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**Volatile (Li, B, F and Cl) mobility during amphibole breakdown in
subduction zones**

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Abstract

Amphiboles are ubiquitous minerals in the altered oceanic crust. During subduction, their breakdown is governed by continuous reactions up to eclogite facies conditions. Amphiboles thus contribute to slab-derived fluid throughout prograde metamorphism and continuously record information about volatile exchanges occurring between the slab and the mantle wedge. However, the fate of volatile elements and especially halogens, such as F and Cl, in amphibole during subduction is poorly constrained. We studied metagabbros from three different localities in the Western Alps: the Chenaillet ophiolite, the Queyras Schistes Lustrés and the Monviso meta-ophiolitic complexes. These samples record different metamorphic conditions, from greenschist to eclogite facies, and have interacted with different lithologies (e.g. sedimentary rocks, serpentinites) from their formation at mid-oceanic ridge, up to their devolatilization during subduction. In the oceanic crust, the initial halogen budget is mostly stored in magmatic amphibole (F = 300-7000 ppm; Cl = 20-1200 ppm) or in amphibole corona (F = 100-7000 ppm; Cl = 80-2000 ppm) and titanite (F = 200-1500 ppm; Cl < 200 ppm) formed during hydrothermal seafloor alteration. It is thus the fate of these phases that govern the halogen fluxes between the crust and the overlying mantle and/or the plate interface in subduction zones. Li and B are poorly stored in the oceanic crust (< 5 ppm). In subduction zones, prograde metamorphism of metagabbros is first marked by the crystallization of glaucophane at the expense of magmatic and amphibole coronas. This episode is accompanied with a decrease of halogen concentrations in amphiboles (< 200 ppm of F and Cl) suggesting that these elements can be transferred to the mantle wedge by fluids. In the Queyras Schistes Lustrés complex, the intense deformation and the abundant devolatilization of metasedimentary rocks produce large fluid flows that promote rock chemical hybridization (metasomatic mixing with hybrid composition between metasedimentary rock and metagabbro) at the metasedimentary rock/ metagabbro contacts. Such fluid/rock interactions result in a strong addition of Li in glaucophane (up to 600 ppm) whereas halogen concentrations are unaffected. At eclogite facies conditions, metagabbros display low halogens concentrations (< 20 ppm of F and < 100 ppm of Cl) relative to altered oceanic crust (F = 40-650 ppm; Cl = 40-1400 ppm) suggesting that these elements are continuously released by fluids during the first 30-80 km of subduction whatever the tectonic environment (e.g. slab, plate interface) and the considered fluid/rock interactions.

Keywords: amphibole, metagabbros, volatile, fluids, subduction

1. Introduction

Magmas erupted at arc volcanoes are generated by partial melting of metasomatized mantle wedge peridotites, and are enriched in H₂O and volatile elements relative to Mid-Oceanic Ridge Basalts (MORB) or Oceanic Island Basalts (e.g. Straub and Layne, 2003; Le Voyer et al., 2010; Rose-Koga et al., 2014). The distinct geochemical signatures and physical properties of arc lavas result from volatile transfer from the slab to the mantle wedge (e.g. Bouilhol et al., 2009; Dalou et al., 2012; Kendrick et al., 2012). Quantitative assessments of these chemical fluxes require knowledge about the pressure and temperature conditions at which slab-derived fluids are released and transferred to the mantle wedge and the volatile composition evolution of the slab during prograde metamorphism. Slab dehydration occurs between 40 and 200 km (e.g. Magni et al., 2014; Schmidt and Poli, 2014) and is related to the stability of hydrous phases such as serpentine (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997), chlorite (Grove et al., 2006, 2009), amphiboles, lawsonite, and/or mica (Pawley and Holloway, 1993; Poli and Schmidt, 1995). The evolution of volatile abundance, during the breakdown of hydrous phases in the slab, is critical to establish the mass balance of the fluxes between the slab, the surface and the deep mantle. However, it remains a significant challenge because multiple metamorphic reactions or fluid/rock interactions occur during subduction.

The composition of primitive arc magmas, recorded in olivine-hosted melt inclusions, is enriched in halogens, such as F and Cl, relative to MORB demonstrating that these elements are mobile in slab derived fluids (e.g. Straub and Layne, 2003; Le Voyer et al., 2010; Rose-Koga et al., 2014). Unlike many fluid mobile elements, such as B or Li (e.g. Zack et al., 2003; Scambelluri et al., 2004a,b; Bebout et al., 2007, 2013; Marschall et al., 2007, 2009; Vils et al., 2010; Penniston-Dorlan et al., 2010; 2012; Scambelluri and Tonarini, 2012), the behavior of halogens during subduction is poorly constrained (see Kendrick et al., 2012). Halogens are present in OH sites within hydrous minerals, such as sheet silicates or amphibole (e.g. Volfinger et al., 1985; Oberti et al., 1993; Anselmi et al., 2000). Those minerals, which are generally formed after seawater-lithosphere interactions at mid-oceanic ridges, can contain significant concentrations of halogens (up to several thousand of ppm; Ito et al., 1983; Vanko 1986; Coogan et al., 2001; Barnes and Sharp, 2006). During prograde metamorphism, the devolatilization of serpentinites and metagabbros is accompanied with a decrease in halogen concentration suggesting that this process can trigger the transfer of a significant amount of halogens in fluids to the mantle wedge (Phillippot et al., 1998; Bonifacie et al., 2008; John et al., 2011; Kendrick et al., 2011). On the other hand, Cl seems to be retained in metasedimentary rocks during subduction (Selverstone and Sharp, 2015). At depth, the devolatilization of slab serpentinites is believed to be a significant source of water and fluid mobile

elements for arc magmas (e.g. Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997; Scambelluri et al., 2004a; Kendrick et al., 2011; Sambelluri and Tonarini, 2012). However, mass balance calculation suggests that this process, alone, cannot explain the observed halogen anomalies of arc magmatism, notably F concentrations. As such additional components in the subducted oceanic lithosphere must act as significant halogen reservoirs during subduction (Debret et al., 2014).

Amphibole is a common component in the altered oceanic crust and its crystal structure can incorporate a wide range of lithophile and volatile elements (e.g. Volfinger et al., 1985; Messiga et al., 1995; Coogan et al., 2001; Gillis et al., 2003). In oceanic settings, amphibole-bearing metagabbros are formed by crystallization of silicate melt at temperature greater than 850°C, and by continuous metamorphic reactions during lithosphere cooling and hydration between 850 to 300 °C (Gilbert et al., 1982; Vanko, 1986; Messiga and Tribuzio, 1991; Spear, 1993; Tribuzio et al., 1995; Coogan et al., 2001; Debret et al., 2013a). During subduction, amphibole breakdown in the slab is governed by continuous reactions occurring below 3 GPa (Poli and Schmidt, 1995) that release a significant amount of water (up to 2 wt%), mostly to the forearc region. It is clear that the breakdown of amphibole during subduction prograde metamorphism could be responsible for delivering a large flux of slab-derived fluid to the overlying mantle wedge. This mineral thus plays a significant role during element fractionation between the fluid and residual slab, and records continuous information about volatile transfer from slab to mantle wedge. However, while there are an increasing number of *in situ* studies focusing on the fate of volatile elements in the hydrous phases composing the subducted lithosphere (e.g. Scambelluri et al., 2004a; Bebout et al., 2007, 2013, Vils et al., 2010; Lafay et al., 2013; Debret et al., 2013b, 2014; Vitale Brovarone et al., 2014), most of them have examined micas, serpentines and/or lawsonites and the potential volatile, especially halogens, losses from amphiboles during subduction remain poorly constrained.

This study aims to determine the volatile (F, Cl, Li and B) fluxes between the different lithologies composing the slab and the mantle wedge. The approach taken is an *in situ* (Secondary ion mass spectrometry and microprobe analyses) and detailed study of amphiboles major and volatile element composition in metagabbros from a suite of Western Alps meta-ophiolites. The micro analytical methods employed here aim to separate oceanic, prograde and retrograde metamorphic evolution of amphiboles and thus better decipher the mobility of volatile elements during metamorphism than bulk rock studies. Metagabbros from 6 different Western Alps meta-ophiolites, which metamorphic conditions span from greenschist to eclogite facies, were selected for a detailed petro-geochemical study. These samples have interacted with different lithologies (e.g. sedimentary rocks, serpentinites) during subduction leading to the released of halogens (F and Cl) to fluids.

2. Geological setting and petrographic observations

Western Alps meta-ophiolites represent hectometric to kilometeric size mafic and ultramafic bodies formed at magma poor settings, and are related to the opening of the Ligurian Ocean in the middle Jurassic (Lagabrielle and Cannat, 1990; Müntener et al., 2010). These meta-ophiolites represent the first few kilometers of the Ligurian oceanic lithosphere, which structure is similar to the lithosphere generated at slow- or ultra-slow spreading ridges (Tricart and Lemoine, 1986; Bernoulli et al., 2003; Manatschall et al., 2011; Lagabrielle et al., 2014). This study focuses on the Piemont zone of the south-western Alps (Figs 1a and b) where ophiolitic units were metamorphosed and juxtaposed during alpine subduction and collision in Late Cretaceous to Tertiary (e.g. Tricart, 1984). We sampled metagabbros from 6 meta-ophiolites on a transect of ~20 km through the Queyras Schistes Lustrés complex, from the Montgenevre to the Monviso (Fig. 1b).

The studied meta-ophiolites belong to two different domains. (i) The Queyras Schistes Lustrés complex consists of 10% of meta-ophiolites and 90% of metasedimentary rocks and is interpreted as a paleo-sedimentary wedge (Tricart and Schwartz, 2006). The Queyras meta-ophiolites form metric to kilometeric bodies embedded in dominant Jurassic to Lower Cretaceous clastic metasedimentary rocks (Lagabrielle et al., 1984, Lemoine et al., 1987). They have experienced strong interactions between mafic lithologies and sediment derived fluid during subduction (Lafay et al., 2013). In this complex, three tectono-metamorphic units record variable P-T conditions (Fig. 1b, c), increasing from low-temperature blueschist facies conditions (LT-blueschist; 320-360°C and 9-11 kbar) in western Queyras to medium-temperature (MT-blueschist; 340-390°C and 10-12 kbar) and high-temperature blueschist (HT-blueschist; 380-470°C and 12-18 kbar) conditions toward to the East (Balleve et al., 1990; Agard et al., 2001; Tricart and Schwartz, 2006; Schwartz et al., 2013; Lagabrielle et al., 2014). (ii) The Monviso meta-ophiolite corresponds to a remnant of the oceanic lithosphere preserving multiple slices of the oceanic crust embedded in serpentinites and re-equilibrated at eclogitic facies P-T conditions (Schwartz et al., 2001; Angiboust et al., 2011). Unlike the Queyras meta-ophiolites, the massif evolved during subduction without interacting with external fluids (Lafay et al., 2013).

For reference, we also studied the Chenaillet massif. This massif is considered to be representative of the pre-subduction alpine oceanic lithosphere since it has been poorly affected by alpine subduction/collision and related metamorphism (e.g. Mével et al., 1978; Caby, 1995; Schwartz et al., 2013; Manatschall et al., 2011; Lafay et al., 2013; Lagabrielle et al., 2014). The massif is interpreted as an obducted portion of the Tethyan oceanic lithosphere (e.g. Caby, 1995). It preserves a complete section of the oceanic lithosphere composed of serpentinite intruded by metagabbros and topped by basalts and rare sediments (Manatschall et al., 2011). The

massif mostly records an oceanic metamorphism, ranging from granulite to greenschist facies conditions, during lithosphere cooling and hydration (Mével et al., 1978).

2.1 *The Chenaillet Ophiolite*

The Chenaillet ophiolite (Fig. 1b) is a thin tectonic nappe resting upon the Queyras Schistes Lustrés complex. The massif preserves pre-Alpine structure and basement-cover relationship between serpentinized mantle, metagabbros, sediments and metabasalts. The metagabbroic pods are less than 1 km in diameter and show coarse-grained textures. Locally, they show porphyroclast stretching and foliation (Fig. 2a) characterizing a post-magmatic deformation during cooling (e.g. Debret et al., 2013a). They are composed of clinopyroxene, plagioclase, ilmenite, Ti-magnetite, low pressure-amphiboles (LP amphiboles), titanite, chlorite, albite and epidote.

Based on petrographic observations, three different generations of amphiboles can be distinguished in Chenaillet metagabbros. These amphiboles will be referred as (1) amphibole porphyroclasts, (2) amphibole coronas and (3) actinolites in the rest of the paper (Fig. 2b, c). (1) Amphibole porphyroclasts correspond to melt derived brown amphiboles crystals of 0.5 mm to 1 cm width displaying planar grain boundaries (Fig. 2b, c). (2) Amphibole coronas are formed during the cooling and hydration of the lithosphere on the seafloor. They partly to fully replace magmatic clinopyroxene or amphibole porphyroclasts and display an optical zoning from brownish-green to green toward to porphyroclast rims (Fig. 2b, c). Amphibole coronas contain titanite inclusions of ~ 20 μm width. (3) Actinolites are concentrated in the plagioclase domain or at the rims of amphibole or clinopyroxene porphyroclasts. They are associated with small grains of chlorite, albite and/or epidote needles of < 50 μm width (Fig. 2b, c). The formation of these assemblages can be related to late seafloor or obduction/exhumation metamorphism. Some ilmenites crystallize as irregular interstitial grains of 200-500 μm width within plagioclase and clinopyroxene domains. They are surrounded by a titanite corona of ~ 100 μm width. Rare magmatic olivines are replaced by tremolite and chlorite aggregates.

2.2 *The Queyras Schistes Lustrés complex*

The Queyras Schistes Lustrés complex (Fig. 1b) is composed of metamorphosed Mesozoic oceanic sediments, which have been strongly deformed during alpine subduction. The complex includes boudinaged units of serpentinites, metagabbros and metabasalts from meter to kilometer size that can be associated with their original sedimentary cover (Lagabrielle and Polino, 1988; Tricart and Lemoine, 1986). The Queyras metagabbros record various blueschist facies P-T conditions (Fig 1b, c). They are mainly composed of

magmatic clinopyroxene relics, LP-amphibole, ilmenite, titanite, glaucophane, lawsonite, chlorite, +/- albite, +/- epidote and +/- quartz. In these rocks, textural relationships show that glaucophane and lawsonite (+/- epidote, quartz) replaced LP amphiboles and the plagioclase domain.

The Chabrière meta-ophiolite (Fig. 1a) is a hectometric massif embedded within metasedimentary rocks, and composed of pillow lavas, metadiorites, metagabbros and serpentinites. The metagabbros show coarse-grained textures and locally display a magmatic deformation characterized by porphyroclast stretching and a foliation. They record LT-blueschist facies P-T conditions (300-350°C, 8-11 kbar; Fig. 1c). Within these rocks the oceanic LP-assemblages are well preserved. They are composed of clinopyroxene, amphibole porphyroclast, amphibole corona, actinolite and interstitial ilmenite surrounded by titanite corona (Fig. 3a). At the contact of the plagioclase domain, LP-amphiboles are partly recrystallized into glaucophane forming coronas of ~ 300 µm width (Fig. 3a). The plagioclase domain is fully recrystallized into elongated crystals of lawsonite up to ~ 50 µm long and interstitial albite (Fig. 3a).

The Clausis meta-ophiolite (Fig. 1b) is a hectometric body composed of metagabbroic and serpentinite boudins recording M-T blueschist facies conditions (340-390°C, 10-12 kbar; Fig. 1c). The contact between metasedimentary rocks and metagabbros is marked by quartzite veins composed of coarse quartz, glaucophane and small titanite grains. In these metasomatic zones, the glaucophane displays idiomorphic textures suggesting that it is in equilibrium with quartz. In the metagabbros, the clinopyroxene and the LP-amphiboles are poorly preserved. Glaucophane coronas of 100-300 µm width replace the amphibole coronas and contain titanite inclusions of 50 µm width, whereas glaucophanes crystallizing in plagioclase domain are titanite free (Fig. 3b). The plagioclase domain is finely recrystallized into lawsonite, +/- phengite, zoisite and quartz crystals of less than 50 µm width. Retrograde epidote and albite have been observed at the contact between lawsonite and glaucophane (Fig. 3b). As previously observed, interstitial ilmenites are surrounded by titanite coronas.

The Echassier meta-ophiolite is located to the East of the Clausis meta-ophiolite. Both massifs record similar P-T conditions (Schwartz et al., 2013). The Echassier meta-ophiolite is composed of hectometric serpentinite and metagabbroic pods and rare metabasalts embedded within metasedimentary rocks. Metagabbros display coarse-grained texture and similar metamorphic assemblages to that of Clausis metagabbros. The contact between metagabbros and metasedimentary rocks is characterized by metasomatic zones composed of interstitial calcite and chlorite and randomly orientated tremolite and diopside needles of 50 µm long. At the contact of these zones, we have sampled a metabasalt which has been finely recrystallized into idiomorphic glaucophane and chlorite of 100 µm width with interstitial calcite and small aggregates of titanite (Fig. 3 c-d).

The Tour Real meta-ophiolite is located to the East of the study area and is metamorphosed at HT-blueschist facies conditions during subduction (380-470°C, 12-18 kbar; Figs 1b, c). It represents a kilometric segment of oceanic lithosphere and is characterized by metagabbroic pods embedded in serpentinites. The contact between metagabbros and serpentinites is composed of fibrous serpentine associated with titanite and chlorite. We sampled glaucophane bearing shear zone crossing metagabbros (Fig. 3e). These rocks are characterized by the absence of LP amphiboles. They are composed of clinopyroxene porphyroclasts of ~ 200 µm width surrounded by glaucophane coronas of 200 µm width (Fig. 3f). The plagioclase domain is fully recrystallized into lawsonite, epidote, magnetite and chlorite. The preferential crystallization of hydrous phases in these shear zones, relative to the host rock, suggests that these zones localized fluid circulation during subduction.

2.3 The Monviso meta-ophiolite

The Monviso meta-ophiolite is located in the extreme east of the study area (Fig. 1b) and is separated from the Queyras Schist Lustres complex by a ductile normal fault (Ballèvre et al., 1990). This meta-ophiolite extends over 30 km and is composed of hectometric lenses of metabasites embedded within highly deformed serpentinites with rare metasedimentary rocks (Lombardo et al., 1978; Schwartz et al., 2001; Angiboust et al., 2011). The massif records various eclogite facies metamorphic conditions with a maximum P-T estimated at 550-620°C and 1.9-2.6 GPa (Schwartz et al., 2001; Angiboust et al., 2011). The massif consists primarily of metagabbros and serpentinites with few metasedimentary rocks (< 10%) relative to the Queyras Schiste Lustres complex. The metagabbros display heterogeneous deformation, which is characterized by porphyroclast stretching and the formation of bandings. Relative to blueschist facies metagabbros from the Queyras, the eclogitic metagabbros of the Monviso meta-ophiolite are characterized by a low abundance of glaucophane (less than 10%), the absence of titanite and lawsonite, and the crystallization of idiomorphic garnet, omphacite, quartz, small rutile grains of ~ 20 µm in width, and ^{+/} phengite and zoisite (Fig. 4).

3. Methods

3.1 Sample preparation

Standard thin sections of 30 µm thickness were prepared from hand samples. After detailed petrographic description, areas of approximately 2 by 2 mm size were selected and cut out of the thin sections. These areas contain mineral assemblages that are representative of the main stages of metagabbro recrystallization during prograde metamorphism. Typically, ten to twelve pieces were placed on a single mount filled with indium. This technique minimizes the number of sample changes during analyses and contributes to better analytical stability.

Laboratory synthesized glasses, doped with in F and Cl, were also inserted into every mount and used to monitor for machine drift. Gold coating was used for IMS 1270 SIMS analyses, and carbon coating for IMS 7f and electron microprobe analysis. In order to avoid multiphase analyses, optical microscope and SEM images were used to identify minerals in the thin section and to select spots for SIMS analyses. After to the SIMS analyses, we performed microprobe analyses to ensure correct mineral phase was analysed.

3.2 *Electron microprobe*

Major element analyses of metagabbroic minerals have been performed with a Cameca SX100 at the Laboratoire Magmas et Volcans (Clermont-Ferrand, France). The primary acceleration voltage was 15 kV, and a 15 nA beam current was used for all mineral analyses. Amphiboles with high F and Cl concentrations were also measured by electron microprobe. To avoid Fe peak interference on the light element detector, three thallium acid phthalate crystals were used to simultaneously measure F for a 300 s total counting time. A pentaerythritol crystal was used for Cl measurements for 100 s counting time. The machine was calibrated with a CaF₂ and a scapolite. KE12 glass was used as an external standard. The detection limits of this procedure are about 350 and 60 ppm for F and Cl, respectively.

3.3 *Secondary ion mass spectrometer*

A Cameca IMS 1270 at CRPG (Nancy, France) was used to determine the concentrations of F and Cl. Measurements were conducted with a ~10µm beam size for all analyses, using a Cs⁺ primary beam with primary and secondary accelerating voltage of 10kV, and no energy offset was applied. ¹⁹F, ³⁵Cl, ³¹P and ³²S measurements were obtained with an electron multiplier. Backgrounds were measured at mass 17.5. A high mass-resolution (MRP=3000 minimum) was set to separate major molecular interferences. ²⁸Si, ¹⁸O and 17.5 measurements were obtained with a Faraday cup. Each analysis consists of 10 cycles. 17.5, ¹⁸O, ¹⁹F, ²⁸Si, ³¹P, ³²S, and ³⁵Cl were counted for 4 seconds each, with 1 or 2 seconds waiting time. The intensity measured at masses ¹⁹F, ³⁵Cl and ³²S were normalized to ¹⁸O. Signals of P and S were often weak and erratic; we did not report these data in this study. The F and Cl contents were determined by measuring international glass standards and laboratory standards (ML3B, ATHO, T1g, Alv2390, and KE12; Appendix A for calibration and see Van den Bleeken and Koga, in press, for long term reproducibility and matrix issues). As reported in Debret et al (2014), we found that ¹⁸O referenced calibration curves provide coherent and reproducible fits among mixed standard samples instead of Si. Our compilation of standard analyses indicates that O signal variability was about 20% less than that of Si normalization.

A Cameca IMS 7f at Institut Jean Lamour (Nancy, France) was used for concentration measurements of Li and B. A primary beam of O_2^- was accelerated to 10 kV, no energy filtering was used, and a 40 eV width energy window was centered around 0 offset. The size of primary beam was approximately 30 μm . The intensity was measured at masses ^6Li , ^{11}B , and ^{28}Si , for 1, 5 and 1 second counting time, respectively. An electron multiplier was used for ^6Li and ^{11}B , and a faraday cup was used for ^{28}Si . Each analysis consists of 20 cycles. Linear concentration calibration curves were established using NIST standards (NBS 610, 612, 614, and 616, see Appendix B for calibration).

4. Mineral chemistry

A set of 16 metagabbros were selected as they were considered representative of metamorphic mineral reactions occurring during crust cooling and hydration in oceanic setting and prograde subduction zone metamorphism (Table 1). Major element compositions of minerals are reported in Table C1, volatile (F, Cl, Li and B) abundances are listed in Table 2.

4.1 Oceanic assemblages of Chenaillet metagabbros

To constrain the behavior of volatiles during oceanic crust cooling and hydration, 4 samples from the Chenaillet ophiolite preserving LP-parageneses have been analyzed (Table 1). The magmatic paragenesis is composed of clinopyroxene, plagioclase, ilmenite and amphibole. The magmatic clinopyroxenes are diopside in composition and are characterized by X_{Mg} ($= \text{Mg}/[\text{Mg} + \text{Fe}]$ in mol fraction) ranging from 0.76 to 0.83 and CaO and Al_2O_3 contents varying from 21.3 to 24.6 wt% and 0.35 to 3.1 wt%, respectively. Magmatic amphibole porphyroclasts display an edenite composition characterized by TiO_2 and Al_2O_3 contents ranging from 2.5 to 4 wt% and from 7 to 11 wt% respectively. Amphibole coronas display lower TiO_2 ($= 0.2\text{-}2.1$ wt%) and highly variable Al_2O_3 ($= 2\text{-}13$ wt%) contents relative to amphibole porphyroclasts (Fig. 5). Their compositions vary from Mg- or Fe-hornblende to edenite. Amphibole coronas commonly present a TiO_2 zoning decreasing toward crystal rims. Titanite inclusions in amphibole coronas or surrounding interstitial ilmenite (Fig. 2b) show TiO_2 and Al_2O_3 contents ranging from 34.7 to 43.6 wt% and from 0.2 to 2.9 wt% respectively. Actinolites are associated with Fe-chlorite and epidote. They are characterized by low TiO_2 (< 1 wt%) and Al_2O_3 (< 3 wt%) contents relative to amphibole coronas (Fig. 5).

Magmatic clinopyroxenes and ilmenites display low halogens concentrations (F = 2–5 ppm, Cl = 17–68 ppm) relative to amphibole porphyroclasts (F = 1225–2011 ppm, Cl = 28–280 ppm) in Chenaillet metagabbros. This

observation is in good agreement with previous studies on Mid-Atlantic Ridge (MAR) metagabbros where magmatic amphibole F and Cl concentrations range from 1000 to 4200 ppm and from 20 to 130 ppm, respectively (Cortesogno et al., 2000; Coogan et al., 2001). Among magmatic minerals, no variations in B or Li concentrations have been observed. The B and Li concentrations of magmatic minerals range from 0.5 to 5 ppm and 0.2 to 2 ppm, respectively. The recrystallization of amphibole porphyroclasts to amphibole corona is accompanied with a decrease of F (90-1970 ppm) and an increase of Cl (80-2060 ppm) and B (0.6-34 ppm) concentrations (Figs 6a-c). In contrast, Li (0.4-6 ppm) concentrations remain constant during the recrystallization of amphibole porphyroclasts into amphibole coronas (Fig. 6d). The actinolite-chlorite-epidote assemblages display low F (5-260 ppm) and Cl (17-652 ppm), concentrations relative to amphibole coronas and similar B (1-6 ppm) and Li (0.3-15 ppm) concentrations (Figs 6a-d). Coronitic titanite surrounding ilmenite displays higher F (933-1534 ppm) and Cl (76-97 ppm) concentrations relative to that of ilmenite.

4.2 Prograde metamorphism in the Queyras and Monviso metagabbros

To constrain the behavior of volatiles during subduction, 8 metagabbros from the Queyras Schistes Lustrés complex (Chabrière, Clausis, Tour Real) and 2 eclogites from the Monviso meta-ophiolite have been analyzed (Table 1). In addition, 2 metasomatic zones in the Echassier and Clausis meta-ophiolites were analyzed to decipher the behavior of volatile during metasedimentary rock/metagabbro interactions.

Queyras metagabbros can preserve relicts of oceanic metamorphism in low metamorphic grade meta-ophiolites (Chabrière and Clausis, Fig. 3a,b). The major element concentrations of oceanic assemblages are similar to that described in Chenaillet metagabbros. Only amphibole porphyroclasts have a wider range of composition ranging from edenite ($\text{TiO}_2 = 2.8\text{-}5 \text{ wt\%}$; $\text{Al}_2\text{O}_3 = 7\text{-}10 \text{ wt\%}$) to kaersutite ($\text{TiO}_2 > 5 \text{ wt\%}$; $\text{Al}_2\text{O}_3 = 9.7 \text{ wt\%}$). Kaersutites have been observed in one sample (metadiorite - QE32) and are associated with igneous apatites which act as a sink for halogens during magmatic differentiation (Nash, 1976). These amphiboles have abnormally low F (= 281-381 ppm) and high Cl (35-1224 ppm) concentrations relative to other magmatic amphibole from alpine or MAR metagabbros (Figs 6e,f). Other magmatic phases in Queyras metagabbros (ilmenite, clinopyroxene and edenite) are characterized by higher F and Li concentrations relative to the one of Chenaillet metagabbros (Table 2, Fig. 6). However, as previously observed, the recrystallizations of amphibole porphyroclasts (F ~ 7120 ppm; Cl ~ 210 ppm) into amphibole coronas result in a decrease of F (210-7740 ppm) and an increase of Cl (= 155-2090 ppm) concentrations (Figs 6e,f) whereas no significant changes of B (3-10 ppm) and Li (0.1-36 ppm) concentrations are observed (Figs 6g,h).

The Queyras metagabbros display the progressive recrystallization of oceanic parageneses into blueschist facies assemblages and are composed of glaucophane, lawsonite, albite and epidote (+/ actinolite). Glaucophanes display a homogenous major element composition in the different studied ophiolites. They are characterized by low TiO_2 (< 0.3 wt%) contents relative to LP-amphiboles (Fig. 5) and variables Al_2O_3 contents (3.9-12.3 wt%). Glaucophane has lower F and Cl, and higher Li concentrations relative to LP-amphiboles (Fig. 7). Their volatile concentrations range from 17 to 125 ppm for F, from 17 to 360 ppm for Cl, from 6 to 184 ppm for Li and from 1 to 18 ppm for B. Among the different studied meta-ophiolites, glaucophanes in shear zones (Tour Real) are characterized by the lowest F concentrations (Fig. 7a). Lawsonite and epidote has low F (5-51 ppm), Li (0.4-23 ppm) and similar Cl (21-114 ppm), B (3-13 ppm) to that of glaucophane (Table 2). In the metasomatic zones, glaucophane and titanite are characterized by high Li concentrations ranging from 180 to 620 ppm (Fig. 7c, Table 2).

The eclogitic paragenesis of Monviso metagabbros is composed of glaucophane, garnet, omphacite, quartz and rutile. Glaucophane from the Monviso meta-ophiolite displays low TiO_2 contents (< 0.2 wt%) and a wide range of Al_2O_3 contents (= 7.8-11.3 wt%) overlapping the compositions of glaucophane from blueschist terrains (Fig. 5). Garnets display a mixed composition between almandine and grossular end-members with low pyrope content (Table C1). Glaucophane from Monviso meta-ophiolite is characterized by higher F and similar Cl, Li and B concentrations relative to glaucophane from blueschist terrains (Fig. 7). Their volatile concentrations range from 91 to 214 ppm for F, from 25 to 146 ppm for Cl, from 14 to 115 ppm for Li and from 1 to 5 ppm for B. Omphacite has low F (6-22 ppm) and similar Cl (21-200 ppm), Li (20-71 ppm) and B (1-4 ppm) concentrations relative to glaucophane. Garnet (F = 4-19 ppm; Cl = 9-64 ppm; Li = 0.6-1.3 ppm; B = 0.5-1.1 ppm) and rutile (F = 9-16 ppm; Cl = 6-12 ppm) has low volatile concentrations relative to other eclogitic minerals.

5. Discussion

During oceanic and subduction metamorphism, the different phase transitions of amphiboles are accompanied with variations in F, Cl, Li and B concentrations (Figs 6 and 7) suggesting that these elements are mobile in fluids on a large scale. In order to better constrain the fate of F, Cl, Li and B, we adapted a method combining the in situ F, Cl, Li and B measurements of the minerals with their respective estimated modal proportions to calculate the bulk volatile composition (Appendix C, Table C3 and Fig. 8). This reconstitution of bulk composition by mineral paragenesis was expected to track the evolution of bulk budget of F, Cl, Li and B in

metagabbros from their crystallization and hydration at the ridge to their devolatilization in subduction zones and thus to give insight into gains or losses during fluid/rock interactions. Indeed, the fate of volatile elements in metagabbros during subduction is difficult to evaluate with direct bulk rock measurements since prograde metamorphism leads to the progressive, but incomplete, recrystallization of LP-paragenesis into HP-paragenesis (Fig. 3). Furthermore, these rocks can also partly record a late metamorphism during massif exhumation (Fig. 3b). Bulk rock measurements of volatile elements integrate all these metamorphic processes and are thus not representative of different recrystallization stages of metagabbro during subduction. It is important to note that few studied metagabbros contain igneous apatites (Table 1) which can incorporate high halogens concentrations (up to several wt%, e.g. Nash, 1976). However, this mineral is poorly affected by prograde metamorphism in metagabbros. Indeed, experimental studies have shown that this mineral is stable up to 7.5 GPa and 950°C in a typical eclogite assemblage (Konzett and Frost, 2009). Furthermore, it should be noted that apatite abundance in an altered oceanic gabbros is about 0.1 wt% (based on $P_2O_5 = 0.04$ wt%, Hart et al 1999), which is low relative to amphibole abundance in these rocks (> 10 wt%). Therefore apatite breakdown does not greatly affect halogen transfers between the slab and the source of arc magmas in subduction zones and have not been considered in the bulk composition reconstitution.

5.1 The oceanic crust before its subduction

To characterize fluid and chemical exchanges in subduction zones, it is crucial to determine the composition of the material that enters in the subduction zone. The Ligurian oceanic lithosphere is characterized by a heterogeneous crust (metabasalts and metagabbros) associated with serpentinites and metasedimentary rocks of various origin (Tricart and Lemoine, 1986; Bernouilli et al., 2003; Manatschal et al., 2011; Lagabrielle et al., 2014). The volatile concentrations of these three different reservoirs are summarized in Table 3. Relative to other lithologies, metagabbros can integrate a significant amount of halogens and thus play an important role in these elements cycle in subduction zones. At the opposite, metagabbros B and Li concentrations are low compared to other lithologies (Table 3).

During oceanic spreading, the igneous crust is continuously modified by the percolation of fluids. This process leads to the crystallization of several generations of amphiboles (amphibole porphyroclasts, amphibole coronas and actinolites), of which the pressure and temperature of crystallization can be assess by the Ca-amphibole thermobarometer of Ernst and Liu (1998). The Ernst and Liu (1998) thermometer is based on the TiO_2 content of amphiboles and requires an excess of Ti in the system, such conditions are met when Ti is present as an oxide

(ilmenite, rutile) or in titanite. The accuracy of the thermometer has been estimated at the Institut für Mineralogie (Hannover, Germany) using published and unpublished experimental data, and temperature estimates are accurate to $\pm 40^\circ\text{C}$ (J. Koepke, pers. comm.). The equilibration temperature of Ca-amphiboles progressively decreases from amphibole porphyroclasts to amphibole coronas. The amphibole porphyroclasts display near solidus magmatic temperature ranging from 1000°C to 880°C whereas temperature equilibration of amphibole coronas ranges from 830°C in light brown amphiboles to 520°C in green amphiboles. Amphibole porphyroclasts record pressures less than 0.5 GPa, which is in agreement with the emplacement of the gabbros at LP in the oceanic lithosphere. Ernst and Liu (1998) predict a decrease of Al_2O_3 contents in amphiboles during the isobaric cooling of metagabbros. However, amphibole coronas display a wide range of Al_2O_3 contents that correspond to unrealistic pressure equilibrations ranging from negative values to 1.7 GPa. Indeed, amphibole coronas can exsolve TiO_2 as titanite (Fig. 2b), whereas there is no evidence of Al_2O_3 redistribution during oceanic lithosphere cooling explaining these unrealistic pressure estimates (Ernst and Liu, 1998; Debret et al., 2013a). The actinolite-chlorite-epidote paragenesis is typical from low temperature greenschist facies conditions (e.g. Spear, 1991). It represents the last stages of metamorphism recorded by ophiolitic metagabbros before subduction and/or during massif exhumation/obduction.

LP-amphiboles and titanites have the highest F and/or Cl concentrations of all the mineral phases in metagabbros and are significant carrier of halogens in these rocks (Fig. 8). Ultimately it is the fate of these phases that control the F-Cl budget of the crust during its cooling and hydration in oceanic setting. Amphibole porphyroclasts display higher F and similar Cl concentrations relative to other magmatic phases (Fig. 9a). The calculated bulk rock composition shows that amphibole porphyroclasts crystallization could be accompanied with an increase of F concentrations (300-650 ppm) relative to MORB composition (11-100 ppm). Such high F concentrations can be explained by the addition of F during melt crystallization (e.g. assimilation of previously hydrothermally altered crust; France et al., 2013) and/or by the release of a F-depleted component during fractional crystallization (Coogan et al., 2001). Amphibole coronas display a wide range of F concentrations overlapping that of amphibole porphyroclasts (Fig. 6a-e and 8a). However, in the same rock, F concentrations systematically decrease by a factor of 2 to 10 during amphibole porphyroclasts recrystallization into amphibole corona (see samples Ch 3.3, 3.5, 5.1, 5.2, and 5.4; Ch 3.1 is an exception, Table 2). This apparent decrease of F abundance during lithosphere cooling can be explained by (i) a redistribution of F between F-rich titanite and amphibole coronas during amphibole porphyroclasts recrystallization or (ii) a leaching of F by fluids. The calculated bulk rock composition ranges from 200 to 500 ppm, which is similar to previous estimates (300 to

650 ppm, Fig. 8), suggesting that F leaching in metagabbros during seafloor metamorphism is minimal. Chlorine concentrations in amphibole coronas are systematically higher than those of magmatic phases. Furthermore, bulk rock reconstitution show that the crystallization of amphibole coronas is accompanied with an increase of metagabbros Cl concentrations (Fig. 8). Given high Cl concentration in seawater, the high concentration of amphibole coronas are usually interpreted as resulting of seawater/rock interaction during lithosphere cooling and hydration (e.g. Vanko, 1986; Coogan et al., 2001). Actinolite, epidote and chlorite greenschist paragenesis has low F and Cl concentrations relative to amphibole porphyroclasts or amphibole corona (Fig. 9a).

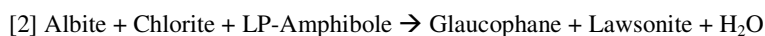
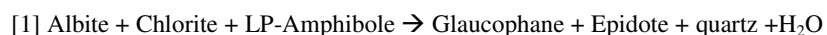
Li and B concentrations of calculated bulk rocks are relatively constant throughout oceanic crust cooling and hydration. The Li concentrations of amphibole coronas overlap that of magmatic minerals or MORB (Fig. 9b) suggesting that Li is immobile during HT oceanic metamorphism. The Li concentrations of amphibole coronas are thus assumed to be inherited from magmatic minerals (clinopyroxene, plagioclase or amphibole porphyroclasts). In the Chenaillet massif, few analyses of epidote and chlorite display higher Li concentrations relative to amphibole porphyroclasts or amphibole coronas (Table 2, Fig. 9b). However, we did not detect significant Li addition in the bulk calculation. Such enrichments can thus be interpreted as localized late fluid circulations occurring in an open system during massif oceanization, subduction or obduction (see discussion below). The B concentrations of metamorphic minerals formed during oceanic lithosphere hydration are commonly attributed to seafloor derived fluids (Coogan et al., 2001; Gillis et al., 2003; Vils et al., 2008). Nevertheless, the studied metagabbros shows little evidence of a B concentration increase during hydrothermal alteration since amphibole coronas, titanite, actinolite, epidote or chlorite display roughly similar B concentrations relative to magmatic minerals (Fig. 9b) and there is no correlation between B and Cl abundance in amphibole.

5.2 Fate of volatile elements in the slab during amphibole breakdown

Amphibole porphyroclasts, amphibole coronas and titanites have the highest F and Cl concentrations relative to others magmatic or metamorphic phases composing oceanic metagabbros (Fig. 9a). The breakdown of these phases is thus critical to constrain halogens fluxes between the slab and the mantle wedge in subduction zones. In the following discussion, the Queyras Schistes Lustrés complex, a metasedimentary-rich environment interpreted as a paleo-sedimentary wedge (Tricart and Schwartz, 2006), and the Monviso meta-ophiolite, a remnant of the oceanic lithosphere preserving a large portions of the oceanic crust (Angiboust et al., 2011), are discussed separately since in both settings the nature of fluid/rock interaction are different (Lafay et al., 2013).

5.3 Metasedimentary rock/Metagabbros fluid interactions in the Queyras ophiolites

In the Queyras metagabbros, titanite inclusions remain unaffected during amphibole coronas recrystallization into glaucophane (Fig. 3b) suggesting that this mineral is stable at these P-T conditions. The recrystallization of oceanic assemblages at blueschist facies P-T conditions can thus be summarized in a relatively closed system by the following general and unbalanced reactions:



A second possibility to consider is the effect of fluid infiltration/percolation during recrystallization at blueschist facies (e.g. Balleve et al., 2003). The interaction between external fluids and the surrounding lithologies at high pressure results in significant enrichment in fluid mobile elements (Marschall et al., 2009; Penniston-Dorlan et al., 2012; Lafay et al., 2013; Vitale-Brovarone et al., 2014).

The Queyras Schistes Lustrés complex is considered as an open system where fluids released during sediment dehydration has infiltrated the surrounding rocks during subduction (Schwartz et al., 2013; Lafay et al., 2013). Metasomatic contacts between metagabbros and metasedimentary rocks (Fig. 3c) or glaucophane bearing shear zones in metagabbros embedded in serpentinites (Fig. 3e) provide evidence of fluid/rock interaction between these different lithologies during subduction. The calculated bulk rock compositions of Queyras metagabbros show that these rocks display high Li concentrations relative to oceanic metagabbros. Such increase of Li in alpine metamorphic rocks has been reported previously and interpreted as retrograde metamorphic processes (Zack et al. 2003; Marschall et al., 2007; 2009) due to a stronger affinity of Li to silicate mineral over aqueous fluids at temperature lower than 250°C (Berger et al., 1988; Marschall et al., 2007). However, in the studied metagabbros, glaucophane is the main carrier of Li in blueschist metagabbros (Fig. 9). This mineral often replaces LP amphiboles (Fig. 3a, b) and sometimes show euhedral shapes (Fig. 3d) suggesting that it has crystallized at HP during prograde metamorphism and is poorly affected by retrograde metamorphic reactions. Glaucophane displays higher Li concentrations relative to oceanic assemblages, reaching up to 620 ppm in metasomatic zones. We thus propose that Li has been mobilized from surrounding sediments during the first stage of prograde metamorphism, at temperature above 250 °C. These Li-rich fluids could have promoted glaucophane crystallization. Several studies have underlined similar Li enrichments during prograde metamorphism in meta-ophiolitic environments dominated by metasedimentary rocks (e.g. Catalina Schist California, United-States; Penniston-Dorland et al., 2012 or Almirez massif, Spain; Scambelluri et al., 2004a) suggesting that Li can act as a tracer of element influx from metasedimentary rocks during subduction.

Metasedimentary rocks constitute a huge reservoir of B and Li in the oceanic lithosphere before subduction (Table 3). Previous whole rock and in situ studies of the Queyras Schiste Lustres complex have shown that B can be mobile in the fluids released during meta-sediments dehydration whereas Li shows an overall retention behavior (Busigny et al., 2003; Bebout et al., 2007, 2013; Garrofalo, 2012). However, our study presents high Li concentrations in glaucophane and titanite composing metasomatic contacts between metasedimentary rocks and metagabbros relative to glaucophane and titanite from metagabbroic pods (Fig. 7). This suggests that Li can be mobilized in metasedimentary rock derived fluids but this loss insignificantly affects the bulk Li concentrations of metasedimentary rocks (e.g. Penniston-Dorland et al., 2012). On the contrary, no B enrichment has been observed in the minerals composing these contacts as well as in metagabbroic pods. The sole consideration of metagabbros and metasedimentary rocks inter-exchanges is thus inadequate to explain the mass balance of volatile elements in this system. Notably, metagabbroic pods from the Queyras Schist Lustrés complex are also associated with B-rich antigorite schists (Lafay et al., 2013). In this setting, serpentinites are considered to act as sponges and buffer most of fluid mobile elements released during metasedimentary rocks dehydration. However, although Li can be easily stored in chrysotile (up to ~ 100 ppm; Vils et al., 2010; Wunder et al., 2010; Lafay et al., 2013), this element is not easily incorporated at HP in antigorite (less than 10 ppm; Scambelluri et al., 2004a; Wunder et al., 2010; Vils et al., 2010; Debret et al., 2013b; Lafay et al., 2013). Antigorite schists therefore serve as poor sinks for Li. This explains the lack of B enrichment and the significant Li enrichment at the greenschist to blueschist transition in metagabbros. This suggests a partitioning of fluid mobile elements among meta-ophiolite lithologies (metagabbros, serpentinites, and metasedimentary rocks) during subduction. During subduction, in an open system where fluid mobile elements are supplied by the dehydration of metasedimentary rocks, lizardite recrystallization into antigorite acts as a sink for B, while Li is mostly incorporated into glaucophane.

In the Queyras metagabbros, no correlation between Li and halogen concentration in glaucophane has been observed suggesting that halogens are poorly affected by fluid/rock interaction during metasedimentary rocks dehydration. The glaucophane and lawsonite/epidote displays similar halogen concentrations, which are lower than those of LP-amphiboles (Fig. 9) whereas quartz contains only traces of halogens (Table 2). These observations are in agreement with F and Cl released by fluids during the recrystallization of amphibole porphyroclasts and amphibole coronas into glaucophane and lawsonite/epidote during subduction. According to previous studies (Scambelluri et al., 2004a,b; Debret et al., 2014), this suggests that halogens are released in slab-derived fluids during the first stages of subduction.

5.4 Amphibole breakdown in the oceanic crust approaching eclogite facies: the Monviso ophiolite

The eclogitic metagabbros of the Monviso ophiolite are mostly composed of garnet, omphacite, quartz, glaucophane, rutile and phengite. Relative to blueschist metagabbros, they are characterized by a lower modal amount of glaucophane and the disappearance of chlorite, titanite, lawsonite and/or epidote (Tables 1 and A1). Mass balance calculation show that F and Cl abundances of eclogitic metagabbros are lower than that of oceanic metagabbros (Fig 9; Table 3) suggesting that about 90 % and 50 % of the initial budget of F and Cl in metagabbros is lost in fluids during the first 80 km of subduction. This observation is in good agreement with the disappearance of oceanic halogen rich phases in eclogitic metagabbros. It suggests that LP-amphiboles and titanite stabilities control the halogens fluxes between metagabbros and the surrounding environment up to eclogite facies. At greater depth, the fate of halogens can be controlled by omphacite, garnet, phengite and/or glaucophane which are the main carriers of F and Cl in eclogitic metagabbros (Table 2). Phengite is rare in the studied metagabbros and its modal amount is less than 5 %. Its crystallization at HP is dependent on the amount of K₂O in the bulk composition (Poli and Schmidt, 1995) which is expected to be low. Phengite cannot be considered as a significant carrier of F in the studied metagabbros. Glaucophane represent about 5-10% of the rock and its concentration reaches up to 210 ppm of F in eclogite metagabbros. At eclogite facies, the continuous reactions taking place in metagabbros progressively consume glaucophane and change its composition (Spear, 1993; Poli and Schmidt, 2002). F-abundances in glaucophane increase in eclogitic metagabbros relative to that of Queyras metagabbros. Indeed, the incorporation of fluorine in glaucophane can stabilize it at high temperature and pressure (e.g. Holloway and Ford, 1975), in equilibrium with eclogitic paragenesis (Fig. 4). At greater depth, the glaucophane terminal breakdown can release a significant amount of halogens in fluids. However, it should be noted that other minerals with OH-sites (humites, chlorite or micas) or apatite are all potential F hosts (e.g. Koga et al., 2014) in the subducting slab that can persist to higher pressure and temperature conditions. It is thus plausible to expect that some F persist deeper in subduction zone.

As in the Queyras Schistes Lustrés complex, bulk rock Li abundances, estimated by mass balance calculation, increase passing from oceanic to eclogitic metagabbros (Table C3) suggesting that Li is added to metagabbros by fluid during subduction. However, in the Monviso massif, the scarcity of metasedimentary rocks, which represent less than 10% of the massif (Schwartz et al., 2001), suggests that fluid/rock interactions between metasedimentary rocks and metagabbros are limited (e.g. Lafay et al., 2013). In contrast, the Monviso is composed of metagabbroic pods embedded into serpentinites. In this massif, previous studies report strong interactions between these two lithologies (e.g. Angiboust et al., 2014). Considering that lizardite breakdown

can release a significant amount Li in fluids (Vils et al., 2010; Debret et al., 2013b), the observed Li concentrations of metagabbros can reflect such serpentinites/metagabbros fluid interactions during subduction. B abundances of eclogitic metagabbros and minerals are comparable to oceanic ones (Fig. 9) suggesting that this element is immobile in metagabbros throughout prograde metamorphism in subduction zones.

6. Summary

Ligurian ophiolites correspond to the sampling of different levels the oceanic lithosphere. The Chenaillet ophiolite corresponds to a large segment of the Ligurian oceanic crust associated with serpentinites and topped locally by rare metasedimentary rocks. The Queyras meta-ophiolites consist of serpentinites and/or metagabbros that can be associated with their oceanic paleobasement, including ophicalcites, pillowed metabasalts and pillow-metabreccias (Lagabrielle et al. 2014). These ophiolites are embedded in a sedimentary rich environment interpreted as a fossiliferous sedimentary wedge (Tricart and Schwartz, 2006). In both settings, the metagabbros are composed of several generations of magmatic and metamorphic amphiboles (Figs 2, 3a,b) and titanite which store a significant amount of halogens. In contrast, metagabbros store a small amount of B and Li relative to sediments or serpentinites during oceanic spreading (Table 3).

Prior to subduction, amphibole porphyroclast, amphibole corona and titanites constitute the main halogen-bearing phases in metagabbros. It is thus the stability of these phases that governs the flux of halogens between the subducted altered oceanic crust and the mantle wedge in subduction zones. During subduction, the different part of the lithosphere experienced different fluid/rock interactions (Fig. 10). In the Queyras Schistes Lustres complex, the heavy deformation and the abundant devolatilization of metasedimentary rocks produce large fluid flows that promote rock hybridization at metasedimentary rock/metagabbros (Fig. 3c) or serpentinite contacts. Such mixing zones are likely to exist along the slab-mantle interface (e.g. Konrad-Schmolke et al., 2011; Bebout, 2014) and act as a filter for geochemical fluxes in subduction zones. In the present study, metagabbro and serpentinite olistoliths can fix some of the Li and B released during metasedimentary rock dehydration and, probably, transport them to greater depth. In contrast, F and Cl are continuously released to fluids and can be transferred at these depths to mantle wedge where halogen-rich fluids can promote the serpentinization of the mantle wedge (e.g. Guillot et al., 2000). The Monviso meta-ophiolite preserves a large segment of the oceanic crust (Angiboust et al., 2011). The presence of pillow-lavas (Schwartz et al., 2001) indicates that this meta-ophiolite correspond to a sampling of the upper part of the slab, probably located just below the slab-mantle interface (Fig. 10). In this setting, the interaction with the sedimentary original cover is limited and most of volatile escaped the system. Local enrichment in Li suggests fluid/rock interactions between serpentinites and

metagabbros. Such interactions can be linked to local fluid/rock interactions or mark the percolation of deep fluid released by serpentinite dehydration composing the deepest part of the slab (e.g. Debret et al., 2013b).

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Figure Captions

Fig. 1: (a) Map of the Western Alps indicating the location of the studied area. (b) Metamorphic map of the studied area showing the locations of the studied ophiolites. (c) Pressure and temperature estimates of the studied ophiolites. Modified after Schwartz et al. (2013).

Fig. 2: (a) Foliated metagabbro of the Chenaillet ophiolite displaying clinopyroxene porphyroclasts surrounded by thin black coronas of amphibole. (b) Photomicrographs of metagabbro from the Chenaillet ophiolite showing amphibole porphyroclasts (Amp P) partly recrystallized into amphibole coronas (Amp C). The amphibole coronas are zoned from light brown to green toward to the rims. (c) Schematic diagram showing the sequence of amphibole crystallization during lithosphere cooling and hydration.

Fig.3: Photomicrographs under plane polarized light (a, b, d, f) and photo (c, e) of metabasite from the Queyras Schistes Lutres complex. (a) Metagabbro from Chabrière ophiolite displaying a zoned amphibole corona partly recrystallized into glaucophane. The ilmenite is surrounded by a titanite corona. (b) Metagabbro from Clausis ophiolite showing glaucophane surrounding a amphibole corona. Small titanite grains are included in the glaucophane replacing the amphibole corona. Epidote crystallizes at the contact between glaucophane and lawsonite. (c-d) Metasomatic glaucophanite crystallizing at the contact between metagabbroic pods and metasedimentary rocks. It is composed of idiomorphic glaucophane and chlorite and interstitial calcite; Echassier ophiolite. (e-f) Glaucophanite veins crossing metagabbroic pods of Tour Real ophiolite. These veins are composed of glaucophane and lawsonite. The glaucophane can locally surround kink-banded clinopyroxene.

Fig. 4: Eclogite from the Monviso ophiolite displaying an equilibrium paragenesis composed of glaucophane, garnet, omphacite, quartz and rutile.

Fig. 5: Plot of amphibole Al_2O_3 and TiO_2 contents.

Fig. 6: Plots of TiO_2 vs F, Cl, Li and B concentrations of LP-amphiboles in Chenaillet metagabbros (a-d) and LP-amphiboles relic in Queyras Schistes Lustres metagabbros (e-h). Symbol captions: see Fig.5. These figures show the compositional evolution of amphibole during oceanic lithosphere cooling and seafloor metamorphism.

Fig. 7: Plots of F, Cl, Li and B concentrations of amphiboles from greenschist to eclogitic facies metagabbros indicating the change of volatile element concentrations with glaucophane crystallization. Symbol caption: see Fig.5.

Fig. 8: Reconstitution of bulk rock composition (corresponding samples, from left to right: Ch3, Ch5, QE34, QE32, QE9, Cl2, TR11, TR16, QE29, Gala) showing a sharp decrease of halogen concentrations passing from

Chenaillet to Queyras or Monviso metagabbros. *Epidote and actinolite crystallization can be related to late seafloor or obduction/exhumation metamorphism.

Fig. 9 Plots of Cl versus F and B versus Li of (a-b) oceanic (magmatic and metamorphic) assemblages and (c-d) alpine assemblages composing the metagabbros. The seawater value is from Li et al. (1991), the primitive mantle value is from Sun and McDonough (1995) and the MORB value is an average value from Shaw et al. (2010) and Koga (unpublished data, see appendix of Van den Bleeken and Koga, in press). The sediment value is from Li et al. (1991). *values from Cortesogno et al. (2000) and Coogan et al. (2001); **see discussion and Appendix C for more details.

Fig. 10: Schematic view of a subduction zone with possible fluid migration pathways based on alpine meta-ophiolite observations. In the down part of the slab, below the Moho, the deformation is limited and volatiles (F, Cl, Li and B) are transported through channelized fluid flows (see Debret et al., 2013b). In the upper part of the lithosphere, the deformation allows a large scale fluid circulation. In metagabbros, the continuous reactions of amphibole disappearance lead to the release of halogens (F and Cl) in fluids while Li can be locally stored in glaucophane and phengite during serpentinites/metagabbros fluid interactions. Above the slab, sediment dehydration releases a large quantity of volatiles that can be transferred to serpentinites and metagabbros boudins and to the mantle wedge.

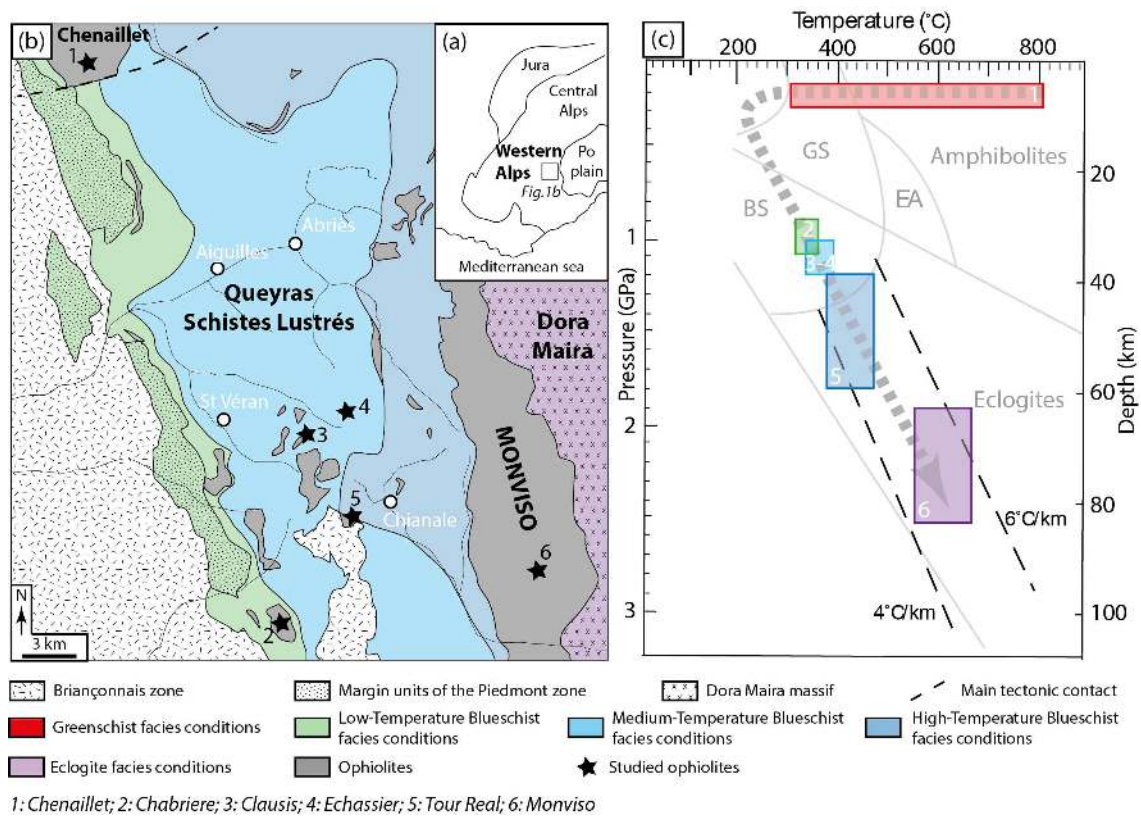


Figure 1

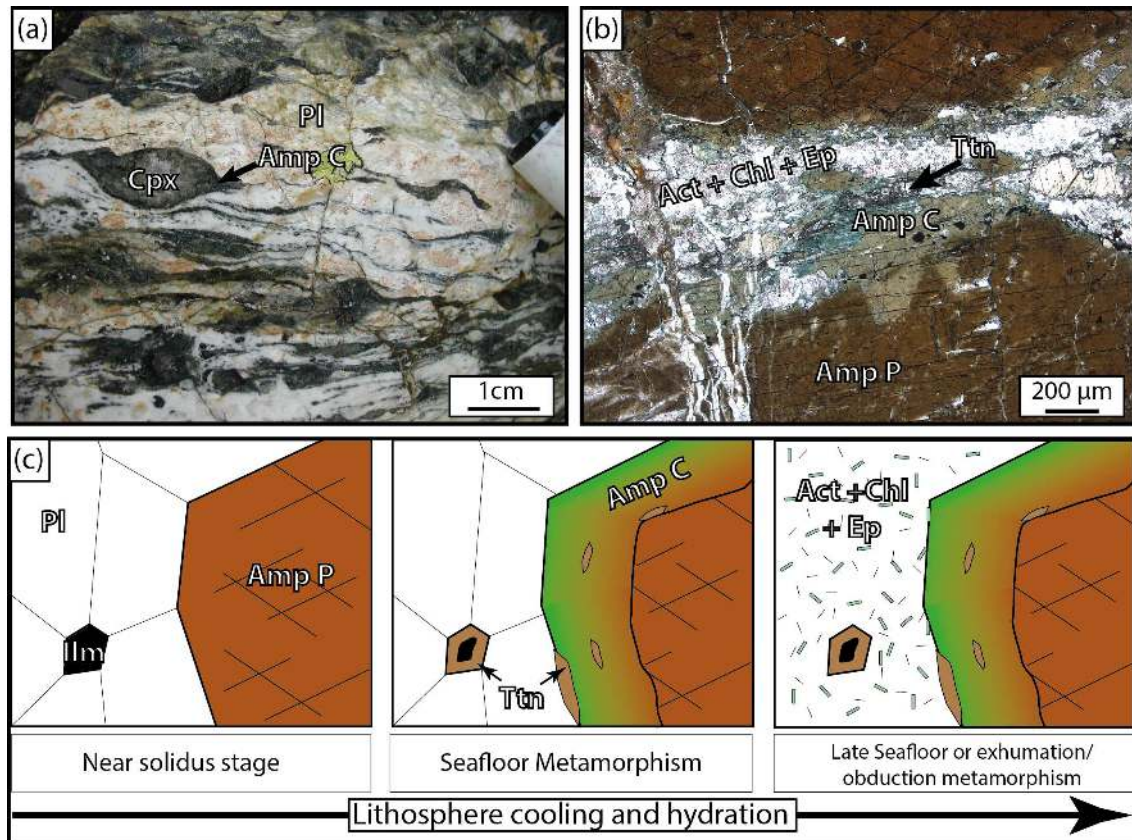


Figure 2

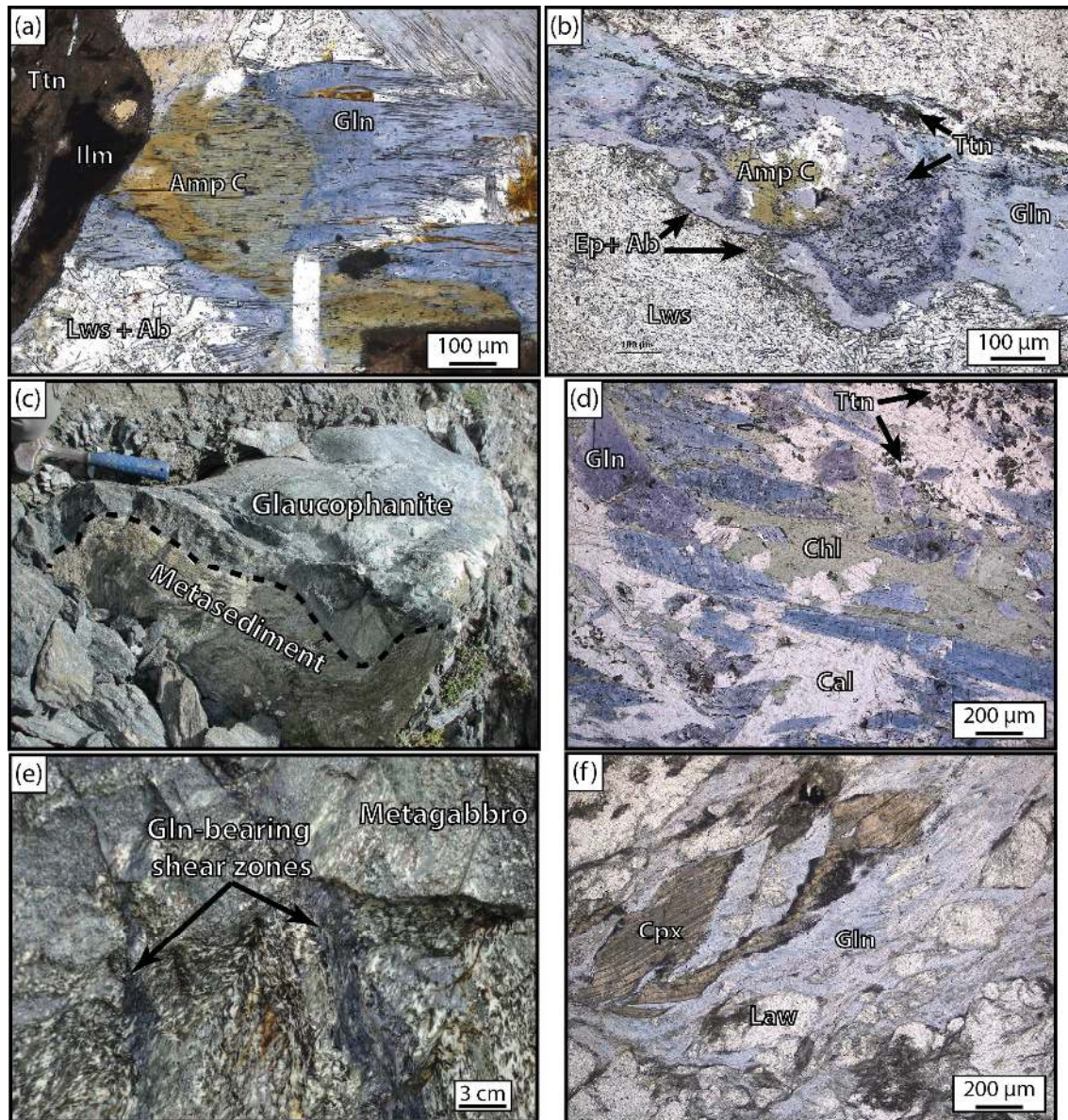


Figure 3

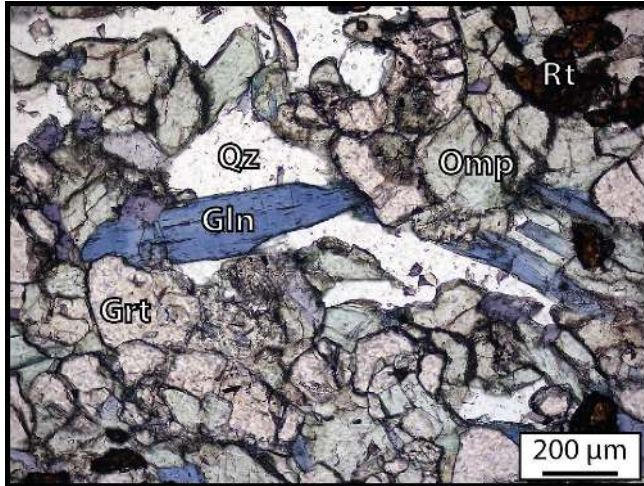


Figure 4

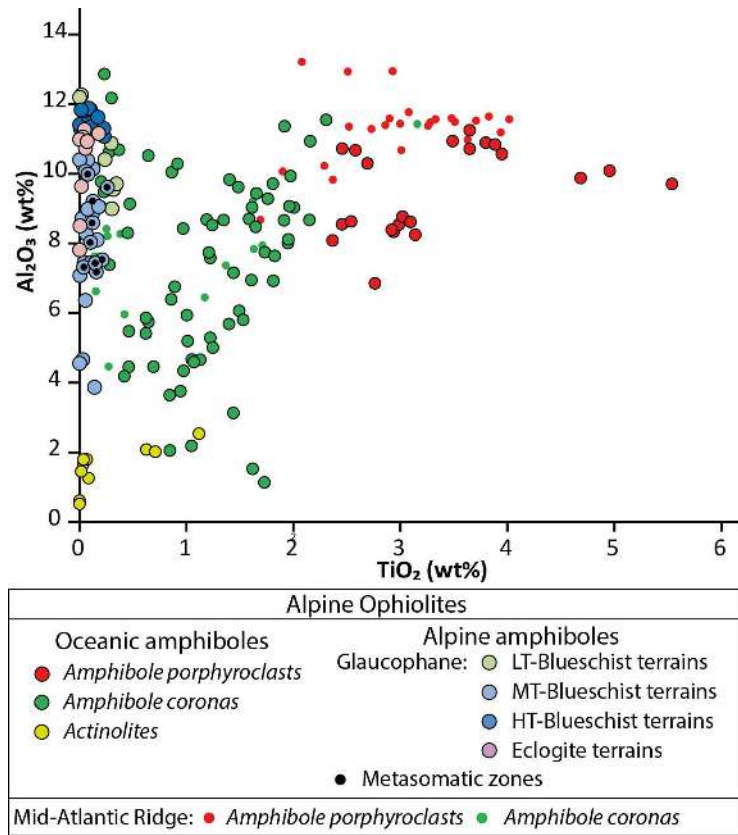


Figure 5

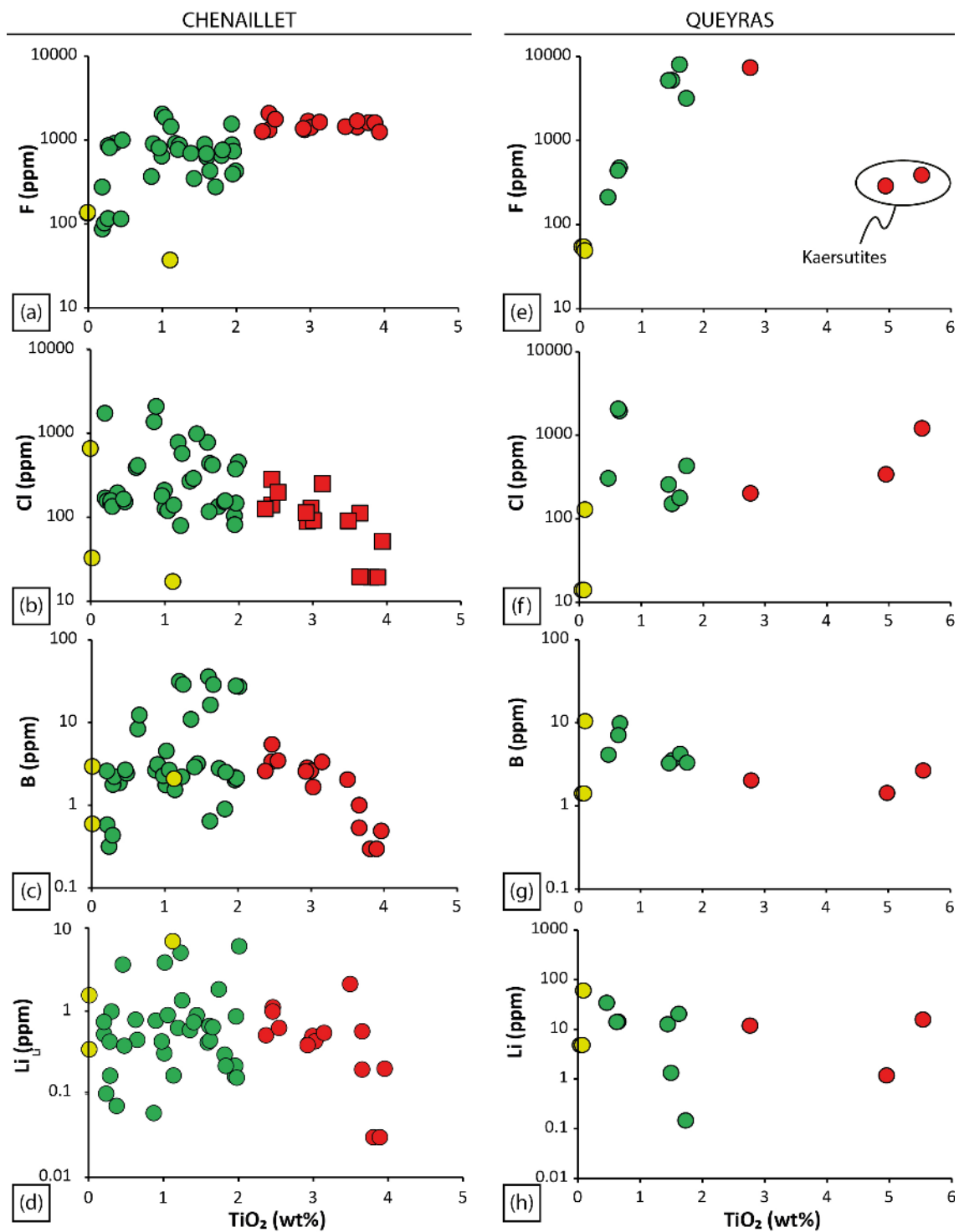


Figure 6

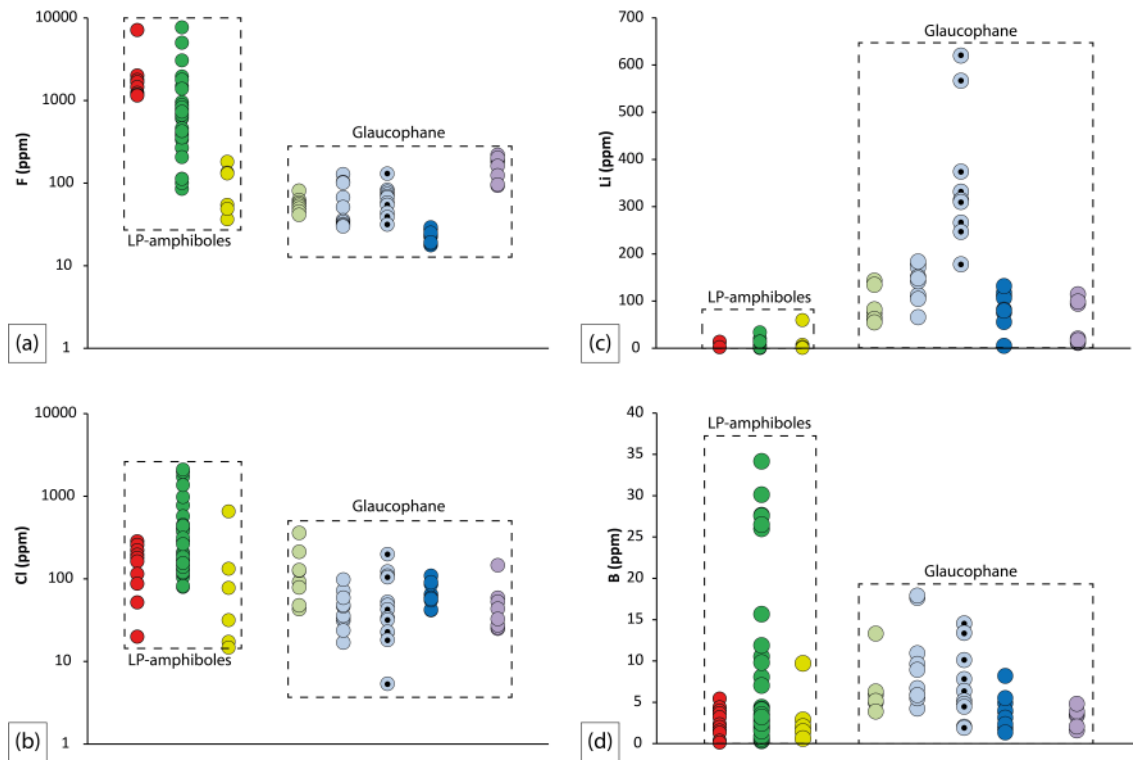


Figure 7

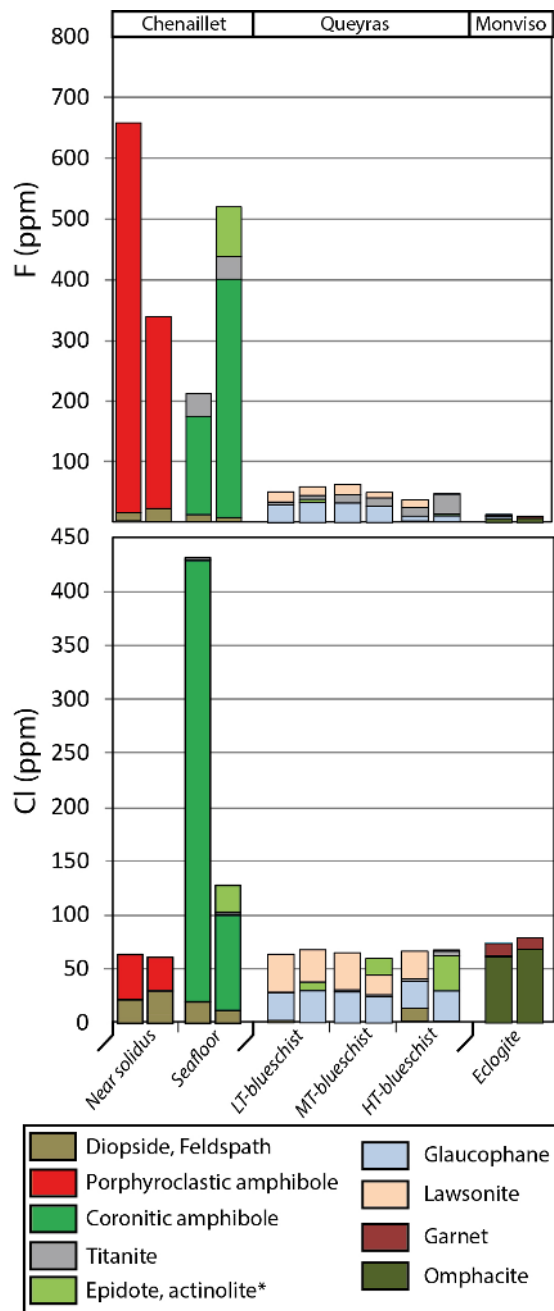


Figure 8

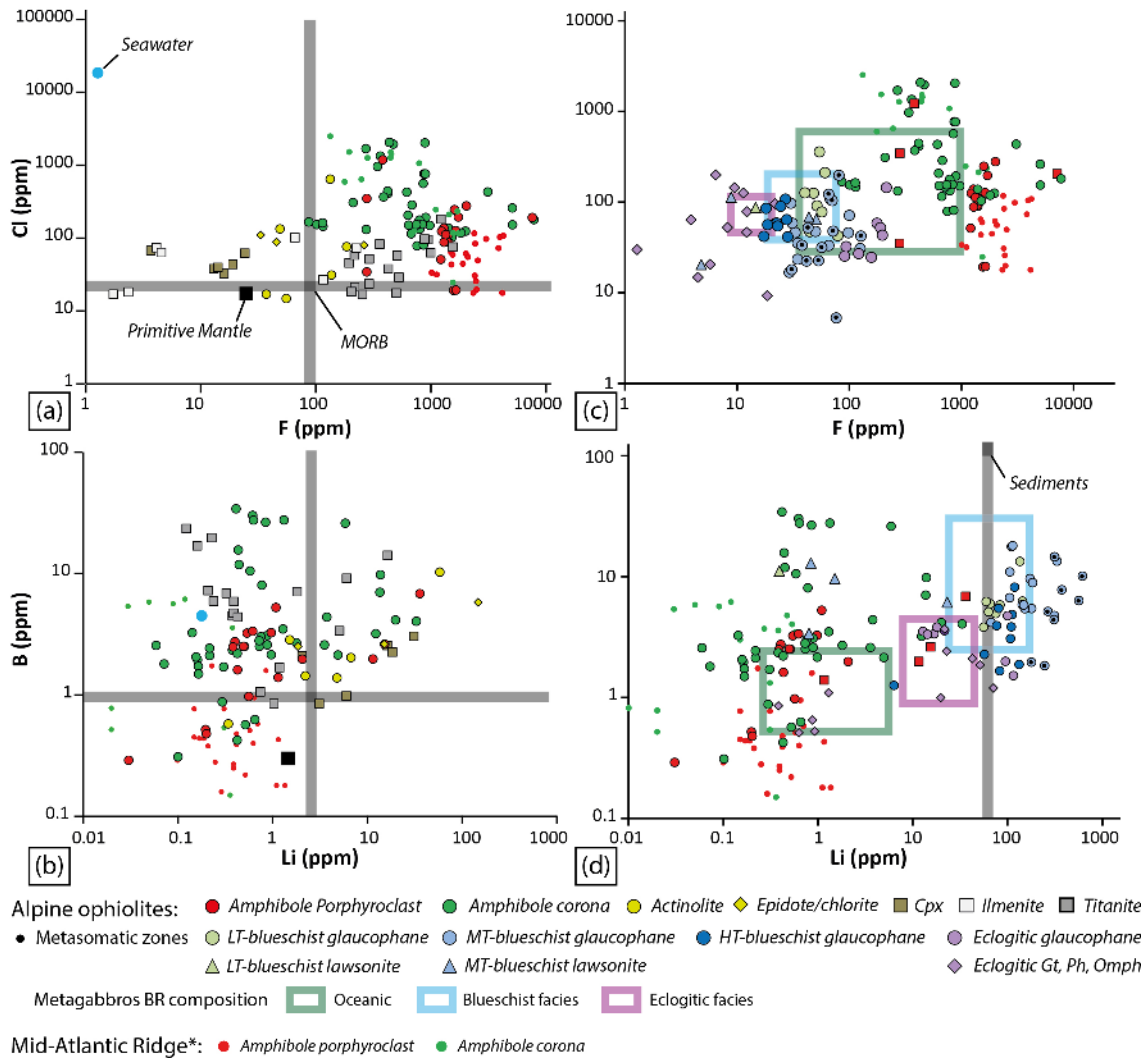


Figure 9

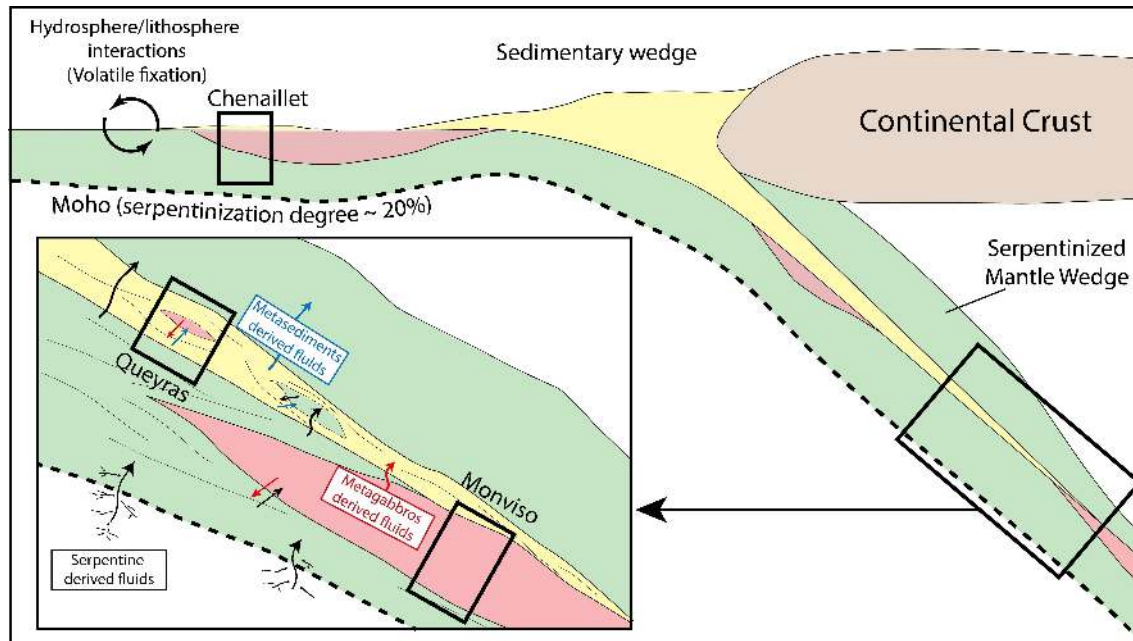


Figure 10

Table 1: Main assemblages composing the studied metagabbros.

| Sample Name | Location | Lithology | Main mineral assemblages | |
|-------------|------------|---------------------|---|---|
| | | | LP metamorphism | alpine HP metamorphism |
| Ch1 | Chenaillet | deformed metagabbro | <i>Cpx-replacive amphibole-actinolite-albite - epidote-chlorite-ilmenite-titanite</i> | |
| Ch5 | | meta-dolerite | <i>Cpx-amphibole porphyroclast s-replacive amphibole-actinolite-albite-epidote-chlorite-ilmenite-titanite</i> | |
| Ch3 | | amphibolite | <i>amphibole porphyroclast s-replacive amphibole-actinolite-albite-epidote-ilmenite-titanite</i> | |
| Ch10 | | amphibolite | <i>amphibole-actinolite-albite-epidote-ilmenite-titanite</i> | |
| QE32 | | Chabriere | meta-diorite | <i>Cpx-ilmenite-⁺apatite-titanite-amphibole porphyroclast s-replacive amphibole-actinolite</i> |

| | | | | |
|-------|---------------------------|---------------------------|--|---|
| QE33 | | meta-dolerite | ilmenite-titanite-replacive amphibole-actinolite | Glaucofane-lawsonite-albite ⁺ /.zoisite |
| QE34 | | metagabbro | ilmenite-titanite-replacive amphibole ⁺ /.apatite | Glaucofane-lawsonite-albite |
| QE6 | | metagabbro | replacive amphibole-titanite | Glaucofane-lawsonite ⁺ /.albite-zoisite-quartz-calcite |
| QE9 | Clausis | metagabbro | Cpx-replacive amphibole-actinolite-ilmenite-titanite | Glaucofane-lawsonite |
| Cl2 | | metagabbro | Cpx-ilmenite-titanite | Glaucofane-lawsonite ⁺ /. epidote |
| Q13 | | metasomatic quartzite | | Quartz-glaucophane-titanite-stiplomelane |
| CE8 | Echasser | metasomatic glaucophanite | | Glaucofane-calcite-chlorite-titanite ⁺ /.ilmenite |
| TR11 | Tour | fracture in a metagabbro | Cpx | Glaucofane-lawsonite-zoisite-chlorite-magnetite |
| TR16 | Real | shear zone in metagabbro | Cpx | Glaucofane-zoisite |
| QE29d | Monviso (Verne) | eclogite | | Omphacite-garnet-glaucophane-quartz-rutile ⁺ /.Phengite |
| Gala | Monviso (Passo Gallarino) | eclogite | | Omphacite-garnet-glaucophane-quartz-Rutile ⁺ /. Phengite |

Table 2: SIMS analyses of pyroxene, amphibole, titanite, ilmenite, lawsonite, epidote, chlorite, rutile, omphacite, garnet, quartz and phengite. 2σ corresponds to the analytical uncertainty.

| Massif | Sample | F | 2σ | Cl | 2σ | B | 2σ | Li | 2σ |
|---------------------------------|---------|-------|-----------|------|-----------|------|-----------|------|-----------|
| pyroxene | | | | | | | | | |
| CHE | Ch1.3 | 3.7 | 0.6 | 68 | 6 | 2.1 | 0.1 | 2.07 | 0.04 |
| TR | TR11.3 | 23.9 | 0.7 | 63 | 6 | 2.6 | 0.2 | 16.4 | 0.7 |
| TR | TR11.3 | 18.8 | 1.0 | 44 | 5 | 3.0 | 0.2 | 31.2 | 1.6 |
| TR | TR16.3 | 15.8 | 0.4 | 33 | 5 | 2.3 | 0.2 | 18.6 | 0.7 |
| TR | TR16.2 | 12.9 | 0.4 | 39 | 6 | 1.0 | 0.2 | 6.1 | 0.3 |
| TR | TR16.1 | 13.9 | 0.6 | 40 | 4 | 0.8 | 0.2 | 3.1 | 0.3 |
| Amphibole porphyroclasts | | | | | | | | | |
| CHE | Ch3.1 | 1285 | 5 | 89 | 3 | 2.7 | 0.2 | 0.40 | 0.07 |
| CHE | Ch3.2 | 1624 | 15 | 128 | 20 | 2.5 | 0.3 | 0.5 | 0.1 |
| CHE | Ch3.3 | 1583 | 7 | 249 | 37 | 3.2 | 0.2 | 0.5 | 0.1 |
| CHE | Ch3.3 | 1710 | 8 | 197 | 10 | 3.3 | 0.3 | 0.6 | 0.1 |
| CHE | Ch3.4 | 1368 | 16 | 91 | 7 | 1.6 | 0.1 | 0.4 | 0.1 |
| CHE | Ch3.4 | 1331 | 14 | 113 | 6 | 2.5 | 0.2 | 0.4 | 0.1 |
| CHE | Ch3.5 | 1279 | 22 | 140 | 13 | 3.3 | 0.3 | 1.0 | 0.2 |
| CHE | Ch3.5 | 1225 | 11 | 126 | 19 | 2.5 | 0.2 | 0.5 | 0.2 |
| CHE | Ch5.1 | 2011 | 13 | 280 | 4 | 5.3 | 0.2 | 1.09 | 0.05 |
| CHE | Ch5.1 | 1386 | 15 | 112 | 7 | 0.52 | 0.12 | 0.20 | 0.05 |
| CHE | Ch5.2 | 1557 | 10 | 19 | 2 | 0.29 | 0.06 | 0.03 | 0.02 |
| CHE | Ch5.2 | 1636 | 9 | 20 | 2 | 1.0 | 0.1 | 0.6 | 0.2 |
| CHE | Ch5.2 | 1208 | 5 | 52 | 7 | 0.48 | 0.07 | 0.20 | 0.06 |
| CHE | Ch5.4 | 1401 | 14 | 90 | 11 | 1.98 | 0.10 | 2.1 | 0.5 |
| CHAB | QE32.1 | 381 | 2 | 1224 | 12 | 2.6 | 0.1 | 15.4 | 0.6 |
| CHAB | QE32.1 | 281 | 5 | 35 | 7 | 6.8 | 0.2 | 36.2 | 1.1 |
| CHAB | QE32.2 | 283 | 3 | 348 | 8 | 1.4 | 0.1 | 1.2 | 0.2 |
| CHAB | QE33b.3 | 7123 | 56 | 206 | 13 | 2.0 | 0.2 | 11.6 | 0.1 |
| Metamorphic Amphiboles | | | | | | | | | |
| CHE | Ch1.1 | 862 | 3 | 772 | 38 | 34.1 | 0.7 | 0.4 | 0.1 |
| CHE | Ch1.1 | 886 | 8 | 770 | 67 | 30.1 | 0.6 | 0.62 | 0.07 |
| CHE | Ch1.1 | 848 | 5 | 569 | 102 | 27.6 | 0.3 | 1.33 | 0.08 |
| CHE | Ch1.1 | 612 | 5 | 434 | 42 | 15.7 | 0.2 | 0.44 | 0.07 |
| CHE | Ch1.1 | N.D. | N.D. | 267 | 25 | 10.5 | 0.3 | 0.58 | 0.07 |
| CHE | Ch1.1 | N.D. | N.D. | 386 | 54 | 8.0 | 0.3 | 0.78 | 0.06 |
| CHE | Ch1.1 | N.D. | N.D. | 410 | 54 | 11.8 | 0.4 | 0.45 | 0.05 |
| CHE | Ch1.3 | 270 | 3 | 1708 | 42 | 2.5 | 0.3 | 0.7 | 0.1 |
| CHE | Ch1.3 | 419 | 5 | 416 | 8 | 27.5 | 0.4 | 0.63 | 0.06 |
| CHE | Ch1.3 | 417 | 8 | 447 | 7 | 26.0 | 0.5 | 5.9 | 0.4 |
| CHE | Ch1.3 | 384 | 13 | 372 | 10 | 26.5 | 0.4 | 0.9 | 0.1 |
| CHE | Ch3.1 | 1973 | 15 | 126 | 6 | 4.4 | 0.4 | 3.8 | 0.5 |
| CHE | Ch3.2 | 1502 | 23 | 104 | 4 | 2.0 | 0.1 | 0.16 | 0.02 |
| CHE | Ch3.2 | 749 | 6 | 79 | 5 | 2.1 | 0.3 | 4.9 | 0.8 |
| CHE | Ch3.2 | 271 | 7 | 133 | 7 | 2.7 | 0.2 | 1.8 | 0.3 |
| CHE | Ch3.3 | 740 | 9 | 156 | 10 | 2.4 | 0.2 | 0.22 | 0.05 |
| CHE | Ch3.4 | 1803 | 8 | 119 | 4 | 2.6 | 0.2 | 0.9 | 0.2 |
| CHE | Ch3.4 | 1399 | 11 | 139 | 20 | 1.5 | 0.1 | 0.17 | 0.04 |
| CHE | Ch3.4 | 113.5 | 1.1 | 164 | 11 | 2.6 | 0.3 | 3.6 | 0.8 |
| CHE | Ch3.5 | 340 | 2 | 975 | 81 | 3.1 | 0.2 | 0.9 | 0.2 |
| CHE | Ch5.1 | 86.0 | 0.8 | 169 | 3 | 0.57 | 0.13 | 0.52 | 0.07 |
| CHE | Ch5.1 | 100.9 | 0.9 | 156 | 5 | 0.3 | 0.1 | 0.10 | 0.01 |
| CHE | Ch5.2 | 360 | 4 | 1357 | 35 | 2.6 | 0.1 | 0.06 | 0.03 |
| CHE | Ch5.2 | 877 | 5 | 2055 | 39 | 3.0 | 0.1 | 0.8 | 0.4 |
| CHE | Ch5.4 | 114.3 | 1.2 | 147 | 2 | 0.4 | 0.1 | 0.4 | 0.2 |
| CHE | Ch10b.1 | 627 | 3 | 208 | 7 | 1.7 | 0.1 | 0.31 | 0.05 |
| CHE | Ch10b.1 | 891 | 7 | 195 | 25 | 1.8 | 0.1 | 0.07 | 0.02 |
| CHE | Ch10b.1 | 677 | 3 | 288 | 24 | 2.8 | 0.2 | 0.73 | 0.08 |
| CHE | Ch10b.1 | 786 | 5 | 179 | 13 | 2.2 | 0.1 | 0.43 | 0.06 |
| CHE | Ch10b.1 | 834 | 4 | 157 | 10 | 1.7 | 0.1 | 0.17 | 0.04 |

| | | | | | | | | | |
|--------------------|---------|-------|------|------|------|------|------|-------|------|
| CHE | Ch10b.2 | 668 | 3 | 116 | 5 | 0.6 | 0.1 | 0.7 | 0.1 |
| CHE | Ch10b.2 | 634 | 4 | 152 | 12 | 0.9 | 0.1 | 0.3 | 0.1 |
| CHE | Ch10b.3 | 790 | 7 | 134 | 18 | 2.1 | 0.1 | 0.98 | 0.09 |
| CHE | Ch10b.3 | 967 | 7 | 151 | 15 | 2.3 | 0.1 | 0.38 | 0.06 |
| CHE | Ch10b.3 | 853 | 7 | 82 | 3 | 2.1 | 0.2 | 0.22 | 0.06 |
| CHE | Ch10b.3 | 716 | 6 | 147 | 6 | 2.1 | 0.2 | 0.16 | 0.03 |
| CHAB | QE34.1 | 5056 | 57 | 155 | 31 | 3.5 | 0.1 | 1.30 | 0.09 |
| CHAB | QE34.1 | 5036 | 44 | 262 | 15 | 3.2 | 0.1 | 12.4 | 0.2 |
| CHAB | QE34.3 | 7738 | 109 | 182 | 7 | 4.2 | 0.2 | 20.1 | 0.6 |
| CHAB | QE34.3 | 3086 | 71 | 437 | 13 | 3.3 | 0.1 | 0.14 | 0.01 |
| CHAB | QE34.3 | 208.7 | 1.3 | 312 | 8 | 4.1 | 0.1 | 33.2 | 0.7 |
| CL | QE6.1 | 466 | 3 | 1970 | 49 | 9.8 | 0.4 | 13.9 | 0.2 |
| CL | QE6.1 | 431 | 3 | 2090 | 29 | 7.0 | 0.2 | 13.7 | 0.4 |
| Actinolite | | | | | | | | | |
| CHE | Ch1.3 | 183 | 4 | 77 | 7 | 1.4 | 0.3 | 2.24 | 0.08 |
| CHE | Ch3.2 | 135 | 2 | 31 | 4 | 0.6 | 0.1 | 0.34 | 0.02 |
| CHE | Ch3.3 | 132.0 | 0.9 | 652 | 89 | 2.9 | 0.3 | 1.5 | 0.2 |
| CHE | Ch5.4 | 36.8 | 0.3 | 17.2 | 1.2 | 2.0 | 1.0 | 7 | 6 |
| CHAB | QE32.1 | 54.0 | 0.3 | 14.5 | 0.3 | 1.4 | 0.06 | 4.7 | 0.07 |
| CHAB | QE32.1 | 48.7 | 0.2 | 132 | 21 | 10.4 | 0.2 | 58.9 | 0.5 |
| Epidote | | | | | | | | | |
| CHE | Ch3.2 | 260 | 10 | 80.0 | 1.9 | 2.51 | 0.13 | 1.85 | 0.28 |
| CL | CI2.1 | 4.81 | 0.17 | 20.6 | 0.3 | 6.13 | 0.10 | 23.0 | 0.2 |
| CL | CI2.1 | 8.9 | 1.4 | 114 | 11 | 3.38 | 0.07 | 0.80 | 0.04 |
| Chlorite | | | | | | | | | |
| CHE | Ch3.3 | 22 | 66 | N.D. | N.D. | 2.62 | 0.07 | 15.4 | 0.3 |
| CHE | Ch5.2 | 44.9 | 0.2 | 90 | 4 | 5.81 | 0.07 | 148.8 | 1.3 |
| CHE | Ch5.4 | 32.72 | 0.15 | 113 | 4 | 4.38 | 0.11 | 0.43 | 0.01 |
| EC | CE8A.2 | 33.9 | 0.2 | 68 | 2 | 5.92 | 0.12 | 0.24 | 0.01 |
| EC | CE8A.2 | 30.78 | 0.12 | 29 | 2 | 5.88 | 0.12 | 0.39 | 0.02 |
| EC | CE8A.3 | 35.2 | 0.3 | 109 | 5 | 7.25 | 0.13 | 0.21 | 0.02 |
| TR | TR11.1 | 44.7 | 0.9 | 593 | 28 | 8.88 | 0.10 | 185 | 2 |
| Titanite | | | | | | | | | |
| CHE | Ch3.4 | 1534 | 3 | 76 | 4 | 0.85 | 0.06 | 1.04 | 0.11 |
| CHE | Ch3.4 | 933 | 6 | 97 | 8 | 1.06 | 0.09 | 0.75 | 0.07 |
| CHAB | QE34.1 | 504 | 4 | 58 | 3 | 9.14 | 0.13 | 6.11 | 0.07 |
| CHAB | QE34.1 | 521.2 | 1.0 | 29 | 2 | 16.9 | 0.2 | 0.16 | 0.01 |
| CHAB | QE34.3 | 421.5 | 1.3 | 38.3 | 1.2 | 19.7 | 0.3 | 0.23 | 0.02 |
| CHAB | QE34.3 | 494.0 | 1.7 | 17.9 | 0.2 | 23.5 | 0.2 | 0.12 | 0.01 |
| CL | CI2.1 | 202.2 | 1.2 | 18.6 | 0.4 | 7.09 | 0.13 | 1.83 | 0.04 |
| CL | CI2.1 | 192.0 | 0.9 | 46 | 3 | 4.73 | 0.11 | 0.39 | 0.03 |
| CL | CI2.1 | 214.3 | 0.7 | 59 | 4 | 4.38 | 0.11 | 0.43 | 0.01 |
| CL | CI2.2 | 288.0 | 0.6 | 52 | 2 | 5.92 | 0.12 | 0.24 | 0.01 |
| CL | CI2.2 | 355.6 | 1.7 | 84 | 5 | 5.88 | 0.12 | 0.39 | 0.02 |
| CL | CI2.2 | 287.3 | 0.9 | 24 | 2 | 7.25 | 0.13 | 0.21 | 0.02 |
| CL | CI2.3 | 251.1 | 1.1 | 17.1 | 0.3 | 6.9 | 0.2 | 0.33 | 0.03 |
| CL | CI2.3 | 215.9 | 1.6 | 21.6 | 1.1 | 4.48 | 0.12 | 0.38 | 0.02 |
| CL | Q13.2 | 983 | 2 | 64 | 6 | 14.1 | 1.2 | 16.5 | 0.5 |
| CL | Q13.2 | 1210 | 3 | 185 | 7 | 1.68 | 0.15 | 1.19 | 0.17 |
| CL | Q13.3 | 871.2 | 1.9 | 98 | 5 | 3.4 | 0.2 | 5.1 | 0.3 |
| Ilmenite | | | | | | | | | |
| CHE | Ch5.1 | 2.33 | 0.10 | 18 | 2 | N.D. | N.D. | N.D. | N.D. |
| CHE | Ch5.2 | 1.72 | 0.11 | 17.2 | 1.5 | N.D. | N.D. | N.D. | N.D. |
| CHE | Ch5.4 | 4.1 | 0.4 | 75 | 4 | N.D. | N.D. | N.D. | N.D. |
| CHE | Ch5.4 | 4.5 | 0.3 | 64 | 4 | N.D. | N.D. | N.D. | N.D. |
| CHAB | QE34.3 | 65.1 | 1.1 | 103 | 4 | N.D. | N.D. | N.D. | N.D. |
| CHAB | QE34.1 | 114.8 | 0.4 | 27 | 3 | N.D. | N.D. | N.D. | N.D. |
| CHAB | QE34.1 | 222.2 | 0.9 | 74 | 27 | N.D. | N.D. | N.D. | N.D. |
| Glaucophane | | | | | | | | | |
| CHAB | QE34.3 | 51.6 | 0.9 | 92 | 15 | 5.9 | 0.1 | 65.7 | 0.8 |

| | | | | | | | | | |
|------------------|---------|-------|------|------|------|-------|------|-------|------|
| CHAB | QE34.3 | 57.1 | 0.7 | 78 | 7 | 6.2 | 0.1 | 59.7 | 1.1 |
| CHAB | QE34.3 | 79 | 2 | 43 | 9 | 4.9 | 0.1 | 75.3 | 1.3 |
| CHAB | QE33b.3 | 54 | 3 | 360 | 101 | 5.8 | 0.1 | 83.4 | 1.1 |
| CHAB | QE33b.3 | 44.5 | 0.4 | 48 | 8 | 6.3 | 0.1 | 144.0 | 1.5 |
| CHAB | QE34.1 | 48.1 | 1.0 | 126 | 17 | 5.09 | 0.09 | 63.0 | 0.8 |
| CHAB | QE34.1 | 40 | 2 | 127 | 45 | 3.81 | 0.08 | 56.0 | 1.1 |
| CHAB | QE32.2 | 61 | 3 | 213 | 58 | 13.3 | 0.3 | 136 | 3 |
| CL | QE6.1 | 125.3 | 0.9 | 31 | 5 | 4.2 | 0.1 | 67.1 | 0.5 |
| CL | QE6.1 | 65.7 | 0.7 | 33 | 3 | 10.9 | 0.1 | 105.8 | 0.7 |
| CL | QE6.1 | 100.4 | 0.5 | 72 | 2 | 17.6 | 0.3 | 110.2 | 1.0 |
| CL | QE6.1 | 98.5 | 1.6 | 46 | 6 | 17.9 | 0.3 | 113.6 | 1.3 |
| CL | CI2.3 | 34.8 | 0.4 | 35.5 | 1.9 | 5.4 | 0.2 | 180 | 6 |
| CL | CI2.3 | 29.3 | 0.4 | 16.9 | 1.5 | 9.6 | 0.2 | 173 | 5 |
| CL | CI2.1 | 34.7 | 0.4 | 24 | 2 | 5.4 | 0.1 | 152 | 3 |
| CL | CI2.1 | 33.0 | 0.5 | 46 | 3 | 5.8 | 0.1 | 142.7 | 1.6 |
| CL | CI2.1 | 30.2 | 0.9 | 98 | 9 | 6.7 | 0.2 | 105.3 | 1.9 |
| CL | CI2.2 | 50.1 | 0.2 | 48 | 7 | 8.9 | 0.2 | 185 | 4 |
| CL | CI2.2 | 31.2 | 0.4 | 59 | 7 | 5.8 | 0.1 | 149 | 3 |
| CL | Q13.3 | 67.9 | 0.8 | 109 | 16 | 5 | 1 | 267 | 8 |
| CL | Q13.3 | 70 | 2 | 104 | 20 | 4.8 | 0.9 | 312 | 6 |
| CL | Q13.3 | 81 | 2 | 198 | 22 | 1.8 | 0.1 | 247 | 7 |
| CL | Q13.2 | 66 | 2 | 123 | 20 | 4.4 | 0.2 | 310 | 5 |
| CL | Q13.2 | 71.9 | 1.2 | 48 | 7 | 2.0 | 0.2 | 179 | 3 |
| EC | CE8A.3 | 38.0 | 0.5 | 34 | 7 | 13.4 | 0.2 | 332 | 4 |
| EC | CE8A.3 | 127.3 | 1.6 | 42 | 3 | 13.4 | 0.2 | 332 | 4 |
| EC | CE8A.3 | 30.8 | 0.3 | 18 | 4 | 14.5 | 0.2 | 314 | 8 |
| EC | CE8A.3 | 41.8 | 0.4 | 23 | 4 | 14.5 | 0.2 | 314 | 8 |
| EC | CE8A.3 | 56.9 | 0.7 | 32 | 4 | 14.5 | 0.2 | 314 | 8 |
| EC | CE8A.1 | 53.3 | 0.3 | 22.7 | 1.8 | 6.3 | 0.1 | 567 | 6 |
| EC | CE8A.2 | 76.7 | 0.9 | 5.3 | 0.6 | 7.8 | 0.2 | 375 | 10 |
| EC | CE8A.2 | 42.9 | 1.2 | 52 | 8 | 10.1 | 0.2 | 620 | 9 |
| TR | TR11.1 | 27 | 2 | 108 | 12 | 3.8 | 0.1 | 110 | 2 |
| TR | TR11.2 | 27.8 | 0.1 | 64 | 5 | 4.8 | 0.1 | 112 | 3 |
| TR | TR11.2 | 28.4 | 0.9 | 42 | 8 | 3.9 | 0.6 | 77 | 17 |
| TR | TR16.3 | 17.4 | 0.5 | 42 | 7 | 8.1 | 0.2 | 119 | 2 |
| TR | TR16.3 | 22.0 | 0.4 | 59 | 19 | 3.1 | 0.2 | 108 | 2 |
| TR | TR16.3 | 18.1 | 0.3 | 86 | 12 | 1.7 | 0.2 | 82.6 | 1.5 |
| TR | TR16.2 | 22.6 | 0.5 | 59 | 9 | 1.9 | 0.1 | 132.6 | 1.5 |
| TR | TR16.1 | 23.1 | 1.6 | 55 | 6 | 2.3 | 0.2 | 57 | 2 |
| TR | TR16.1 | 24.5 | 0.5 | 91 | 13 | 1.3 | 0.1 | 6.3 | 0.3 |
| TR | TR16.1 | 18.8 | 0.3 | 57 | 17 | 5.4 | 0.2 | 81 | 2 |
| MV | QE29d.3 | 177 | 2 | 59 | 7 | 3.5 | 0.1 | 12.8 | 0.2 |
| MV | QE29d.3 | 190.1 | 1.8 | 53 | 7 | 3.35 | 0.07 | 16.8 | 0.2 |
| MV | QE29d.3 | 214.2 | 1.6 | 146 | 51 | 3.32 | 0.08 | 14.3 | 0.2 |
| MV | QE29d.4 | 197.6 | 1.4 | 43 | 6 | 3.6 | 0.2 | 21.7 | 0.5 |
| MV | QE29d.4 | 157.4 | 1.9 | 24.8 | 1.1 | 3.8 | 0.2 | 18.0 | 0.3 |
| MV | Gala.1 | 91.0 | 1.3 | 26 | 3 | 1.51 | 0.08 | 115.4 | 0.9 |
| MV | Gala.4 | 121.4 | 1.7 | 27 | 3 | 2.0 | 0.2 | 95.1 | 0.4 |
| MV | Gala.4 | 93.9 | 0.6 | 32 | 4 | 4.7 | 0.2 | 100 | 3 |
| Lawsonite | | | | | | | | | |
| CHAB | QE32.1 | 14.7 | 1.4 | 88 | 8 | 11.10 | 0.09 | 0.39 | 0.08 |
| CL | QE6.1 | 50.8 | 1.1 | 65 | 8 | 9.59 | 0.14 | 1.50 | 0.04 |
| CL | QE6.1 | 43.8 | 1.2 | 69 | 9 | 12.91 | 0.09 | 0.84 | 0.01 |
| Rutile | | | | | | | | | |
| MV | Gala.1 | 15.72 | 0.04 | 12.0 | 0.5 | N.D. | N.D. | N.D. | N.D. |
| MV | Gala.4 | 9.17 | 0.04 | 6.12 | 0.13 | N.D. | N.D. | N.D. | N.D. |
| Omphacite | | | | | | | | | |
| MV | Gala.1 | 12.3 | 0.4 | 79 | 10 | 2.10 | 0.04 | 42.36 | 0.16 |
| MV | Gala.1 | 11.4 | 0.5 | 127 | 8 | 1.20 | 0.03 | 71.1 | 0.3 |
| MV | Gala.1 | 9.5 | 0.2 | 145 | 7 | 1.20 | 0.03 | 71.1 | 0.3 |

| | | | | | | | | | |
|-----------------|---------|-------|------|------|-----|-------|------|------|------|
| MV | QE29d.4 | 21.9 | 0.7 | 97 | 5 | 2.40 | 0.12 | 22.8 | 0.4 |
| MV | QE29d.4 | 12.2 | 0.3 | 46.7 | 1.5 | 3.68 | 0.08 | 21.7 | 0.3 |
| MV | Gala.4 | 5.78 | 0.05 | 20.8 | 0.7 | 1.00 | 0.03 | 19.7 | 0.3 |
| MV | Gala.4 | 6.48 | 0.11 | 200 | 12 | 1.86 | 0.08 | 51.2 | 0.3 |
| Garnet | | | | | | | | | |
| MV | QE29d.3 | 8.2 | 0.3 | 53 | 7 | 0.53 | 0.03 | 0.92 | 0.02 |
| MV | Gala.1 | 3.89 | 0.13 | 64 | 4 | 1.09 | 0.05 | 1.29 | 0.03 |
| MV | QE29d.4 | 18.61 | 0.13 | 9.4 | 0.7 | 0.65 | 0.09 | 0.87 | 0.04 |
| MV | Gala.4 | 4.5 | 0.3 | 14.9 | 1.0 | 0.51 | 0.08 | 0.63 | 0.05 |
| Quartz | | | | | | | | | |
| MV | Gala.4 | 1.3 | 0.1 | 30 | 2 | 0.85 | 0.12 | 0.38 | 0.03 |
| Phengite | | | | | | | | | |
| MV | QE29d.3 | 428 | 2 | 65 | 5 | 104.8 | 0.8 | 0.95 | 0.01 |
| MV | QE29d.4 | 348 | 3 | 37.5 | 0.7 | 130.6 | 0.4 | 1.35 | 0.03 |
| MV | QE29d.4 | 305 | 2 | 43 | 3 | 198.0 | 0.7 | 0.99 | 0.02 |

CHE: Chenaillet; TR: Tour Real; CHAB : Chabrière ; CL : Clausis ; EC : Echassier ; MV : Monviso

Table 3: Volatile (F, Cl, B and Li) contents of lithosphere reservoirs during oceanic and subduction metamorphism

| Lithologies | F (ppm) | Cl (ppm) | B (ppm) | Li (ppm) | ref. |
|---|------------------|------------------|-------------------|-------------------|-----------|
| <i>Oceanic lithospheric budget</i> | | | | | |
| Serpentinities | 50-520* | 260-7100 | 10.4-65 | 0.1-3.4 | 1,2,3,4,5 |
| Sediments | 400-1300 | 21-2000 | 100-230 | 5.4-74 | 6,7,8,9 |
| MORB | 11-100 | 6.-50 | 0.5 | 5.4-6.9 | 10,11 |
| AOC | 160-216 | 79-1432 | 0.2-6 | 9-33 | 12,13,14 |
| Chenaillet/Chabrière metagabbros | 42-657 (317†) | 38-425 (123†) | 0.6-1.9 (1.4†) | 0.3-2.3 (1.8†) | |
| <i>Western Alps Subduction</i> | | | | | |
| Queyras serpentinites | - | - | 30-174* | 0.1-4 | 15 |
| Queyras metasedimentary rocks | - | - | 32-374 | 10-127 | 15, 16 |
| Queyras metagabbros | 27-62 (50†) | 57-68 (63†) | 4-24 (10†) | 29-140 (62†) | |
| Queyras metasomatic zones | 57 | 131 | 13 | 143 | |
| Monviso metagabbros | 10-16 (13†) | 71-79 (75†) | 1-4 (3†) | 9-34 (20†) | |
| Monviso serpentinites | 3.6-11.3* | 20-246* | 10-11* | 0.2 | 1, 15 |

1 Debret et al., 2014; 2 Orberger et al., 1999; 3 Bonifacie et al., 2008; 4 Vils et al., 2008; 5 Barnes and Sharp, 2006; 6 Li, 1982; 7 Li, 1991; 8 John et al., 2011; 9 Bouman et al., 2004; 10 Hart et al., 1999; 11 Salters and Stracke, 2004; 12 Wedepohl and Hartmann, 1994; 13 Straub and Layne, 2003; 14 Sano et al., 2008; 15 Lafay et al., 2013; 16 Bebout et al., 2013; **in situ* measurements; †mean value.

Highlights:

We track the fate of F, Cl, Li and B in the subducted oceanic crust

Halogen budget of metagabbros is mostly stored in amphibole and titanite

Li acts as a tracer of sediment/metagabbros interactions during prograde metamorphism

90 to 50 % of metagabbro halogen budget is lost to fluid during subduction