ca)-Amp: Na-(Ca)-amphibole; Omp: omphacite, Ph: phengite, Rt: rutile, Qz: quartz.

7.3 Methods

7.3.1 Bulk rock chemistry

Bulk rock major and trace element compositions of the Tso Moriri samples (except for CH208) are determined by X-ray fluorescence (XRF) after fusion of rock powder with 50/50 $\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$ at the Université de Lyon, and compositions of the Sulu samples (and CH208) are determined by XRF with 79/21 $\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$ + 1% LiBr at the University of Ottawa. Bulk rock major and trace element compositions of samples from Sulu were determined by XRF at the University of Ottawa. For the latter, powdered samples weighing 0.8 ± 0.0002 g were combined with 7.2 ± 0.0002 g of in-house 79/21 $\text{Li}_2\text{B}_4\text{O}_7/\text{LiBO}_2$ + 1% LiBr non-wetting agent. A Claisse M4 fluxer was used to digest samples over 24 minutes and generate glass beads for XRF. Samples were analyzed for all major rock-forming elements and select traces using a Rigaku Supermini 200 benchtop XRF under vacuum. International reference materials used for calibration curves include UB-N, UM-2, MRG-1, PM-S, BCR-2, WS-E, SY-3 BHVO-2, BM, AN-G, BCR-032 and PC-1016. Standards SY-3, MRG-1 and BCR-032 were used for drift correction, and GSP-2 and BHVO-1 were used as checks. Method precision and accuracy is verified by the analysis of SY-3 and MRG-1, yielding average relative variation over six analytical runs of 1.9%, and average relative variation over published values of 2.7%.

Bulk B concentrations of all samples are determined on 1.0 g of finely ground sample material by Activation Laboratories (Ancaster, Ontario, Canada) by prompt gamma neutron activation analysis (PGNAA) with a 2 ppm detection limit. Accuracy of the technique is verified by analysis of two geologic reference materials (SY-2 and SY-3).

7.3.2 Halogen extraction: pyrohydrolysis + IC/ICP-MS

Halogens are extracted from 0.5 g of finely ground sample using a modified pyrohydrolysis technique (Pagé et al., 2016). Fluorine and Cl contents are determined using a

Dionex ICS-2100 ion chromatography system equipped with KOH eluent generator, and Br (^{79}Br) and I (^{127}I) contents are determined using an Agilent Technologies 7700 series inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Ottawa. Instrumental detection limits (3σ) are 0.023 ppm F, 0.021 ppm Cl, 0.083 ppb Br and 0.023 ppb I. Samples for ICP-MS are diluted 5x to minimize the effects of Na precipitate, and 1% NH_3 is added to stabilize the anions in solution. The method blank, as determined by repeat extractions without sample or catalyst, is 0.011 ppm F, 0.108 ppm Cl, 4.1 ppb Br and 2.7 ppb I. Average standard deviations (1σ) of repeat extractions ($n=2$ or 3) are 6.7 % for F, 17 % for Cl, 44 % for Br and 13 % for I. The inferior precision of Br may be related to its instability in solution or minor contamination from the plastic vials or boats if Br is used as a flame retardant in these products. Accuracy of the pyrohydrolysis technique is verified by the analysis of four reference standards (BCR-2, JB-1, JB-3 and MRG-1; Pagé et al., 2016).

7.3.3 Mineral chemistry: electron probe microanalysis (EPMA)

Minerals was analyzed at the University of Ottawa with a JEOL 8230 electron microprobe using a wavelength dispersive spectrometer. A 5 μm diameter 20 nA beam accelerated to 20 kV was used for analysis of silicates. Peak counting times were 10s per element for the $K\alpha$ lines of Fe, Mn and Si, 20s for K, Ca, P, Al, Ti, Na and Mg, and 50s for Cl and 150 s for F. The high beam current and longer counting time for F were used to overcome low count rates for light element X-rays associated with the conventional TAP diffraction crystal. Instrument calibration used sanidine (Si, Al, K), diopside (Ca, Mg), albite (Na), hematite (Fe), tephroite (Mn), San Carlos olivine (Ni), rutile (Ti), chromite (Cr), apatite (P), Mg-mica or fluorite (F) and tugtupite (Cl). Mineral formulae of phengite and the amount of Fe^{3+} were calculated based on stoichiometric composition and charge balance using 11(O).

The analytical conditions for apatite were 10 kV accelerating voltage, 4 nA beam current, and 10 μm diameter beam size for optimal analysis of fluorochlorapatites. Each grain was analyzed in 1–3 spot(s), depending on grain size. Peak counting times were 10 s per element for Si ($K\alpha$), Fe ($K\alpha$), Mg ($K\alpha$), K ($K\alpha$), S ($K\alpha$), Ce ($L\alpha$), La ($L\alpha$) and As ($L\alpha$), 20 s for Al ($K\alpha$), Ca ($K\alpha$), Na ($K\alpha$), P ($K\alpha$), Sr ($L\alpha$) and Cl ($K\alpha$), and 50 s for F ($L\alpha$). Instrument calibration used sanidine (Si, Al, K), hematite (Fe), diopside (Mg), apatite (Ca, P, F), albite (Na), celestine (S, Sr), CePO_4 (Ce), LaPO_4 (La), GaAs (As) and tugtupite (Cl). A synthetic multi-layered diffraction crystal, LDE1, was used to enhance the count rate for F. Apatite mineral formulae were calculated based on normalizing to 13 (O, OH, F, Cl).

Detection limits were ~ 50 ppm for Cl, and either ~ 150 ppm F using the TAP crystal for silicates or ~ 440 ppm F using the LDE1 crystal for apatite.

7.4 Results

7.4.1 Bulk rock chemistry

All samples have low SiO_2 (39.7–50.9 wt% SiO_2 ; Table A V-1). The Sulu eclogites have alkali element contents (2.6–3.1 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$; Table A V-1) similar to N-MORB values (< 2.8 wt % $\text{Na}_2\text{O} + \text{K}_2\text{O}$; White & Klein, 2014), while the Tso Moriri eclogites are slightly more alkaline (3.2–4.3 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$).

Eclogite protoliths are classified using V versus Ti/1000 (Figure 7-4A; Shervais, 1982) and Zr versus Zr/Y (Figure 7-4B; Pearce & Norry, 1979) tectonic discrimination diagrams. These discrimination plots were used because abundances of Ti, V and Zr in basaltic rocks greatly exceed their detection limit in XRF analysis, making accurate determination reasonably easy. The original Ti-V diagram was originally based on variations of partial melting partition coefficients of V as a function of oxygen fugacity (Shervais, 1982), and has been validated more

recently by statistical methods (Vermeesch, 2006). The ratio of high field strength elements Zr and Y is insensitive to fractionation in the shallow mantle, but the behaviour of Y changes in the deeper mantle due to its increased compatibility with garnet.

Two Tso Moriri samples plot within the MORB field of the V-Ti diagram ($\text{Ti/V} \approx 20\text{--}50$), while the others straddle the boundary of MORB and OIB ($\text{Ti/V} \approx 50$; Figure 7-4A), and all samples fall within the Within Plate Basalt (WPB) field of the Zr-Y diagram (Figure 7-4B). This supports previous suggestions that these eclogites are metamorphosed Panjal Traps – OIB-like basalts associated with the break-up of Gondwana (Shellnut et al., 2015) – based on enriched REE patterns, Hf -Nd isotope data and elevated concentrations of incompatible elements including TiO_2 (up to 2.8 wt%), P_2O_5 (up to 0.34 wt%) and K_2O (up to 1.2 wt%) (e.g., di Sigoyer et al., 2000; Ahmad et al., 2006; Kouketsu et al., 2017). In contrast, the Sulu eclogites have low Ti (< 1 wt%) and Ti/V ratios (>20; Figure 7-4A), indicating an arc basalt protolith, as previously suggested to explain HFSE depletions (Li et al., 1993; Chen et al., 2007b) and ϵNd – ϵHf compositions (Liu et al., 2015) of UHP rocks from this area.

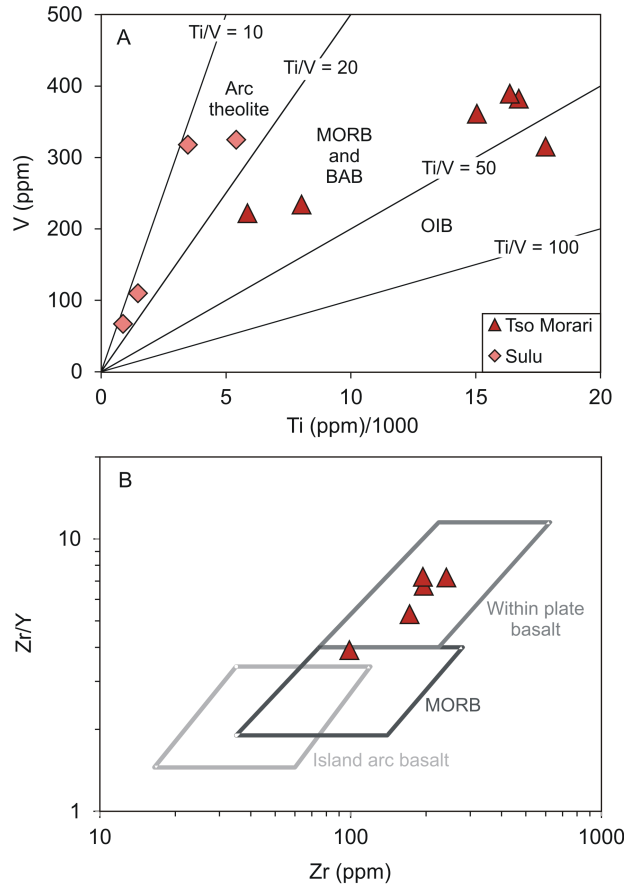


Figure 7-4: Tectonic discrimination diagrams for eclogites from the Tso Morari UHP unit, Himalaya and the Sulu UHP belt. The Sulu eclogites plot in the arc theolite field with $Ti/V < 20$. The Tso Morari eclogites plot in the ‘within plate basalt’ field of the Zr versus Zr/Y diagram. (A) modified after Shervais (1982); (B) modified after Pearce & Norry (1979).

7.4.2 Halogen abundances

Bulk Cl concentrations of the Tso Morari and Sulu eclogites cover a wide range (8-90 ppm and 12-96 ppm, respectively) and are two to three orders of magnitude greater than those of Br (0.011–0.18 ppm and 0.037-0.38 ppm, respectively; Table A V-2; Figure 7-5). Their Br/Cl ratios for Tso Morari (0.0006–0.0054) and Sulu (0.0015-0.0048) are comparable. Iodine contents of the Sulu eclogites are below the pyrohydrolysis method detection limit (0.0029 ppm; Table A

V-2) except for one sample (0.0042 ppm I). The Tso Morari samples are comparatively more I-enriched (0.05-0.25 ppm; Table A V-2; Figure 7-5B), and consequently have greater I/Cl ratios (0.00051–0.0104) than the Sulu sample (0.00007; Table A V-2; Figure 7-6A). Fluorine is the most abundant halogen in the Tso Morari (142-363 ppm) samples, with corresponding F/Cl ratios of 3.4 to 45 (Table A V-2; Figure 7-5C & Figure 7-6B). The Sulu samples also have relatively high F (61-272 ppm), but lower F/Cl (0.92-5.3) than the Tso Morari samples.

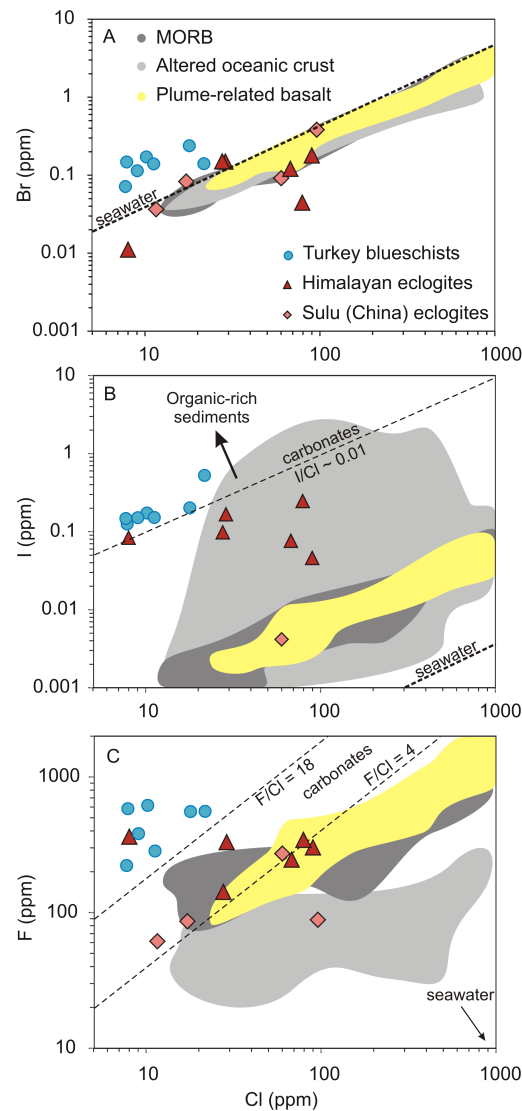


Figure 7-5: Halogen content of bulk eclogites of the Tso Morari UHP unit, Himalaya and the Sulu UHP belt. Chlorine is plotted against (A) Br, (B) I and (C) F. Chlorine and Br contents are

positively correlated along the calculated slope of seawater (Li, 1982) and overlap with the low end of values for the presumed protoliths of plume-related basalts (Kendrick et al., 2017), mid-oceanic ridge basalt (MORB; Kendrick et al., 2017) and altered oceanic crust (Kendrick et al., 2019). In contrast, I is variably enriched relative to Cl in the eclogites, similar to the enrichment observed for altered oceanic crust. Iodine and F compositions extend toward estimated slopes for carbonate minerals (Claret et al., 2010; Kendrick et al., 2019). Halogen data for blueschists from Turkey (Pagé et al., 2016) are shown for comparison.

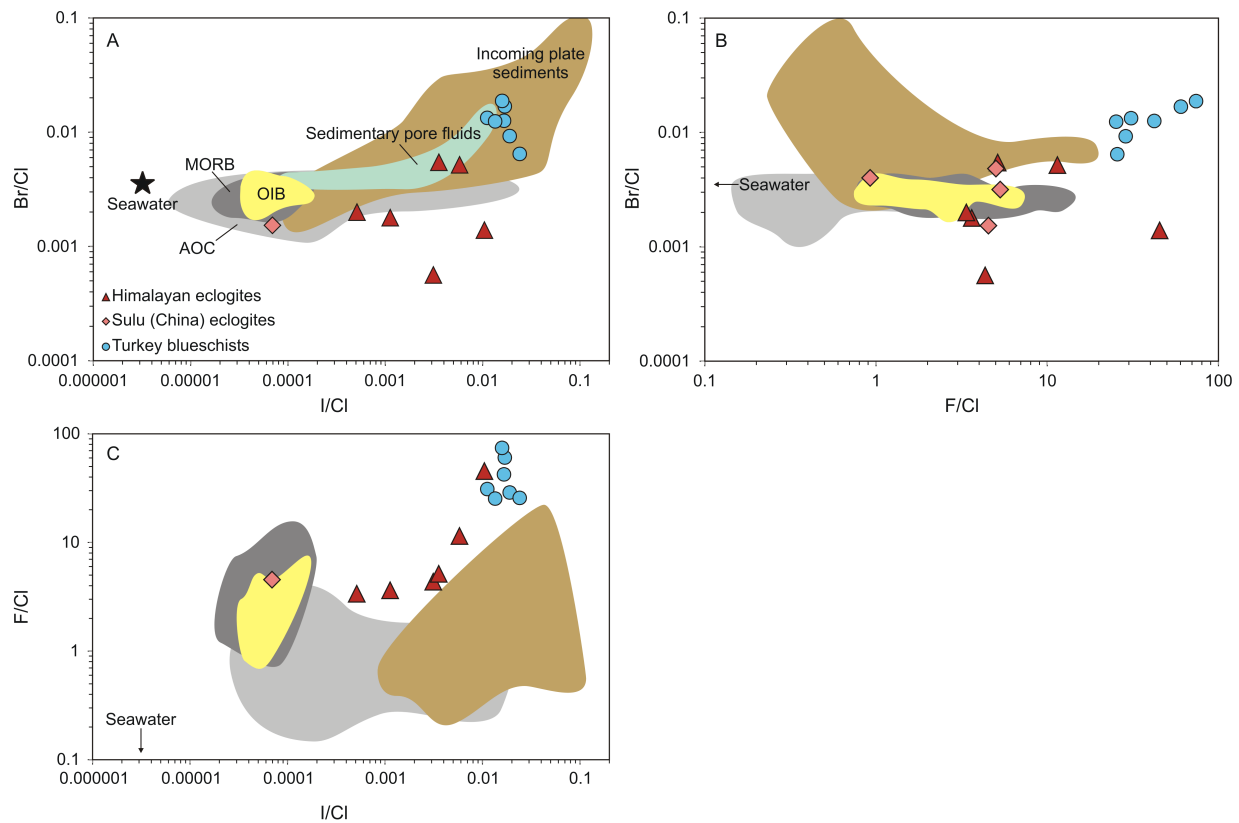


Figure 7-6: Compilation of halogen ratios in eclogites of the Tso Moriri UHP unit, Himalaya and the Sulu UHP belt, and blueschists from the Tavsanlı zone, NW Turkey (Pagé et al., 2016). Data for unaltered MORB (Kendrick et al., 2017), altered oceanic crust (Kendrick et al., 2019), plume-related basalt (Kendrick et al., 2017), incoming plate sediments (John et al., 2011),

sedimentary pore fluids (Fehn et al., 2000; 2007; Mahn & Geiskes, 2001; Muramatsu et al., 2007) and seawater (Li, 1982) are shown for reference. Ratios of Br/Cl are similar to unaltered and altered oceanic crust and plume-related basalts, while I/Cl and F/Cl ratios are elevated.

7.4.3 Mineral chemistry

7.4.3.1 Phengite

Phengite compositions for Tso Morari samples CH165, CH171, CH208, CH266 and all Sulu samples are listed in Table A V-3. Most white mica grains in the Tso Morari eclogites are indeed phengites with Si_{pfu} ranging from 3.3 to 3.6 (Figure 7-7) with minor intercalated paragonite in CH165 and CH208. White mica in the Sulu samples generally have lower Si (3.2-3.4 pfu) and atomic ratios of K/Na (6-12) compositions than those of the Tso Morari samples (Figure 7-7). In the Tso Morari samples, average Cl concentrations of 1-3 analyses/phengite grain for 5-18 grains/sample range from 31 ± 23 ppm to 56 ± 35 ppm (Figure 7-8). Average F concentrations range from 710 ± 310 ppm to 1800 ± 560 ppm and F/Cl ratios range from 24 ± 10 to 78 ± 41 (Figure 7-8). In the Sulu samples, average Cl concentrations of 1-3 analyses/phengite grain for 3-9 grains/sample range from 29 ± 19 ppm to 92 ± 44 ppm (Figure 7-8). Average F concentrations range from 643 ± 330 ppm to 1110 ± 510 ppm and F/Cl ratios range from 8.5 ± 4.7 to 28 ± 20 (Figure 7-8). Similarly large relative standard deviations are observed for EPMA-determined F and Cl contents and ratios of phengites from other eclogite rocks (Svensen et al., 2001), and are attributed to analytical uncertainties inherent in the EPMA method at low F (<1000 ppm) and Cl (<100 ppm) concentrations, in addition to chemical heterogeneities within the samples. Analytical uncertainties arise from low count rates at these concentrations, as well as sample damage and volatile migration caused by the electron beam curing long count times.

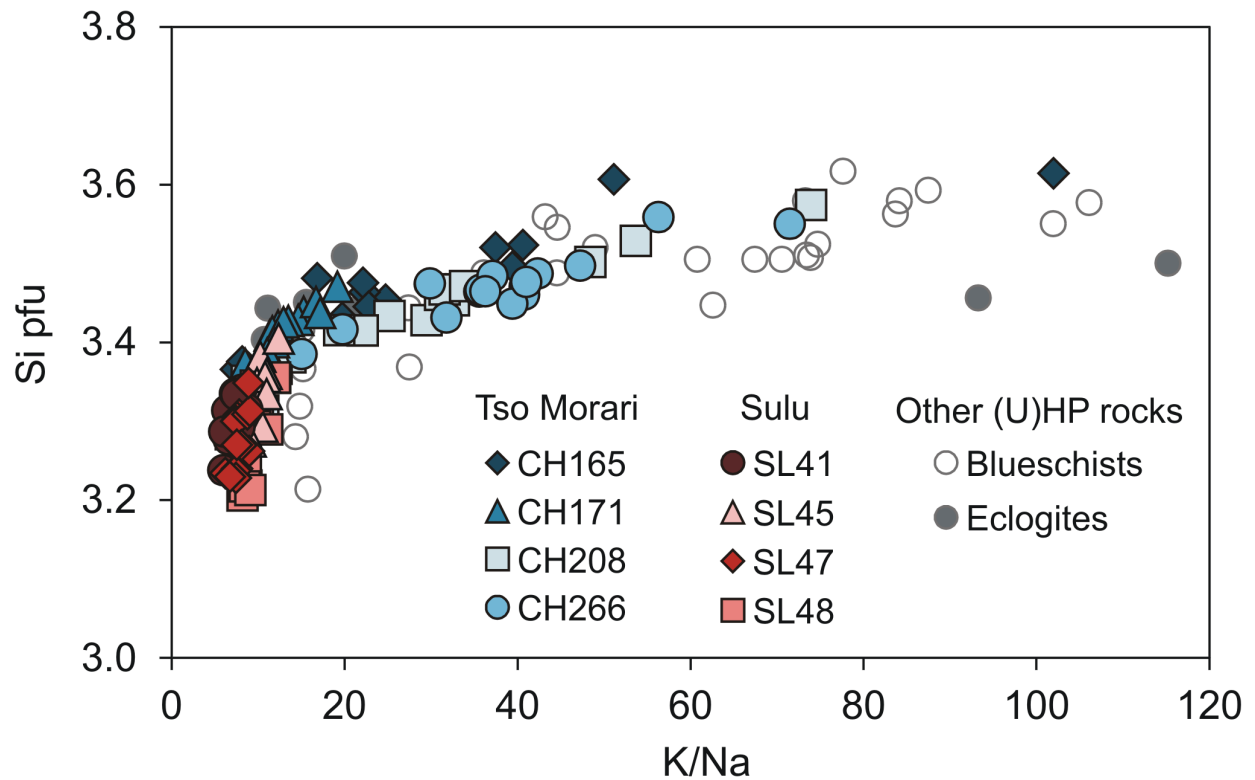


Figure 7-7: Composition of phengite from eclogites of the Tso Morari UHP unit, Himalaya and the Sulu UHP belt. Atomic ratios of K/Na increases with increasing Si atoms per formula unit (pfu). The compositions are similar to phengite in blueschists and eclogites from other terranes, including New Caledonia (Spandler et al., 2003), the Catalina Schist in California (Bebout et al., 2007) and the Tavsanli Zone in NW Turkey (Davis and Whitney, 2006; Pagé et al., 2016).

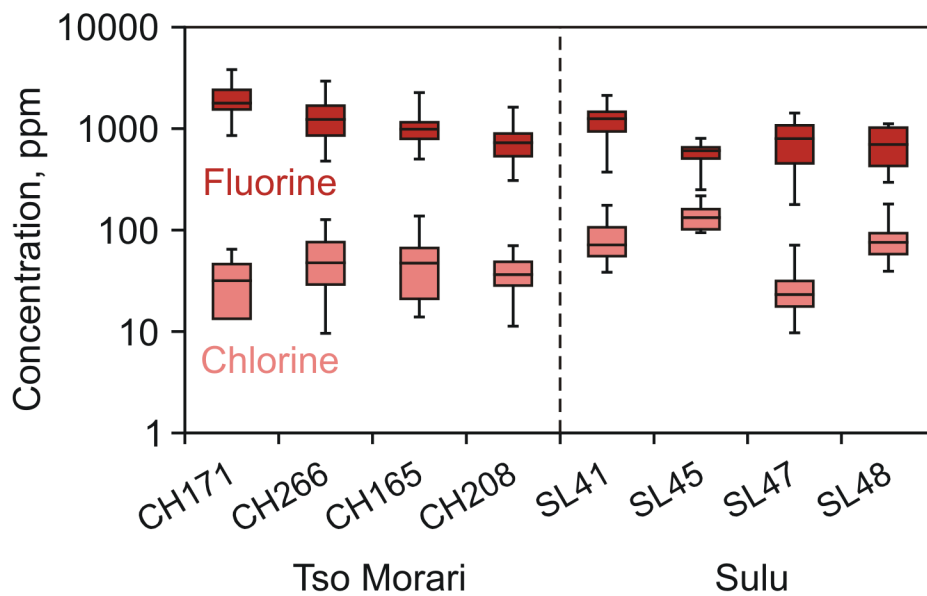


Figure 7-8: Box-and-whisker plot displaying F and Cl contents of phengite from eclogites of the Tso Morari UHP unit, Himalaya and the Sulu UHP belt.

7.4.3.2 Apatite

All four Tso Morari samples contain fluorapatites (avg. 2.09–2.97 wt% F) with low Cl contents (avg. 0.01–0.21 wt%; Figure 7-9; Table A V-4). Average F/Cl ratios for CH171, CH208 and CH266 are similar (31 ± 13 , 10 ± 11 and 17 ± 4 , respectively), whereas CH165 show high ratios (420 ± 93). In addition to CaO and P₂O₅, most samples contain minor amounts of Na₂O (<0.05 wt%), MgO (<0.11 wt%), K₂O (<0.11 wt%), SiO₂ (<0.20 wt%), Al₂O₃ (<0.07 wt%), TiO₂ (<0.37 wt%), MnO (<0.03 wt%), FeO (<0.32 wt%), SrO (<0.71 wt%), As₂O₅ (<0.04 wt%), La₂O₃ (<0.30 wt%), Ce₂O₃ (<0.21 wt%) and SO₃ (<0.02 wt%). Apatite grains in samples SL47 and SL48 have higher Cl contents (avg. 0.16–0.60 wt%) than the Tso Morari samples and slightly lower F contents (avg. 1.89–2.03 wt%; Table A V-4; Figure 7-9), resulting in lower F/Cl ratios (3.4 ± 0.3 to 12 ± 1.1). Sulu apatite grains contain minor amounts of Na₂O (<0.10 wt%), MgO

(<0.02 wt%), K₂O (<0.02 wt%), TiO₂ (<0.04 wt%), MnO (<0.04 wt%), FeO (<0.18 wt%), SrO (<0.32 wt%), Ce₂O₃ (<0.11 wt%) and SO₃ (<0.21 wt%).

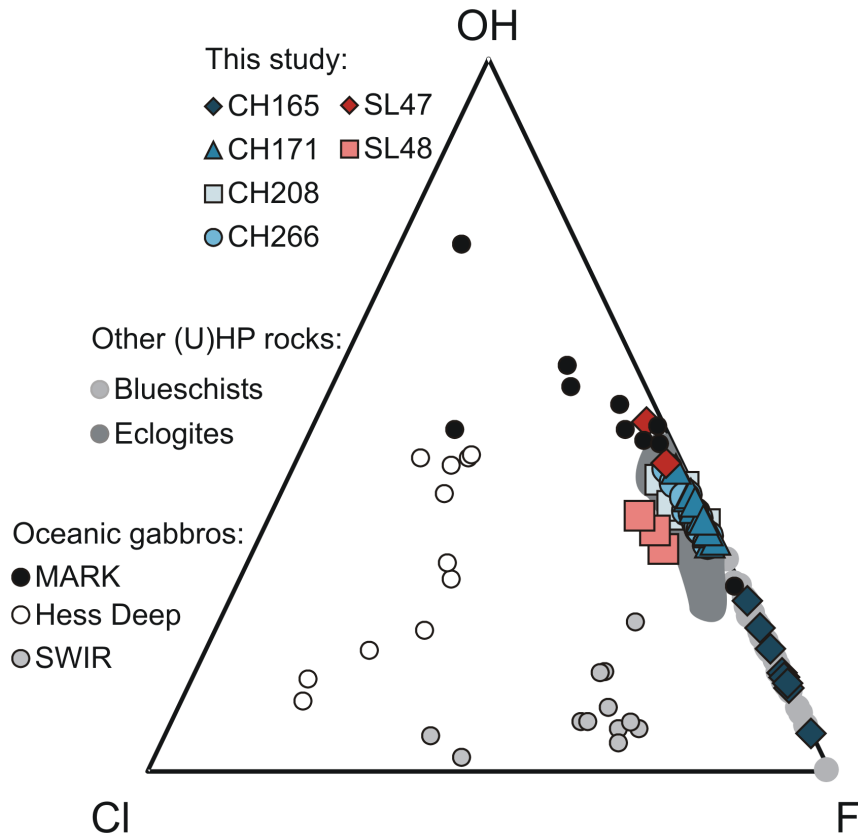


Figure 7-9: Volatile contents (atomic proportion) in apatite from eclogites of the Tso Morari UHP unit, Himalaya and the Sulu UHP belt. Hydroxyl component calculated by difference ($X_{OH} = 1 - X_F - X_{Cl}$). There is overlap with apatites from other (U)HP belts (e.g. Svensen et al., 2001; John et al., 2008; Pagé et al., 2016; Hughes et al., 2018). Apatites of oceanic gabbros contain more Cl and OH (Meurer & Natland, 2001).

7.5 Discussion

7.5.1 Halogens in eclogite facies rocks

The Sulu and Tso Morari eclogites are primarily characterized by prograde mineral assemblages with minimal retrogression (Table 7-1; Figure 7-3), therefore their halogen contents are considered to represent those present in the deep (>100 km) slab and not acquired at shallow depth during exhumation.

The Tso Morari and Sulu eclogites have lower Cl and Br contents than their presumed protoliths. Plume-related basalts contain ~580 ppm Cl and ~1.7 ppm Br (Kendrick et al., 2017) and island arc basalts contain ~790 ppm Cl and ~3.3 ppm Br (John et al., 2011). This is consistent with the loss of up to 75% of Cl from rocks and pore fluids of subducting slab before 15 km depth (Jarrard, 2003) and the loss of Cl and Br from the slab before or during blueschist facies metamorphism (Pagé et al., 2016). Similar Br/Cl ratios among the eclogites and their protoliths (Figure 7-6 B) suggest coherent loss from the subducting slab prior to, or during eclogite facies metamorphism. Similarly low bulk Cl contents are recorded for other eclogites from the island of Syros, Greece (30-60 ppm; Marschall et al., 2009) and estimated from mineral compositions and abundances for eclogitic metabasalts and metagabbros of the Western Alps (10-80 ppm; Debret et al., 2016; Hughes et al., 2018).

On the contrary, I contents and I/Cl ratios of the Tso Morari eclogites are greater than their presumed protolith of plume-related basalt (Figure 7-5B & Figure 7-6A). This enrichment may be attributed to I-rich shallow water sediments on the margin of the subducting Indian continent, as previously suggested for high I in mantle wedge serpentinites associated with the Tso Morari UHP unit (Pagé et al., 2018). Indeed, I/Cl ratios of these eclogites are similar to those of sedimentary pore fluids and incoming plate sediments (Figure 7-6A). However, Br/Cl ratios of the eclogites extend to lower values than those associated with organic sediments. An enrichment

of I over Br may be attributed to I-rich, Br-poor fluids from dehydrating carbonate-bearing sediments in the slab during subduction (Figure 7-5A). In seawater, I can exist as iodide (I^-) or as its oxidised form, iodate (IO_3^- ; e.g., Fuge & Johnson, 1986). The substitution of IO_3^- for CO_3^{2-} in carbonates (Lu et al., 2010) increases the compatibility of I relative to Cl and Br in these minerals (Kitano et al. 1975; Okumura et al. 1986). Based on an estimate of ~2 ppm I in marine carbonates (Claret et al., 2010) and measurements of ~200 ppm Cl in carbonates associated with the Atlantis Bank gabbros (SW Indian Ridge ; Kendrick et al., 2019), the I/Cl ratio of marine carbonates is estimated at ~0.01 (Figure 7-5A). Additional I in the eclogites may have also been sourced from subducting abyssal serpentinites during the lizardite-antigorite phase transition which is accompanied by the release of fluids and halogens (Pagé & Hattori, 2017).

The Tso Moriri and Sulu eclogites have similar F contents to their presumed protoliths (Figure 7-5C), and F/Cl ratios that extend to higher values (Figure 7-6C). The high F coupled with high I of these eclogites suggests F may also be sourced from clay- or carbonate-bearing sediments either prior to subduction along bend-related extensional faults at the outer rise or during subduction from dehydrating sediments in the channel. In general, the F content of sediment pore fluids are low (similar to seawater) due to the low solubility of F in aqueous fluids (Mahn & Geiskes, 2001). However, enrichment of F in isolated pore fluids may take place in deep water below the carbonate compensation depth, ~ 3000-4000 m (Andel, 1975), where marine carbonates that contain up to 1700 ppm F (Rude & Aller, 1991) and high F/Cl ratios (~4-8; Carpenter, 1969) dissolve. Dehydration of carbonates and clay minerals (~1000 ppm F; Carpenter, 1969) during subduction may also release F to be incorporated in the altered oceanic crust.

Average F concentrations (~220 ppm) and F/Cl ratios (~10) of the Tso Moriri and Sulu eclogites are similar to concentrations (avg. 340 ppm F) and ratios (~19) estimated for eclogite

facies metabasalts of the Western Alps based on modal abundances and their measured concentrations in minerals (Hughes et al., 2018), but slightly lower than blueschists from the Tavsanlı zone in NW Turkey (~460 ppm F and F/Cl≈40; Pagé et al., 2016). This may be the result of dehydrating F-bearing Na-amphiboles (Pagé et al., 2016) during the blueschist-eclogite transition, however this interpretation is purely speculative given the limited halogen data from metamorphosed mafic crust. In very broad terms, the difference is consistent with progressive loss of FME from the subducting slab.

7.5.2 Halogens in eclogite facies minerals

Fluorine contents of the Tso Moriri and Sulu eclogites broadly correlate with bulk K₂O, P₂O₅ and TiO₂ (Figure A V-1), suggesting it may be hosted in phengite, apatite – the primary K-bearing and P-bearing phases of these rocks – and Ti-rich minerals, such as titanite. *In situ* analyses of representative samples from Tso Moriri and Sulu confirm that abundant F and some Cl in phengite and apatite. Chlorine contents of phengite (< 200 ppm; Figure 7-8) and apatite (<0.7 wt%; Figure 7-9) are variably low, while F contents are high (up to 1800 ppm and 3.0 wt%, respectively). Phengite F contents are slightly elevated relative to those from the Tavsanlı blueschists (~500 ppm F; Pagé et al., 2016), while F contents in apatite are lower than those of the blueschists (~3.5 wt%; Pagé et al., 2016). Apatite halogen compositions are similar to those of apatite grains from other eclogites of HP and UHP terranes, such as Tianshan in China, the Western Alps and the Norwegian Caledonides (Svensen et al., 2001; John et al., 2008; Hughes et al., 2018; Figure 7-9). The relatively low Cl content of apatites from eclogites reflects low Cl activity of the fluids during high pressure metamorphism as apatite is known to be easily re-equilibrated with fluids even at low temperatures (Brennan, 1993).

High F/Cl ratios for phengite (up to 78) and apatite (up to 420) among the Tso Moriri and Sulu eclogite samples indicate these minerals preferentially accommodate F over Cl in their

crystal structures. As discussed in Pagé et al. (2016), this is attributed to the smaller size and higher electronegativity of F. The ionic radius of F (1.33 Å) is most similar to that of OH⁻ (1.35 Å) compared with the heavier halogens, making it more compatible for substitution in hydrous minerals, such as phengite. Furthermore, the substitution of F⁻ for OH⁻ in micas produces a more stable structure by replacing the K⁺-H⁺ repulsion with K⁺-F⁻ attraction and reducing the misfit between the tetrahedral and octahedral sheets (Gianfagna et al. 2007). Additional F may be incorporated into the O²⁻ (1.21 Å) site of silicate minerals, coupled with the substitution of Al³⁺ for Si⁴⁺ (e.g., Beyer et al., 2012). Fluorine is preferentially incorporated into apatite from fluids relative to Cl (Spear & Pyle, 2002; Li & Hermann, 2015). Under high pressures, the smaller F ion is preferentially accommodated in the columnar anion site over Cl or OH⁻ (Page et al., 2016). Similar to rocks from other (U)HP terranes, F is preferentially concentrated in apatite over phengite (Li & Hermann, 2015; Pagé et al., 2016).

The relative contribution of coexisting phengite and apatite to the bulk F budget of these rocks is calculated based on the assumption that all P₂O₅ is in apatite and all K₂O is in phengite. In the Tso Moriri eclogites, phengite contributes 27-37% of total F in bulk samples, and apatite contributes 20-61%, and in the Sulu eclogites, phengite and apatite comprise 9-16% and 27-56% of total bulk F, respectively (Figure 7-10). The lower contribution of phengite in the Sulu samples reflects its lower modal abundance (1-4 vol.%; Table 7-1) and average F content (720 ppm) compared to phengite in the Tso Moriri samples (3-11 vol.% and 1070 ppm F, respectively). The remaining F in these eclogites may reside in Ti-bearing minerals, as previously noted by a broad positive correlation between bulk F and TiO₂ in these rocks (Figure A V-1). Residual Na-amphibole and paragonite may also host F, as reported in eclogitic metagabbros of the Monviso meta-ophiolite (Italy) (Debret et al., 2016). Indeed, some of our

samples contain these minerals, but their F concentrations are too low to be determined by EPMA.

Apatite grains may also host Br and I in their crystal structures. Indeed, up to 8 ppm Br has been measured by secondary ion mass spectrometry and total reflection X-ray fluorescence in apatites from the Mt. Saint Hilaire plutonic complex in Canada and the Ødegården metagabbro in Norway (Marks et al., 2012), and experimental studies demonstrate incorporation of iodate (IO_3^-) into hydroxylapatite until at least 550 °C (Campayo et al., 2011). However, their concentrations in the eclogites are too low to be measured by EPMA.

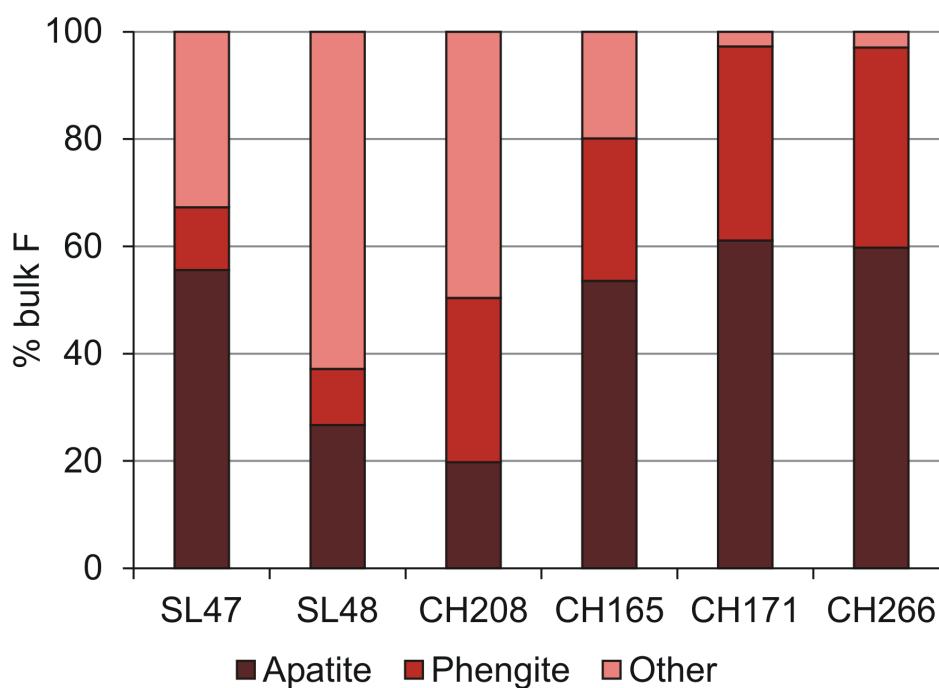


Figure 7-10: Distribution of bulk F among phengite, apatite and other minerals in eclogites of the Tso Moriri UHP unit, Himalaya and the Sulu UHP belt.

7.5.3 *Implications for deep halogen cycling*

Apatite and phengite have wide stabilities. Apatite is stable to 7.5 Gpa (Konzett & Frost, 2009) and phengite to 10 Gpa (Schmodt & Poli, 1998) at ~900°C. In cold subduction zones where geothermal gradients are low, ~5°C/km, the stability limits of apatite and phengite correspond to depths of 200 km and 300 km, respectively. Given the high F/Cl ratios in these minerals, the resulting fluids or melt from their decomposition at these depths are also anticipated to be high. Indeed, across arc studies reveal F/Cl ratios of arc melt inclusions increase with increasing distance from the trench (i.e., increasing slab depth; Ishikawa et al., 1980; Churikova et al., 2007), and in general, F/Cl ratios of back-arc basalts are elevated (up to 2; Bézoz et al., 2009) compared to those of volcanic arcs (typically <1; Heath et al., 1998; Bouvier et al., 2008; John et al., 2011). Unaltered kimberlites from Lac de Gras (Canada) also contain elevated F/Cl ratios (~4-10; Kjarsgaard et al., 2009) compared to the primitive mantle (0.65 ppm; Kendrick et al., 2017), and Archean komatiites of the Abitibi greenstone belt (Canada) have slightly elevated F/Nd ratios (up to 34; Sobolev et al., 2016) compared to primitive mantle values (~19.2; Sun & McDonough, 1989).

The large contribution of apatite and phengite (up to 97%; Figure 7-10) to the overall F budget of the Tso Moriri and Sulu eclogites confirms their importance as reservoirs for F in the slab at (U)HP conditions and for the delivery of F to the deeper mantle.

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Chapter 8.

Global Summary

Summary

A systematic investigation of halogen (+/- B and N) abundances and distributions in a variety of subduction-related lithologies using bulk rock and in situ analytical techniques has constrained the inventory of these elements for transfer to the mantle through subduction. This chapter provides a summary of the work documented in this thesis.

Elevated halogen abundances in abyssal serpentinites relative to their mantle protoliths illustrate their compatibility in serpentine minerals. Abyssal lizardite-serpentinites, such as those from the Tertiary subduction complex in Dominican Republic, are particularly enriched in Cl, Br and I (Chapter 2). Absolute and relative abundances (i.e., Br/Cl and I/Cl ratios) indicate incorporation from seawater and sediments to serpentine minerals during serpentinization on the seafloor. On the contrary, F contents of these serpentinites show little to no enrichment, which is consistent with low F in seawater and pelagic sediment pore fluids. Subducted antigorite-serpentinites of the same complex have higher contents of F but much lower contents of Cl, Br and I than their lizardite counterparts, suggesting loss of the latter elements during the lizardite-antigorite phase transition. Fluorine enrichment is considered to occur during additional serpentinization along fractures at the outer rise of the slab immediately prior to subduction (Figure 8-1). Fluorine is likely mobilized from dissolving minerals, such as marine carbonates or phosphorites, in shallow trench sediments.

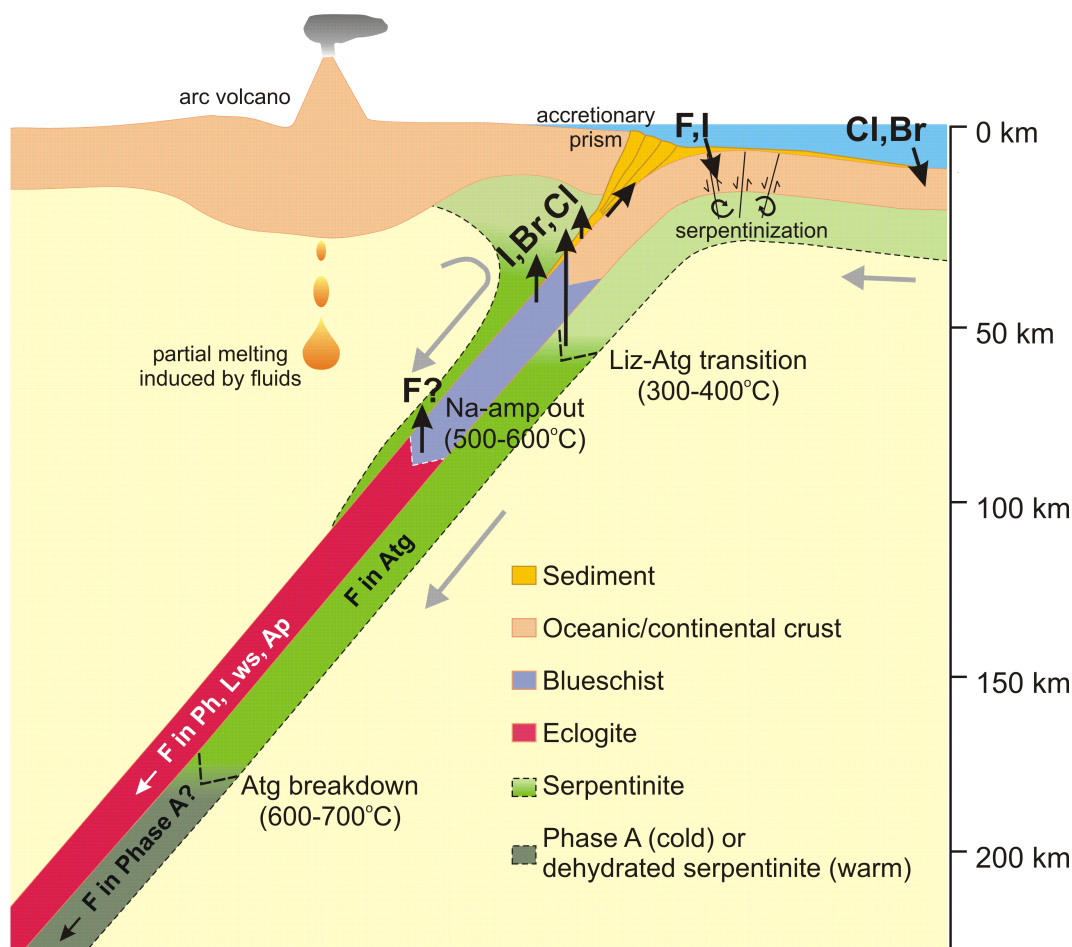


Figure 8-1: Schematic cross section of a cold subduction zone showing the behaviour of halogens in the subducting oceanic lithosphere. Serpentinization of abyssal peridotite and hydration of the oceanic crust occurs on or near the seafloor and along fractures of the bending slab at the outer rise. Seawater provides Cl and Br while I and F are sourced from sediment-modified fluids. During shallow (< 50 km) subduction, Cl, Br and I are lost from sediments, altered oceanic crust and lizardite-serpentinites but F is retained. Some F may be lost from the deeper slab as sodic amphibole (Na-Amp) decomposes during the blueschist-eclogite transition. In the slab, minerals including antigorite, phase A (after antigorite decomposition), apatite, lawsonite and phengite host significant F (and minor Cl, Br and I) to depths beyond those associated with arc magma genesis (< 100 km) and may contribute to their transport to the

deeper mantle. The approximate depths of the lizardite (Liz)–antigorite (Atg) transition and decompositions of antigorite and sodic amphibole decomposition are based on a geothermal gradient of ~ 5 °C/km.

During subduction, fluids released from the slab are either refluxed back to the ocean or transferred to the overlying mantle wedge where they are incorporated into forearc mantle serpentinites (Figure 8-1). Halogen compositions of forearc mantle lizardite-serpentinites from the Dominican Republic suggest their hydration by fluids released from subducting altered oceanic crust, with only minor sediment contribution. This is in contrast with shallow (<25 km) forearc serpentinites from Mariana and deep (>100 km) mantle wedge serpentinites associated with the Tso Moriri UHP unit in NW Himalaya (Chapter 3), whose heavy halogen abundance demonstrates significant contribution from subducted shallow water sediments. The Tso Moriri antigorite-serpentinites are enriched in the halogens relative to the depleted MORB mantle, but contain lower absolute concentrations of Cl, Br and I than forearc lizardite-serpentinites of Mariana (considered a shallow level analog for the Tso Moriri samples). This suggests that as serpentinites in the mantle wedge are dragged downwards due to mantle corner flow, the heavy halogens are expelled from the serpentine structure during the lizardite-antigorite transition, consistent with observations for serpentinites of the subducting slab. This behaviour is attributed to antigorite's tighter crystal structure which inhibits accommodation of the larger halogen anions in the OH⁻ site. On the contrary, F contents of the Tso Moriri antigorite-serpentinites are similar or elevated with respect to a shallow level analog, indicating preferential accommodation of F due to its smaller size than heavy halogens and possibly a late influx of F from the deeper slab (Chapter 6). These results suggest that serpentinites have the capacity to transport halogens

to at least 100 km depth in the mantle wedge, and perhaps even deeper in cold slabs. Considering a model for oceanic lithosphere produced at fast-spreading ridges, lizardite-serpentinites of 500 m thickness constitute 2% of the F, 26% Cl, 23% Br and 31% I entering subduction zones, and antigorite-serpentinites contribute 2% of the residual F, 37% Cl, 56% Br and 50% I remaining in the metamorphosed slab (Chapter 5). However, it is important to note that these calculations are based on a conservative estimate for the volume of serpentinites entering subduction zones, and in most subduction zones serpentinites likely make an ever greater contribution to the incoming and residual halogen budgets of the subducting slab.

The altered oceanic crust is also an important reservoir for the halogens, particularly F, entering subduction zones. Blueschist facies metabasites from the Tavsanlı zone, NW Turkey (Chapter 4) and eclogite facies metabasites from the Tso Moriri ultra-high pressure (UHP) unit, NW Himalaya and Sulu UHP belt, China (Chapter 6) contain high F, low Cl and Br and variable I relative to their basaltic-gabbroic protoliths, suggesting the preferential retention of F relative to the heavier halogens in the subducting slab. Bulk Cl, Br and I contents of the blueschist rocks and their mineral separates are positively correlated, suggesting their coherent behaviour during subduction. The blueschists and eclogites preserve I/Cl and Br/Cl ratios similar to those of sedimentary pore fluids and incoming plate sediments, suggesting input from sedimentary sources. Enrichments of F and some I in the metamorphosed crust may be attributed to fluids released from subducting (carbonate-bearing) marine sediments, suggesting geochemical exchange among subducting lithologies.

The apparent retention of F in the blueschists and eclogites relative to the other halogens is attributed to a preferential accommodation of F in the OH⁻ site of hydrous minerals, such as phengite, and the M2 site of apatite due to its smaller ionic radius and higher electronegativity. Some F may also be incorporated into hydrous or nominally anhydrous minerals by coupled

substitution where $\text{Si}^{4+} + \text{O}^{2-}$ are replaced by Fe^{3+} or $\text{Al}^{3+} + \text{F}^-$. Indeed, apatite and phengite are the major host of halogens in these rocks as demonstrated by high F in these minerals – blueschists contain up to 3.5 wt% and 500 ppm F, respectively, and eclogites contain up to 2.3 wt% and 1600 ppm F, respectively. Combined, apatite and phengite constitute 40-85% of the total bulk F in the blueschists (Appendix IV) and 40-97% of the total F in the eclogites (Chapter 6). Other halogen-bearing hydrous minerals in the blueschists include lawsonite, Na-amphibole +/- chlorite (Chapter 4). In these rocks, Cl partitioning follows apatite > phengite $\approx$ Na-amphibole > lawsonite, and F partitioning follows apatite $\gg$ phengite $\approx$ lawsonite > Na-amphibole. Based on bulk rock chemistry, other halogen-bearing phases in the eclogites likely include Ti-bearing phases such as titanite, or residual sodic amphibole (Chapter 6). Bulk F contents of the eclogites are slightly lower than those of the blueschists. This is attributed to a loss of F during the dehydration of sodic amphibole associated with the blueschist-eclogite transition (Figure 8-1). As previously eluded to, the liberated fluids and F may be incorporated into overlying deep mantle wedge serpentinites. Considering a model for oceanic lithosphere produced at fast-spreading ridges, eclogitic basalt and gabbro constitute 87% of the residual F, 60% Cl, 40% Br and 4% I remaining in the metamorphosed slab (Chapter 5). If a model for lithosphere produced at slow spreading ridges is utilized, the contribution of the metacrust decreases to 12% for Cl, 5% for Br and 1% for I, but it remains the major reservoir of F, contributing 74% of residual F in the metamorphosed slab.

Mass balance estimates indicate 90-101% of subducted F, 11-14% Cl, 7-12% Br and 4-5% I are retained in the metamorphosed slab to HP-UHP conditions, presumably beyond depths associated with arc magmatism (Chapter 5; Figure 8-2). Given the stability of antigorite, apatite, lawsonite and phengite to depths of 200-300 km in cold subduction zones with geothermal

gradients of $\sim 5^{\circ}\text{C}/\text{km}$ and the accommodation of halogens in their crystal structures, these minerals likely transport F and some Cl, Br and I beyond subarc depths and contribute to the their abundances in magmas derived from the deeper mantle (Figure 8-2).

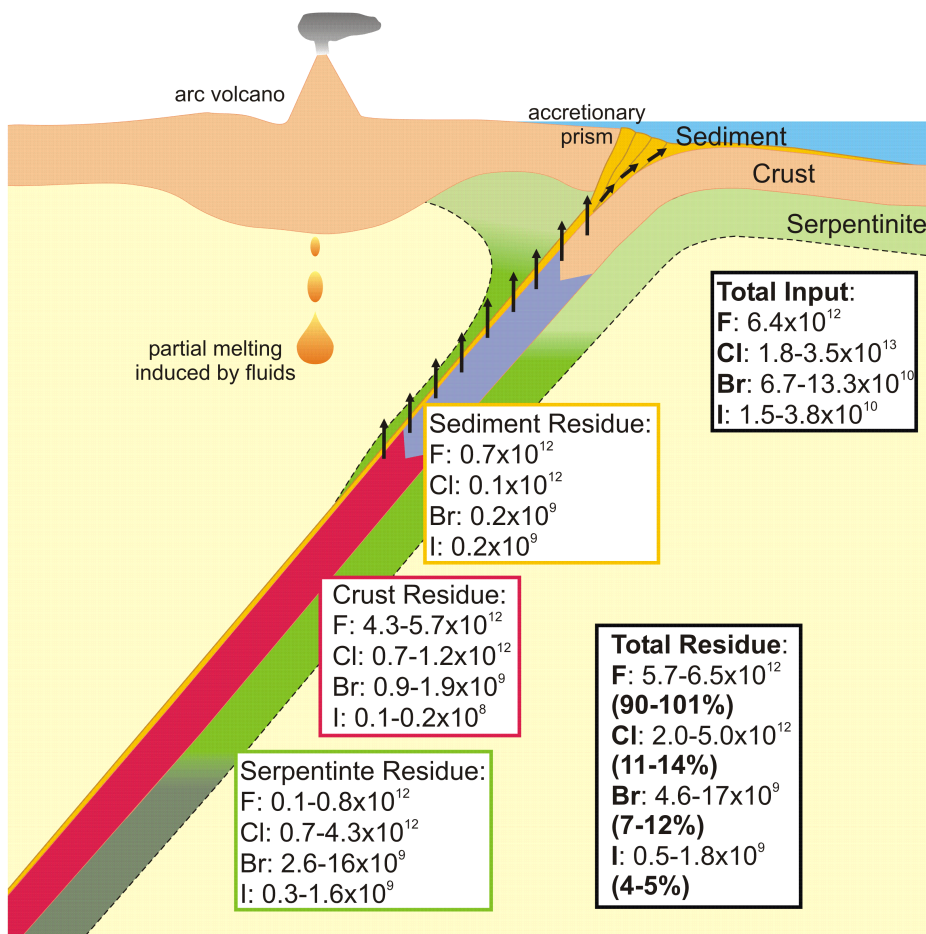


Figure 8-2: Schematic cross section illustrating halogen fluxes (g/yr) through subduction zones. Input and residual flux calculations are from Chapter 5. Ranges reflect calculations for oceanic lithosphere produced fast- and slow- spreading ridges. Nearly all subducted F, up to 14% Cl, 12% Br and 5% I are retained in the metamorphosed slab to subarc depths.

Similar to the halogens, B and N are also enriched in the serpentinitized lithosphere relative to primitive and depleted MORB mantle values. The high B content and B/Cl ratios of

abyssal lizardite-serpentinites from the Dominican Republic are attributed to serpentinization by sediment-modified fluids on the seafloor (Chapter 2). The subducted antigorite-serpentinites from this study area have similarly high B concentrations, indicating B is retained in the crystal structure of serpentine minerals during subduction and there may be additional input by B-rich trench sediments. High B contents are also observed for the deep mantle wedge antigorite-serpentinites associated with the Tso Moriri UHP unit and are similar to those of shallow level lizardite-bearing analogs (Chapter 3). *In situ* analyses of the Tso Moriri serpentinites confirm B is in serpentine minerals. Boron likely replaces tetrahedral Si in these minerals and therefore, it is expected to be retained in the mineral structure during the phase change. In addition to the halogens and B, antigorite-serpentinites from the Tso Moriri UHP unit are also enriched in N relative to mantle values (Chapter 3). This enrichment is also attributed to fluids released from marine sediments on the margin of the Indian continent. Nitrogen abundances of the Tso Moriri serpentinites are the highest ever reported for peridotitic lithologies. Typically N is present as NH_4^+ replacing K^+ in silicates, but no correlation exists between N and alkali elements (e.g., Rb) in these rocks. If N is present as N^{3-} replacing structural O^{2-} (coupled with the substitution of Al^{3+} for Mg^{2+} or As^{5+} for Si^{4+}), then it is likely to be retained during the lizardite-antigorite phase transition. These results show antigorite-serpentinites can transport B and N to at least 100 km depth in the mantle wedge, and, as previously stated for the halogens, perhaps even deeper in the slab in cold subduction zones. Antigorite-serpentinites make a significant contribution to the residual B and N in the metamorphosed slab, constituting 28-80% of residual B and 7-41% of residual N depending on the volume of serpentinites entering subduction zones.

Appendix I.

Published and unpublished supplementary material for Chapter 3

I.1 Published supplementary material

I.1.1 Sample petrography

Serpentine species were previously identified using micro-Raman spectrometry and X-ray powder diffraction (ref. 1). Samples of the Northern Terrane and fault zones are composed of hourglass-textured lizardite pseudomorphs after olivine, along with minor, dusty magnetite. Samples of the tectonic mélanges are comprised of blades of antigorite overprinting the original rock/mineral textures, along with fine-grained magnetite. Mélange sample RD94 consists of pseudomorphic lizardite replacing olivine and minor, penetrative antigorite blades. Primary olivine is preserved in fault-zone sample RD68, and mélange sample RD94, while primary orthopyroxene is identified in fault-zone samples RD18b, RD68, RD34 and mélange sample RD94.

Table A I-1: Summary of the occurrences and mineralogy of serpentinites from the northern Dominican Republic as modified from Saumur et al. (2010).

Geologic context	Location	Samples ^a	Serpentine phase	Accessory minerals ^b	Protolith
‘Northern Terrane’ ophiolite complexes	Puerto Plata complex	4, 6a, 31	Lizardite	Mag, Chr	Obducted abyssal
	Gasper Hernandez	8b	Lizardite	Mag, Chr	Obducted abyssal
Mélanges	Arroyo Sabana	87, 89	Antigorite		Subducted abyssal
	Jagua Clara	21a, 91, 6-50c, 6-52a, 6-54a, 94*	Antigorite (+ lizardite*)	1°Ol, 1°Opx	Subducted abyssal
Fault zones	Camú	9a, 18b, 6-80, 6-81	Lizardite	Mag, Chr	Forearc mantle
	Septentrional	34a, 34c, 68, 6-36a, 6-36c Rio Cuevas: 45, 48, 60	Lizardite	Mag, Chr 1°Ol, 1°Opx	Forearc mantle

^a Prefix of RD is omitted.

^b Abbreviations: Mag – magnetite, Chr – chromite, 1°Ol – primary olivine, 1°Opx – primary orthopyroxene

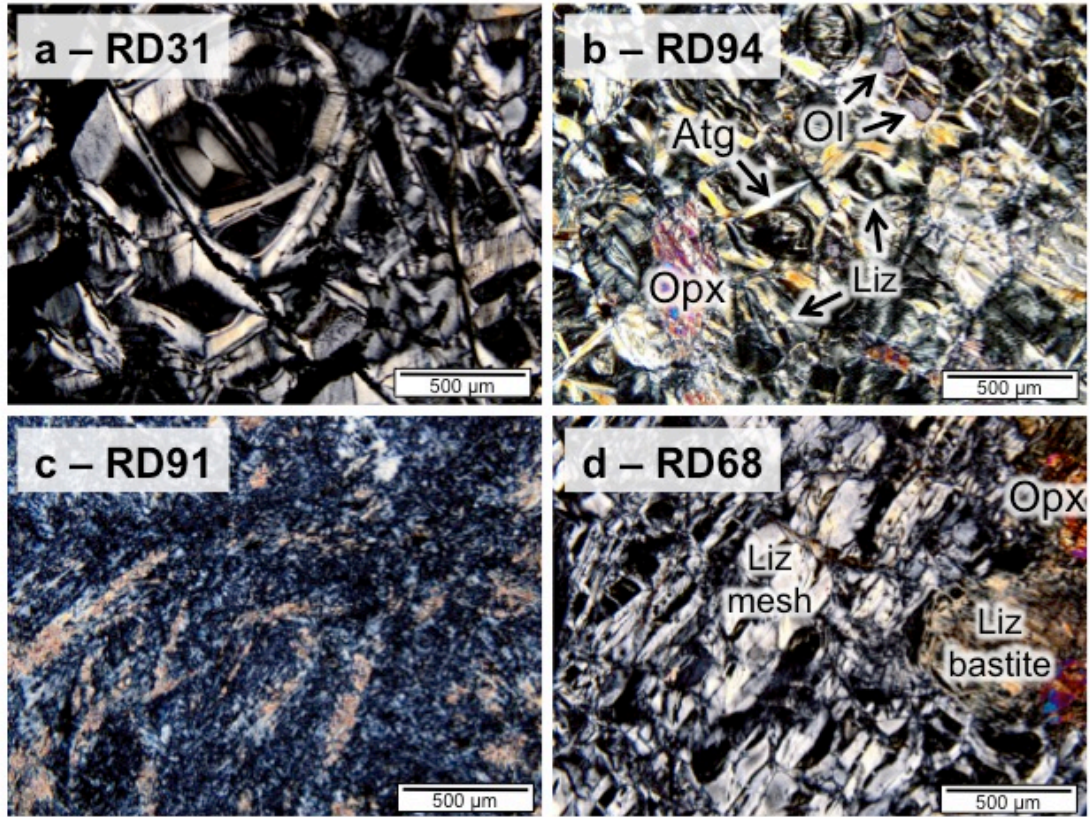


Figure A I-1: Photomicrographs of serpentinite samples under crossed polars. (a) Pseudomorphic lizardite with hourglass texture in obducted abyssal sample RD31. (b) Antigorite blades cross-cutting pseudomorphic lizardite and relic primary olivine and orthopyroxene in subducted abyssal sample RD94. (c) Antigorite blades in antigorite-rich matrix in subducted abyssal sample RD91. (d) Lizardite mesh after olivine and lizardite bastite after orthopyroxene in forearc mantle sample RD68. Atg – antigorite, Liz – lizardite, Ol – olivine, Opx – orthopyroxene

1.1.2 Serpentine protoliths

The Dominican Republic serpentinite samples are classified into three types: i) obducted abyssal ii) subducted abyssal, and iii) forearc mantle serpentinites. Bulk rock and Cr-spinel compositions were used to determine the protolith (abyssal versus forearc mantle peridotite) of each sample (ref. 1). Serpentinites along the fault zones have more refractory protoliths than those of the Northern Terrane and tectonic mélanges, as indicated by higher MgO (up to 40 wt%) and lower Al₂O₃ (< 0.7 wt%) content. The fault-zone serpentinites plot within the field of forearc mantle peridotites on the diagram of Al/Si versus Mg/Si, whereas the samples from the Northern Terrane and mélanges plot within the abyssal peridotite field (ref. 1). The platinum group element (PGE) contents of the fault-zone samples also support a highly refractory protolith, with an enrichment of Iridium-group PGEs (Ir, Os and Ru) and a depletion of Palladium-group PGEs (Pt, Pd and Rh). Furthermore, the high Cr# (up to 0.7) of spinel grains in the fault-zone serpentinites suggest a forearc mantle origin, since abyssal peridotites formed a slow spreading ridges typically contain spinel with a much lower Cr# (<0.4; ref. 2).

The tectonic mélanges represent a serpentinite-rich subduction channel, as suggested by the occurrence of eclogitic fragments in the mélanges (ref. 3), and high-temperature antigorite overprinting pre-existing lizardite in the serpentinite samples. In contrast, the serpentinites of the Northern Terrane ophiolite complex are comprised of low-temperature lizardite, supporting that they have not undergone subduction.

I.2 Unpublished supplementary material

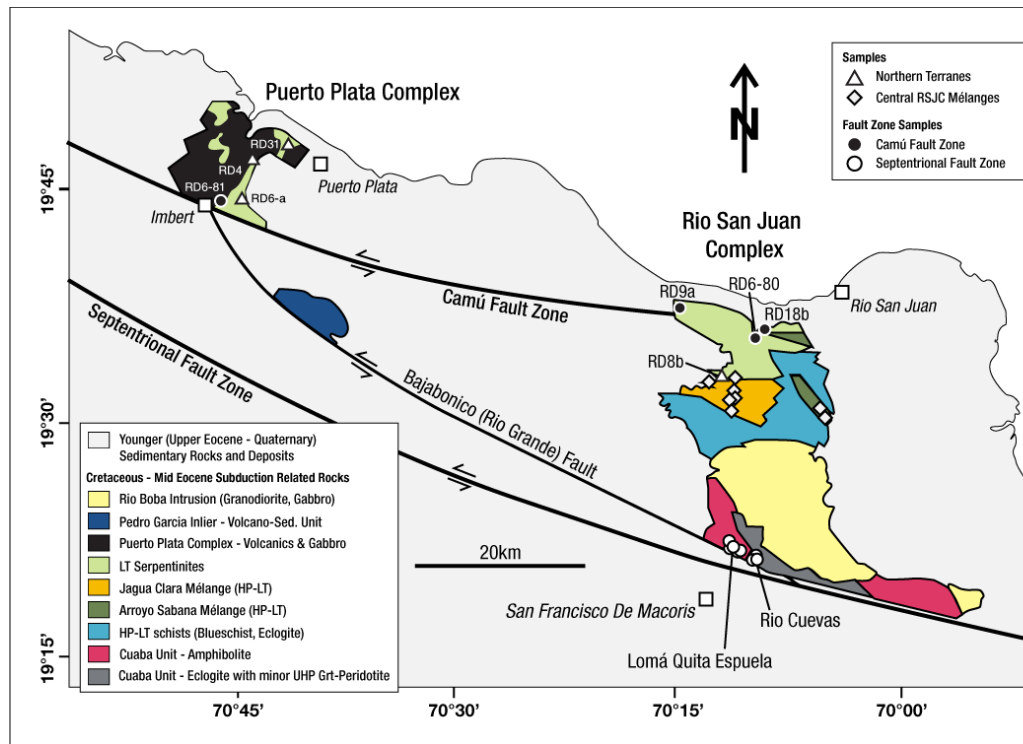


Figure A I-2: Simplified geologic map of the investigated area in Dominican Republic with sample locations. Serpentinite samples were collected from the northern terranes (white triangles) in the Puerto Plata Complex (RD31, RD4, RD6a) and the Gaspar Hernandez serpentinites of the northern Rio San Juan Complex (RD8b), the tectonic mélanges (white diamonds) in the central Rio San Juan Complex including two from the Arroyo Sabana mélange (RD87, RD89) and six from the Jagua Clara mélange (RD21a, RD91, RD94, RD6–50c, RD6–52a, RD6–54a), the Septentrional fault zone (white circles) in the southern part of the Rio San Juan Complex including five from Lomá Quita Espuela (RD34a, RD34c, RD68, RD6–36a, RD6–36c) and three from Rio Cuevas (RD45, RD48, RD60), and the Camú fault zone (black circles) including one in the Puerto Plata Complex (RD6-81) and the northern Rio San Juan Complex (RD9A, RD18b, RD6–80). Modified from Saumur et al. (2010) and Saumur & Hattori (2013).

Table A I-2: Trace element concentrations and B isotopes in serpentine minerals from the Dominican Republic determined by SIMS.

Sample ID		RD4	RD94	RD652	RD87	RD45
Type		Obducted abyssal	Subducted abyssal	Subducted abyssal	Subducted abyssal	Forearc mantle
Phase		Lizardite	Lizardite	Antigorite	Antigorite	Lizardite
H₂O	wt%	10.08	12.17	12.56	11.08	12.90
F	ppm	486	1500	63	905	501
Cl	ppm	437	434	26	34	470
B	ppm	107	347	12	104	70
Li	ppm	0.2	0.6	0.4	0.5	0.1
Sr	ppm	4.4	3.3	0.3	2.2	1.1
Y	ppm	1.2	0.05	0.3	2.9	0.1
Ce	ppm	0.01	0.02	0.02	0.5	0.04
δ¹¹B	‰	3.4	-2.6	4.0	-3.3	-13
1σ	‰	0.5	0.2	1.2	0.5	1.0
nd - not detected						

Table A I-3: Major element and halogen concentrations in serpentine minerals from the Dominican Republic. Mineral formulae and the amount of Fe³⁺ are calculated based on stoichiometric composition and charge balance using 7(O). Liz – lizardite; Atg – antigorite

Sample ID	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4	RD 4
Grain ID	1	2	3	4	5	6	7	8	9	10	11
Phase	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz
Notes	Bastite	Mesh vein	Mesh vein	Mesh vein	Mesh vein	Mesh vein	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center
SiO2	43.26	44.37	42.73	42.73	42.61	42.98	40.25	41.40	41.41	41.84	41.44
TiO2	0.01	0.01	0.02	0.01	0.00	0.00	0.00	0.02	0.02	0.00	0.01
Al2O3	1.71	0.83	0.76	0.70	0.98	0.61	0.84	0.77	0.83	0.83	0.69
FeO	4.53	5.77	3.84	3.28	4.23	3.58	8.34	5.87	6.17	7.88	7.00
MnO	0.04	0.06	0.03	0.04	0.04	0.05	0.05	0.06	0.06	0.05	0.06
MgO	34.56	36.19	38.55	39.54	38.77	39.00	34.15	36.62	36.48	35.65	35.89
NiO	0.39	0.46	0.20	0.13	0.17	0.16	0.54	0.58	0.60	0.59	0.63
CaO	0.16	0.16	0.07	0.05	0.08	0.07	0.13	0.11	0.10	0.16	0.13
Na2O	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01
P2O5	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.04
K2O	0.00	0.01	0.01	0.01	0.00	0.01	0.02	0.00	0.01	0.00	0.00
F	0.058	0.049	0.000	0.000	0.025	0.000	0.027	0.055	0.000	0.036	0.000
Cl	0.023	0.036	0.021	0.020	0.023	0.022	0.152	0.092	0.099	0.128	0.101
Sub-total	84.76	87.96	86.27	86.52	86.94	86.47	84.50	85.58	85.78	87.20	86.01
O=F,Cl	0.03	0.03	0.00	0.00	0.02	0.01	0.05	0.04	0.02	0.04	0.02
Total	84.73	87.93	86.27	86.51	86.92	86.47	84.46	85.53	85.76	87.15	85.99
7(O)											
Si	2.0824	2.0756	2.0228	2.0125	2.0078	2.0271	2.0051	2.0078	2.0058	2.0110	2.0104
Ti	0.0005	0.0002	0.0007	0.0002	0.0001	0.0000	0.0001	0.0006	0.0007	0.0000	0.0005
Al	0.0971	0.0457	0.0426	0.0391	0.0544	0.0336	0.0493	0.0441	0.0474	0.0470	0.0394
Fe3+	0.0006	0.0025	0.0023	0.0007	0.0003	0.0006	0.0010	0.0002	0.0008	0.0017	0.0014
Fe2+	0.1818	0.2232	0.1497	0.1285	0.1664	0.1406	0.3464	0.2378	0.2491	0.3150	0.2826
Mn	0.0015	0.0025	0.0013	0.0015	0.0016	0.0019	0.0022	0.0024	0.0024	0.0020	0.0026
Mg	2.4802	2.5239	2.7207	2.7764	2.7235	2.7421	2.5363	2.6477	2.6343	2.5545	2.5958
Ni	0.0153	0.0174	0.0075	0.0050	0.0066	0.0059	0.0217	0.0226	0.0234	0.0229	0.0247
Ca	0.0083	0.0078	0.0036	0.0027	0.0039	0.0037	0.0070	0.0058	0.0050	0.0080	0.0066
Na	0.0004	0.0021	0.0017	0.0000	0.0001	0.0001	0.0000	0.0002	0.0000	0.0016	0.0013
P	0.0001	0.0000	0.0007	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000	0.0007	0.0016
K	0.0001	0.0004	0.0006	0.0007	0.0002	0.0005	0.0010	0.0000	0.0008	0.0001	0.0000
F	0.0089	0.0072	0.0000	0.0000	0.0037	0.0000	0.0042	0.0084	0.0000	0.0055	0.0000
Cl	0.0019	0.0028	0.0017	0.0016	0.0018	0.0018	0.0128	0.0076	0.0081	0.0105	0.0083
OH	1.9892	1.9900	1.9983	1.9984	1.9944	1.9982	1.9830	1.9840	1.9919	1.9841	1.9917

Table A I-3 continued:

Sample ID	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94	RD 94
Grain ID	1	2	3	4	5	6	7	8	9	10	11
Serpentine phase	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz	Liz
Notes	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh center	Mesh vein
SiO2	43.61	42.84	42.98	40.58	43.52	43.79	40.42	42.13	41.02	42.07	42.56
TiO2	0.01	0.01	0.01	0.00	0.00	0.02	0.01	0.02	0.01	0.01	0.00
Al2O3	0.05	0.01	0.07	0.15	0.24	0.23	0.17	0.00	0.01	0.11	0.01
FeO	8.39	8.23	8.20	9.71	7.75	7.60	8.48	11.68	11.21	9.09	3.30
MnO	0.18	0.03	0.09	0.06	0.13	0.16	0.09	0.10	0.06	0.10	0.05
MgO	32.62	33.27	32.76	34.84	32.54	32.84	36.17	30.17	33.06	34.06	39.72
NiO	0.45	0.42	0.39	0.11	0.50	0.50	0.42	0.36	0.23	0.48	0.04
CaO	0.09	0.08	0.08	0.05	0.05	0.04	0.03	0.12	0.05	0.07	0.02
Na2O	0.02	0.03	0.00	0.02	0.02	0.05	0.01	0.02	0.05	0.02	0.00
P2O5	0.01	0.00	0.01	0.00	0.03	0.00	0.00	0.03	0.01	0.00	0.00
K2O	0.01	0.01	0.00	0.00	0.01	0.03	0.01	0.07	0.04	0.00	0.00
F	0.006	0.081	0.074	0.011	0.112	0.076	0.034	0.000	0.006	0.000	0.000
Cl	0.071	0.095	0.090	0.025	0.084	0.088	0.057	0.065	0.118	0.128	0.016
Sub-total	85.51	85.10	84.75	85.56	84.99	85.42	85.89	84.76	85.86	86.13	85.73
O=F,Cl	0.02	0.06	0.05	0.01	0.07	0.05	0.03	0.01	0.03	0.03	0.00
Total	85.50	85.04	84.70	85.55	84.93	85.37	85.86	84.75	85.83	86.10	85.72
7(O)											
Si	2.1251	2.1014	2.1146	2.0043	2.1283	2.1281	1.9838	2.1107	2.0340	2.0551	2.0236
Ti	0.0002	0.0004	0.0002	0.0001	0.0001	0.0007	0.0004	0.0007	0.0004	0.0003	0.0000
Al	0.0026	0.0005	0.0039	0.0088	0.0137	0.0129	0.0096	0.0000	0.0004	0.0061	0.0006
Fe3+	0.0029	0.0031	0.0004	0.0021	0.0024	0.0067	0.0010	0.0061	0.0071	0.0020	0.0001
Fe2+	0.3390	0.3345	0.3370	0.3989	0.3145	0.3021	0.3470	0.4832	0.4577	0.3693	0.1311
Mn	0.0073	0.0011	0.0038	0.0026	0.0055	0.0064	0.0037	0.0043	0.0026	0.0042	0.0021
Mg	2.3697	2.4329	2.4028	2.5655	2.3723	2.3793	2.6465	2.2534	2.4439	2.4804	2.8156
Ni	0.0177	0.0165	0.0156	0.0043	0.0199	0.0196	0.0165	0.0147	0.0091	0.0188	0.0016
Ca	0.0047	0.0044	0.0041	0.0025	0.0026	0.0022	0.0015	0.0062	0.0027	0.0035	0.0011
Na	0.0020	0.0027	0.0004	0.0020	0.0019	0.0050	0.0006	0.0018	0.0047	0.0019	0.0000
P	0.0005	0.0001	0.0002	0.0000	0.0012	0.0000	0.0000	0.0013	0.0002	0.0000	0.0000
K	0.0009	0.0004	0.0000	0.0001	0.0005	0.0017	0.0004	0.0043	0.0023	0.0001	0.0001
F	0.0009	0.0126	0.0115	0.0017	0.0173	0.0117	0.0052	0.0000	0.0009	0.0000	0.0000
Cl	0.0058	0.0079	0.0075	0.0021	0.0070	0.0072	0.0047	0.0055	0.0099	0.0106	0.0013
OH	1.9933	1.9795	1.9811	1.9962	1.9757	1.9811	1.9901	1.9945	1.9892	1.9894	1.9987

Table A I-3 continued:

Sample ID	RD 94	RD 94	RD 94	RD 94	RD 94	RD 652	RD 652	RD 652	RD 652	RD 652	RD 652
Grain ID	12	13	14	15	16	1	2	3	4	5	6
Serpentine phase	Liz	Liz	Liz	Liz	Liz	Atg	Atg	Atg	Atg	Atg	Atg
Notes	Mesh vein	Mesh vein	Mesh vein	Mesh vein	Mesh vein	Blade	Blade	Blade	Blade	Blade	Blade
SiO2	42.56	42.35	39.92	41.83	42.84	45.13	44.99	45.31	45.17	45.42	45.12
TiO2	0.00	0.00	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.00
Al2O3	0.00	0.01	0.03	0.02	0.01	0.25	0.29	0.11	0.25	0.08	0.13
FeO	4.48	4.09	6.60	4.37	5.41	5.08	4.63	4.09	4.75	4.17	4.48
MnO	0.09	0.09	0.02	0.05	0.06	0.07	0.08	0.07	0.05	0.04	0.06
MgO	38.54	38.60	38.44	38.89	36.45	37.62	38.00	38.22	37.80	38.54	37.98
NiO	0.04	0.14	0.32	0.10	0.26	0.20	0.17	0.18	0.25	0.22	0.24
CaO	0.02	0.04	0.02	0.04	0.06	0.02	0.03	0.02	0.01	0.01	0.00
Na2O	0.01	0.00	0.01	0.02	0.03	0.02	0.01	0.00	0.01	0.00	0.00
P2O5	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.04
K2O	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.01	0.00
F	0.050	0.060	0.000	0.012	0.000	0.000	0.003	0.007	0.000	0.007	0.000
Cl	0.042	0.043	0.121	0.040	0.126	0.005	0.000	0.004	0.003	0.004	0.001
Sub-total	85.83	85.43	85.51	85.38	85.28	88.39	88.21	88.02	88.31	88.53	88.06
O=F,Cl	0.03	0.03	0.03	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00
Total	85.80	85.39	85.48	85.37	85.25	88.39	88.21	88.02	88.31	88.53	88.06
7(O)											
Si	2.0339	2.0315	1.9529	2.0119	2.0683	2.0878	2.0817	2.0941	2.0885	2.0889	2.0891
Ti	0.0000	0.0001	0.0004	0.0003	0.0008	0.0001	0.0004	0.0002	0.0002	0.0002	0.0000
Al	0.0000	0.0004	0.0017	0.0009	0.0006	0.0136	0.0157	0.0062	0.0138	0.0046	0.0072
Fe3+	0.0005	0.0004	0.0009	0.0023	0.0039	0.0017	0.0009	0.0004	0.0008	0.0005	0.0002
Fe2+	0.1785	0.1636	0.2691	0.1735	0.2145	0.1948	0.1782	0.1576	0.1829	0.1598	0.1733
Mn	0.0035	0.0035	0.0010	0.0020	0.0024	0.0026	0.0030	0.0027	0.0021	0.0017	0.0023
Mg	2.7458	2.7605	2.8035	2.7885	2.6235	2.5946	2.6212	2.6335	2.6055	2.6424	2.6217
Ni	0.0015	0.0054	0.0124	0.0039	0.0100	0.0076	0.0062	0.0066	0.0092	0.0082	0.0088
Ca	0.0012	0.0023	0.0013	0.0019	0.0029	0.0008	0.0013	0.0008	0.0007	0.0005	0.0002
Na	0.0005	0.0002	0.0008	0.0014	0.0025	0.0016	0.0009	0.0000	0.0008	0.0000	0.0000
P	0.0002	0.0000	0.0007	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0005	0.0017
K	0.0000	0.0002	0.0001	0.0009	0.0014	0.0001	0.0000	0.0004	0.0000	0.0005	0.0002
F	0.0076	0.0091	0.0000	0.0017	0.0000	0.0000	0.0004	0.0010	0.0000	0.0010	0.0000
Cl	0.0034	0.0035	0.0100	0.0033	0.0103	0.0004	0.0000	0.0003	0.0002	0.0003	0.0001
OH	1.9890	1.9874	1.9900	1.9950	1.9897	1.9996	1.9996	1.9987	1.9998	1.9987	1.9999

Table A I-3 continued:

Sample ID	RD 652	RD 652	RD 652	RD 652	RD 87	RD 87	RD 87	RD 87	RD 87	RD 87
Grain ID	7	8	9	10	1	2	3	4	5	6
Serpentine phase	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg
Notes	Blade	Blade	Matrix	Matrix	Blade	Matrix	Matrix	Matrix	Matrix	Matrix
SiO2	44.68	44.77	44.79	44.65	42.59	43.10	41.58	42.94	41.70	42.61
TiO2	0.00	0.02	0.01	0.01	0.01	0.02	0.03	0.01	0.02	0.00
Al2O3	0.48	0.58	0.09	0.05	1.37	1.89	3.00	1.80	4.50	2.04
FeO	4.92	4.54	2.49	2.91	7.55	8.16	8.24	7.88	6.78	7.93
MnO	0.05	0.05	0.07	0.10	0.12	0.16	0.10	0.14	0.06	0.12
MgO	38.00	37.82	39.38	38.99	35.22	33.77	32.90	33.46	33.43	34.37
NiO	0.78	0.18	0.03	0.02	0.13	0.40	0.39	0.36	0.36	0.27
CaO	0.01	0.01	0.04	0.03	0.02	0.05	0.08	0.06	0.15	0.03
Na2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
P2O5	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
K2O	0.01	0.00	0.00	0.01	0.00	0.02	0.01	0.00	0.02	0.01
F	0.024	0.000	0.000	0.030	0.04	0.067	0.072	0.106	0.16	0.06
Cl	0.000	0.002	0.005	0.004	0.00	0.000	0.003	0.004	0.01	0.00
Sub-total	88.97	87.97	86.91	86.81	87.06	87.63	86.41	86.77	87.19	87.46
O=F,Cl	0.01	0.00	0.00	0.01	0.02	0.03	0.03	0.05	0.07	0.03
Total	88.96	87.97	86.91	86.79	87.04	87.60	86.38	86.72	87.12	87.43
7(O)										
Si	2.0617	2.0758	2.0808	2.0821	2.0327	2.0487	2.0080	2.0582	1.9799	2.0278
Ti	0.0001	0.0007	0.0003	0.0004	0.0003	0.0006	0.0010	0.0005	0.0008	0.0002
Al	0.0260	0.0316	0.0051	0.0027	0.0770	0.1058	0.1707	0.1017	0.2518	0.1150
Fe3+	0.0006	0.0000	0.0000	0.0008	0.0003	0.0012	0.0008	0.0005	0.0019	0.0006
Fe2+	0.1892	0.1760	0.0967	0.1127	0.3010	0.3231	0.3319	0.3153	0.2671	0.3151
Mn	0.0021	0.0021	0.0026	0.0040	0.0050	0.0065	0.0042	0.0056	0.0025	0.0048
Mg	2.6141	2.6142	2.7274	2.7106	2.5058	2.3930	2.3687	2.3909	2.3663	2.4382
Ni	0.0289	0.0065	0.0011	0.0006	0.0051	0.0151	0.0151	0.0139	0.0137	0.0103
Ca	0.0007	0.0007	0.0022	0.0015	0.0009	0.0023	0.0042	0.0029	0.0075	0.0017
Na	0.0000	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0003	0.0007	0.0000
P	0.0004	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0002	0.0000	0.0001
K	0.0006	0.0000	0.0000	0.0007	0.0003	0.0012	0.0008	0.0002	0.0012	0.0006
F	0.0035	0.0000	0.0000	0.0045	0.0057	0.0101	0.0110	0.0161	0.0242	0.0091
Cl	0.0000	0.0002	0.0004	0.0003	0.0001	0.0000	0.0002	0.0003	0.0005	0.0002
OH	1.9965	1.9998	1.9996	1.9952	1.9941	1.9899	1.9888	1.9836	1.9753	1.9906

Table A I-3 continued:

Sample ID	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89	RD 89
Grain ID	1	2	3	4	5	6	7	8	9	10	11
Serpentine phase	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg
Notes											
SiO2	39.54	39.62	40.86	42.58	43.86	43.58	43.46	43.75	43.12	36.82	36.44
TiO2	0.04	0.04	0.02	0.02	0.00	0.01	0.01	0.01	0.02	0.03	0.04
Al2O3	5.57	5.76	4.26	2.32	0.26	0.64	0.99	0.93	1.17	8.81	9.43
FeO	7.69	8.39	8.41	8.23	7.06	7.35	7.20	7.56	6.49	7.46	8.15
MnO	0.06	0.09	0.07	0.09	0.14	0.12	0.10	0.12	0.09	0.02	0.05
MgO	31.91	30.86	32.82	33.55	36.07	35.69	35.62	35.24	36.27	32.08	31.18
NiO	0.68	0.98	0.56	0.51	0.21	0.28	0.25	0.23	0.20	0.30	0.39
CaO	0.10	0.12	0.07	0.07	0.03	0.01	0.01	0.02	0.02	0.05	0.05
Na2O	0.01	0.03	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01
P2O5	0.04	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.03
K2O	0.04	0.03	0.02	0.02	0.01	0.00	0.00	0.02	0.00	0.02	0.03
F	0.02	0.060	0.00	0.05	0.038	0.03	0.01	0.034	0.027	0.00	0.00
Cl	0.01	0.025	0.02	0.02	0.021	0.02	0.01	0.015	0.010	0.02	0.02
Sub-total	85.72	86.00	87.13	87.48	87.71	87.74	87.67	87.92	87.44	85.61	85.82
O=F,Cl	0.01	0.03	0.00	0.03	0.02	0.02	0.01	0.02	0.01	0.00	0.01
Total	85.71	85.97	87.13	87.45	87.69	87.72	87.66	87.90	87.42	85.60	85.82
7(O)											
Si	1.9240	1.9315	1.9603	2.0299	2.0714	2.0609	2.0539	2.0645	2.0376	1.7941	1.7782
Ti	0.0016	0.0015	0.0007	0.0008	0.0000	0.0003	0.0004	0.0002	0.0006	0.0009	0.0014
Al	0.3191	0.3309	0.2406	0.1309	0.0145	0.0358	0.0552	0.0516	0.0652	0.5059	0.5426
Fe3+	0.0033	0.0046	0.0033	0.0027	0.0004	0.0006	0.0001	0.0010	0.0000	0.0015	0.0029
Fe2+	0.3096	0.3374	0.3342	0.3257	0.2784	0.2902	0.2843	0.2973	0.2564	0.3023	0.3298
Mn	0.0026	0.0037	0.0029	0.0037	0.0055	0.0047	0.0040	0.0047	0.0036	0.0010	0.0021
Mg	2.3149	2.2429	2.3477	2.3840	2.5395	2.5161	2.5096	2.4792	2.5552	2.3301	2.2682
Ni	0.0268	0.0383	0.0217	0.0198	0.0080	0.0107	0.0096	0.0086	0.0077	0.0119	0.0155
Ca	0.0054	0.0061	0.0038	0.0033	0.0015	0.0007	0.0007	0.0012	0.0010	0.0027	0.0027
Na	0.0005	0.0028	0.0019	0.0017	0.0000	0.0004	0.0000	0.0000	0.0000	0.0004	0.0008
P	0.0017	0.0000	0.0001	0.0002	0.0007	0.0001	0.0001	0.0000	0.0007	0.0000	0.0012
K	0.0028	0.0018	0.0013	0.0010	0.0004	0.0002	0.0001	0.0010	0.0000	0.0011	0.0021
F	0.0033	0.0092	0.0000	0.0082	0.0057	0.0051	0.0011	0.0050	0.0040	0.0000	0.0000
Cl	0.0011	0.0021	0.0015	0.0014	0.0017	0.0012	0.0008	0.0012	0.0008	0.0017	0.0020
OH	1.9955	1.9887	1.9985	1.9904	1.9927	1.9937	1.9981	1.9938	1.9952	1.9983	1.9980

Table A I-3 continued:

Sample ID	RD 91	RD 91	RD 91	RD 91	RD 91	RD 91	RD 91	RD 91	RD 91	RD 45	RD 45
Grain ID	1	2	3	4	5	6	7	8	9	1	2
Serpentine phase	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Atg	Liz	Liz
Notes	HourglassHourglass										
SiO2	43.26	42.70	43.34	43.49	43.30	43.28	43.29	42.68	43.30	42.64	42.99
TiO2	0.01	0.01	0.02	0.00	0.02	0.02	0.02	0.02	0.03	0.00	0.00
Al2O3	1.35	1.06	0.92	0.83	0.91	0.94	0.84	1.56	0.88	0.04	0.03
FeO	6.51	5.79	6.06	6.34	6.05	6.10	6.11	6.32	6.11	3.10	2.45
MnO	0.04	0.03	0.04	0.04	0.02	0.04	0.05	0.04	0.03	0.07	0.04
MgO	36.38	36.17	37.10	36.74	37.39	36.98	37.86	36.97	37.46	39.79	40.53
NiO	0.32	0.26	0.24	0.29	0.16	0.18	0.18	0.22	0.20	0.37	0.31
CaO	0.01	0.01	0.00	0.02	0.00	0.02	0.01	0.01	0.02	0.04	0.03
Na2O	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P2O5	0.00	0.01	0.00	0.00	0.01	0.00	0.03	0.01	0.03	0.00	0.00
K2O	0.01	0.09	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
F	0.000	0.000	0.035	0.000	0.000	0.009	0.000	0.000	0.000	0.02	0.02
Cl	0.024	0.005	0.004	0.003	0.003	0.003	0.004	0.000	0.001	0.10	0.11
Sub-total	87.93	86.14	87.77	87.77	87.87	87.58	88.39	87.85	88.06	86.17	86.52
O=F,Cl	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03
Total	87.92	86.13	87.75	87.77	87.87	87.57	88.39	87.85	88.06	86.14	86.49
7(O)											
Si	2.0333	2.0411	2.0367	2.0454	2.0314	2.0374	2.0214	2.0075	2.0284	2.0213	2.0218
Ti	0.0005	0.0003	0.0006	0.0001	0.0007	0.0009	0.0006	0.0008	0.0010	0.0001	0.0001
Al	0.0749	0.0595	0.0508	0.0458	0.0501	0.0524	0.0464	0.0867	0.0488	0.0020	0.0017
Fe3+	0.0007	0.0056	0.0016	0.0016	0.0007	0.0004	0.0000	0.0003	0.0004	0.0005	0.0005
Fe2+	0.2552	0.2259	0.2365	0.2477	0.2366	0.2397	0.2386	0.2483	0.2389	0.1227	0.0960
Mn	0.0015	0.0013	0.0014	0.0016	0.0009	0.0014	0.0018	0.0017	0.0012	0.0027	0.0017
Mg	2.5491	2.5776	2.5991	2.5760	2.6151	2.5953	2.6356	2.5924	2.6161	2.8118	2.8419
Ni	0.0122	0.0099	0.0091	0.0111	0.0059	0.0068	0.0067	0.0083	0.0077	0.0139	0.0116
Ca	0.0007	0.0006	0.0000	0.0008	0.0000	0.0008	0.0004	0.0005	0.0008	0.0018	0.0013
Na	0.0000	0.0001	0.0016	0.0012	0.0004	0.0002	0.0000	0.0000	0.0004	0.0003	0.0004
P	0.0000	0.0005	0.0000	0.0001	0.0002	0.0000	0.0014	0.0006	0.0010	0.0001	0.0000
K	0.0007	0.0054	0.0000	0.0004	0.0003	0.0002	0.0000	0.0003	0.0000	0.0002	0.0001
F	0.0000	0.0000	0.0052	0.0000	0.0000	0.0014	0.0000	0.0000	0.0000	0.0037	0.0032
Cl	0.0019	0.0004	0.0003	0.0002	0.0002	0.0002	0.0003	0.0000	0.0001	0.0081	0.0086
OH	1.9981	1.9996	1.9945	1.9998	1.9998	1.9984	1.9997	2.0000	1.9999	1.9882	1.9882

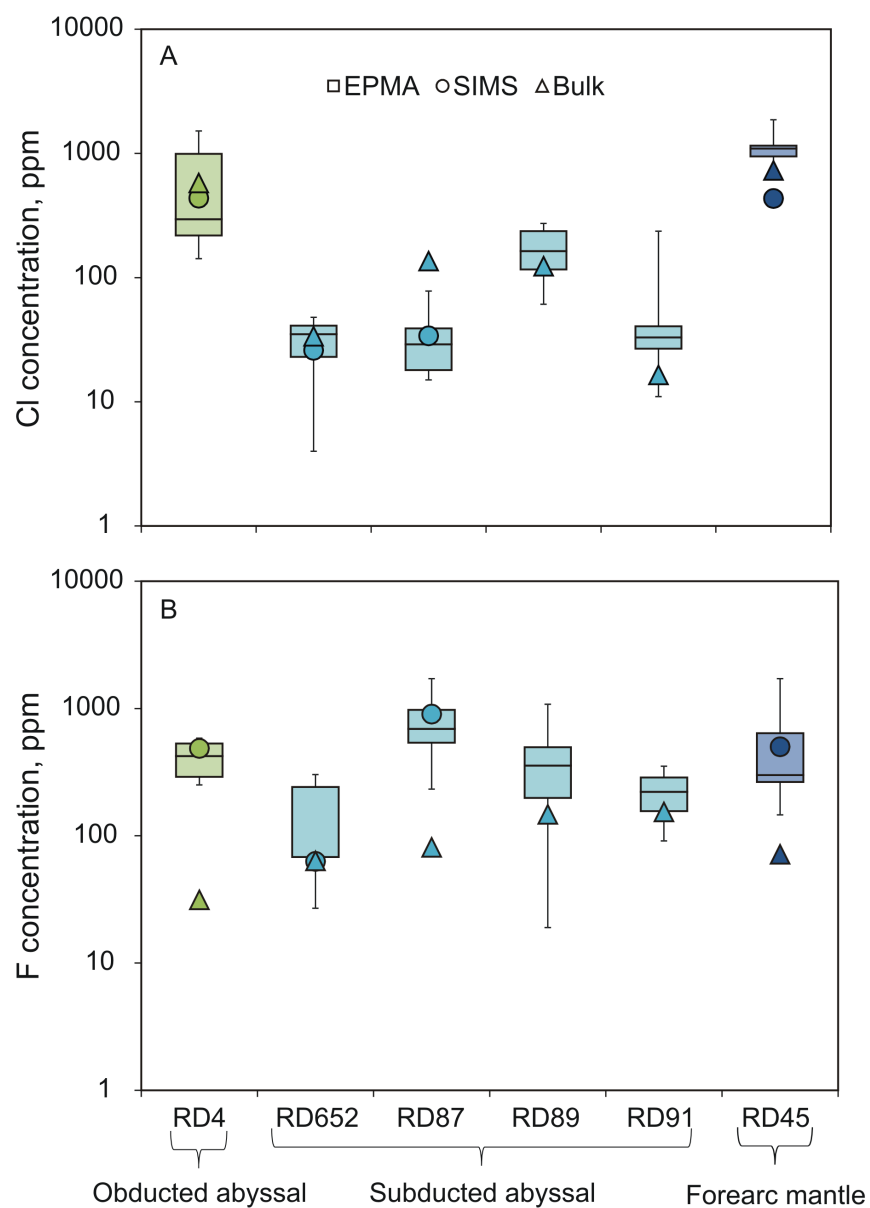


Figure A I-3: Box-and-whisker plots displaying Cl (A) and F (B) concentrations in serpentine grains from Dominican Republic serpentinites as determined by EPMA. Average in situ concentrations determined by SIMS and bulk rock concentrations determined by pyrohydrolysis + IC are shown for reference.

References

- Saumur, B. M., Hattori, K. H., & Guillot, S. Contrasting origins of serpentinites in a subduction complex, northern Dominican Republic. *Geol. Soc. Am. Bull.* **122(1-2)**, 292-304 (2010).
- Michael, P. J., & Bonatti, E. Peridotite composition from the North Atlantic: regional and tectonic variations and implications for partial melting. *Earth Planet. Sci. Lett.*, **73(1)**, 91-104 (1985).
- Krebs, M. *et al.* The dynamics of intra-oceanic subduction zones: a direct comparison between fossil petrological evidence (Rio San Juan Complex, Dominican Republic) and numerical simulation. *Lithos*, **103(1)**, 106-137 (2008).

Appendix II.

Published and unpublished supplementary material for Chapter 4

II.1 Published supplementary material

II.1.1 Sample petrography

All samples are moderately to intensely sheared and comprised of >90% antigorite, along with primary chromite rimmed by magnetite (**Error! Reference source not found.**). Antigorite commonly forms millimetric blades defining schistosity, but pseudomorphs of olivine and pyroxene are identified in some samples (CH430, CH432, CH433). Most samples contain Mg-rich ($Fo > 96$; Hattori and Guillot, 2007) secondary olivine with magnetite inclusions and minor talc cross-cutting the earlier antigorite, indicating the olivine is not primary. Rare veinlets of chrysotile or lizardite cross-cutting antigorite are observed in a few samples (CH98A, CH98B, CH146, CH187) and minor late carbonates are observed in CH433, while the remaining samples (CH422, CH423, CH430, CH432) do not show any evidence of late recrystallization or alteration.

Table A II-1: Mineralogy of investigated Himalayan serpentinite samples.

Mineral	CH98A	CH98B	CH146	CH187	CH422	CH423	CH430	CH432	CH433
Atg	90	90	94	94	93	93	90	95	92
2° Olv	5	5			3	3	4		3
Mag	3	3	2	3	1	1	3	3	3
Talc			1	<1	1	1	1		
Chr	1	1	2	2	2	2	2	2	2
Ctl/Lz	<1	<1	<1	<1					
Chl		<1	<1	<1					
Cal									<1

Note: Atg – antigorite; 2° Olv – secondary olivine after antigorite; Mag – magnetite; Chr – chromite; Mgs – magnesite; Ctl/Lz – chrysotile/lizardite; Chl – chlorite; Cal – calcite

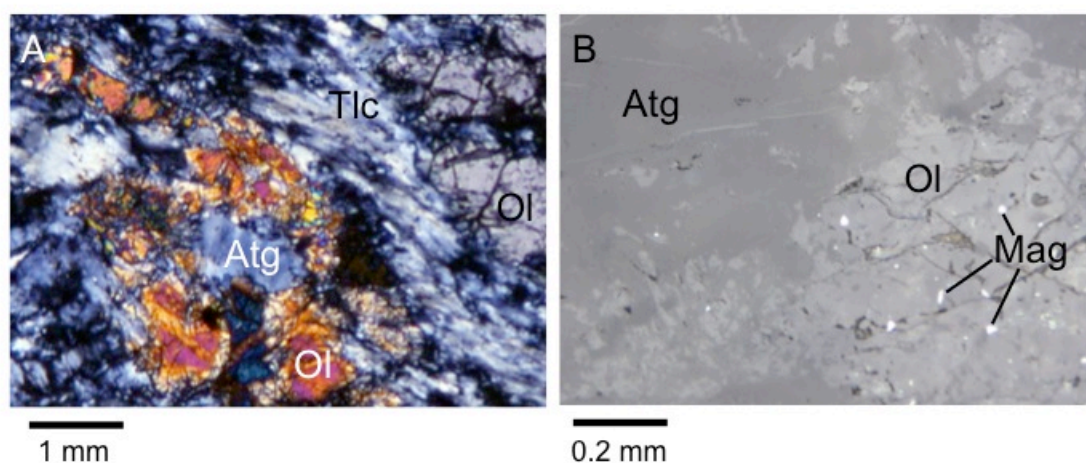


Figure A II-1: Photomicrographs of Himalayan sample CH98B with A) crossed polarized light and B) backscattered electron imaging showing antigorite (Atg) replaced by secondary olivine (Ol) and magnetite (Mag) inclusions in Ol. Tlc-talc.

II.1.2 Methods

II.1.2.1 Halogens

All samples are thoroughly washed prior to grinding to remove any adsorbed elements or soluble organics. Halogens are extracted from 0.5 g of pulverized sample using a pyrohydrolysis technique with the accuracy of the technique verified by the analysis of four references (BCR-2, JB-1, JB-3, MRG-1; Pagé et al., 2016). Fluorine and Cl contents are determined using a Dionex ICS-2100 ion chromatography system equipped with KOH eluent generator, and Br (^{79}Br) and I (^{127}I) contents are determined using an Agilent Technologies 7700 series inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Ottawa. Samples for ICP-MS are diluted 5x to minimize the effects of Na precipitate, and 1% NH_3 is added to stabilize the anions in solution. Instrument detection limits and blanks are reported in Pagé & Hattori, 2017. Average

standard deviations (1σ) of repeat extractions ($n=2$ or 3) are 5.2 % for F, 9.8 % for Cl, 38 % for Br and 6.6 % for I.

II.1.2.2 Nitrogen

Nitrogen contents are determined using an Elementar vario EL cube elemental analyzer in CNS mode (combustion at 1150°C). To improve peak resolution, N is separated from other gases by chemical traps and carried by He to the detector. Powdered samples (~400 mg) mixed with Sn and WO₂ powders (~100 mg each) are placed in large (20x10x8 mm) Sn capsules.

Atmospheric N is removed from samples and references by placing them under vacuum in the auto-sampler ball valve for 20 seconds prior to combustion. The calibration curve is created using references B-2150 and B-2152 and the concentration values obtained from the curve are reported. The average standard deviation (1σ) of repeat sample analyses ($n=3$) is 4.9 %.

Accuracy of the technique is assessed by the analysis of four references (BHVO-2, SO-3, SCo-1, MAG-1; Table S2). Overall, the obtained values were slightly lower than previously reported.

Method blanks and detection limit are reported as the integration value (area under N peak of raw time-count graphs) and compared to that of a typical sample (Table S3; Fig. S1).

II.1.2.3 Boron

Bulk B concentrations are determined on 1.0 g of samples by Activation Laboratories (Ancaster, Ontario, Canada) by prompt gamma neutron activation analysis (PGNAA) with a 0.5 ppm detection limit. Accuracy of the technique is verified by the analysis of two references (SY-2, SY-3).

Table A II-2: Nitrogen content of international reference materials determined using elemental analyzer.

Standard n=4	N ppm	SD ppm	RSD %	Published data
BHVO-2	15	2.8	19	36±5*; 23 [†]
SO-3	119	6.9	5.8	171±18*; 140±50 [†] ; 152±9 [§]
SCo-1	572	5.0	0.87	644±42*; 580±30 [§]
MAG-1	2971	35	1.2	2863±78*; 2840±55 [§]

Note: SD – standard deviation; RSD – relative SD
 *Kubota, 2009
[†]Govindaraju, 1994
[§]Terashima, 1993

Table A II-3: Background and limit of detection of N determination by elemental analyzer.

Integration value*	
Background (n=5)	3±4
Sn capsule only (n=6)	7±4
Capsule + 100 mg Sn + 100 mg WO ₂ (n=7) [†]	18±9
LOD [§]	27
Sample CH146 (n=3)	296±4

*Nitrogen peak area on time-count graph (Figure S2)
[†]Standard deviation used to calculate LOD
[§]LOD – limit of detection (3σ)

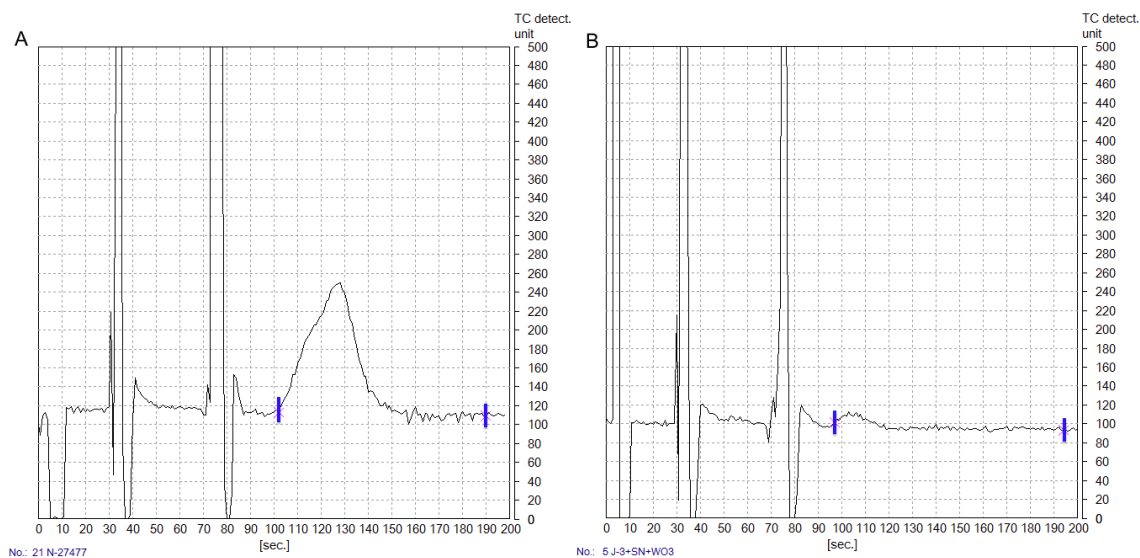


Figure A II-2: Time versus counts received at detector for N determination by elemental analyzer. A) N peak observed for typical sample (CH146 shown here). B) N peak observed for blank (i.e., Sn capsule with Sn and WO₂ powders). Blue lines designate portion of curve integrated to determine N area.

Table A II-4: Fluid-mobile element concentrations of investigated Himalayan serpentinite samples and selected references.

	F (ppm)	Cl (ppm)	Br (ppm)	I (ppm)	B (ppm)	N (ppm)	As[^] (ppm)	Rb[^] (ppm)
Sample (n=2)								
CH98a	104	21	0.209	0.42	83	26	275	0.08
CH98b	96	13	0.095	0.17	104	36	54	0.07
CH146	140	10	0.194	0.19	60	23	6	0.033
CH187	50	35	0.206	0.15	54	46	145	0.11
CH422	649	9	0.045	0.029	21	9	27	0.1
CH423	298	14	0.076	0.18	60	15	49	0.11
CH430	132	12	0.252	0.13	24	22	48	0.32
CH432	100	14	0.106	0.064	38	5	55	0.04
CH433	96	9	0.027	0.049	20	ND*	62	0.14
<i>Average</i>	<i>185</i>	<i>15</i>	<i>0.135</i>	<i>0.16</i>	<i>51</i>	<i>23</i>	<i>80</i>	<i>0.11</i>
References^{†§}								
DM	12	5	0.013	0.0003	0.06	0.09	0.0074	0.088
SW	1	19000	67	0.06	4.44	0.4	0.0018	0.12
Marine sediments	1300	21000	70	28	230	600	20	110
*ND – not determined								
[^] Published in Hattori & Guillot, 2007; As and Rb determined by hydride generator-atomic adsorption and isotopic dilution, respectively								
[†] Abbreviations: DM – depleted mantle; SW – seawater								
[§] References cited: DM – Palme & O’Neil (2003), Salters & Stracke (2004), Marty (2012) and Kendrick et al. (2017); SW – Li (1982); Marine sediments – Li & Schoonmaker (2003)								

II.2 Unpublished supplementary material

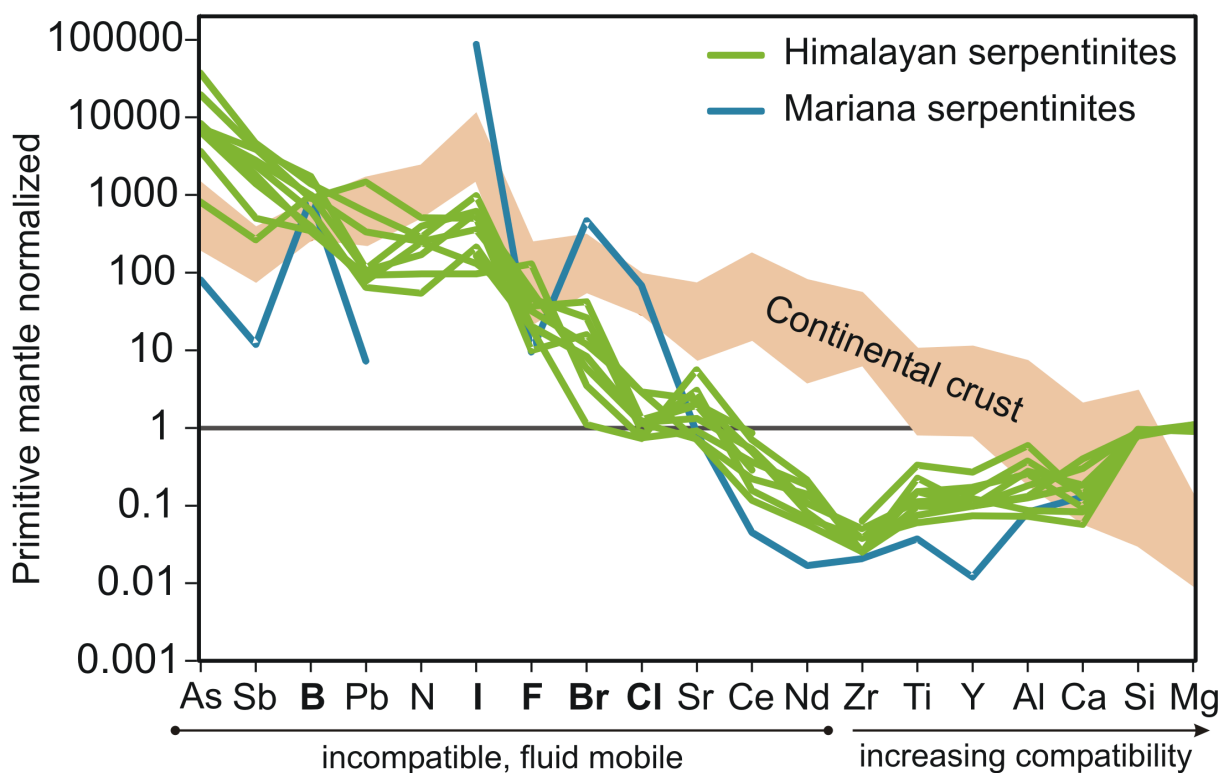


Figure A II-3: Normalized concentrations of fluid-mobile and fluid-immobile elements in antigorite-serpentinites from Himalaya compared to samples of shallow forearc mantle lizardite-serpentinites (Savov et al., 2005; Wei et al., 2005; Kodolanyi et al., 2011; Kendrick et al., 2013) and continental crust (Rudnick & Gao, 2003). Most fluid-mobile elements have similar compatibility with light rare earth elements during partial melting but are on the left side of the diagram to show their enrichment and to clarify the diagram. Fluid-immobile elements are listed in order of compatibility with mantle minerals during partial melting. Samples are normalized to primitive mantle values (Palme & O'Neil, 2003; Kendrick et al., 2017).

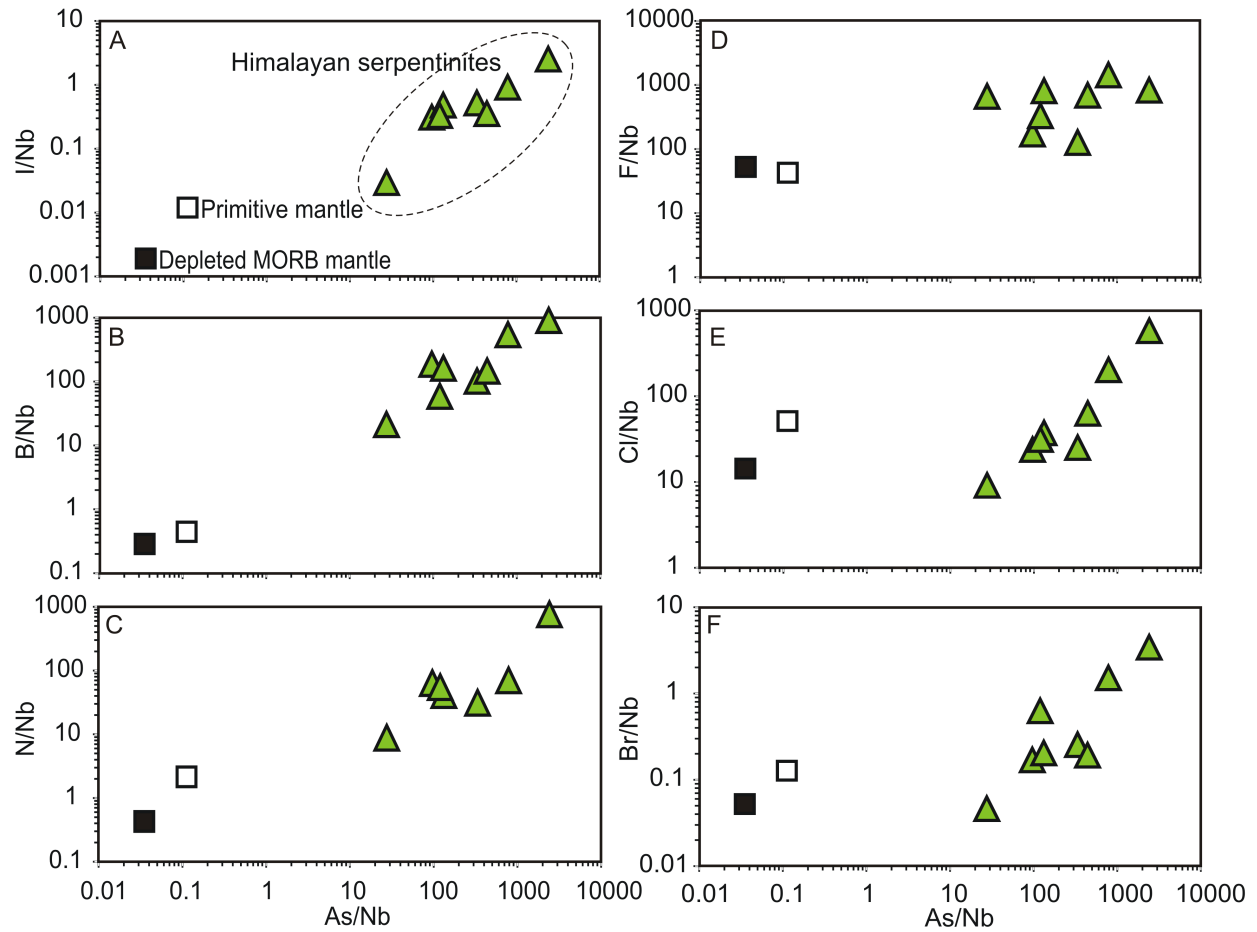


Figure A II-4: Halogen/Nb, B/Nb and N/Nb versus As/Nb ratios of Himalayan serpentinites.

Ratios of I/Nb (A), B/Nb (B) and N/Nb (C) are higher than primitive mantle (PM) and depleted MORB mantle (DMM) values and correlate well with As/Nb. F/Nb ratios (D) are also elevated but do not correlate with As/Nb. Cl/Nb (E) and Br/Nb (F) ratios overlap with the PM and DMM. References for mantle values are in Table 1.

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- Kendrick, M. A., Hémond, C., Kamenetsky, V. S., Danyushevsky, L., Devey, C. W., Rodemann, T., ... & Perfit, M. R. (2017). Seawater cycled throughout Earth's mantle in partially serpentinized lithosphere. *Nature geoscience*, 10(3), 222.

Appendix III.

Published and unpublished supplementary material for Chapter 5

III.1 Published supplementary material

III.1.1 *Pyrohydrolysis method for halogen extraction*

A 0.5 g weight of finely ground sample was combined in a silica boat with an equal weight of reagent grade V_2O_5 (Elemental Microanalysis Ltd) previously heated to 325°C for 24 hours. A wet oxygen gas flow of 0.8 Lmin⁻¹ was created using an Erlenmeyer flask of water on low heat connected to a tank of UHP oxygen gas. The main silica tube was housed in a Lindberg Blue M tube furnace set at an initial temperature of 500°C. A glass rod was used to insert a silica wool plug into the main tube and position it just beyond the wall of the furnace. The purpose of plug was to prevent solid material from entering the trap and clogging the frit. The sample was slowly introduced to the main tube and positioned directly in the middle of the furnace. Once the system was reconnected, the furnace temperature was increased to 1100°C for 15 minutes. The temperature on the output end of the main tube beyond the furnace was maintained at 120°C+ with heating tape to prevent condensation. The evolved gas was passed through a frit inside the trap to maximize surface area contact with the 7 mL of 25 mM NaOH trap solution (prepared from extra pure N₂-flushed NaOH pellets from Acros Organics). The collection vessel was submerged in an ice bath during collection to promote condensation of the halogens in solution. After 15 minutes the furnace temperature was reduced to 500°C before expelling the sample and quartz wool from the main tube. The system was purged with oxygen for 10-15 minutes, fresh quartz wool and the next sample were inserted, and a clean collection vessel was connected to the trap. All glassware was cleaned with deionized water after every two to three runs (i.e. duplicates or triplicates of one sample). Collected solutions were diluted 5x for ICP-MS analysis, and 1% NH₃ was added to stabilize anions in solution. Dilution was not necessary for IC analysis.

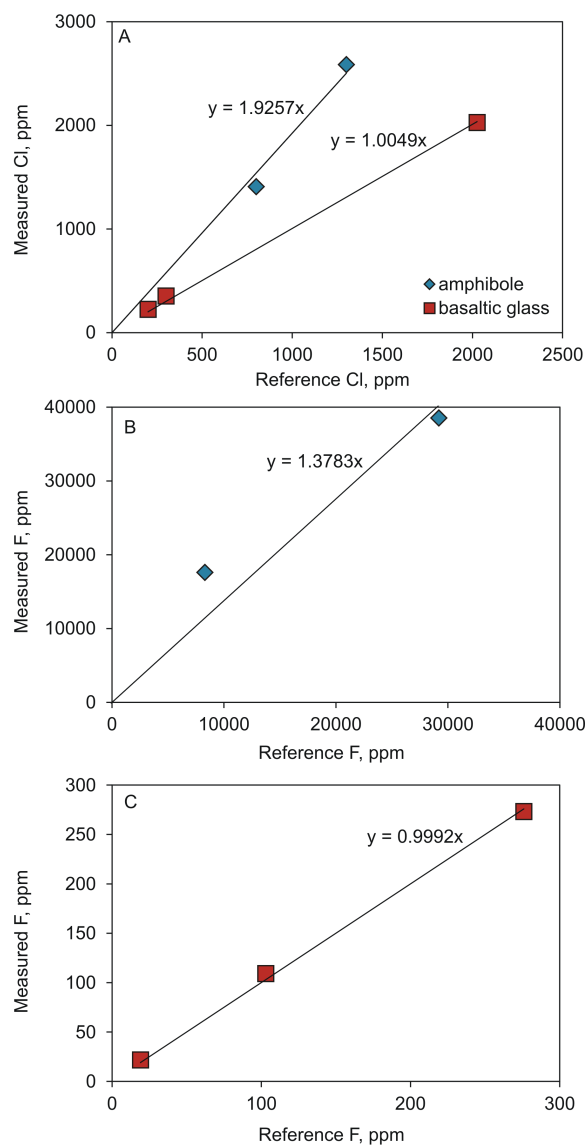


Figure A III-1: Measured halogen concentrations of standards using SIMS, relative to literature values. Slopes of best fit lines are taken as correction factors and applied to analyzed samples. Amphibole standards used for amphibole and phengite correction, and basaltic glass standards used for lawsonite correction. A) Cl in amphibole and basaltic glass standards, B) F in amphibole standards, C) F in basaltic glass standards.

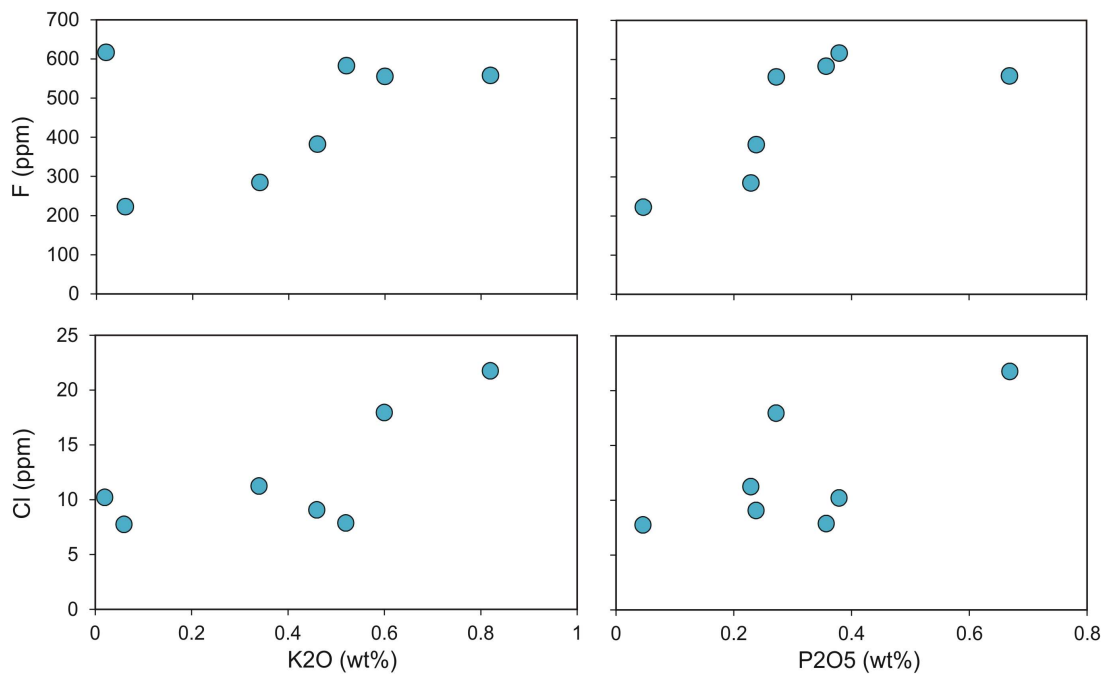


Figure A III-2: Bulk rock concentrations of Tavsanlı Zone blueschists showing positive correlations between the halogens (F and Cl), and K₂O and P₂O₅. This suggests phengite and apatite may control the bulk halogen concentrations in these rocks.

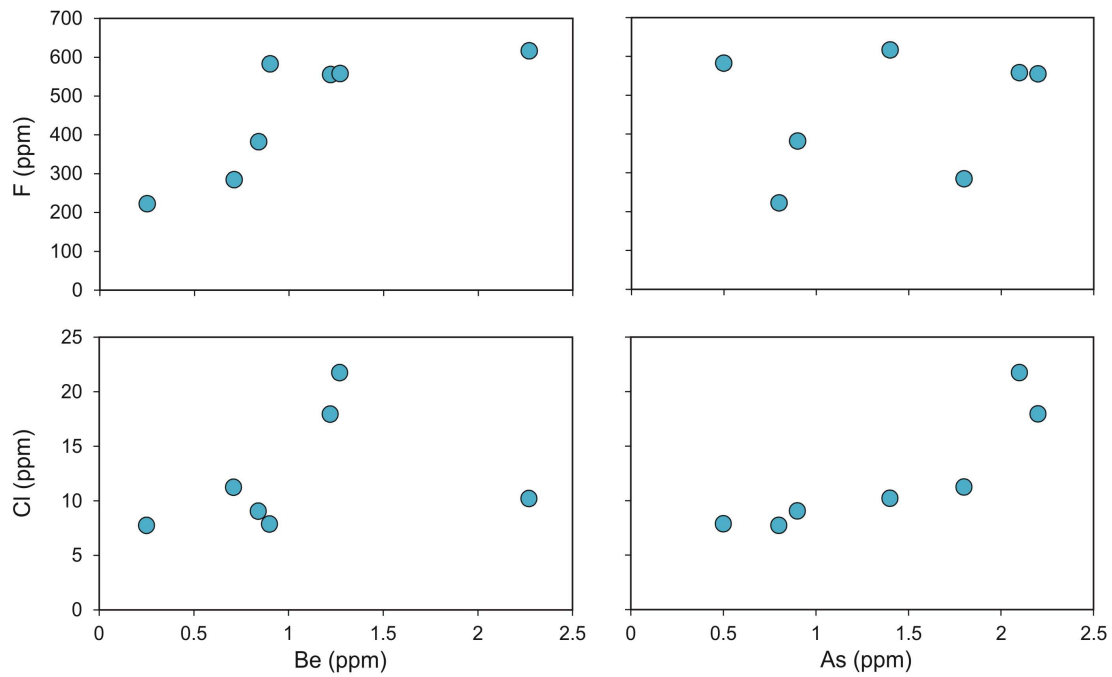


Figure A III-3: Bulk rock concentrations of Tavsanlı Zone blueschists showing the relationships between the halogens and other fluid-mobile elements. Fluorine is positively correlated with Be, but not As, while Cl is broadly correlated with As, but not with Be.

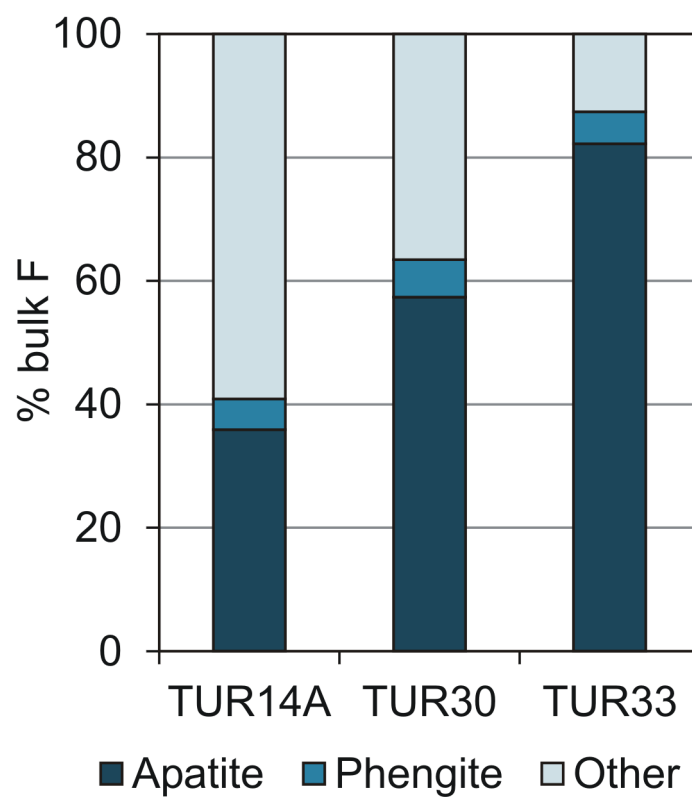


Figure A III-4: Contribution of minerals to bulk F of lawsonite blueschists from the Tavsanlı Zone, northwestern Turkey.

Table A III-1: Major, minor and trace element bulk rock compositions of lawsonite blueschists from the Tavsanlı Zone, northwestern Turkey.

		Method	TUR12	TUR14	TUR23	TUR30	TUR31	TUR32	TUR33
SiO ₂	wt %	XRF	44.41	52.13	45.9	50.47	57.98	46.2	47.32
TiO ₂	wt %	XRF	3.11	1.16	2.09	1.64	1.72	0.46	2.09
Al ₂ O ₃	wt %	XRF	15.41	10.91	14.64	14.01	12.02	19.24	15.05
Fe ₂ O ₃ (t)	wt %	XRF	9.67	9.19	11.2	9.11	10.27	8.2	9.25
MnO	wt %	XRF	0.09	0.24	0.15	0.1	0.17	0.23	0.16
MgO	wt %	XRF	4.69	13.14	7.06	5.42	4.92	5.89	7.61
CaO	wt %	XRF	12.71	3.9	9.14	9.53	4.56	9.74	8.14
Na ₂ O	wt %	XRF	2.86	2.47	3.11	2.92	2.69	2.06	2.6
K ₂ O	wt %	XRF	0.02	0.6	0.46	0.34	0.52	0.06	0.82
P ₂ O ₅	wt %	XRF	0.379	0.272	0.238	0.229	0.357	0.046	0.669
Cr ₂ O ₃	wt %	XRF	0.01	0.12	0.04	0.03	0.02	0.03	0.06
SrO	wt %	XRF	0.04	0.01	0.02	0.02	0.02	0.01	0.03
BaO	wt %	XRF	<0.01	0.02	0.01	0.01	0.01	0.01	0.02
LOI	wt %	XRF	5.72	5.54	5.89	5.97	4.54	7.69	5.91
Total	wt %	XRF	99.13	99.69	99.94	99.77	99.78	99.88	99.74
Mg#			0.49	0.74	0.56	0.54	0.49	0.59	0.62
B	ppm	PGNAA	3	20	15	13	5	4	12
As	ppm	ICP-MS	1.4	2.2	0.9	1.8	0.5	0.8	2.1
Ba	ppm	ICP-MS	<10	150	50	20	80	10	160
Be	ppm	ICP-MS	2.27	1.22	0.84	0.71	0.9	0.25	1.27
Bi	ppm	ICP-MS	0.15	0.17	0.04	0.11	0.29	0.11	0.21
Cd	ppm	ICP-MS	0.16	0.1	0.22	0.15	0.1	0.13	0.14
Ce	ppm	ICP-MS	103	69.5	34.5	32.9	88.9	3.94	92.7
Co	ppm	ICP-MS	33.3	67.3	41.2	27.1	33.7	39.5	39.7
Cr	ppm	ICP-MS	40	704	202	151	120	169	294
Cs	ppm	ICP-MS	<0.05	0.75	0.28	0.22	0.88	<0.05	0.97
Cu	ppm	ICP-MS	59.3	52.1	71.9	65.8	36.3	33.5	37.8
Ga	ppm	ICP-MS	21.5	14.1	18.7	15	17.8	14.85	18.7
Ge	ppm	ICP-MS	0.14	0.11	0.1	0.08	0.15	0.08	0.17
Hf	ppm	ICP-MS	1.9	0.1	0.4	1	0.5	0.2	1.4
In	ppm	ICP-MS	0.081	0.071	0.085	0.066	0.096	0.039	0.084
La	ppm	ICP-MS	51.2	30.3	16.3	15.7	42.3	2.2	41.8
Li	ppm	ICP-MS	30.4	48.1	19.9	17.9	38.5	19.2	36
Mn	ppm	ICP-MS	741	1930	1170	809	1300	1800	1310
Mo	ppm	ICP-MS	2.1	0.11	2.49	1.11	0.05	0.09	0.34

			Method	TUR12	TUR14	TUR23	TUR30	TUR31	TUR32	TUR33
Nb	ppm	ICP-MS		63.3	1.9	20.7	15.8	40.2	0.8	40
Ni	ppm	ICP-MS		71	683	129	91.1	127.5	109	359
P	ppm	ICP-MS		1810	1280	1110	1090	1640	210	3050
Pb	ppm	ICP-MS		12.5	8.5	4.2	8.6	9.7	7.5	13.9
Rb	ppm	ICP-MS		0.2	17.2	5.7	6.1	18	0.1	20.5
Re	ppm	ICP-MS		<0.002	<0.002	0.002	<0.002	<0.002	<0.002	0.002
Sb	ppm	ICP-MS		0.51	0.14	0.24	0.28	0.3	0.29	0.44
Sc	ppm	ICP-MS		17.6	18	29	24.4	17.5	42.2	16.6
Se	ppm	ICP-MS		2	1	1	1	1	1	2
Sn	ppm	ICP-MS		1.9	0.9	1.3	1.2	2.1	0.3	1.9
Sr	ppm	ICP-MS		390	133.5	169.5	143.5	187.5	135.5	245
Ta	ppm	ICP-MS		3.87	0.13	1.18	0.92	2.3	<0.05	2.42
Te	ppm	ICP-MS		<0.05	0.26	<0.05	<0.05	0.06	<0.05	0.1
Th	ppm	ICP-MS		5.5	6	1.4	1.2	6.7	<0.2	6.4
Tl	ppm	ICP-MS		<0.02	0.16	0.05	0.03	0.16	<0.02	0.17
U	ppm	ICP-MS		1.2	0.6	0.4	0.4	0.8	0.2	1
V	ppm	ICP-MS		306	137	221	206	159	197	169
W	ppm	ICP-MS		0.3	0.1	0.3	0.3	0.5	0.1	0.3
Y	ppm	ICP-MS		27.2	20.4	22.7	23.2	26.9	17.1	32.7
Zn	ppm	ICP-MS		91	108	104	72	135	110	98
Zr	ppm	ICP-MS		52.9	3.5	7.4	14.2	17.6	1.9	64.3

Fe total expressed as Fe₂O₃ (t)

Mg# - atomic Mg/[Mg + Fe₂O₃ (t)]

XRF - x-ray fluorescence; PGNAA - prompt gamma neutron activation analysis; ICP-MS - inductively coupled plasma-mass spectrometry

Table A III-2: Major and minor element compositions of representative sodic amphibole (Na-amp) grains from the Tavsanlı Zone blueschists, northwestern Turkey.

Sample ID	TUR12	TUR12	TUR12	TUR14A	TUR14A	TUR14A	TUR23	TUR23	TUR30	TUR30
Grain ID	G1	G2	G3	G1	G2	G3	G2	G2b	G2	G3
Mineral	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp
# of analyses	3	3	3	3	3	3	2	4	3	3
SiO₂	56.11	55.82	56.29	57.82	57.78	57.86	56.23	56.39	56.78	56.79
TiO₂	0.03	0.04	0.04	0.00	0.01	0.01	0.09	0.20	0.04	0.19
Al₂O₃	5.37	5.34	5.89	6.13	5.82	5.98	5.25	7.23	6.10	5.37
Cr₂O₃	0.08	0.00	0.01	0.04	0.02	0.04	0.05	0.25	0.07	0.00
FeO	17.26	17.07	16.88	14.62	14.63	14.58	18.75	16.83	15.43	14.61
MnO	0.22	0.19	0.21	0.25	0.27	0.25	0.17	0.16	0.18	0.21
MgO	9.81	9.97	9.52	11.23	11.40	11.27	8.56	7.91	10.48	11.50
NiO	0.02	0.01	0.02	0.09	0.09	0.06	0.00	0.02	0.01	0.02
CaO	1.73	2.10	1.62	0.76	0.99	0.81	0.94	0.76	1.39	2.88
Na₂O	5.61	5.58	5.77	6.24	6.19	6.21	6.37	6.43	6.07	5.31
K₂O	0.02	0.03	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.03
F	0.01	0.00	0.00	0.01	0.03	0.01	0.01	0.01	0.00	0.02
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sub-total	96.28	96.15	96.29	97.23	97.26	97.11	96.44	96.21	96.58	96.93
O=F.Cl	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.01
Total	96.28	96.15	96.29	97.22	97.25	97.11	96.43	96.21	96.58	96.92
23(O)										
Si	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000
Ti	0.0029	0.0041	0.0047	0.0004	0.0013	0.0010	0.0097	0.0213	0.0043	0.0198
Al	0.9027	0.9013	0.9848	0.9995	0.9492	0.9739	0.8802	1.2081	1.0088	0.8884
Cr	0.0086	0.0005	0.0013	0.0048	0.0027	0.0043	0.0052	0.0281	0.0076	0.0000
Fe³⁺	0.8273	0.6800	0.8296	0.9881	1.0022	1.0593	1.1257	0.8195	0.7591	0.5980
Fe²⁺	1.2304	1.3659	1.1770	0.7029	0.6917	0.6268	1.1052	1.1779	1.0612	1.1277
Mn	0.0265	0.0225	0.0253	0.0292	0.0322	0.0287	0.0207	0.0198	0.0215	0.0245
Mg	2.0858	2.1294	2.0175	2.3163	2.3526	2.3239	1.8146	1.6727	2.2024	2.4136
Ni	0.0022	0.0009	0.0025	0.0102	0.0100	0.0072	0.0005	0.0022	0.0017	0.0024
Ca	0.2642	0.3229	0.2486	0.1129	0.1466	0.1205	0.1430	0.1154	0.2110	0.4343
Na	1.5506	1.5494	1.5885	1.6746	1.6607	1.6647	1.7553	1.7672	1.6572	1.4509
K	0.0037	0.0051	0.0040	0.0035	0.0057	0.0044	0.0048	0.0045	0.0036	0.0055
F	0.0049	0.0000	0.0000	0.0039	0.0119	0.0043	0.0053	0.0057	0.0008	0.0091
Cl	0.0006	0.0002	0.0003	0.0000	0.0003	0.0010	0.0000	0.0001	0.0004	0.0004
OH	1.9946	1.9998	1.9997	1.9961	1.9878	1.9947	1.9947	1.9942	1.9987	1.9905

Table A III-2 continued:

Sample ID	TUR31	TUR31	TUR31	TUR31	TUR31	TUR31	TUR32	TUR32	TUR33	TUR33	TUR33
Grain ID	G1	G2	G3	G4	G5	G6	G2	G3	G1	G2	G3
Mineral	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp	Na-amp
# of analyses	1	1	1	1	1	1	1	3	3	3	3
SiO2	55.50	55.83	54.73	54.38	54.81	54.45	58.21	55.41	56.32	56.20	56.85
TiO2	0.13	0.21	0.16	0.07	0.09	0.09	0.04	0.04	0.02	0.05	0.02
Al2O3	9.18	11.09	8.11	7.39	9.24	7.77	8.68	3.16	7.51	7.69	6.63
Cr2O3							0.01	0.03	0.01	0.01	0.01
FeO	17.50	15.79	19.18	20.22	18.29	20.54	10.17	18.06	17.54	18.50	17.65
MnO	0.06	0.05	0.09	0.04	0.05	0.07	0.26	0.33	0.19	0.23	0.16
MgO	0.91	0.66	1.15	0.47	0.54	0.52	11.46	10.60	7.84	7.31	8.43
NiO	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.03	0.01	0.00	0.00
CaO	1.79	1.63	1.69	0.75	1.08	0.83	0.29	0.44	0.32	0.47	0.42
Na2O	12.74	13.08	12.63	13.18	13.07	13.32	6.82	6.26	6.58	6.50	6.52
K2O	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.02	0.02	0.02	0.01
F	0.000	0.000	0.000	0.000	0.000	0.000	0.06	0.08	0.01	0.01	0.02
Cl	0.000	0.004	0.002	0.000	0.000	0.001	0.00	0.01	0.00	0.00	0.00
Sub-total	97.81	98.35	97.77	96.49	97.17	97.61	96.02	94.47	96.37	96.99	96.70
O=F,Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.00	0.00	0.01
Total	97.81	98.35	97.77	96.49	97.17	97.60	96.00	94.44	96.37	96.99	96.69
23(O)											
Si	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000
Ti	0.0143	0.0226	0.0175	0.0081	0.0104	0.0094	0.0044	0.0040	0.0017	0.0055	0.0024
Al	1.5594	1.8728	1.3971	1.2812	1.5894	1.3454	1.4059	0.5379	1.2572	1.2895	1.0986
Cr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0013	0.0031	0.0008	0.0010	0.0006
Fe3+	0.5281	0.0767	0.4118	0.9416	0.4435	0.5744	0.7606	1.4535	0.7705	0.6046	1.0601
Fe2+	1.5812	1.8153	1.9325	1.5458	1.7888	1.9491	0.4082	0.7279	1.3134	1.5982	1.0166
Mn	0.0068	0.0066	0.0115	0.0044	0.0064	0.0090	0.0308	0.0405	0.0233	0.0272	0.0186
Mg	0.1954	0.1418	0.2514	0.1022	0.1167	0.1143	2.3480	2.2827	1.6604	1.5504	1.7677
Ni	0.0000	0.0000	0.0013	0.0000	0.0000	0.0012	0.0000	0.0030	0.0009	0.0002	0.0001
Ca	0.2764	0.2502	0.2647	0.1177	0.1689	0.1303	0.0429	0.0685	0.0480	0.0721	0.0626
Na	3.5602	3.6336	3.5791	3.7590	3.6984	3.7941	1.8171	1.7521	1.8111	1.7938	1.7789
K	0.0001	0.0000	0.0014	0.0000	0.0000	0.0011	0.0023	0.0035	0.0044	0.0028	0.0025
F	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0248	0.0383	0.0029	0.0041	0.0077
Cl	0.0000	0.0008	0.0005	0.0000	0.0000	0.0003	0.0002	0.0021	0.0002	0.0008	0.0000
OH	2.0000	1.9992	1.9995	2.0000	2.0000	1.9997	1.9750	1.9596	1.9969	1.9951	1.9923

Table A III-3: Major and minor element compositions of representative lawsonite (Lws) from the Tavsanlı Zone blueschists, northwestern Turkey.

Sample ID	TUR12	TUR12	TUR14A	TUR14A	TUR14A	TUR23	TUR23	TUR23	TUR30	TUR30	TUR30
Grain ID	L2	L3	L1	L2	L3	L1	L2	L3	L1	L2	L3
Mineral	Lws	Lws	Lws	Lws	Lws	Lws	Lws	Lws	Lws	Lws	Lws
# of analyses	3	3	3	3	3	3	3	3	3	3	3
SiO ₂	40.03	39.88	39.89	39.83	39.74	39.93	39.74	39.44	39.31	39.42	39.68
TiO ₂	0.16	0.15	0.19	0.06	0.06	0.24	0.31	0.52	0.07	0.14	0.28
Al ₂ O ₃	32.12	32.44	31.55	31.96	30.90	32.26	31.72	31.82	31.39	31.68	31.27
Cr ₂ O ₃	0.01	0.01	0.01	0.06	0.93	0.04	0.05	0.06	0.06	0.05	0.04
FeO	1.21	1.04	1.94	1.85	1.82	0.88	1.02	1.05	1.59	1.49	1.51
MnO	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
MgO	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.05	0.01	0.02
NiO	0.00	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00
CaO	17.54	17.57	17.57	17.55	17.53	17.39	17.32	17.42	17.10	17.63	17.53
Na ₂ O	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
F	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sub-total	91.10	91.12	91.22	91.37	91.00	90.77	90.20	90.33	89.60	90.46	90.39
O=F,Cl	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Total	91.10	91.12	91.21	91.37	91.00	90.77	90.20	90.33	89.60	90.46	90.39
8(O)											
Si	2.0342	2.0258	2.0308	2.0234	2.0330	2.0341	2.0387	2.0230	2.0331	2.0229	2.0370
Ti	0.0061	0.0058	0.0072	0.0022	0.0022	0.0092	0.0120	0.0199	0.0025	0.0054	0.0108
Al	1.9236	1.9416	1.8928	1.9133	1.8628	1.9365	1.9176	1.9232	1.9133	1.9155	1.8920
Cr	0.0003	0.0004	0.0005	0.0026	0.0376	0.0015	0.0022	0.0023	0.0025	0.0022	0.0016
Fe ³⁺	0.0516	0.0440	0.0826	0.0787	0.0780	0.0374	0.0439	0.0451	0.0687	0.0641	0.0650
Mn	0.0000	0.0003	0.0004	0.0005	0.0003	0.0005	0.0004	0.0004	0.0010	0.0003	0.0004
Mg	0.0004	0.0004	0.0008	0.0005	0.0008	0.0003	0.0002	0.0002	0.0038	0.0007	0.0012
Ni	0.0002	0.0005	0.0003	0.0001	0.0002	0.0001	0.0002	0.0001	0.0000	0.0002	0.0001
Ca	0.9550	0.9563	0.9584	0.9553	0.9606	0.9492	0.9520	0.9574	0.9471	0.9692	0.9643
Na	0.0009	0.0003	0.0005	0.0008	0.0001	0.0002	0.0002	0.0003	0.0001	0.0004	0.0013
K	0.0002	0.0000	0.0001	0.0001	0.0000	0.0003	0.0002	0.0000	0.0003	0.0000	0.0003
F	0.0009	0.0000	0.0043	0.0006	0.0006	0.0001	0.0000	0.0000	0.0000	0.0021	0.0019
Cl	0.0000	0.0000	0.0002	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002
OH	1.9991	2.0000	1.9955	1.9993	1.9993	1.9999	2.0000	2.0000	2.0000	1.9978	1.9979

Table A III-3 continued:

Sample ID	TUR31	TUR31	TUR31	TUR32	TUR32	TUR33	TUR33	TUR33
Grain ID	L1	L2	L3	L1	L2	L1	L2	L3
Mineral	Lws	Lws	Lws	Lws	Lws	Lws	Lws	Lws
# of analyses	3	3	3	3	3	3	3	3
SiO2	39.52	39.41	39.56	39.68	39.84	40.08	39.56	39.76
TiO2	0.35	0.06	0.03	0.10	0.41	0.04	0.39	0.06
Al2O3	31.97	32.06	32.07	32.05	32.06	31.68	31.43	31.16
Cr2O3	0.04	0.06	0.07	0.04	0.05	0.01	0.01	0.00
FeO	0.94	0.98	0.81	1.37	1.01	1.41	1.65	1.97
MnO	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00
NiO	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00
CaO	17.47	17.41	17.35	17.65	17.61	17.57	17.49	17.57
Na2O	0.00	0.01	0.02	0.00	0.01	0.01	0.00	0.00
K2O	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
F	0.09	0.04	0.07	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sub-total	90.40	90.04	90.01	90.91	91.02	90.83	90.59	90.54
O=F,Cl	0.04	0.02	0.03	0.00	0.00	0.00	0.00	0.00
Total	90.36	90.02	89.98	90.91	91.02	90.83	90.59	90.54
8(O)								
Si	2.0261	2.0269	2.0343	2.0238	2.0276	2.0441	2.0272	2.0390
Ti	0.0134	0.0024	0.0012	0.0037	0.0157	0.0014	0.0151	0.0025
Al	1.9316	1.9433	1.9434	1.9264	1.9228	1.9040	1.8979	1.8828
Cr	0.0016	0.0024	0.0027	0.0017	0.0019	0.0006	0.0004	0.0001
Fe3+	0.0402	0.0420	0.0348	0.0584	0.0430	0.0601	0.0708	0.0845
Mn	0.0001	0.0001	0.0004	0.0004	0.0003	0.0005	0.0005	0.0003
Mg	0.0005	0.0002	0.0006	0.0006	0.0003	0.0003	0.0005	0.0000
Ni	0.0002	0.0000	0.0000	0.0000	0.0004	0.0002	0.0005	0.0002
Ca	0.9598	0.9593	0.9558	0.9642	0.9604	0.9603	0.9599	0.9652
Na	0.0000	0.0006	0.0018	0.0000	0.0007	0.0011	0.0002	0.0001
K	0.0005	0.0000	0.0003	0.0004	0.0001	0.0002	0.0000	0.0001
F	0.0148	0.0060	0.0111	0.0003	0.0005	0.0000	0.0008	0.0000
Cl	0.0000	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000
OH	1.9852	1.9940	1.9889	1.9996	1.9995	2.0000	1.9992	2.0000

Table A III-4: Major and minor element compositions of representative phengite (Ph) from the Tavsanlı Zone blueschists, northwestern Turkey.

Sample ID	TUR14A	TUR14A	TUR14A	TUR30	TUR30	TUR30
Grain ID	P1	P2	P3	P1	P2	P3
Mineral	Ph	Ph	Ph	Ph	Ph	Ph
# of analyses	2	2	3	3	2	2
SiO₂	52.85	52.73	52.33	55.07	56.94	56.89
TiO₂	0.15	0.13	0.16	0.06	0.04	0.02
Al₂O₃	22.93	22.25	22.47	20.68	19.11	19.57
Cr₂O₃	0.36	0.57	0.03	0.07	0.14	0.01
FeO	4.84	4.87	4.71	3.63	3.23	2.90
MnO	0.04	0.01	0.04	0.03	0.05	0.06
MgO	4.26	4.46	4.77	5.38	6.26	6.01
NiO	0.02	0.01	0.01	0.00	0.01	0.00
CaO	0.02	0.00	0.03	0.04	0.04	0.04
Na₂O	0.14	0.10	0.10	0.09	0.06	0.06
K₂O	10.85	11.13	10.82	11.05	11.12	11.27
F	0.05	0.07	0.08	0.07	0.10	0.08
Cl	0.01	0.00	0.00	0.00	0.00	0.00
Sub-total	96.49	96.33	95.56	96.19	97.09	96.92
O=F.Cl	0.02	0.03	0.03	0.03	0.04	0.04
Total	96.47	96.30	95.53	96.16	97.05	96.89
11(O)						
Si	3.4963	3.5061	3.4872	3.6457	3.7262	3.7339
Ti	0.0072	0.0067	0.0079	0.0030	0.0020	0.0012
Al	1.7873	1.7433	1.7642	1.6139	1.4737	1.5143
Cr	0.0187	0.0300	0.0017	0.0038	0.0072	0.0006
Fe³⁺	0.2515	0.2435	0.2551	0.1338	0.1215	0.0576
Fe²⁺	0.0160	0.0273	0.0073	0.0672	0.0550	0.1015
Mn	0.0022	0.0007	0.0020	0.0019	0.0030	0.0034
Mg	0.4196	0.4421	0.4740	0.5304	0.6107	0.5873
Ni	0.0012	0.0003	0.0006	0.0003	0.0007	0.0002
Ca	0.0013	0.0001	0.0022	0.0028	0.0028	0.0027
Na	0.0178	0.0134	0.0134	0.0120	0.0073	0.0082
K	0.9152	0.9441	0.9200	0.9335	0.9283	0.9437
F	0.0101	0.0148	0.0168	0.0144	0.0202	0.0174
Cl	0.0006	0.0001	0.0003	0.0004	0.0002	0.0001
OH	1.9893	1.9851	1.9830	1.9853	1.9796	1.9825

Table A III-4 continued:

Sample ID	TUR31	TUR31	TUR31	TUR31	TUR33	TUR33	TUR33
Grain ID	P2	P4	P5	P6	P1	P2	P3
Mineral	Ph	Ph	Ph	Ph	Ph	Ph	Ph
# of analyses	1	1	1	1	3	3	3
SiO2	50.85	49.17	48.60	48.59	56.74	52.79	51.96
TiO2	0.07	0.19	0.11	0.17	0.04	0.10	0.06
Al2O3	25.83	25.71	25.06	26.13	17.69	21.88	25.11
Cr2O3					0.01	0.01	0.00
FeO	4.58	5.63	6.34	5.75	4.38	5.23	3.94
MnO	0.07	0.03	0.11	0.03	0.06	0.05	0.05
MgO	3.58	3.04	4.78	3.04	6.15	4.04	3.34
NiO	0.01	0.02	0.01	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.00	0.00	0.06	0.07	0.05
Na2O	0.25	0.44	0.38	0.46	0.03	0.09	0.22
K2O	10.36	10.03	8.99	9.97	10.85	10.48	10.52
F	0.139	0.093	0.282	0.208	0.09	0.03	0.05
Cl	0.000	0.001	0.004	0.002	0.00	0.01	0.00
Sub-total	95.74	94.36	94.66	94.35	96.11	94.79	95.31
O=F.Cl	0.06	0.04	0.12	0.09	0.04	0.01	0.02
Total	95.68	94.32	94.54	94.27	96.07	94.78	95.29
11(O)							
Si	3.3684	3.3187	3.2134	3.2800	3.7610	3.5551	3.4672
Ti	0.0035	0.0099	0.0056	0.0088	0.0018	0.0052	0.0029
Al	2.0165	2.0450	1.9527	2.0787	1.3824	1.7366	1.9745
Cr	0.0000	0.0000	0.0000	0.0000	0.0003	0.0005	0.0000
Fe3+	0.2537	0.3177	0.3505	0.3246	0.1611	0.2209	0.1547
Fe2+	0.0000	0.0000	0.0000	0.0000	0.0817	0.0734	0.0649
Mn	0.0037	0.0019	0.0061	0.0020	0.0035	0.0026	0.0030
Mg	0.3535	0.3059	0.4712	0.3059	0.6080	0.4056	0.3326
Ni	0.0007	0.0010	0.0006	0.0001	0.0001	0.0002	0.0001
Ca	0.0000	0.0000	0.0000	0.0000	0.0043	0.0052	0.0035
Na	0.0318	0.0582	0.0481	0.0597	0.0045	0.0112	0.0285
K	0.8754	0.8635	0.7582	0.8585	0.9174	0.8999	0.8951
F	0.0292	0.0198	0.0590	0.0443	0.0179	0.0054	0.0101
Cl	0.0000	0.0001	0.0004	0.0002	0.0005	0.0009	0.0005
OH	1.9708	1.9801	1.9406	1.9555	1.9817	1.9937	1.9894

Table A III-5: Major and minor element compositions of representative apatite (Ap) grains from the Tavsanlı Zone blueschists, northwestern Turkey.

Sample ID	TUR12	TUR14	TUR14	TUR14	TUR23	TUR23	TUR23	TUR23	TUR30	TUR30	TUR30	TUR30
Grain ID	Ap1	Ap1	Ap2	Ap3	Ap1	Ap2	Ap3	Ap4	Ap1	Ap2	Ap3	Ap4
# of analyses	3	3	3	3	3	1	2	1	2	2	3	1
SiO ₂	0.05	0.05	0.06	0.10	0.16	0.37	0.07	0.27	1.15	0.13	0.71	0.15
Al ₂ O ₃	0.01	0.02	0.02	0.01	0.03	0.04	0.02	-	0.05	0.05	0.27	-
FeO	0.32	0.11	0.41	0.11	0.43	0.71	0.19	0.81	0.41	0.43	0.41	0.20
MgO	0.01	0.02	0.02	0.01	0.02	0.03	<0.01	0.08	0.01	0.01	0.01	-
CaO	54.66	54.57	54.81	54.78	54.78	55.39	55.16	53.77	54.59	54.77	53.47	54.60
Na ₂ O	-	0.01	-	0.02	0.03	0.09	-	0.08	<0.01	0.02	0.02	0.01
K ₂ O	0.06	0.03	0.01	0.02	0.04	0.05	-	-	0.01	-	0.04	0.02
P ₂ O ₅	40.91	41.39	42.01	41.89	41.44	41.52	41.91	40.29	40.27	42.56	41.46	42.44
SO ₃	-	0.04	0.11	0.14	0.10	0.12	0.18	0.55	-	0.02	0.08	-
SrO	0.21	0.16	0.16	0.06	0.20	0.16	0.02	0.05	0.06	0.12	0.06	0.13
Ce ₂ O ₃	0.41	0.27	0.24	0.07	0.04	0.43	-	0.24	0.08	0.25	0.30	0.37
La ₂ O ₃	-	-	0.09	-	0.01	0.03	0.23	-	-	0.04	0.33	0.31
As ₂ O ₅	0.09	-	0.08	0.06	-	0.06	0.04	-	0.06	0.01	0.06	0.11
F	3.06	3.06	3.13	2.99	3.28	3.18	3.28	3.38	2.89	2.96	2.99	2.99
Cl	-	0.01	<0.01	0.01	0.01	-	0.02	-	-	<0.01	-	0.01
Sub-total	99.78	99.75	101.17	100.28	100.57	102.17	101.12	99.51	99.58	101.36	100.21	101.34
O=F,Cl	1.29	1.29	1.32	1.26	1.38	1.34	1.38	1.42	1.21	1.25	1.26	1.26
Total	98.49	98.46	99.85	99.02	99.19	100.84	99.74	98.08	98.36	100.12	98.95	100.08
12.5(O,OH,Cl,F)												
Si	0.0044	0.0043	0.0050	0.0086	0.0138	0.0321	0.0064	0.0242	0.1063	0.0117	0.0642	0.0127
Al	0.0006	0.0018	0.0022	0.0007	0.0037	0.0039	0.0021	-	0.0056	0.0047	0.0283	-
Fe	0.0235	0.0081	0.0301	0.0081	0.0323	0.0518	0.0137	0.0609	0.0313	0.0313	0.0312	0.0147
Mg	0.0013	0.0025	0.0029	0.0019	0.0023	0.0038	0.0006	0.0103	0.0009	0.0009	0.0019	-
Ca	5.1989	5.1614	5.1217	5.1257	5.1796	5.1870	5.1583	5.1806	5.2481	5.0805	5.0792	5.0706
Na	-	0.0022	-	0.0035	0.0057	0.0145	-	0.0131	0.0008	0.0041	0.0027	0.0022
K	0.0067	0.0035	0.0010	0.0025	0.0042	0.0057	-	-	0.0015	-	0.0045	0.0019
P	3.0747	3.0933	3.1020	3.0973	3.0964	3.0724	3.0971	3.0674	3.0587	3.1196	3.1122	3.1144
S	-	0.0027	0.0073	0.0093	0.0066	0.0080	0.0121	0.0368	-	0.0010	0.0053	-
Sr	0.0105	0.0084	0.0081	0.0029	0.0103	0.0080	0.0012	0.0024	0.0034	0.0060	0.0030	0.0066
Ce	0.0131	0.0089	0.0078	0.0023	0.0013	0.0137	-	0.0080	0.0024	0.0078	0.0095	0.0116
La	-	-	0.0030	-	0.0004	0.0011	0.0072	-	-	0.0011	0.0105	0.0100
As	0.0042	-	0.0037	0.0028	-	0.0029	0.0018	-	0.0029	0.0006	0.0028	0.0050
F	0.8591	0.8532	0.8644	0.8249	0.9149	0.8790	0.9054	0.9612	0.8205	0.8105	0.8388	0.8196
Cl	-	0.0016	0.0004	0.0013	0.0016	-	0.0025	-	-	0.0004	-	0.0011
OH	0.1409	0.1452	0.1352	0.1738	0.0836	0.1210	0.0921	0.0388	0.1795	0.1892	0.1612	0.1794

Table A III-5 continued:

Sample ID	TUR31	TUR32	TUR32	TUR32	TUR32	TUR33	TUR33	TUR33
Grain ID	Ap1	Ap1	Ap2	Ap3	Ap4	Ap1	Ap2	Ap3
# of analyses	3	1	1	1	1	3	3	3
SiO2	0.04	0.07	0.12	0.07	-	0.07	0.02	0.05
Al2O3	0.02	0.01	0.01	<0.01	0.01	-	0.02	0.01
FeO	0.28	-	0.74	-	0.25	0.21	0.07	0.66
MgO	0.01	-	0.01	0.02	-	-	0.01	0.02
CaO	55.58	54.82	54.41	54.65	55.81	54.94	55.04	54.96
Na2O	<0.01	<0.01	0.05	<0.01	0.02	0.01	0.01	0.02
K2O	0.06	0.15	0.01	0.03	-	0.02	-	0.01
P2O5	41.67	42.87	41.89	41.58	43.06	42.20	41.54	42.11
SO3	-	0.12	-	0.06	0.12	0.04	0.10	0.11
SrO	0.10	-	-	0.32	-	0.01	0.12	0.18
Ce2O3	0.17	-	-	0.15	-	0.03	0.25	0.19
La2O3	-	-	-	-	0.18	-	0.19	-
As2O5	0.03	-	0.13	0.06	0.01	0.09	0.06	0.05
F	3.51	3.10	3.23	3.25	3.14	2.94	2.90	2.78
Cl	0.01	0.02	<0.01	-	0.01	0.04	0.01	0.02
Sub-total	101.47	101.17	100.61	100.20	102.61	100.61	100.34	101.17
O=F,Cl	1.48	1.31	1.36	1.37	1.32	1.25	1.23	1.18
Total	99.99	99.86	99.24	98.83	101.29	99.36	99.12	100.00
12.5(O,OH,Cl,F)								
Si	0.0036	0.0063	0.0108	0.0065	-	0.0064	0.0021	0.0043
Al	0.0016	0.0012	0.0006	0.0004	0.0006	-	0.0017	0.0012
Fe	0.0205	-	0.0542	-	0.0182	0.0153	0.0049	0.0476
Mg	0.0013	-	0.0019	0.0032	-	-	0.0019	0.0023
Ca	5.2267	5.0662	5.1289	5.1573	5.1064	5.1193	5.1577	5.1066
Na	0.0004	0.0003	0.0089	0.0004	0.0041	0.0015	0.0015	0.0028
K	0.0067	0.0160	0.0010	0.0029	-	0.0025	-	0.0013
P	3.0963	3.1306	3.1202	3.1006	3.1132	3.1068	3.0761	3.0914
S	-	0.0079	-	0.0040	0.0078	0.0026	0.0067	0.0072
Sr	0.0051	-	-	0.0161	-	0.0004	0.0060	0.0089
Ce	0.0056	-	-	0.0049	-	0.0010	0.0081	0.0061
La	-	-	-	-	0.0055	-	0.0060	-
As	0.0012	-	0.0061	0.0026	0.0005	0.0039	0.0027	0.0024
F	0.9737	0.8456	0.8987	0.9052	0.8480	0.8099	0.8032	0.7634
Cl	0.0011	0.0035	0.0004	-	0.0011	0.0057	0.0019	0.0024
OH	0.0409	0.1509	0.1010	0.0948	0.1510	0.1845	0.1949	0.2342

Table AIII-6: Halogen content of bulk samples and mineral fractions for lawsonite blueschists from the Tavsanli Zone, northwestern Turkey. All values are in ppm.

Sample	Major mineral	Dionex IC				ICP-MS				F/Cl	Br/Cl	I/Cl	Br/I
		F	sd	Cl	sd	79 Br	sd	127 I	sd				
TUR12	Bulk	616	2.1	10	1.7	0.17	4.99	0.17	16.72	60.4	0.017	0.017	0.989
TUR14	Amp-rich	608	10	29	24	0.26	18.10	0.43	12.95	21.1	0.009	0.015	0.612
	Lws-rich	733	7.9	20	16	0.25	18.49	0.35	23.73	37.2	0.013	0.018	0.695
	Ph-rich	647	1.0	19	16	0.25	2.34	0.31	21.39	34.3	0.013	0.016	0.804
	Bulk	555	3.1	18	0.30	0.24	48.3	0.20	9.4	30.9	0.013	0.011	1.187
TUR23	Bulk	382	3.5	9.0	13	0.11	3.75	0.15	8.81	42.2	0.013	0.017	0.755
TUR30	Amp-rich	397	0.8	10	13	0.16	9.11	0.19	2.00	38.4	0.015	0.019	0.801
	Lws-rich	120	11	14	8.0	0.14	20.55	0.30	10.14	8.8	0.010	0.022	0.470
	Bulk	284	0.38	11	8.7	0.14	50.1	0.15	3.8	25.3	0.012	0.013	0.919
TUR31	Bulk	582	2.2	7.9	5.7	0.15	19.56	0.13	4.04	74.1	0.019	0.016	1.177
TUR32	Amp-rich	265	15	11	4.0	0.17	24.51	0.12	14.26	24.1	0.016	0.011	1.449
	Lws-rich	198	13	7.9	6.7	0.16	13.48	0.14	3.72	25.1	0.021	0.018	1.138
	Bulk	222	2.0	7.7	2.1	0.07	53.0	0.15	13.2	28.7	0.009	0.019	0.485
TUR33	Amp-rich	322	0.34	40	36	0.22	19.65	1.01	3.16	7.9	0.005	0.025	0.214
	Lws-rich	955	1.7	56	31	0.47	11.63	1.37	29.26	17.0	0.008	0.024	0.340
	Bulk	558	0.021	22	8.3	0.14	76.0	0.52	11.5	25.7	0.006	0.024	0.267
Instrument LOD, 3 σ		0.0017		0.0034		0.000022		0.0000041					
Method LOD, 3 σ		0.019		0.12		0.0041		0.0029					

IC – ion chromatography; ICP-MS – inductively coupled plasma-mass spectrometry

Amp – amphibole; Lws – lawsonite; Ph – phengite

LOD – limit of detection; sd – standard deviation; bd – below detection limit

Table A III-7: Comparison of measured bulk rock halogen content with calculated bulk rock estimates based on in situ F and Cl measurements of minerals and their respective estimated modal proportions. All values are in ppm.

Sample	Analysis	Mineral	F	Cl	Modal mineralogy
TUR30	pyrohydrolysis + IC	Bulk	284	11	
	SIMS	Na-amphibole	390	18	30
		Lawsonite	383	33	35
		Phengite	572	21	3 ^a
	EMPA	Apatite	29563	60	0.5 ^b
		<i>Bulk estimate</i>	<i>416</i>	<i>18</i>	
TUR32	pyrohydrolysis + IC	Bulk	222	8	
	SIMS	Na-amphibole	256	46	30
		Lawsonite	295	27	50
	EMPA	Apatite	31800	113	0.1 ^a
		<i>Bulk estimate</i>	<i>256</i>	<i>27</i>	
TUR33	pyrohydrolysis + IC	Bulk	558	22	
	SIMS	Na-amphibole	84	87	35
		Lawsonite	538	46	35
		Phengite	372	69	8 ^a
	EMPA	Apatite	28767	253	1.5 ^b
		<i>Bulk estimate</i>	<i>679</i>	<i>56</i>	
Bulk estimate is based on average halogen concentrations in minerals as determined by SIMS or EMPA, combined with their modal abundance. The estimates are slightly higher than measured bulk rock values by pyrohydrolysis because of the presence of minor halogen-free phases, such as quartz.					
^a Phengite modal mineralogy based on bulk rock K ₂ O					
^b Apatite modal mineralogy based on bulk rock P ₂ O ₅					

III.2 Unpublished supplementary material

Table A III-8: Trace element concentrations and B isotopes in blueschist facies minerals from the Tavsanlı Zone, northwestern Turkey determined by SIMS.

	B	Li	Sr	Y	Ce	δ11B	1σ
	ppm	ppm	ppm	ppm	ppm	‰	‰
Phengite							
TUR14A	92	22	5.0	0.04	0.02	-5.8	0.4
TUR30	93	10	11	0.5	0.1	-12.3	0.4
TUR33	98	6.2	2.3	0.04	0.1	-8.0	0.4
<i>Average</i>	<i>95</i>	<i>13</i>	<i>6.1</i>	<i>0.2</i>	<i>0.1</i>	<i>-8.7</i>	<i>0.4</i>
Na-amphibole							
TUR12	3.6	74	1.6	0.1	0.01	-13	1.2
TUR14A	3.2	123	0.8	0.2	nd	-15	1.3
TUR30	13	16	2	0.2	0.05	-5.8	1.3
TUR32	1.6	46	0.4	0.01	0.03	-11	1.8
TUR33	2.3	140	1.0	0.05	0.04	nd	
<i>Average</i>	<i>4.7</i>	<i>80</i>	<i>1.2</i>	<i>0.1</i>	<i>0.03</i>	<i>-11</i>	<i>1.4</i>
Lawsonite							
TUR12	0.2	0.19	6801	285	5870	nd	
TUR23	0.4	0.03	253	10	34	nd	
TUR30	4.2	0.07	223	5.3	43	-13.3	3.2
TUR31	1.4	0.02	1329	68	567	nd	
TUR32	5.4	0.04	86	30	4.1	nd	
TUR33	0.4	0.11	377	22	21	nd	
<i>Average</i>	<i>2.0</i>	<i>0.08</i>	<i>1512</i>	<i>70</i>	<i>1090</i>	<i>-13.3</i>	<i>3.2</i>
nd - not detected							

Appendix IV.

Published supplementary material for Chapter 6

IV.1 Published supplementary material

Table A IV-1: Mineralogy of eclogitic metasediments from the Tso Morari UHP unit, NW

Himalaya based on petrographic observation and scanning electron microprobe (SEM) analyses.

	102b	211	157a	TS58c	223d
Quartz	X	X	X	X	X
Phengite	X	X	X	X	X
Paragonite	X	X	X	X	X
Garnet	X	X	X	X	X
Apatite	X	X	X	X	X
Zircon	X	X	X	X	X
Rutile	X	X	X	X	X
Ilmenite	X	X	X	X	X
Chloritoid	X		X		
Na-amphibole	X		X	X	
Chlorite	X	X	X	X	
Biotite			X	X	X
Jadeite	X	X	X		X
Plagioclase		X	X		
Zoisite			X		X
Allanite	X				
Titanite		X			
Calcite					X
Fluorite		X			

Table A IV-2: Bulk rock halogen and B contents of metasediments from the Tso Morari UHP unit, NW Himalaya. All concentrations and standard deviations in ppm.

Sample	Dionex IC				ICP-MS				PGNAA
	F	sd	Cl	sd	79 Br	sd	127 I	sd	B
CH102	214	12	11	1.4	0.03	0.02	0.05	0.003	24
CH157	113	5.1	9	2.0	0.02	0.02	0.09	0.02	19
TS58c	534	49	13	0.9	bdl	bdl	0.03	0.02	30
CH223d	296	16	35	3.0	0.14	0.02	0.18	0.04	16
CH211	967	23	43	3.8	0.08	0.01	0.14	0.02	55
Instrument LOD (3σ)	0.0017		0.0034		0.000022		0.0000041		
Method LOD (3σ)	0.019		0.12		0.0041		0.0029		
IC – ion chromatography; ICP-MS – inductively-coupled plasma mass spectrometry; PGNAA - prompt gamma neutron activation analysis									
LOD – limit of detection; sd – standard deviation; bdl – below detection limit									

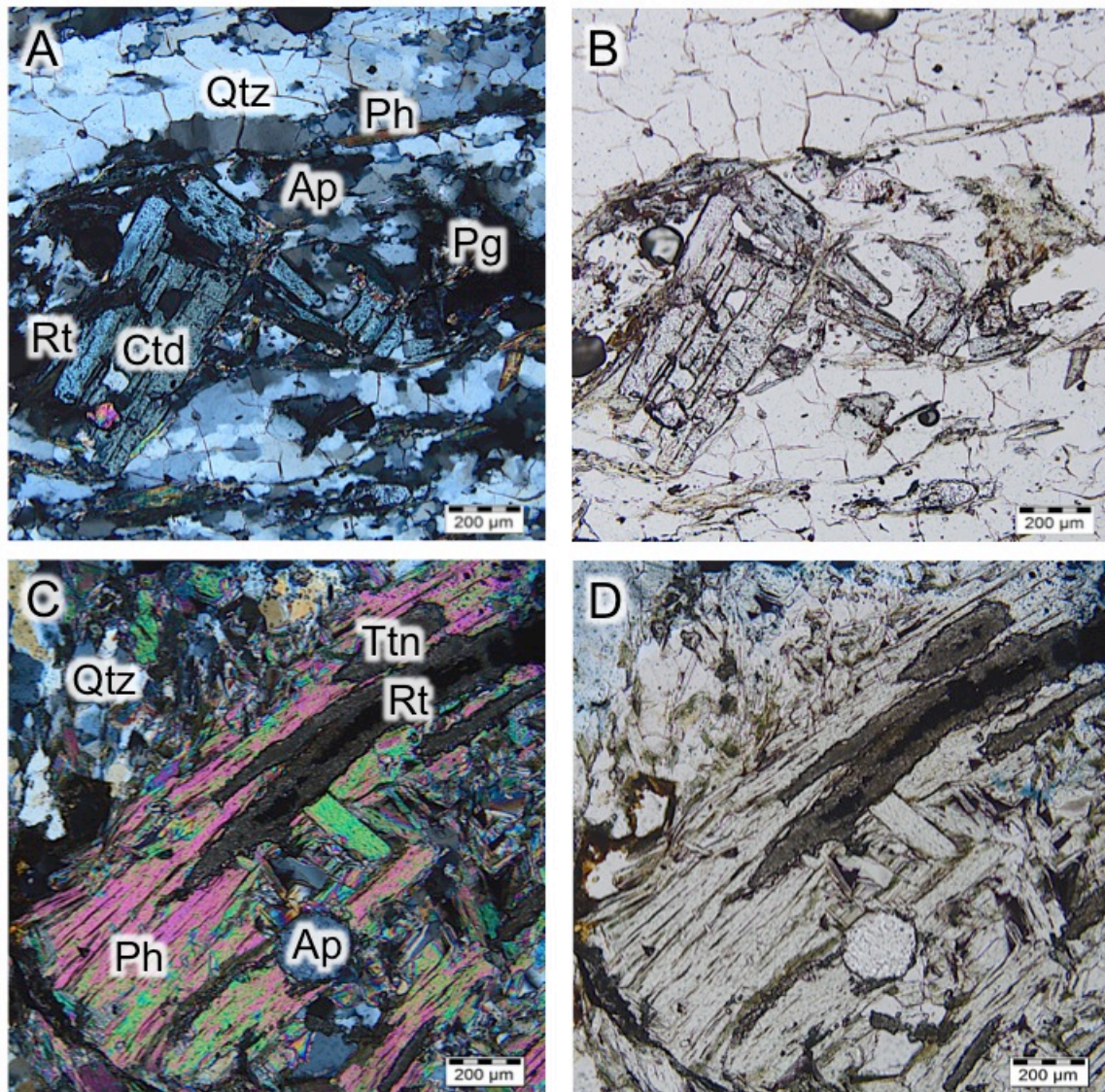


Figure A IV-1: Photomicrographs of Tso Morari metasediment samples CH102b (A,B) and CH211 (C, D) under cross polarized (A,C) and plane polarized (B,D) light. Ap – apatite; Ctd – chlorotoid; Pg – paragonite; Ph – phengite; Rt – rutile; Ttn – titanite; Qtz – quartz.

Appendix V.

Supplementary material for Chapter 7

Table A V-1: Bulk rock major and trace element compositions of eclogites from the Tso Morari (Himalaya) and Sulu (China) UHP units.

Element	Method*		Tso Morari						Sulu			
			CH163	CH165	CH171	CH208	CH266	Ts34	SL41	SL45	SL47	SL48
SiO ₂	wt %	XRF	40.23	45.98	49.99	50.90	45.25	46.19	44.78	47.58	48.40	47.17
TiO ₂	wt %	XRF	2.97	2.51	1.34	0.98	2.79	2.73	0.15	0.25	0.90	0.58
Al ₂ O ₃	wt %	XRF	15.74	15.39	15.57	13.54	15.47	14.93	26.99	17.72	17.77	15.66
Fe ₂ O ₃ (t)	wt %	XRF	14.03	14.29	12.36	11.57	13.83	13.22	5.79	8.70	11.16	11.92
MnO	wt %	XRF	0.17	0.21	0.20	0.15	0.20	0.24	0.09	0.12	0.15	0.15
MgO	wt %	XRF	6.73	6.45	7.16	9.42	7.03	6.87	5.94	9.77	6.39	9.66
CaO	wt %	XRF	6.36	9.77	9.65	7.48	9.55	9.50	12.70	12.25	11.50	11.36
Na ₂ O	wt %	XRF	3.00	2.75	2.85	2.27	2.47	3.36	2.61	2.85	2.14	2.98
K ₂ O	wt %	XRF	0.83	1.03	0.33	1.15	1.21	0.91	0.07	0.21	0.43	0.14
P ₂ O ₅	wt %	XRF	0.28	0.26	0.16	0.09	0.34	0.24	0.04	0.15	0.34	0.05
LOI	wt %	XRF	8.20	1.69	0.56	2.10	1.66	1.36	0.68	0.31	0.68	0.19
Total	wt %	XRF	98.54	100.33	100.17	99.65	99.80	99.55	99.82	99.92	99.87	99.86
Ba	ppm	XRF	65	103	40	na	117	70	na	na	na	na
Co	ppm	XRF	56	52	52	31	51	55	na	na	na	na
Cr	ppm	XRF	30	196	402	285	159	209	97	241	45	679
Cu	ppm	XRF	26	43	43	90	58	65	14	29	46	29
Nb	ppm	XRF	4	10	10	21	9	8	na	na	na	na
Ni	ppm	XRF	81	91	157	256	93	96	96	150	32	204
Rb	ppm	XRF	49	76	29	bdl	130	61	23	14	24	24
Sc	ppm	XRF	31	35	29	na	35	33	na	na	na	na
Sr	ppm	XRF	168	192	137	155	255	218	1476	223	660	52
V	ppm	XRF	315	361	234	222	382	389	na	na	na	na
Y	ppm	XRF	29	27	25	na	33	33	na	na	na	na
Zr	ppm	XRF	196	194	99	62	241	172	bdl	13	65	33
B	ppm	PGNAA	6	5	9	8	6	9	2	<2	4	3

Fe total expressed as Fe₂O₃ (t)

XRF - x-ray fluorescence; PGNAA - prompt gamma neutron activation analysis

*Tso Morari samples analysed by XRF at the Université de Lyon, France (except for CH208) and Sulu samples (+ CH 208) at the University of Ottawa, Canada

bdl - below detection limit; na - not analyzed

Table A V-2: Halogen content of bulk samples for eclogites of the Tso Morari (Himalaya) and Sulu (China) UHP units. All values are in ppm.

Sample ID	n	Dionex IC		ICP-MS				F/Cl	Br/Cl	I/Cl	
		F sd	Cl sd	79 Br	sd	127 I	sd				
Tso Morari											
CH163	2	344 44	79 18	0.044	0.0047	0.25	0.019	4.3	0.00056	0.0031	
CH165	2	363 1.1	8.0 0.8	0.011	0.0047	0.084	0.017	45	0.0014	0.010	
CH171	2	142 3.8	28 1.0	0.15	0.049	0.10	0.0005	5.1	0.0054	0.0036	
CH208	2	246 13	68 5.4	0.12	0.0038	0.076	0.0091	3.6	0.0018	0.0011	
CH266	2	302 4.7	90 2.9	0.18	0.026	0.046	0.014	3.4	0.0020	0.00051	
TS34	2	330 12	29 1.7	0.15	0.029	0.17	0.015	11	0.0052	0.0058	
Sulu											
SL41	2	61 5.6	12 2.0	0.037	0.032	bdl	bdl	5.3	0.0032	bdl	
SL45	2	89 6.4	96 14	0.38	0.049	bdl	bdl	0.92	0.0040	bdl	
SL47	2	272 42	60 18	0.092	0.040	0.0042		4.5	0.0015	0.000069	
SL48	2	86 10	177 8	0.083	0.14	bdl	bdl	5.0	0.0048	bdl	
Instrument LOD (3σ) 0.0017 0.0034 0.000022 0.0000041											
Method LOD (3σ) 0.019 0.12 0.0041 0.0029											
IC – ion chromatography; ICP-MS – inductively coupled plasma-mass spectrometry											
LOD – limit of detection; sd – standard deviation; bdl – below detection limit											

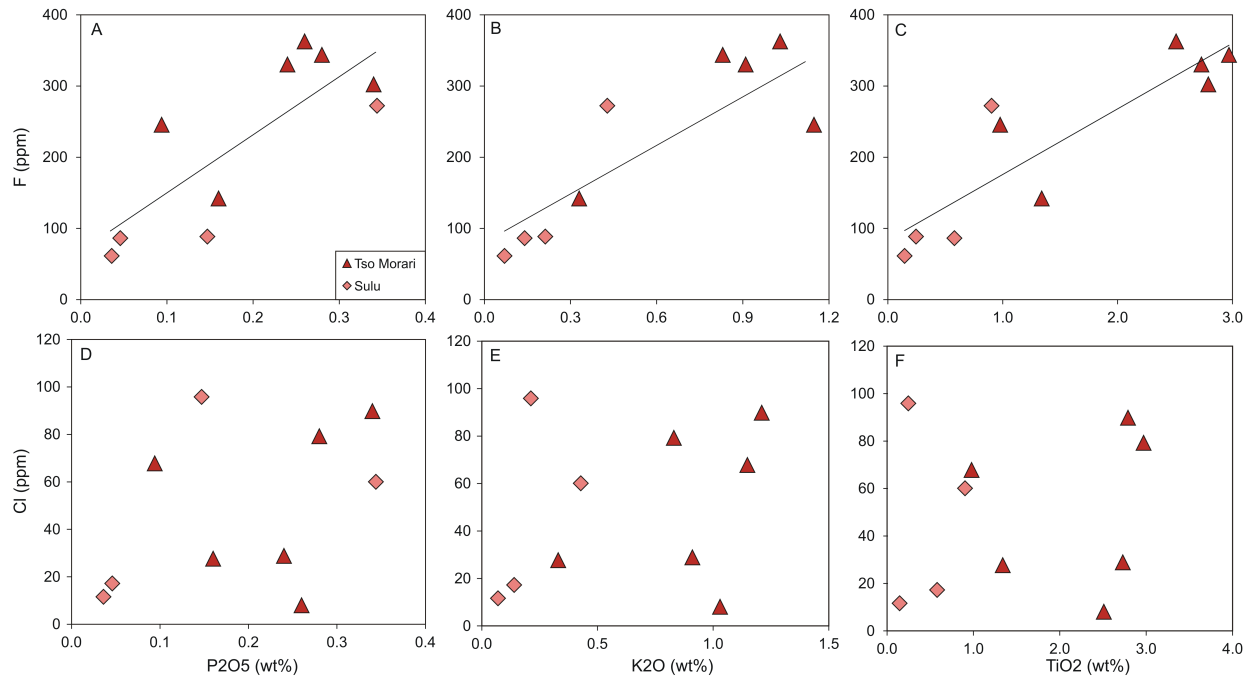


Figure A V-1: Bulk rock concentrations of eclogites of the Tso Morari (Himalaya) and Sulu (China) UHP units showing broad positive correlations between F and K₂O, P₂O₅ and TiO₂. This suggests phengite, apatite and Ti-bearing minerals may control the bulk F content in these rocks.

Table A V-3: Major element and halogen compositions of representative white mica from eclogites of the Tso Morari (Himalaya) and Sulu (China) UHP units.

Sample ID	CH165	CH165	CH165	CH165	CH165	CH165	CH165	CH171	CH171	CH171	CH171	CH171
Mineral	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica
Grain ID	1	2	3	4	5	6	7	1	2	3	4	5
# of analyses	3	2	1	3	2	1	2	2	3	2	6	4
SiO2	52.24	50.78	50.72	53.03	51.75	52.82	51.48	51.51	51.05	51.39	51.26	50.43
TiO2	0.25	0.26	0.22	0.18	0.26	0.17	0.27	0.26	0.26	0.36	0.25	0.31
Al2O3	25.86	28.15	24.21	23.50	26.43	24.56	26.16	26.90	27.28	27.09	26.78	27.65
FeO	1.53	1.27	1.20	1.36	1.40	1.41	1.30	0.91	0.96	0.97	1.07	1.03
MnO	0.01	0.01	-	<0.01	-	-	-	-	-	<0.01	<0.01	<0.01
MgO	4.52	3.81	4.84	5.21	4.41	5.05	4.55	4.22	4.09	4.15	4.23	3.95
CaO	-	-	-	-	-	-	-	-	-	-	-	-
Na2O	0.34	0.85	0.17	0.17	0.47	0.19	0.34	0.51	0.57	0.54	0.50	0.67
K2O	10.74	10.12	10.41	10.42	10.39	10.78	10.83	10.50	10.41	10.27	10.51	10.19
F	0.15	0.09	0.09	0.10	0.07	0.04	0.08	0.21	0.14	0.25	0.23	0.08
Cl	<0.01	<0.01	<0.01	<0.01	0.01	-	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sub-total	95.65	95.33	91.87	93.97	95.18	95.01	95.00	95.03	94.76	95.02	94.84	94.32
O=F,Cl	0.07	0.04	0.04	0.04	0.03	0.02	0.03	0.09	0.06	0.11	0.10	0.03
Total	95.59	95.29	91.83	93.93	95.15	94.99	94.97	94.94	94.70	94.91	94.75	94.29
11(O)												
Si	3.4468	3.3523	3.4722	3.5442	3.4182	3.4985	3.4174	3.4166	3.3925	3.4041	3.4092	3.3619
Ti	0.0125	0.0128	0.0114	0.0092	0.0128	0.0084	0.0133	0.0130	0.0128	0.0177	0.0126	0.0155
Al	2.0109	2.1898	1.9533	1.8521	2.0575	1.9169	2.0467	2.1026	2.1363	2.1148	2.0990	2.1727
Fe3+	0.0844	0.0699	0.0686	0.0759	0.0775	0.0779	0.0723	0.0506	0.0533	0.0535	0.0597	0.0575
Fe2+	-	-	-	-	-	-	-	-	-	-	-	-
Mn	0.0004	0.0003	-	0.0002	-	-	-	-	-	0.0001	0.0001	0.0002
Mg	0.4451	0.3748	0.4945	0.5185	0.4340	0.4983	0.4504	0.4172	0.4051	0.4098	0.4194	0.3923
Ca	-	-	-	-	-	-	-	-	-	-	-	-
Na	0.0435	0.1091	0.0231	0.0220	0.0598	0.0243	0.0434	0.0650	0.0729	0.0693	0.0643	0.0871
K	0.9043	0.8519	0.9089	0.8888	0.8753	0.9111	0.9170	0.8882	0.8821	0.8681	0.8919	0.8669
F	0.0321	0.0195	0.0205	0.0209	0.0152	0.0091	0.0158	0.0450	0.0297	0.0524	0.0485	0.0173
Cl	0.0002	0.0001	0.0002	0.0004	0.0007	-	0.0008	0.0003	0.0002	0.0003	0.0000	0.0001
OH	1.9677	1.9804	1.9793	1.9787	1.9841	1.9909	1.9834	1.9548	1.9701	1.9473	1.9514	1.9825

Table A V-3 continued:

Sample ID	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH208
Mineral	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica
Grain ID	1	2	3	4	5	6	7	8	9	10	11	12
# of analyses	1	1	1	2	1	1	2	1	1	1	1	1
SiO2	48.98	48.62	48.65	50.22	52.82	49.93	48.98	50.61	49.09	51.00	50.58	49.34
TiO2	0.24	0.28	0.43	0.25	0.22	0.23	0.29	0.23	0.22	0.16	0.20	0.30
Al2O3	28.98	29.34	29.13	27.71	24.36	28.26	28.97	26.27	28.07	26.14	26.63	28.94
FeO	2.01	2.06	2.45	1.26	1.39	1.58	1.96	1.22	1.66	1.40	1.35	2.04
MnO	<0.01	-	0.01	-	-	-	-	<0.01	-	0.01	0.01	0.02
MgO	3.20	3.01	2.79	3.83	4.99	3.51	3.10	4.22	3.48	4.43	4.15	3.11
CaO	-	-	-	-	-	-	-	-	-	-	-	-
Na2O	0.92	0.94	0.85	0.53	0.13	0.76	0.81	0.24	0.71	0.28	0.32	0.64
K2O	9.85	9.78	9.90	10.45	10.83	10.10	10.02	10.75	9.92	10.82	10.63	10.26
F	0.06	0.09	0.05	0.09	0.04	0.04	0.05	0.07	0.10	0.07	0.08	0.05
Cl	-	<0.01	<0.01	-	-	-	<0.01	<0.01	<0.01	<0.01	-	<0.01
Sub-total	94.25	94.14	94.27	94.34	94.79	94.42	94.18	93.61	93.23	94.30	93.95	94.71
O=F,Cl	0.02	0.04	0.02	0.04	0.02	0.02	0.02	0.03	0.04	0.03	0.03	0.02
Total	94.22	94.10	94.25	94.31	94.77	94.41	94.15	93.58	93.19	94.28	93.91	94.69
11(O)												
Si	3.2737	3.2547	3.2607	3.3540	3.5097	3.3298	3.2800	3.4094	3.3130	3.4112	3.3935	3.2877
Ti	0.0121	0.0142	0.0217	0.0124	0.0111	0.0116	0.0145	0.0117	0.0110	0.0080	0.0100	0.0152
Al	2.2828	2.3150	2.3004	2.1813	1.9076	2.2214	2.2863	2.0858	2.2325	2.0602	2.1055	2.2729
Fe3+	0.1126	0.1155	0.1373	0.0706	0.0775	0.0880	0.1099	0.0688	0.0936	0.0785	0.0758	0.1136
Fe2+	-	-	-	-	-	-	-	-	-	-	-	-
Mn	0.0001	-	0.0008	-	-	-	-	0.0002	-	0.0004	0.0006	0.0014
Mg	0.3188	0.3004	0.2791	0.3817	0.4941	0.3492	0.3093	0.4242	0.3499	0.4418	0.4146	0.3093
Ca	-	-	-	-	-	-	-	-	-	-	-	-
Na	0.1191	0.1218	0.1104	0.0690	0.0171	0.0986	0.1046	0.0313	0.0929	0.0366	0.0412	0.0821
K	0.8400	0.8356	0.8464	0.8904	0.9180	0.8594	0.8564	0.9234	0.8537	0.9231	0.9095	0.8720
F	0.0119	0.0188	0.0110	0.0187	0.0089	0.0092	0.0112	0.0144	0.0204	0.0139	0.0172	0.0115
Cl	-	0.0005	0.0004	-	-	-	0.0000	0.0002	0.0001	0.0005	-	0.0005
OH	1.9881	1.9808	1.9887	1.9813	1.9911	1.9908	1.9888	1.9854	1.9794	1.9857	1.9828	1.9881

Table A V-3 continued:

Sample ID	CH208	CH208	CH208	CH208	CH208	CH208	CH208	CH266	CH266	CH266	CH266	CH266
Mineral	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica
Grain ID	13	14	15	16	17	18	19	1	2	3	4	5
# of analyses	1	1	1	1	1	3	1	2	3	6	3	2
SiO ₂	49.66	49.53	51.46	53.17	50.93	51.74	52.29	50.56	51.18	51.94	52.18	51.45
TiO ₂	0.21	0.22	0.26	0.17	0.29	0.24	0.26	0.58	0.42	0.28	0.28	0.23
Al ₂ O ₃	28.83	27.73	25.77	23.10	26.73	25.61	24.59	26.59	25.31	24.97	24.70	25.23
FeO	1.23	1.39	1.50	1.71	1.33	1.61	1.64	2.39	1.82	1.87	1.75	1.79
MnO	-	-	-	0.02	0.02	0.01	-	0.01	<0.01	0.01	<0.01	0.01
MgO	3.47	3.78	4.50	5.18	4.14	4.41	4.82	3.76	4.50	4.54	4.71	4.48
CaO	-	-	-	-	-	-	-	-	-	-	-	-
Na ₂ O	0.82	0.57	0.22	0.10	0.36	0.22	0.15	0.40	0.19	0.18	0.14	0.18
K ₂ O	10.13	10.43	10.82	10.89	10.72	10.91	11.16	10.29	10.75	10.63	10.92	10.78
F	0.06	0.06	0.07	0.11	0.05	0.07	0.16	0.12	0.06	0.09	0.18	0.17
Cl	<0.01	<0.01	0.01	0.01	-	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
Sub-total	94.42	93.72	94.59	94.46	94.56	94.82	95.06	94.70	94.23	94.51	94.87	94.32
O=F,Cl	0.03	0.03	0.03	0.05	0.02	0.03	0.07	0.05	0.03	0.04	0.08	0.07
Total	94.40	93.69	94.56	94.41	94.54	94.79	94.99	94.64	94.21	94.47	94.80	94.25
11(O)												
Si	3.3110	3.3328	3.4312	3.5566	3.3970	3.4482	3.4854	3.3730	3.4293	3.4658	3.4788	3.4478
Ti	0.0104	0.0110	0.0129	0.0088	0.0144	0.0119	0.0131	0.0290	0.0212	0.0142	0.0139	0.0118
Al	2.2652	2.1992	2.0250	1.8209	2.1013	2.0118	1.9315	2.0903	1.9983	1.9639	1.9411	1.9926
Fe ³⁺	0.0687	0.0780	0.0836	0.0956	0.0744	0.0899	0.0912	0.1332	0.1019	0.1045	0.0978	0.1002
Fe ²⁺	-	-	-	-	-	-	-	-	-	-	-	-
Mn	-	-	-	0.0013	0.0011	0.0003	-	0.0007	0.0001	0.0004	0.0001	0.0004
Mg	0.3448	0.3790	0.4473	0.5169	0.4118	0.4378	0.4788	0.3739	0.4492	0.4512	0.4683	0.4472
Ca	-	-	-	-	-	-	-	-	-	-	-	-
Na	0.1062	0.0748	0.0282	0.0126	0.0470	0.0289	0.0196	0.0512	0.0247	0.0238	0.0187	0.0239
K	0.8617	0.8949	0.9206	0.9289	0.9119	0.9272	0.9491	0.8753	0.9187	0.9046	0.9288	0.9215
F	0.0135	0.0135	0.0145	0.0230	0.0097	0.0138	0.0334	0.0260	0.0125	0.0188	0.0378	0.0364
Cl	0.0003	0.0002	0.0006	0.0007	-	0.0006	0.0000	0.0007	0.0005	0.0001	0.0005	0.0011
OH	1.9861	1.9862	1.9848	1.9763	1.9903	1.9856	1.9666	1.9733	1.9870	1.9811	1.9617	1.9625

Table A V-3 continued:

Sample ID	SL41	SL41	SL41	SL41	SL41	SL41	SL41	SL41	SL45	SL45	SL45
Mineral	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica
Grain ID	1	2	3	4	5	6	7	8	1	2	3
# of analyses	1	1	1	1	1	2	2	3	2	3	3
SiO2	48.99	49.05	49.01	48.76	48.24	48.95	49.35	48.10	49.82	49.85	48.61
TiO2	0.42	0.41	0.38	0.43	0.42	0.50	0.53	0.51	0.45	0.39	0.46
Al2O3	29.06	27.99	28.81	29.21	29.15	28.45	28.38	29.64	27.82	27.63	28.91
FeO	1.60	1.68	1.64	1.71	1.63	1.49	1.45	1.60	1.05	1.10	1.17
MnO	0.01	0.00	0.00	0.00	0.02	0.00	0.01	0.01	0.00	0.01	0.00
MgO	3.02	3.21	3.06	2.89	2.72	3.12	3.21	2.82	3.69	3.74	3.37
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na2O	0.79	0.82	0.76	0.84	0.83	0.94	0.88	1.01	0.66	0.57	0.65
K2O	9.98	10.01	10.09	9.86	9.86	9.82	9.88	9.53	10.02	9.98	9.99
F	0.18	0.10	0.20	0.08	0.03	0.09	0.12	0.10	0.04	0.08	0.04
Cl	0.02	0.01	0.02	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.01
Sub-total	94.07	93.29	93.97	93.79	92.90	93.34	93.79	93.34	93.54	93.37	93.21
O=F,Cl	0.08	0.04	0.09	0.04	0.01	0.04	0.05	0.04	0.02	0.04	0.02
Total	93.99	93.25	93.88	93.75	92.89	93.30	93.74	93.29	93.52	93.33	93.19
11(O)											
Si	3.2879	3.3241	3.2973	3.2781	3.2763	3.31	3.32	3.24	3.35	3.35	3.28
Ti	0.0212	0.0209	0.0192	0.0217	0.0214	0.03	0.03	0.03	0.02	0.02	0.02
Al	2.2984	2.2355	2.2843	2.3143	2.3331	2.27	2.25	2.36	2.20	2.19	2.30
Fe3+	0.0898	0.0952	0.0923	0.0961	0.0926	0.08	0.08	0.09	0.06	0.06	0.07
Fe2+	0.0000	0.0000	0.0000	0.0000	0.0000	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.0006	0.0000	0.0000	0.0000	0.0012	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.3022	0.3243	0.3069	0.2897	0.2754	0.31	0.32	0.28	0.37	0.38	0.34
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.1028	0.1077	0.0991	0.1095	0.1093	0.12	0.11	0.13	0.09	0.07	0.08
K	0.8544	0.8653	0.8659	0.8456	0.8542	0.85	0.85	0.82	0.86	0.86	0.86
F	0.0382	0.0214	0.0425	0.0170	0.0064	0.02	0.03	0.02	0.01	0.02	0.01
Cl	0.0023	0.0011	0.0023	0.0011	0.0000	0.00	0.00	0.00	0.00	0.00	0.00
OH	1.9595	1.9774	1.9552	1.9819	1.9936	1.98	1.97	1.98	1.99	1.98	1.99

Table A V-3 continued:

Sample ID	SL47	SL47	SL47	SL47	SL47	SL47	SL47	SL48	SL48	SL48	SL48	SL48
Mineral	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica	Mica
Grain ID	1	2	3	4	5	6	7	1	2	3	4	5
# of analyses	3	1	2	3	1	2	3	1	1	1	3	4
SiO2	48.58	48.88	48.59	47.80	47.90	47.83	48.48	48.82	48.20	47.60	48.45	48.12
TiO2	0.59	0.74	0.61	0.56	0.63	0.49	0.55	0.79	0.69	0.89	0.85	0.84
Al2O3	29.33	28.59	28.83	30.11	29.28	29.87	28.27	28.25	28.07	30.26	30.04	28.91
FeO	2.12	2.26	2.28	2.20	2.10	2.17	2.11	1.23	1.18	1.50	1.30	1.65
MnO	0.00	0.02	0.01	0.02	0.00	0.00	0.00	-	0.02	0.01	<0.01	-
MgO	2.76	3.05	2.94	2.65	2.84	2.66	3.06	3.46	3.40	2.92	3.05	3.35
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	-	-
Na2O	0.89	0.86	0.79	0.86	0.73	0.86	0.76	0.66	0.73	0.75	0.75	0.66
K2O	9.66	9.78	9.81	9.80	9.94	9.61	9.82	9.99	10.03	9.90	10.00	9.94
F	0.05	0.11	0.09	0.11	0.09	0.05	0.05	0.02	<0.01	0.03	0.09	0.06
Cl	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01
Sub-total	94.00	94.28	93.96	94.11	93.51	93.52	93.11	93.23	92.33	93.86	94.53	93.54
O=F,Cl	0.02	0.05	0.04	0.05	0.04	0.02	0.02	0.01	<0.01	0.01	0.04	0.03
Total	93.98	94.23	93.92	94.06	93.47	93.49	93.09	93.22	92.33	93.85	94.49	93.51
11(O)												
Si	3.26	3.2738	3.26	3.20	3.2339	3.22	3.29	3.2953	3.2914	3.1892	3.23	3.24
Ti	0.03	0.0373	0.03	0.03	0.0320	0.02	0.03	0.0400	0.0354	0.0448	0.04	0.04
Al	2.32	2.2567	2.28	2.38	2.3297	2.37	2.26	2.2470	2.2588	2.3898	2.36	2.29
Fe3+	0.12	0.1266	0.13	0.12	0.1186	0.12	0.12	0.0695	0.0674	0.0841	0.07	0.09
Fe2+	0.00	0.0000	0.00	0.00	0.0000	0.00	0.00	0.0000	0.0000	0.0000	-	-
Mn	0.00	0.0011	0.00	0.00	0.0000	0.00	0.00	0.0000	0.0009	0.0004	<0.01	-
Mg	0.28	0.3045	0.29	0.26	0.2859	0.27	0.31	0.3481	0.3460	0.2917	0.30	0.34
Ca	0.00	0.0000	0.00	0.00	0.0000	0.00	0.00	0.0000	0.0000	0.0000	-	-
Na	0.12	0.1117	0.10	0.11	0.0955	0.11	0.10	0.0862	0.0971	0.0976	0.10	0.09
K	0.83	0.8355	0.84	0.84	0.8560	0.82	0.85	0.8598	0.8732	0.8459	0.85	0.85
F	0.01	0.0233	0.02	0.02	0.0192	0.01	0.01	0.0045	0.0009	0.0057	0.02	0.01
Cl	0.00	0.0000	0.00	0.00	0.0000	0.00	0.00	0.0007	0.0013	0.0006	<0.01	<0.01
OH	1.99	1.9767	1.98	1.98	1.9808	1.99	1.99	1.9949	1.9978	1.9937	1.98	1.99

Table A V-4: Major element and halogen compositions of representative apatite (Ap) from eclogites of the Tso Morari (Himalaya) and Sulu (China) UHP units.

Sample ID	CH165	CH165	CH165	CH165	CH165	CH165	CH165	CH165	CH165	CH171	CH171	CH171
Grain ID	Ap1	Ap2	Ap3	Ap4	Ap5	Ap6	Ap7	Ap8	Ap9	Ap1	Ap2	Ap3
Spot ID	1	1	1	1	1	1	1	1	1	1	1	1
SiO2	-	-	-	-	-	-	-	-	0.03	-	-	-
TiO2	0.09	-	-	0.07	-	0.11	0.01	0.02	0.02	-	-	-
Al2O3	-	-	-	-	-	<0.01	-	-	0.01	0.01	-	-
FeO	0.11	0.17	0.16	0.12	0.22	0.09	0.09	0.12	0.17	0.07	0.09	0.12
MnO	-	-	0.01	0.02	0.02	<0.01	-	-	-	-	0.02	-
MgO	0.02	0.03	0.04	0.03	0.02	0.03	0.02	0.02	0.06	<0.01	0.02	0.01
CaO	55.72	55.27	55.62	55.47	53.56	53.01	52.43	55.64	55.34	55.52	55.76	55.87
Na2O	0.01	<0.01	0.02	0.02	0.01	0.02	<0.01	0.03	<0.01	<0.01	0.02	0.03
K2O	0.02	0.03	0.03	0.03	0.02	0.05	0.11	0.02	0.06	0.02	0.01	0.02
P2O5	43.70	39.90	38.81	39.56	43.90	37.95	38.00	38.40	38.26	40.95	41.56	41.38
SO3	-	<0.01	-	0.01	0.01	-	0.01	0.01	-	0.01	<0.01	0.01
SrO	0.59	0.71	0.63	0.49	0.14	0.42	0.64	0.10	0.45	0.39	0.51	0.42
Y2O3	-	0.01	-	-	0.01	-	-	0.01	-	-	<0.01	-
La2O3	-	-	0.06	-	-	-	-	0.22	0.05	0.15	-	0.17
Ce2O3	0.11	-	0.21	-	-	-	0.01	0.08	0.19	0.11	-	0.03
As2O3	-	0.02	-	-	0.03	-	-	-	<0.01	-	-	-
F	2.82	2.80	2.98	3.08	3.18	2.90	2.92	2.84	3.24	2.37	2.22	2.35
Cl	0.01	0.01	0.01	0.01	<0.01	0.01	-	0.01	0.01	0.10	0.10	0.07
Sub-total	103.20	98.95	98.58	98.92	101.12	94.61	94.25	97.52	97.89	99.72	100.31	100.47
O=F,Cl	1.19	1.18	1.26	1.30	1.34	1.22	1.23	1.20	1.37	1.02	0.96	1.01
Total	102.01	97.77	97.32	97.62	99.78	93.39	93.02	96.32	96.52	98.70	99.35	99.46
12.5(O,OH,Cl,F)												
Si	-	-	-	-	-	-	-	-	0.0024	-	-	-
Ti	0.0054	-	-	0.0049	-	0.0078	0.0005	0.0013	0.0014	-	-	-
Al	-	-	-	-	-	0.0004	-	-	0.0008	0.0008	-	-
Fe	0.0076	0.0127	0.0118	0.0087	0.0152	0.0070	0.0072	0.0086	0.0123	0.0053	0.0064	0.0082
Mn	-	-	0.0004	0.0013	0.0017	0.0002	-	-	-	-	0.0013	-
Mg	0.0029	0.0034	0.0046	0.0044	0.0021	0.0036	0.0028	0.0024	0.0079	0.0001	0.0030	0.0018
Ca	4.8814	5.1285	5.2277	5.1665	4.7595	5.1551	5.1178	5.2721	5.2554	5.0703	5.0404	5.0574
Na	0.0011	0.0002	0.0040	0.0027	0.0021	0.0042	0.0004	0.0048	0.0007	0.0008	0.0040	0.0044
K	0.0019	0.0030	0.0036	0.0033	0.0020	0.0054	0.0132	0.0028	0.0067	0.0024	0.0013	0.0021
P	3.0250	2.9259	2.8825	2.9117	3.0828	2.9163	2.9313	2.8750	2.8707	2.9549	2.9684	2.9595
S	-	0.0002	-	0.0008	0.0009	-	0.0006	0.0008	-	0.0009	0.0001	0.0003
Sr	0.0281	0.0355	0.0320	0.0247	0.0066	0.0222	0.0340	0.0049	0.0230	0.0194	0.0249	0.0204
Y	-	0.0005	-	-	0.0003	-	-	0.0006	-	-	0.0000	-
La	-	-	0.0021	-	-	-	-	0.0072	0.0017	0.0048	-	0.0052
Ce	0.0034	-	0.0068	-	-	-	0.0003	0.0025	0.0062	0.0033	-	0.0010
As	-	0.0009	-	-	0.0012	-	-	-	0.0002	-	-	-
F	0.7301	0.7660	0.8276	0.8476	0.8340	0.8335	0.8427	0.7948	0.9090	0.6380	0.5924	0.6289
Cl	0.0013	0.0018	0.0009	0.0015	0.0002	0.0013	-	0.0013	0.0012	0.0148	0.0141	0.0102
OH	0.2686	0.2321	0.1715	0.1510	0.1658	0.1652	0.1573	0.2040	0.0899	0.3472	0.3935	0.3609

Table A V-4 continued:

Sample ID	CH171	CH171	CH171	CH171	CH171	CH171	CH208	CH208	CH208	CH208	CH208	CH208
Grain ID	Ap4	Ap5	Ap6	Ap7	Ap8	Ap9	Ap1	Ap2	Ap3	Ap4	Ap5	Ap6
Spot ID	1	1	2	4	3	2	2	1	2	2	2	2
SiO2	-	-	-	-	-	-	-	-	-	-	-	-
TiO2	0.06	0.06	0.12	0.37	-	0.03	0.02	0.10	0.04	-	0.06	-
Al2O3	-	<0.01	-	-	-	-	-	-	-	-	-	-
FeO	0.05	0.15	0.10	0.05	0.07	0.04	0.08	0.18	0.24	0.21	0.12	0.22
MnO	-	-	-	0.01	-	0.03	0.02	0.01	0.03	0.03	<0.01	0.03
MgO	0.04	0.03	0.02	0.02	0.03	0.01	0.01	-	0.02	0.02	0.03	0.01
CaO	56.10	55.24	55.83	55.73	55.85	55.71	55.57	55.81	55.99	55.44	55.40	55.71
Na2O	0.02	0.04	<0.01	0.01	0.01	0.01	0.01	-	0.01	0.01	0.01	<0.01
K2O	0.03	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01
P2O5	40.96	42.32	42.20	42.04	42.38	42.36	42.14	38.45	41.48	39.22	39.04	41.64
SO3	-	-	0.01	0.01	0.01	0.02	-	-	0.01	0.01	0.01	0.02
SrO	0.50	0.35	0.52	0.34	0.52	0.48	0.13	0.05	0.16	0.12	0.17	0.02
Y2O3	-	0.01	0.01	<0.01	<0.01	<0.01	0.03	0.05	<0.01	0.01	0.01	<0.01
La2O3	-	-	0.04	0.09	-	0.01	0.01	0.09	0.04	0.15	0.03	-
Ce2O3	-	0.11	0.05	0.01	0.04	0.15	0.01	0.05	0.06	0.01	<0.01	0.03
As2O3	0.04	0.01	-	<0.01	<0.01	-	-	-	-	0.01	0.01	-
F	2.40	2.04	2.31	2.23	2.38	2.33	1.98	2.06	2.14	2.03	2.23	2.10
Cl	0.04	0.09	0.08	0.06	0.07	0.06	0.29	0.26	0.23	0.09	0.06	0.30
Sub-total	100.24	100.46	101.28	100.99	101.37	101.25	100.32	97.13	100.46	97.40	97.21	100.07
O=F,Cl	1.02	0.88	0.99	0.95	1.02	0.99	0.90	0.93	0.95	0.88	0.95	0.95
Total	99.22	99.58	100.29	100.04	100.36	100.26	99.42	96.20	99.51	96.52	96.26	99.12
12.5(O,OH,Cl,F)												
Si	-	-	-	-	-	-	-	-	-	-	-	-
Ti	0.0038	0.0037	0.0074	0.0233	-	0.0021	0.0011	0.0067	0.0023	-	0.0042	-
Al	-	0.0002	-	-	-	-	-	-	-	-	-	-
Fe	0.0033	0.0105	0.0069	0.0033	-0.0049	0.0027	0.0056	0.0136	0.0166	0.0154	0.0089	0.0153
Mn	-	-	-	0.0005	-	0.0020	0.0012	0.0006	0.0022	0.0019	0.0001	0.0022
Mg	0.0053	0.0039	0.0025	0.0026	-0.0033	0.0015	0.0017	-	0.0022	0.0024	0.0044	0.0010
Ca	5.0984	4.9537	4.9914	4.9881	-4.9866	4.9771	5.0044	5.2765	5.0672	5.1970	5.2100	5.0438
Na	0.0026	0.0062	0.0005	0.0014	-0.0017	0.0022	0.0019	-	0.0021	0.0021	0.0016	0.0001
K	0.0033	0.0016	0.0006	0.0014	-0.0019	0.0016	0.0021	0.0014	0.0020	0.0024	0.0022	0.0012
P	2.9415	2.9986	2.9813	2.9734	-2.9899	2.9905	2.9893	2.8729	2.9566	2.9050	2.9014	2.9724
S	-	-	0.0004	0.0007	-0.0003	0.0013	-	-	0.0004	0.0008	0.0004	0.0012
Sr	0.0247	0.0172	0.0249	0.0167	-0.0253	0.0234	0.0065	0.0027	0.0076	0.0062	0.0086	0.0009
Y	-	0.0003	0.0003	0.0001	-0.0002	0.0000	0.0013	0.0023	0.0002	0.0006	0.0003	0.0001
La	-	-	0.0012	0.0029	-	0.0002	0.0002	0.0030	0.0012	0.0048	0.0011	-
Ce	-	0.0033	0.0015	0.0004	-0.0012	0.0046	0.0005	0.0015	0.0019	0.0003	0.0002	0.0009
As	0.0016	0.0005	-	0.0001	-0.0001	-	-	-	-	0.0004	0.0003	-
F	0.6438	0.5404	0.6087	0.5896	-0.6268	0.6137	0.5255	0.5753	0.5704	0.5631	0.6181	0.5599
Cl	0.0053	0.0128	0.0106	0.0082	-0.0097	0.0084	0.0421	0.0395	0.0320	0.0141	0.0095	0.0431
OH	0.3509	0.4467	0.3807	0.4022	(0.3635)	0.3779	0.4324	0.3852	0.3976	0.4228	0.3725	0.3970

Table A V-4 continued:

Sample ID	CH266	CH266	CH266	CH266	CH266	CH266	CH266	CH266	CH266	CH266	CH266	CH266
Grain ID	Ap1	Ap2	Ap3	Ap4	Ap5	Ap6	Ap7	Ap8	Ap9	Ap10	Ap11	Ap12
Spot ID	1	1	1	1	1	1	1	1	2	1	1	2
SiO2	-	0.20	-	-	-	-	-	0.24	0.17	-	-	-
TiO2	0.04	0.04	-	0.04	-	-	-	-	-	-	-	-
Al2O3	-	0.04	-	-	-	-	-	0.07	0.05	-	-	-
FeO	0.07	0.21	0.16	0.18	0.07	0.06	0.06	0.31	0.24	0.08	0.07	0.12
MnO	-	0.02	-	0.03	-	0.01	0.03	0.02	0.00	0.04	-	0.01
MgO	-	0.11	0.01	0.02	0.01	-	0.01	0.13	0.11	0.01	0.01	0.00
CaO	55.82	54.19	55.79	55.62	55.77	55.86	55.50	55.62	55.03	55.80	55.46	55.56
Na2O	0.04	0.01	0.03	0.01	0.01	0.02	0.02	0.03	0.02	0.05	0.04	0.03
K2O	0.01	0.01	0.03	0.01	0.00	0.02	0.02	0.01	0.01	0.04	0.03	0.03
P2O5	42.25	40.37	41.83	41.72	41.73	41.69	42.41	42.41	42.05	42.75	41.60	42.54
SO3	0.02	-	-	-	-	-	-	0.03	0.03	0.00	-	-
SrO	0.42	1.25	0.80	0.99	0.81	0.82	0.38	0.18	0.77	0.77	0.89	0.97
Y2O3	-	-	0.05	0.03	-	-	0.08	0.02	0.02	0.00	0.02	0.02
La2O3	0.08	-	-	0.12	0.06	-	-	-	0.04	0.30	-	0.09
Ce2O3	-	-	-	0.11	-	-	0.05	0.13	0.11	-	0.11	0.05
As2O3	-	-	-	-	-	0.01	0.00	0.01	-	0.04	-	-
F	2.39	2.08	2.25	2.32	2.27	1.98	2.21	2.19	2.07	2.29	2.23	2.18
Cl	0.09	0.12	0.11	0.14	0.11	0.18	0.18	0.11	0.17	0.11	0.12	0.14
Sub-total	101.21	98.65	101.05	101.33	100.84	100.64	100.96	101.50	100.89	102.28	100.58	101.74
O=F,Cl	1.03	0.90	0.97	1.01	0.98	0.88	0.97	0.94	0.91	0.99	0.96	0.95
Total	100.18	97.75	100.08	100.33	99.86	99.77	99.99	100.55	99.98	101.29	99.62	100.79
12.5(O,OH,Cl,F)												
Si	-	0.0171	-	-	-	-	-	0.0200	0.0140	-	-	-
Ti	0.0023	0.0029	-	0.0023	-	-	-	-	-	-	-	-
Al	-	0.0037	-	-	-	-	-	0.0069	0.0046	-	-	-
Fe	0.0047	0.0153	0.0112	0.0124	0.0048	0.0042	0.0043	0.0213	0.0169	0.0059	0.0051	0.0086
Mn	-	0.0015	-	0.0024	-	0.0008	0.0019	0.0017	0.0002	0.0027	-	0.0005
Mg	-	0.0143	0.0016	0.0028	0.0006	-	0.0015	0.0157	0.0142	0.0015	0.0009	0.0002
Ca	4.9937	5.0006	5.0138	5.0030	5.0243	5.0319	4.9662	4.9417	4.9344	4.9451	5.0117	4.9479
Na	0.0065	0.0012	0.0045	0.0015	0.0011	0.0028	0.0038	0.0047	0.0025	0.0072	0.0068	0.0050
K	0.0008	0.0011	0.0030	0.0015	0.0003	0.0017	0.0020	0.0013	0.0014	0.0040	0.0037	0.0033
P	2.9867	2.9436	2.9710	2.9650	2.9708	2.9680	2.9987	2.9777	2.9784	2.9937	2.9709	2.9937
S	0.0010	-	-	-	-	-	-	0.0019	0.0020	0.0001	-	-
Sr	0.0201	0.0624	0.0387	0.0482	0.0396	0.0399	0.0183	0.0085	0.0371	0.0368	0.0435	0.0468
Y	-	-	0.0022	0.0014	-	-	0.0036	0.0007	0.0010	0.0000	0.0008	0.0008
La	0.0023	-	-	0.0038	0.0019	-	-	-	0.0012	0.0093	-	0.0028
Ce	-	-	-	0.0033	-	-	0.0016	0.0039	0.0033	-	0.0033	0.0015
As	-	-	-	-	-	0.0004	0.0001	0.0003	-	0.0015	-	-
F	0.6309	0.5679	0.5971	0.6147	0.6043	0.5276	0.5841	0.5734	0.5475	0.5988	0.5938	0.5718
Cl	0.0128	0.0173	0.0155	0.0201	0.0156	0.0251	0.0258	0.0150	0.0242	0.0161	0.0174	0.0193
OH	0.3563	0.4148	0.3875	0.3652	0.3801	0.4473	0.3901	0.4116	0.4283	0.3851	0.3887	0.4089

Table A V-4 continued:

Sample ID	CH266	CH266	CH266	CH266	SL47	SL47	SL48	SL48	SL48
Grain ID	Ap14	Ap15	Ap16	Ap17	Ap1	Ap2	Ap1	Ap2	Ap3
Spot ID	3	1	1	1	2	2	2	3	2
SiO2	0.08	-	-	-	-	-	-	-	-
TiO2	0.02	-	0.01	-	0.01	<0.01	-	<0.01	0.02
Al2O3	-	-	-	-	-	-	-	-	-
FeO	0.05	0.14	0.09	0.06	0.09	0.07	0.09	0.13	0.09
MnO	0.02	-	0.01	-	0.03	0.02	0.01	<0.01	0.01
MgO	0.01	<0.01	0.02	0.01	0.02	0.02	0.05	0.06	0.02
CaO	55.56	55.39	55.63	55.66	55.40	55.68	55.35	55.15	55.58
Na2O	0.02	0.02	0.02	0.01	0.09	0.09	0.09	0.06	0.07
K2O	0.01	0.04	0.02	0.02	0.02	0.02	0.02	0.01	0.02
P2O5	42.23	42.23	42.05	41.43	44.14	41.68	39.54	40.52	41.14
SO3	<0.01	0.01	-	0.01	0.20	0.17	0.19	0.12	0.15
SrO	0.29	0.71	0.89	0.46	0.03	0.04	0.28	0.21	0.13
Y2O3	0.02	-	0.04	-	<0.01	0.02	0.01	<0.01	0.01
La2O3	0.03	-	0.09	-	-	0.04	-	-	-
Ce2O3	0.07	0.19	0.13	-	-	0.05	0.01	0.01	0.09
As2O3	0.01	-	-	-	-	-	-	0.01	-
F	2.29	2.31	2.33	2.38	1.81	1.96	1.89	2.03	2.15
Cl	0.14	0.14	0.13	0.13	0.16	0.16	0.65	0.58	0.59
Sub-total	100.85	101.19	101.47	100.15	102.01	100.02	98.18	98.89	100.06
O=F,Cl	1.00	1.01	1.01	1.03	0.80	0.86	0.94	0.99	1.04
Total	99.86	100.18	100.45	99.12	101.21	99.16	97.24	97.90	99.02
12.5(O,OH,Cl,F)									
Si	0.0070	-	-	-	-	-	-	-	-
Ti	0.0012	-	0.0009	-	0.0006	0.0001	0.0001	0.0013	-
Al	-	-	-	-	-	-	-	-	-
Fe	0.0035	0.0100	0.0060	0.0042	0.0065	0.0049	0.0089	0.0067	0.0066
Mn	0.0013	-	0.0006	-	0.0019	0.0015	0.0003	0.0007	0.0010
Mg	0.0010	0.0006	0.0022	0.0009	0.0027	0.0025	0.0071	0.0026	0.0061
Ca	4.9782	4.9640	4.9860	5.0481	4.8399	5.0199	5.0799	5.0561	5.1535
Na	0.0039	0.0033	0.0025	0.0012	0.0148	0.0153	0.0093	0.0109	0.0150
K	0.0008	0.0042	0.0025	0.0018	0.0017	0.0022	0.0008	0.0017	0.0019
P	2.9902	2.9909	2.9779	2.9688	3.0408	2.9690	2.9446	2.9540	2.9090
S	0.0002	0.0003	-	0.0003	0.0120	0.0108	0.0081	0.0095	0.0122
Sr	0.0140	0.0345	0.0434	0.0223	0.0015	0.0018	0.0105	0.0065	0.0141
Y	0.0009	-	0.0017	-	0.0000	0.0009	0.0001	0.0006	0.0003
La	0.0008	-	0.0028	-	-	0.0012	-	-	-
Ce	0.0021	0.0059	0.0039	-	-	0.0014	0.0003	0.0027	0.0005
As	0.0005	-	-	-	-	-	0.0006	-	-
F	0.6057	0.6123	0.6173	0.6358	0.4676	0.5227	0.5522	0.5765	0.5204
Cl	0.0196	0.0197	0.0184	0.0188	0.0225	0.0229	0.0841	0.0847	0.0959
OH	0.3747	0.3679	0.3643	0.3454	0.5099	0.4545	0.3637	0.3388	0.3837

Table A V-5: Major element compositions of representative garnet from eclogites of the Tso

Morari (Himalaya) and Sulu (China) UHP units.

Sample ID	CH171	CH171	CH171	CH171	CH171	CH171	CH266	CH266	CH266	CH266	CH266
Mineral	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet
Grain ID	1	2	3	4	5	6	1	2	3	4	5
# of analyses	2	2	2	4	5	4	1	1	1	1	1
SiO₂	38.58	37.99	38.58	38.72	39.01	38.04	38.02	37.61	38.19	38.09	37.32
TiO₂	0.01	0.06	0.05	0.01	0.03	0.06	<0.01	0.07	0.01	0.02	0.18
Al₂O₃	22.07	21.21	21.74	21.95	21.99	21.74	21.84	21.40	21.74	21.74	21.17
FeO	23.47	27.84	23.69	24.95	22.80	24.66	25.74	26.29	26.38	26.27	25.50
MnO	0.18	0.61	0.36	0.24	0.37	0.59	0.22	0.35	0.28	0.52	0.63
MgO	8.49	3.27	7.07	7.92	8.47	6.33	6.93	5.19	6.76	6.74	3.76
CaO	7.18	9.25	8.31	6.44	7.64	8.18	6.96	8.37	6.96	6.42	11.06
Na₂O	0.01	0.02	0.01	0.02	0.01	0.02	0.04	0.04	0.01	0.02	0.02
K₂O	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02
Total	100.02	100.27	99.85	100.28	100.33	99.64	99.767	99.330	100.344	99.837	99.664
12(O)											
Si	2.9458	2.9893	2.9718	2.9661	2.9670	2.9520	2.9430	2.9507	2.9465	2.9555	2.9335
Ti	0.0007	0.0036	0.0032	0.0008	0.0017	0.0035	0.0003	0.0042	0.0005	0.0013	0.0104
Al	1.9854	1.9666	1.9737	1.9816	1.9712	1.9881	1.9925	1.9785	1.9766	1.9879	1.9610
Fe³⁺	0.1255	0.0527	0.0808	0.0898	0.0943	0.1059	0.1283	0.1194	0.1331	0.1018	0.1560
Fe²⁺	1.3731	1.7789	1.4466	1.5118	1.3583	1.4977	1.5376	1.6051	1.5686	1.6025	1.5197
Mn	0.0117	0.0410	0.0238	0.0155	0.0238	0.0394	0.0143	0.0233	0.0181	0.0343	0.0423
Mg	0.9668	0.3835	0.8084	0.9010	0.9571	0.7267	0.8000	0.6075	0.7779	0.7791	0.4406
Ca	0.5871	0.7793	0.6871	0.5280	0.6234	0.6816	0.5769	0.7032	0.5750	0.5340	0.9314
Na	0.0016	0.0027	0.0023	0.0033	0.0013	0.0031	0.0054	0.0060	0.0015	0.0027	0.0033
K	0.0024	0.0024	0.0023	0.0020	0.0018	0.0020	0.0018	0.0019	0.0022	0.0008	0.0017

Table A V-5 continued:

Sample ID	CH266	CH266	CH266	CH208	CH208	CH208	CH208	CH165	CH165	SL41	SL41	SL41	SL41
Mineral	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet
Grain ID	6	7	8	1	2	3	4	1	2	1	2	3	4
# of analyses	1	2	2	3	3	3	4	3	4	5	3	3	3
SiO2	37.68	38.13	38.07	37.58	37.42	37.49	37.42	36.86	37.51	39.26	39.31	39.24	39.62
TiO2	0.08	0.06	0.03	0.07	0.12	0.11	0.11	0.06	0.07	0.02	0.02	0.02	0.01
Al2O3	21.50	21.60	21.54	20.83	20.74	20.83	20.70	20.87	20.97	22.34	22.19	22.15	22.35
FeO	25.39	25.17	26.37	29.53	29.62	28.93	29.23	22.06	30.39	19.36	19.29	19.73	19.07
MnO	0.80	0.87	0.48	0.85	0.54	1.46	0.67	0.21	0.40	0.37	0.42	0.44	0.36
MgO	5.20	6.23	6.17	2.44	2.50	2.38	2.57	4.98	3.06	9.97	9.03	8.91	9.54
CaO	9.12	8.34	7.28	8.24	8.59	8.51	8.52	6.29	7.23	8.81	9.77	9.56	9.47
Na2O	0.01	0.02	0.02	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	<0.01
K2O	0.03	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total	99.82	100.44	99.99	99.54	99.55	99.72	99.23	91.36	99.64	100.16	100.06	100.05	100.43
12(O)													
Si	2.9388	2.9416	2.9570	3.0044	2.9897	2.9926	2.9969	3.1266	2.9902	2.9510	2.9691	2.9678	2.9734
Ti	0.0046	0.0035	0.0020	0.0040	0.0072	0.0063	0.0064	0.0039	0.0040	0.0013	0.0011	0.0009	0.0007
Al	1.9761	1.9640	1.9720	1.9628	1.9531	1.9591	1.9541	2.0860	1.9703	1.9789	1.9753	1.9743	1.9765
Fe3+	0.1410	0.1498	0.1145	0.0211	0.0553	0.0448	0.0406	-	0.0424	0.1178	0.0859	0.0903	0.0760
Fe2+	1.5151	1.4750	1.5983	1.9533	1.9231	1.8857	1.9166	1.5636	1.9833	1.0991	1.1325	1.1575	1.1204
Mn	0.0530	0.0575	0.0314	0.0574	0.0366	0.0988	0.0456	0.0151	0.0272	0.0239	0.0271	0.0284	0.0231
Mg	0.6052	0.7140	0.7143	0.2904	0.2976	0.2829	0.3072	0.6298	0.3639	1.1176	1.0166	1.0043	1.0675
Ca	0.7623	0.6907	0.6062	0.7060	0.7350	0.7281	0.7312	0.5730	0.6175	0.7093	0.7908	0.7744	0.7617
Na	0.0013	0.0024	0.0025	0.0005	0.0021	0.0012	0.0011	0.0019	0.0009	0.0010	0.0014	0.0021	0.0005
K	0.0026	0.0016	0.0019	0.0002	0.0001	0.0005	0.0003	0.0002	0.0002	0.0002	0.0002	0.0001	0.0002

Table A V-5 continued:

Sample ID	SL45	SL45	SL45	SL45	SL45	SL47	SL47	SL47	SL47	SL47	SL47	SL47	SL47
Mineral	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet
Grain ID	1	2	3	4	5	1	2	3	4	5	6	7	8
# of analyses	3	2	2	3	5	4	4	1	1	1	3	3	4
SiO2	39.73	39.65	39.76	39.90	40.07	38.88	38.81	39.16	38.47	38.72	38.91	38.86	38.65
TiO2	0.02	0.01	0.01	0.02	0.01	0.02	0.03	0.02	0.03	0.01	0.02	0.02	0.02
Al2O3	22.74	22.44	22.47	22.52	22.50	21.72	21.71	21.60	21.27	21.62	21.64	21.86	21.51
FeO	18.36	18.78	18.72	18.49	17.84	21.57	21.05	20.12	23.70	23.18	21.21	21.42	21.89
MnO	0.30	0.35	0.36	0.35	0.32	0.44	0.39	0.32	0.81	0.55	0.37	0.40	0.61
MgO	11.54	11.57	11.15	11.54	12.48	7.47	7.27	7.47	5.82	6.56	7.81	7.48	7.18
CaO	7.64	7.31	7.84	7.66	7.17	9.58	10.15	10.53	9.19	9.21	9.27	9.66	9.18
Na2O	0.01	0.02	<0.01	0.01	0.01	0.02	<0.01	0.01	-	0.01	0.02	0.01	0.01
K2O	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	<0.01	<0.01	0.01
Total	100.36	100.13	100.33	100.50	100.41	99.70	99.41	99.24	99.31	99.87	99.25	99.70	99.05
12(O)													
Si	2.9545	2.9584	2.9658	2.9653	2.9656	2.9808	2.9833	3.0071	2.9999	2.9863	2.9907	2.9779	2.9904
Ti	0.0011	0.0005	0.0006	0.0010	0.0005	0.0013	0.0017	0.0013	0.0017	0.0007	0.0013	0.0013	0.0011
Al	1.9924	1.9729	1.9755	1.9719	1.9626	1.9623	1.9670	1.9553	1.9546	1.9649	1.9599	1.9737	1.9616
Fe3+	0.0990	0.1119	0.0925	0.0978	0.1068	0.0765	0.0635	0.0302	0.0422	0.0620	0.0587	0.0698	0.0572
Fe2+	1.0427	1.0595	1.0752	1.0509	0.9974	1.3068	1.2894	1.2618	1.5032	1.4333	1.3042	1.3026	1.3598
Mn	0.0190	0.0224	0.0230	0.0220	0.0202	0.0284	0.0255	0.0211	0.0538	0.0361	0.0241	0.0259	0.0402
Mg	1.2797	1.2874	1.2398	1.2788	1.3770	0.8537	0.8334	0.8551	0.6769	0.7548	0.8951	0.8541	0.8271
Ca	0.6090	0.5845	0.6266	0.6101	0.5683	0.7872	0.8355	0.8660	0.7676	0.7609	0.7635	0.7928	0.7607
Na	0.0020	0.0024	0.0003	0.0018	0.0013	0.0029	0.0004	0.0021	-	0.0009	0.0025	0.0019	0.0013
K	0.0005	0.0002	0.0006	0.0004	0.0002	0.0001	0.0003	0.0002	0.0001	-	0.0000	0.0000	0.0005

Table A V-5 continued:

Sample ID	SL48	SL48	SL48	SL48	SL48	SL48	SL48
Mineral	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet	Garnet
Grain ID	1	2	3	4	5	6	7
# of analyses	5	1	1	1	1	2	4
SiO2	39.70	39.63	39.65	39.46	39.68	39.71	39.57
TiO2	0.02	<0.01	0.04	0.02	0.01	0.02	0.02
Al2O3	22.18	22.13	22.16	22.14	22.33	22.16	22.25
FeO	19.09	19.26	19.31	19.03	19.40	19.23	19.30
MnO	0.33	0.31	0.31	0.31	0.28	0.30	0.33
MgO	9.94	10.09	10.14	9.92	9.89	9.99	9.89
CaO	9.11	8.96	8.74	9.26	9.26	8.87	9.15
Na2O	0.01	-	0.02	0.02	0.01	-	0.01
K2O	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total	100.37	100.38	100.38	100.14	100.85	100.28	100.53
12(O)							
Si	2.9766	2.9706	2.9714	2.9649	2.9631	2.9810	2.9641
Ti	0.0009	0.0001	0.0025	0.0011	0.0008	0.0010	0.0010
Al	1.9604	1.9552	1.9574	1.9605	1.9655	1.9606	1.9646
Fe3+	0.0856	0.1034	0.0983	0.1103	0.1076	0.0756	0.1067
Fe2+	1.1114	1.1036	1.1120	1.0850	1.1035	1.1314	1.1023
Mn	0.0208	0.0198	0.0197	0.0196	0.0175	0.0193	0.0207
Mg	1.1117	1.1279	1.1333	1.1107	1.1005	1.1178	1.1047
Ca	0.7314	0.7194	0.7018	0.7451	0.7407	0.7131	0.7345
Na	0.0009	-	0.0033	0.0027	0.0008	-	0.0013
K	0.0002	0.0000	0.0002	0.0001	0.0000	0.0002	0.0002

Table A V-6: Major element compositions of representative pyroxene (Px) from eclogites of the Tso Morari (Himalaya) and Sulu (China) UHP units.

Sample ID	CH171	CH171	CH171	CH171	CH266	CH266	CH165	CH165	CH165	SL41	SL41	SL41	SL41
Mineral	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px
Grain ID	1	2	3	4	1	2	1	2	3	1	2	3	4
# of analyses	3	2	2	3	3	3	1	1	2	3	3	3	3
SiO₂	57.21	50.26	57.12	56.72	56.56	56.23	56.24	56.59	56.74	55.58	55.99	56.02	56.26
TiO₂	0.02	0.24	0.02	0.02	0.03	0.02	0.03	0.04	0.04	0.09	0.08	0.07	0.07
Al₂O₃	11.10	12.62	11.29	11.36	10.06	9.69	8.76	9.04	10.00	10.64	10.53	10.34	10.25
FeO	2.61	6.51	2.46	2.25	3.60	3.29	5.93	6.34	5.65	3.43	3.19	3.30	3.09
MnO	0.01	<0.01	0.02	0.02	0.01	0.01	0.03	0.01	0.01	<0.01	0.01	0.01	0.01
MgO	9.17	15.07	9.17	9.22	9.43	9.98	8.34	7.89	7.58	9.18	9.31	9.41	9.59
CaO	14.19	8.61	13.88	13.88	14.59	14.98	13.73	13.02	12.16	14.29	14.47	14.66	14.73
Na₂O	6.48	3.70	6.63	6.52	6.10	5.91	6.82	7.36	7.78	6.49	6.52	6.44	6.33
K₂O	0.02	0.26	0.03	0.02	0.01	0.02	<0.01	<0.01	0.01	<0.01	<0.01	0.01	0.01
Total	100.82	97.28	100.62	100.01	100.40	100.14	99.88	100.30	99.96	99.70	100.10	100.26	100.34
6(O)													
Si	2.008	1.828	2.005	2.002	2.002	1.993	2.010	2.011	2.014	1.974	1.979	1.979	1.986
Ti	0.001	0.007	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.002	0.002	0.002	0.002
Al	0.459	0.541	0.467	0.473	0.420	0.405	0.369	0.379	0.418	0.445	0.439	0.431	0.426
Fe³⁺	-	0.063	-	-	0.003	0.015	0.083	0.106	0.089	0.049	0.046	0.049	0.032
Fe²⁺	0.077	0.135	0.072	0.066	0.104	0.083	0.094	0.083	0.079	0.053	0.049	0.048	0.059
Mn	0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.480	0.817	0.480	0.485	0.498	0.527	0.445	0.418	0.401	0.486	0.491	0.495	0.505
Ca	0.534	0.336	0.522	0.525	0.553	0.569	0.526	0.496	0.462	0.544	0.548	0.555	0.557
Na	0.441	0.261	0.451	0.446	0.419	0.406	0.472	0.507	0.536	0.447	0.447	0.441	0.433
K	0.001	0.012	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table A V-6 continued:

Sample ID	SL45	SL45	SL45	SL45	SL45	SL47	SL47	SL47	SL48	SL48	SL48	SL48	SL48
Mineral	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px	Px
Grain ID	1	2	3	4	5	1	2	3	1	2	4	5	6
# of analyses	3	3	3	2	4	1	1	1	4	2	3	3	3
SiO2	55.82	55.92	56.07	55.86	56.02	55.78	55.80	55.87	56.07	56.20	55.93	55.92	55.95
TiO2	0.07	0.07	0.06	0.08	0.07	0.10	0.09	0.08	0.09	0.07	0.07	0.10	0.09
Al2O3	9.09	9.29	8.62	9.48	8.95	11.01	11.05	11.43	9.99	10.02	9.84	10.09	9.95
FeO	2.95	2.95	3.01	3.04	3.00	4.30	4.28	4.10	3.42	3.32	3.48	3.46	3.49
MnO	<0.01	0.01	0.02	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01	0.02	<0.01
MgO	10.60	10.43	10.98	10.23	10.70	8.31	8.26	8.06	9.63	9.57	9.73	9.61	9.55
CaO	16.17	15.94	16.61	15.64	16.30	13.59	13.62	13.11	15.02	14.75	15.04	14.88	14.91
Na2O	5.54	5.62	5.28	5.92	5.52	6.95	6.80	7.20	6.30	6.40	6.26	6.26	6.26
K2O	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01
Total	100.24	100.25	100.64	100.26	100.57	100.06	99.93	99.86	100.53	100.35	100.37	100.35	100.20
6(O)													
Si	1.977	1.980	1.981	1.975	1.979	1.977	1.983	1.980	1.977	1.984	1.975	1.976	1.981
Ti	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.002
Al	0.380	0.388	0.359	0.395	0.372	0.460	0.463	0.477	0.415	0.417	0.410	0.420	0.415
Fe3+	0.043	0.034	0.038	0.056	0.045	0.060	0.036	0.053	0.057	0.050	0.065	0.052	0.049
Fe2+	0.044	0.054	0.051	0.033	0.044	0.067	0.091	0.068	0.044	0.048	0.037	0.051	0.054
Mn	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000
Mg	0.560	0.551	0.578	0.539	0.563	0.439	0.438	0.426	0.506	0.503	0.512	0.506	0.504
Ca	0.613	0.605	0.629	0.593	0.617	0.516	0.518	0.498	0.567	0.558	0.569	0.563	0.565
Na	0.381	0.386	0.362	0.406	0.378	0.478	0.468	0.495	0.431	0.438	0.429	0.429	0.430
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Appendix VI.

Unpublished data

VI.1 Logatchev hydrothermal field (Mid-Atlantic Ridge)

VI.1.1 Geology and samples

The Logatchev Hydrothermal Field (LHF) is located along the Mid-Atlantic Ridge (MAR) at ~14°45"N, 44°59"W. It is part of an ultramafic-hosted hydrothermal system comprising three short ridge segments separated by non-transform discontinuities (Cannat et al., 1997; Fouquet et al., 2007; Smith et al., 2008). The Logatchev hydrothermal field is characterized by deep (~3500–4500 m) basins and linear ridges along the axis (Fujiwara et al., 2003). The prevalence of tectonic accretion over magma production in this area results in the tectonic uplift and exposure of mantle peridotites and gabbros of the lower crust (Cannat et al., 1997). Spinel and relic olivine compositions of serpentinized peridotites suggest they are highly depleted mantle residues (e.g., Cannat and Casey, 1995; Cannat et al., 1997). Hydrothermal activity at Logatchev is related to depressions in the seafloor called “smoking craters”, a unique style of venting that has only been described at Logatchev, and the ultramafic-hosted Ashadze (Fouquet et al., 2008) and Nibelungen hydrothermal fields (Melchert et al., 2008). Hydrothermal fluids contain abundant CH₄ and H₂ gases, which is attributed to the abundant serpentinization in the area (e.g., Schmidt et al., 2007).

LHF abyssal serpentinite samples were collected during the HYDROMAR M60/3 and MSM03/2 cruises between 2004 and 2007. Sample acquisition methods included TV-guided grab sampling, shallow (<15 m) drilling and dredging (**Error! Reference source not found.**). All samples are composed of 90-95% lizardite with minor chrysotile and magnetite ± pyroxene ± talc (Augustin et al., 2008). Lizardite occurs as mesh-like or hourglass texture after olivine, bastite texture after pyroxene and fibrous or platy texture filling veins. Bulk rock and select microprobe mineral compositions are published in Augustin et al. (2008).

Table A VI-1: Summary of sample location, sample depth, cruise ID and dredge type for serpentinites collected from the Logatchev hydrothermal field, Mid-Atlantic Ridge. All samples are composed of 90-95% lizardite.

Sample ID	Latitude*	Longitude*	Depth (m)*	Cruise	Type	Reference
35GTV-5	14°45.19'N	44°58.74'W	3019	M60/3	TV Grab	1
49GTV-2	14°55.48'N	44°54.34'W	3344	M60/3	TV Grab	1
57GTV-1A-2	14°42.29'N	44°53.67'W	1608	M60/3	TV Grab	1
67GTV-2B	14°42.30'N	44°54.41'W	1967	M60/3	TV Grab	1
67GTV-2C	14°42.30'N	44°54.41'W	1967	M60/3	TV Grab	1
957RD-A	14°45.220'N	44°58.818'W	3045	MSM03/2	Rock drill core	2
957RD-B	14°45.220'N	44°58.818'W	3045	MSM03/2	Rock drill core	2
MSM942-10	14°43.55'N	44°58.85'W	3275	MSM03/2	Dredge	2
MSM949-20	14°43.16'N	44°56.50'W	2745	MSM03/2	Dredge	2
MSM949-24	14°43.16'N	44°56.50'W	2745	MSM03/2	Dredge	2

*Dredge locations and depths are starting points
1 - Augustin et al., 2008; 2- Petersen et al., 2009

VI.1.2 Halogen Results

Table A VI-2: Bulk rock halogen contents of lizardite-serpentinites from the Logatchev

hydrothermal field, Mid-Atlantic Ridge. All concentrations and standard deviations are in ppm.

Sample ID	n	Dionex IC				ICP-MS			
		F	sd	Cl	sd	79 Br	sd	127 I	sd
35GTV-5	2	112	0.5	593	7	1.7	0.4	3.7	0.9
49GTV-2	2	122	5.6	1826	141	4.2	0.2	2.6	0.0
57GTV-1A	2	84	0.7	753	82	2.9	0.3	2.2	0.5
67GTV-2C	2	119	0.1	1103	162	2.7	1.2	2.0	0.2
67GTV-2B	2	130	6.2	1524	97	5.5	0.3	2.2	0.3
957RD-A	2	53	0.4	978	129	2.5	0.5	1.1	0.4
957RD-B	2	62	0.7	1085	90	3.5	1.6	0.9	0.2
MSM942-10	2	104	31	2223	1063	6.5	3.4	1.3	0.3
MSM949-20	2	115	11	1045	201	4.0	0.9	1.5	0.0
MSM949-24	2	97	16	857	10	2.8	0.4	1.7	0.3
Instrument LO (3σ)		0.0017		0.0034		0.000022		0.0000041	
Method LOD (3σ)		0.019		0.12		0.0041		0.0029	
IC – ion chromatography; ICP-MS – inductively-coupled plasma mass spectrometry; PGNA – prompt gamma neutron activation analysis									
LOD – limit of detection; sd – standard deviation									

VI.2 Mariana serpentinite mud volcanoes

Table A VI-3: Bulk rock halogen contents of lizardite-serpentinites from Mariana serpentinite mud volcanoes. All concentrations and standard deviations are in ppm.

Sample ID	n	Dionex IC				ICP-MS				
		F	sd	Cl	sd	79 Br	sd	127 I	sd	
Conical Seamount*										
D030	3	7.7	0.8	459	86	1.8	0.70	17	1.7	
D934	3	0.53		722	135	1.6	1.1	10	2.1	
H916	3	2.3	1.1	384	85	0.80	0.56	2.9	0.83	
H948	3	0.27	0.006	350	28	0.88	0.34	11	2.2	
Ogasawara Seamount†										
KH82-4-4-001	3	154	8.5	952	198	1.9	1.0	17	6.2	
KH80-3-32-2	3	387	20	1234	290	3.3	0.9	13	1.4	
Instrument LOD (3σ)		0.0017		0.0034		0.000022		0.0000041		
Method LOD (3σ)		0.019		0.12		0.0041		0.0029		
IC – ion chromatography; ICP-MS – inductively-coupled plasma mass spectrometry; PGNA – prompt gamma neutron activation analysis										
LOD – limit of detection; sd – standard deviation; bd – below detection limit										
*See Ishii, 1992 for sampling and petrology details; †Sakai et al., 1990 for sampling and petrology details										

VI.3 Dominican Republic metabasites

Table A VI-4: Bulk rock halogen contents of blueschists and eclogites from Dominican Republic metabasites. All concentrations and standard deviations are in ppm.

Sample ID	n	Dionex IC				ICP-MS				F/Cl	Br/Cl	I/Cl
		F	sd	Cl	sd	79 Br	sd	127 I	sd			
Blueschists												
RD82	2	769	0.086	15	0.042	bdl	bdl	0.21	0.10	52	bdl	0.014
RD84	2	936	0.022	28	0.016	bdl	bdl	0.22	0.13	34	bdl	0.0081
Eclogites												
RD97	2	210	0.071	12	0.36	bdl	bdl	0.013	0.00025	17	bdl	0.0010
RD98	2	243	0.032	14	0.086	0.082	0.00063	0.038	0.00011	18	0.0060	0.0027
Instrument LOD (3σ)	0.0017		0.0034		0.000022		0.0000041					
Method LOD (3σ)	0.019		0.12		0.0041		0.0029					
IC – ion chromatography; ICP-MS – inductively coupled plasma-mass spectrometry												
LOD – limit of detection; sd – standard deviation; bdl – below detection limit												

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Appendix VII.

Conference abstracts

Goldschmidt 2013, Florence, Italy [Poster]

Fluorine, Cl, Br & I in serpentinites

Pagé, L. and Hattori, K.

The abundance of F, Cl, Br and I in serpentinites were examined to evaluate their behaviour in subduction zones. Samples include (1) unmetamorphosed, obducted hydrated abyssal peridotites, (2) subducted abyssal peridotites to depth of ~30 km, (3) forearc mantle serpentinites from shallow depth (<30 km) and (4) mantle wedge serpentinites from ~140 km depth in the Himalayas. Samples (1,2,3) from Dominican Republic are composed of lizardite (low temp. serpentine). The Himalayan samples consist of antigorite (high temp. phase).

Abyssal peridotites contain high (<530 ppm) Cl but they lose Cl during their subduction. In the mantle wedge, elevated (<880 ppm) Cl in shallow serpentinites suggests transfer of Cl from subducting slab to the overlying mantle wedge. Lower Cl values (≤ 50 ppm) in deep mantle wedge serpentinites indicate loss of Cl either by pressure increase or transition from lizardite to antigorite. The Br/Cl ratios for obducted abyssal peridotites are comparable to that of seawater, confirming their serpentinization on or near the ocean floor. Bromine appears to mimic Cl in its behaviour; abyssal peridotites partially lose Br during subduction and there is high Br content in shallow mantle wedge serpentinites. However, the degree of Br loss is less than that of Cl with increasing depth, as illustrated by the elevated Br/Cl ratio ($< 12 \times 10^{-3}$) in the deep mantle wedge. Hydrated abyssal peridotites contain relatively high I/Cl ratios up to 240 times seawater. Our results are consistent with data from sea floor serpentinites [1]. The content of I remains relatively constant during their shallow subduction. In the mantle wedge, shallow and deep forearc serpentinites contain similar amounts of I, indicating retention of I during the lizardite to antigorite phase transition.

Fluorine shows significantly different behaviour from the other halogens. The content of F is low (120 ppm) in abyssal peridotites, as expected from low F content in seawater. Upon shallow subduction, F content increases in hydrated abyssal peridotites, likely incorporated from shallow water sediments. Similar F-enhancement is observed for shallow forearc peridotites. Fluorine is further enriched in deep mantle wedge peridotites (<160 ppm) by incorporating F released from slabs and sediments. Serpentinites likely contribute to the transfer of F and I into the deep mantle, whereas Br and Cl likely have shallow cycles in subduction zones.

[1] Kendrick *et al* (2013) *Earth Planet Sc. Lett.* 365, 86-96.

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Behaviour of serpentinite halogens (F, Cl, Br & I) in subduction zones

Pagé, L. and Hattori, K.

The abundance of F, Cl, Br and I in serpentinites were examined to evaluate their behaviour in subduction zones. Samples include (1) unmetamorphosed, obducted hydrated abyssal peridotites, (2) subducted abyssal peridotites to depth of ~30 km, (3) forearc mantle serpentinites from shallow depth (<30 km) and (4) mantle wedge serpentinites from ~140 km depth in the Himalayas. Samples (1,2,3) from Dominican Republic are composed of lizardite (low temp. serpentine). The Himalayan samples consist of antigorite (high temp. phase). Abyssal peridotites contain high (avg. 340 ppm) Cl but they lose Cl during their subduction. In the mantle wedge, elevated (avg. 514 ppm) Cl in shallow serpentinites suggests transfer of Cl from subducting slab to the overlying mantle wedge. Lower Cl values (<40 ppm) in deep mantle wedge serpentinites indicate loss of Cl either by pressure increase or transition from lizardite to antigorite. The Br/Cl ratios for obducted abyssal peridotites are comparable to that of seawater, confirming their serpentinization on or near the ocean floor. Bromine appears to mimic Cl in its behaviour; abyssal peridotites partially lose Br during subduction and there is high Br content in shallow mantle wedge serpentinites. However, the degree of Br loss is less than that of Cl with increasing depth, as illustrated by the elevated Br/Cl ratio (avg. 20×10^{-3}) in the deep mantle wedge. Hydrated abyssal peridotites contain relatively high I/Cl ratios up to 240 times seawater. Our results are consistent with data from sea floor serpentinites [1]. The content of I remains relatively constant during their shallow subduction. In the mantle wedge, shallow and deep forearc serpentinites contain similar amounts of I, indicating retention of I during the lizardite to antigorite phase transition.

Fluorine shows significantly different behaviour from the other halogens. The content of F is low (avg. 13 ppm) in abyssal peridotites, as expected from low F content in seawater. Upon shallow subduction, F content increases in hydrated abyssal peridotites, likely incorporated from shallow water sediments. Similar F-enhancement is observed for shallow forearc peridotites. Fluorine is further enriched in deep mantle wedge peridotites (avg. 149 ppm) by incorporating F released from slabs and sediments.

Serpentinites likely contribute to the transfer of F and I into the deep mantle, whereas Br and Cl likely have shallow cycles in subduction zones.

[1] Kendrick *et al.* (2013) *Earth Planet Sc. Lett.* **365**, 86-96.

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Halogenes, B and Li in lawsonite blueschists

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Blueschists from the Tavsanlı zone in NW Turkey represent the northern margin of the Anatolide-Tauride Block subducted to 80 km depth during the late Cretaceous [1]. They contain Na-amphibole and lawsonite, with minor phengite, omphacitic pyroxene, and quartz. Lawsonite laths (<5 mm) are surrounded by fibrous aggregates of blue Na-amphibole, some of which is retrogressed to chlorite. Bulk rocks contain high MgO (4.7-13 wt%), FeO_{total} (8.2-11 wt%) and TiO₂ (0.46-3.1 wt%), confirming a basaltic protolith. All samples are enriched in fluid-mobile elements (Pb, Sb, Sr, Li), and most are enriched in Cs, Rb and Ba. High Na₂O (<3.1 wt%) is consistent with sea-floor alteration prior to subduction, yet bulk pyrohydrolysis data shows low Cl (8-56 ppm) and Br (0.11-0.47 ppm) relative to seawater. They contain higher I (0.12-1.37 ppm) and F (120-955 ppm) than MORB.

Sodic amphiboles are of the crossite variety with high Fe₂O₃ (<17 wt%). Phengite (3.4-3.9 Si p.f.u.) also has relatively high Fe₂O₃ (<5.3 wt%). Lawsonite contains <2.3 wt% FeO_{total} (mostly Fe²⁺), high Sr (avg. 1512 ppm), Y (avg. 70 ppm) and Ce (avg. 1090 ppm) compared to phengite and amphibole, but low Li (<0.19 ppm) and B (<5.4 ppm). Lithium preferentially partitions into Na-amphibole with K_D(Li) = 2.6-12, and B into phengite (K_D(B) = 7.2-44). Fluorine partitioning follows phengite>lawsonite>Na-amphibole, with average contents of 482, 413 and 257 ppm, respectively. On average, lawsonite contains low Cl (27 ppm) relative to phengite (56 ppm) and Na-amphibole (59 ppm). SIMS analysis of F and Cl for phengite and amphibole used amphibole calibration standards.

This study shows that hydrous minerals lose Cl, but retain F during subduction. Since Na-amphibole, lawsonite and phengite are stable to depths of ~90 km, ~280 km and >300 km, respectively [2], relatively high contents of F in lawsonite, and F and B in phengite suggest their transport by these minerals to the deep upper mantle.

[1] Sherlock et al. (1999) *Contrib. Mineral Petr.* **137**, 46-58.

[2] Schmidt & Poli (1998) *Earth Planet Sci. Lett.* **163**, 361-379.

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Halogens and other volatiles in the UHP Tso Moriri unit, NW Himalaya

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The Tso Moriri eclogitic unit in E-Ladakh, NW Himalaya represents metamorphosed mafic rocks and sediments of the northern margin of the Indian continent that were subducted to 70+ km following closure of the Neo-Tethys and subsequent collision with Asia. Trace element abundances suggest a plume-related origin of these mafic rocks. The UHP unit was exhumed together with lenses of antigorite-bearing serpentinites that represent a deep (>120 km) portion of the hydrated mantle wedge. Eclogites contain garnet, omphacite, glaucophane, phengite, rutile, quartz, zoisite, paragonite and apatite.

Chlorine (<50 ppm), Br (<0.2 ppm) and I (<0.2 ppm) contents of the metapelites are low compared to typical incoming plate sediments, whereas F (up to 960 ppm), B (up to 90 ppm) and N (up to 400 ppm) are high. The heavy halogen/Nb ratios in the metapelites are an order of magnitude lower than those of incoming plate sediments, confirming Cl, Br and I are lost from sediments during subduction. Eclogites contain high F (up to 360 ppm), along with variable Cl (10-140 ppm), low Br (<0.3 ppm) and B (<2 ppm), and elevated I (up to 0.82 ppm). F/Nb ratios of the eclogites are similar to those typical of plume-related basalts, suggesting F may be partially inherited from its protolith, in addition to input from incoming plate sediments. Sediments are also the likely source of higher I contents in the eclogites. A positive correlation between bulk rock F and K₂O suggests F in metapelites is primarily hosted in K-rich phengite, but in eclogites both phengite and apatite host F.

The halogen contents of the mantle wedge serpentinites that overlay the subducting UHP unit are similar to those of the metapelites. Ratios of heavy halogen/Nb of the serpentinites are

similar to typical incoming plate sediments, confirming hydration of the forearc mantle by fluids from dehydrating sediments during early subduction, and their high F/Cl contents suggest serpentinites are capable of transferring F into the deeper mantle.

This study supports our earlier work on lawsonite blueschists from Turkey that Cl and Br are expelled from subducting slabs at shallow depths, where as F and some I are retained even to UHP conditions.

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Halogen systematics of the subducting slab: implications for the recycling of F to the deep mantle

Pagé, L. and Hattori, K.

Subduction provides a mechanism for recycling fluid-mobile elements (FME) from surface reservoirs, including seawater and sediments, into the Earth's mantle. The high abundance of these elements, including the halogens (F, Cl, Br, I), in arc magmas attest to their recycling at convergent plate boundaries. Certain FME have also been detected in magmas originating from the deeper mantle, such as high F in kimberlites and ocean island basalts. The depth of F release from the slab is controlled by the geothermal gradient of the subduction zone and the stability of specific minerals, such as serpentine, amphibole, lawsonite, phengite and apatite. Blueschists from the Tavsanli zone, NW Turkey and eclogites from the Tso Moriri ultra-high pressure (UHP) unit in E-Ladakh, NW Himalaya represent continental margins subducted to 70+ km depth during the closure of the Neo-Tethys. Both sample sets contain bulk Cl (<100 ppm) and Br (<0.3 ppm) contents similar to unaltered MORB, whereas their I and F contents are elevated. High I and F in the slab are attributed to input from sediments on the seafloor and near subduction zones. The blueschists have slightly higher I (up to 0.5 ppm) and F (up to 600 ppm) than the eclogites (< 0.3 ppm I; < 400 ppm F), likely reflecting the dehydration of halogen-bearing amphibole during prograde metamorphism.

Broad positive correlations between bulk F and P_2O_5 and K_2O suggest apatite and phengite may control the bulk halogen concentrations in these rocks. *In situ* analyses support this interpretation with high F in apatite and phengite of the blueschists (up to 3.5 wt% and 500 ppm,

respectively) and eclogites (up to 2.3 wt% and 1600 ppm, respectively) compared with other minerals.

These results show that Cl and Br are expelled from subducting slabs at shallow depths, where as F and some I are retained. Given the stability of apatite and phengite to depths of 200 and 300 km, respectively, they may transport F beyond subarc depths and contribute to the high F in magmas derived from the deeper mantle.