

Fluorine and chlorine fractionation in the sub-arc mantle: an experimental investigation

Célia Dalou

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UNIVERSITÉ BLAISE PASCAL – CLERMONT-FERRAND II

(U. F. R. Scientifique et Technique)

ÉCOLE DOCTORALE DES SCIENCES FONDAMENTALES N°664

THÈSE

Présentée pour obtenir le grade de

DOCTEUR D'UNIVERSITÉ

Spécialité: Pétrologie expérimentale – Géochimie

 par

Célia DALOU

Titulaire du Master 2 Recheche :

"Processus magmatiques et metamorphiques - Volcanologie"

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Pierre Schiano	Professeur, LMV, Clermont-Ferrand	Président
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Fluorine and Chlorine fractionation in the sub-arc mantle:

An experimental investigation

Volatile elements released from the subducting slab play a fundamental role during the formation of arc magmas in the mantle wedge. Advances of melt inclusion studies enlarged the data on volatile abundance in arc magmas, and it is now possible to characterize some volatile contents in arc primary magmas, in particular F and Cl. A recent study of Mt Shasta melt inclusions (Le Voyer et al., 2010) shows that fractionation of F and Cl potentially contain information about arc magma genesis. In order to trace the source of arc magmas, fluorine and chlorine partitioning was investigated.

Here, I present new experimental determinations of Cl and F partition coefficients between dry and hydrous silicate melts and mantle minerals: olivine, orthopyroxene, clinopyroxene, plagioclase, garnet and also pargasite and phlogopite. The values were compiled from more than 300 measurements in 24 melting experiments, conducted between 8 and 25 kbars and between 1180 and 1430°C. The low abundance F, Cl measurements in minerals were done by Cameca IMF 1280 at WHOI using the negative secondary ion mode.

The results show that $D_F^{Opx/melt}$ ranges from 0.123 to 0.021 and $D_F^{Cpx/melt}$ ranges from 0.153 to 0.083, while Cl partition coefficient varies from $D_{Cl}^{Opx/melt}$ from 0.002 to 0.069 and $D_{Cl}^{Cpx/melt}$ from 0.008 to 0.015, as well. Furthermore, $D_F^{Ol/melt}$ ranges from 0.116 to 0.005 and $D_{Cl}^{Ol/melt}$ from 0.001 to 0.004; $D_F^{Grt/melt}$ ranges from 0.012 to 0.166 and $D_{Cl}^{Grt/melt}$ from 0.003 to 0.087 with the increasing water amount and decreasing temperature. I also show that F is compatible in phlogopite ($D_F^{Phl/melt} >$ 1.2) while $D_F^{Amp/melt}$ is incompatible in pargasite ($D_F^{Amp/melt}$ from 0.36 to 0.63). On the contrary, Cl is more incompatible in phlogopite ($D_{Cl}^{Phl/melt} >$ 1.2 on average 0.09 ± 0.02), than in pargasite ($D_{Cl}^{Amp/melt}$ from 0.12 to 0.38).

This study demonstrates that F and Cl are substituted in specific oxygen site in minerals that lead then to be more sensitive than trace elements to crystal chemistry and water amount variations thus melting conditions. Using those new partition coefficients, I modelled melting of potential sub-arc lithologies with variable quantity aqueous-fluid. This model is able to decipher 1) amount of aqueousfluid involved in melting, 2) melting induced by fluid or melting of an hydrous mineral-bearing source and 3) melting of either pargasite-bearing lithology or phlogopite-bearing lithology and shows that sources of some primitive melts, for instance from Italy, bear pargasite and phlogopite, while some primitve melts seem to be the results of fluid-induced melts.

Key words : partition coefficients, fluorine, chlorine, trace elements, high pressure experiments, substitution, subduction zones, hydrous melting, lattice strain models.

Fractionemment du fluor et du chlore dans le manteau sub-arc

Une approche experimentale

Les éléments volatils libérés de la plaque plongeante lors de la subduction joue un rôle fondamental durant la formation des magmas d'arc dans le coin mantellique. Depuis quelques années, les développements des techniques d'analyse par sonde ionique ont permis l'analyse de ces éléments, en particulier F et Cl, dans les magmas d'arc, et notamment dans les magmas d'arc primaires grâce aux avancées des études sur les inclusions magmatiques. Une récente étude des inclusions magmatiques du Mont Shasta (E. U.) (Le Voyer et al., 2010) a montré que le fractionnement du F et du Cl apportait des informations sur la genèse des magmas d'arc. Afin de caractériser la source de ces magmas, j'ai étudié les coefficients de partage du fluor et du chlore.

Dans cette étude, je présente les premiers coefficients de partage du F et du Cl, entre des liquides de fusions silicatés anhydres et hydratés et des minéraux mantelliques tels que olivine, orthopyroxene, clinopyroxene, plagioclase, grenat ainsi que pargasite et phlogopite. Les valeurs sont issues de 300 mesures dans 24 expériences de fusion, réalisées entre 8 et 25 kbars et, 1180 et 1430°C. Les faibles concentrations en F et Cl dans les minéraux ont été analysés par la sonde ionique Cameca IMF 1280 de WHOI en utilisant le mode d'ions secondaires négatifs.

Les résultats montrent que $D_F^{Opx/melt}$ varient de 0.123 à 0.021 et $D_F^{Cpx/melt}$ de 0.153 à 0.083, tandis que $D_{Cl}^{Opx/melt}$ varient de 0.002 à 0.069 et $D_{Cl}^{Cpx/melt}$ de 0.008 à 0.015. De plus, $D_F^{Ol/melt}$ de 0.116 à 0.005 et $D_{Cl}^{Ol/melt}$ de 0.001 à 0.004; $D_F^{Grt/melt}$ de 0.012 à 0.166 et $D_{Cl}^{Grt/melt}$ de 0.003 à 0.087 avec l'augmentation de la teneur en eau et la diminution de la température dans les expériences. Je montre aussi que le F est compatible dans la phlogopite ($D_F^{Phl/melt} > 1.2$) alors qu'il est incompatible dans la pargasite ($D_F^{Amp/melt}$ de 0.36 à 0.63). A l'inverse, Cl est plus incompatible dans la phlogopite ($D_{Cl}^{Phl/melt}$ en moyenne 0.09 \pm 0.02), que dans la pargasite ($D_{Cl}^{Amp/melt}$ de 0.12 à 0.38).

Cette étude démontre que F et Cl sont substitués dans des sites spécifiques de l'oxygène, ce qui les rend plus sensible que les éléments traces aux variations de chimie des cristaux et de la quantité d'eau, et donc aux conditions de fusion. En utilisant ces nouveaux coefficients de partage, j'ai modellisé la fusion de lithologies potentielles du manteau sub-arc permettant de 1) déterminer la quantité de fluide aqueux impliqué dans la fusion, 2) distinguer la fusion induite par apport de fluides de la fusion d'une source à minéraux hydratés et 3) la fusion d'une lithologie à pargasite de celle à phlogopite, et montre que la source de certains magmas primaires d'arc, par exemple d'Italie, contient de la pargasite et de la phlogopite, tandis d'autres magmas primaires d'arc résultent d'une fusion par apport de fluides.

Mots clés: coefficients de partage, fluor, chlore, éléments traces, expériences de hautes pressions, substitution, zones de subduction, fusion hydratée, modèle de "lattice strain".

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L'aventure continue...

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Preface :

Context : arc magmas genesis in subduction zones

"Subduction zones helped nucleate and grow continents, they fertilize and lubricate the Earth's interior, they are the site of most subaerial volcanism and many major earthquakes, and they yield a large fraction of the earth's precious metals." (J. M. Eiler, Preface of "Inside the Subduction Factory"). Since the beginning of the 20^{th} century, those specific areas of our planet have been the subject of many researches leading to the global understanding that they correspond to convergent plate boundaries, where one of the two tectonic plates (mainly oceanic) dives under another plate (oceanic or continental). Models of subduction zones were built inseparably from "the andesite problem"; that is the question about the origin of the arc lavas.

Arc lavas are compositionally different from mid-oceanic basalt (MORB) or oceanic island basalt (OIB). They are generally calc-alkaline andesites, rich in water and in other volatile elements (i.e. elements likely to fractionate to the gaseous phase as H_2O , CO_2 , S and halogens), emitted during explosive eruptions. Those lavas are also depleted in high field strength elements (HFSE, as Ti, Nb, Ta, Zr or Hf) and enriched in large ion lithophile elements (LILE, as K, Rb, Ba, Sr, U, Pb, Th or Cs) compared to MORB. As well, they are also enriched in light rare earth elements (LREE) compared to heavy rare earth elements (HREE), which induces that their rare earth spectra are more fractionated than MORB ones.

Those characteristics indicate the involvement of a water-rich component, which fractionates mobile from immobile elements into this fluid (e.g. Gill, 1981; Kelemen et al., 1993; Arculus, 1994). This component could come directly or indirectly from the various reactions that the cold and hydrous downgoing plate (slab) undergone when it enters into the mantle: metamorphism, dehydration and sometimes partial melting. When it is released, this component (aqueous fluid from dehydration of the slab or silicate melt from the slab melting) interacts with the overlying mantle. Thus, arc magmas have two sources: the mantle wedge and the hydrous component that causes the melting of the mantle, by lowering the melting temperature of mantle peridotite (Kushiro et al., 1972; Ringwood, 1974; Tatsumi, 1986, 1989; Schmidt and Poli, 1998). Furthermore, this mobile component transfer from the slab to the mantle some elements, that give its chemical characteristic to arc magmas.

Scientific issue

The nature and the composition of this component remains nevertheless little known. Is it a fluid or a melt? Is it from the dehydration/melting of metamorphosed phases from the sediments overlaying the slab or from the slab itself? Its composition can be influenced by 1) its source (Peacock, 1993), 2) partition coefficients between minerals and fluids (Brenan et al., 1995b) and 3) interactions with mantle and forming of hydrous minerals (Ayers et al., 1997).

Answering these questions involves access to the primitive compositions of arc magmas. Recent advances in microanalytical techniques allowed to measured major, trace and volatile elements in melt inclusions (trapped primitive magmas in primitive olivines) from different arcs (e.g. Le Voyer, 2009). It appeared that volatile elements (especially F and Cl, which are the less degassed) retained more information about the arc magma sources than other commonly used trace elements (Le Voyer et al., 2010). Le Voyer et al. (2010) showed the selective enrichment in fluid-mobile elements, such as F and Cl, of the basaltic andesite melt inclusions from the Mount Shasta contained the imprints of two distinct slab-derived components.

The question is now: are F and Cl tracers of source? The answer of this question requires knowing the behavior of F and Cl during melting of the mantle in dry and hydrous conditions. Thus, I needed to experimentally determine F and Cl partition coefficients between mantle minerals as olivine, orthopyroxene, clinopyroxene, plagioclase and garnet and dry basaltic melt and between those same minerals, plus amphibole and phlogopite and hydrous silicate melts, at sub-arc mantle conditions.

I have organized this manuscript so that all chapters will build upon one another in a logical way, detailed in the next sections.

Plan of this thesis

This manuscript is made up of 5 chapters briefly described below:

1) The first chapter is an introduction that presents both preliminary works and current knowledges on subduction zones. It details also why volatile elements, as F and Cl, could better constrain the source of arc magmas and it introduces the use of partition coefficients in crystal-chemical and in geochemical perspectives. 2) The second chapter is methological chapter that describes experimental techniques on pistoncylinders and experimental techniques on several instruments. The focus is made on the recent progress on ion probe that allowed me to measure low abundances of F and Cl in anhydrous minerals, for the first time.

3) The third chapter presents the first data on F and Cl partition coefficients between lherzolite minerals and basaltic melt in the dry system. Its aim is to understand how F and Cl can be incorporated in minerals and how those minerals respond to its incorporation. It is presented under the form of a paper submitted to *Contributions in Mineralogy and Petrology* in December 2010 and accepted in May 2011.

4) The chapter four studies the change of F and Cl partition coefficients in hydrous conditions. We show that water abundance has a strong influence on the change of F and Cl partition coefficients. Moreover, it presents F and Cl partition coefficients between pargasite and hydrous basaltic melt and between phlogopite and hydrous shoshonitic melt. At the end of this chapter, I present a paper in preparation on these data.

5) The chapter five presents how F and Cl can help to discriminate the nature of the component or the mantle lithology involved in the sub-arc melting. Indeed, given that each subduction zone is distinct, differing from some aspects from other subduction zones, I suggest new diagrams that allows to easily distinguish melting by addition of an aqueous component from melting of an amphibolebearing or from phlogopite-bearing mantle lithology, that produced the signatures of melt inclusions. This chapter is presented under the form of an article, but this is not its definitive version.

Chapter 1

Subduction zones: definitions and models for arc magmas genesis

This chapter is composed of two main sections. A first section (pages 2 to 30) exhaustively reports the chronology of the science that brought our knowledge on subduction zones to the point where it stands today. This historical aspect of the scientific approach starts from back in 1915 with the discovery of plate tectonics and tackles every aspect of the geology of subduction zones, including geophysics, geochemistry and tectonics. This section does not introduce my PhD research per se, it gives a more general context to the geodynamic Earth and is a reminder of the chronology of past and present scientific leaps in geology.

A second section (pages 32 to 38) introduces the latest challenges that recent experimental results brought to the issue of the nature of the materials participating to arc magmas genesis. These challenges shed a new light on the need of new tracers to decipher the source and nature of these materials. The motivation for my research begins there. The end of this section (pages 39 to 45) details why I looked into the behavior of two volatile elements F and Cl in subduction zones, using the experimental determination of partition coefficients (theory presented from page 45 to page 51) and melting models (described from page 51).

1.1 Arc lavas

A brief petrological presentation of the lavas of subduction zones is presented: As it is presented on Figure 1.1.1, arc lavas are mostly basaltic to andesitic.



Figure 1.1.1: TAS diagram (total alkali vs. silica) for 1946 analyses from ~ 30 island and continental arcs with an emphasis on the more primitive lavas, compiled by Plank and Langmuir (1988).

Arc lavas belong mainly to the calc-alkali serie (basalt – andesite – dacite – rhyolite) of differenciation, and some lavas of tholeiitic and alkaline series are found in subduction context (see Figure 1.1.2). In comparison with the two other series, calc-alkaline lavas have intermediate alkali and iron contents. Another caracteristic of arc lavas is their high water content, which is often underlined by the presence of hydrous minerals such as amphibole or phlogopite phenocrysts.



Figure 1.1.2: AFM diagram (Alkali, Iron, Magnesium) for 1946 analyses from ~ 30 island and continental arcs with an emphasis on the more primitive lavas, compiled by Plank and Langmuir (1988). Arrows represent differenciation trends. FeO* is the sum of FeO and Fe₂O₃.

1.2 Subduction zone models

1.2.1 A century of thoughts

The concept of "subduction", which is a sinking process of a tectonic plate into the mantle, appeared on geophysics textbooks published after late sixties. From the time of Wegener's continental drift theory (Wegener, 1915) until the period in sixties, the presence of big thrust faults were recognized, but the operation of continuous sinking of a plate were not.

Nevertheless, with the first results of seismology, it was observed that seism epicenters were aligned along vast wrinkled regions like the Pacific belt (e.g. Suess, 1892; Coulomb, 1952; Gutenberg and Richter, 1959, Figure 1.2.1).



Figure 1.2.1: Epicenters of main earthquakes (> 5.5 of magnitude), recorded between 1913 and 1933 from Coulomb (1952).

It was also observed that this seismicity coincided with the repartition of some type of volcanoes, still in the Pacific region and that seismicity could reach focal depths of 700 km. However, this deep seismicity was linked to deep fractures in the terrestrial crust. To explain the deep earthquakes, controversial hypotheses were suggested, like the extension of the lower crust down to 700 km deep (Wadati, 1935; Benioff, 1955, Figure 1.2.2).

In the same time, other scientists (Turner and Verhoogen, 1951; Gutenberg and Richter, 1959), pointed out that this "Pacific structure", paralleled to volcanic chains, can be related to a specific kind of eruptive magma predominantly andesitic. The alignment of andesitic volcanoes, called the "andesite line" (Born, 1933) or "Marshall line", was opposed to submarine seismicity region linked to the basaltic "Atlantic Structure".



Figure 1.2.2: Generalized oceanic and continental sections with orogenic fault types after Benioff (1954). Surface relief is exaggerated.

In the late fifties and the early sixties, significant improvements in petrology proved that basalts were primary magmas generated in the mantle and that fractional crystallization caused the evolution of parental magma composition. Experimental petrology from this period already showed that addition of water and other volatile components in basalt sample lowered temperatures of complete melting (Yoder and Tilley, 1962; Kuno, 1967). Furthermore, Kuno and others (Kuno et al., 1957; Kuno, 1959, 1960) and Kushiro and Kuno (1963) stated that the difference of primary magma compositions originates from difference of pressure under which the melting takes place. They concluded primary magmas as tholeiite (of Hawaii) and alkali olivine basalt (of Japan) are generated, at shallower and deeper levels in the mantle, respectively. On the other hand, Yoder and Tilley (1962), referring to experiments on relevant systems, pointed out that tholeiite and olivine tholeiite magmas cannot produce alkali olivine basalt magma, or vice versa, by fractionation under low pressure.

Focusing their interest on volcanoes of the Japanese Islands, Korea and Manchuria, Kuno and others described three series of primary basalt. Today, these corresponds to the three magmatic series (found in the fore arc, volcanic arc and back arc): the tholeiite magma, the high-alumina basalt magma and the alkali olivine basalt magmas and their magmas associated through differentiation (andesite, dacite, trachyte...), as illustrating on Figure 1.2.3.



Figure 1.2.3: Alkali-silica relations of tholeiite series(\bullet)(basalt, andesite, dacite and rhyolite; high-alumina basalt series (+)(basalt, andesite, dacite); alkali rock series (\circ)(basalt, mugearite, trachyandesite, trachyte and alkali rhyolite), occurring along a traverse zone from the Izu Islands, passing through central Honshyu; to the Japan Sea region including Korea and Manchuria (from Kuno, 1967).

Thus, from the Pacific coast to the Korea and Machuria, they observed a continuous variation from silica oversaturated tholeiite magmas to alkali olivine basalt magmas. The average depths of earthquakes foci in the mantle underneath the Japanese Islands and adjacent areas from Sugimura (1959) are aligned with this distribution of basalt magmas (Kuno, 1967). Tholeiite, high-alumina basalt and alkali olivine basalt magmas are therefore generated at successively greater depths (Figure 1.2.4).

This was the first model of arc magma genesis, Figure 1.2.4, even before the term "subduction" appeared. At that time, it was opposed to the vision of Yoder and Tilley (1962), who assumed that magmas were generated at a comparatively uniform depth, of 100 to 150 km (Figure 1.2.5).



Figure 1.2.4: Sections across the circum-Pacific belt and Japan showing the depths of generation of basaltic magmas according to Kuno (1967).



Figure 1.2.5: Sections across the circum-Pacific belt and Japan showing the depths of generation of basalt magmas according to Yoder and Tilley (1962), redrawn from Kuno (1967).

The concept of ocean spreading and oceanic crust formation was demonstrated in the early sixties (Dietz, 1961; Hess, 1962) and recognized by the scientific community. Since the idea of an "expanding Earth" (see Carey, 1975) was dropped, the principles of crust recycling had to be advanced. If the Earth's crust was expanding along the oceanic ridges, it must be shrinking elsewhere. Hess suggested that new oceanic crust continuously spreads away from the ridges in a conveyor belt-like motion. Many millions of years later, the oceanic crust eventually descends into the oceanic trenches-very deep, narrow canyons along the rim of the Pacific Ocean basin. According to Hess, the Atlantic Ocean was expanding while the Pacific Ocean was shrinking.

From seventies, subduction concept was well established. New results in geophysics, especially highresolution seismology, allowed to better constrain strengths, speeds, slab volume or slope...in subduction zones. Though, subducted slabs are delineated by their seismicity, they also influence the travel times and paths taken by seismic waves from the earthquake source to the seismic station that records their arrival. An early discovery in the plate tectonic paradigm was that slabs affect travel times (Davies and McKenzie, 1969). Later, the alternative seismic-wave paths accounting for slabs (Mitronovas and Isacks, 1971) were recognized and were related to the material properties of subducting lithosphere (Sleep, 1971). However, the seismic wave anomalies due to slabs were ultimately appreciated for the information they bore concerning slab mineralogy (Solomon and U, 1975). For the first time, detailed studies of slab wave speeds concluded that the slab of subducted lithosphere differs in temperature, bulk composition and detailed mineralogy from the mantle. Furthermore, the up-dip travel times observed by Suyehiro and Sacks (1979) in the upper 350 km of the slab led them to propose a two-layer slab model with an upper layer 40 – 50 km thick. In parallel, mineralogy of ultrahigh-pressure metamorphic terrains, having recorded depths down to 100 km, were described and, combined with experimental petrology (e.g. Pawley and Holloway, 1993; Schmidt and Poli, 1998), it allowed the description of constituent mineralogy, the metamorphism and some dehydration processes of the subducting crust (see e.g. Peacock, 1993; Peacock et al., 1994; Ulmer and Trommsdorff, 1995; Peacock, 1996). It was then proposed that dehydration reactions can produce deep intraslab earthquakes (e.g. Savage, 1969; Kirby, 1995; Silver et al., 1995; Kirby et al., 1996; Stein and Stein, 1996).

Since then, subduction zone models are closed to that shown in Figure 1.2.6.



Figure 1.2.6: Petrologic model of a mature subduction zone after Peacock (1996). (A) Mineralogical changes in subducting oceanic crust. Large amounts of H_2O are released by continuous dehydration reactions that occur in subducting oceanic crust during blueschist \rightarrow eclogite facies metamorphism. Proposed mineralogy of the subducting slabs shown in boxes; hydrous minerals are marked by asterisks. (B) Mineralogic changes in mantle wedge, proposed by Peacock (1996). Integrated over time, H_2O released from the subducting oceanic crust causes extensive hydration of the mantle wedge at shallow depths and adjacent to the subducting slab. Possible hydrous minerals stable at different depths are shown in boxes. Water-rich fluids that infiltrate the core of the convecting wedge may trigger partial melting (see next section 1.2.2 for details).

1.2.2 Controversies about arc magma genesis

The following reservoirs, which were proposed over several decades, can contribute to arc magma genesis:

- the mantle wedge.
- the subducted oceanic lithosphere, made of mafic lithology (like the altered oceanic crust, AOC) and sediments. It can contribute to arc magma genesis by slab flux, fluids from slab dehydration or melts from slab melting.
- the continental or oceanic crust, above the mantle wedge.

First petrological model and melting of the upper mantle

It was considered, during the sixties, that basalt magma could form either by complete or nearly complete melting of an eclogite source or by partial melting of a wide variety of ultrabasic rocks other than the pure olivine dunite rock (Yoder and Tilley, 1962; Kushiro and Kuno, 1963). It was thus a problem to explain the various chemical composition of basalt magma. Several factors were suggested to explain this variety: the composition of the source rock , the temperature and pressure conditions at the source, and the history of fractional crystallization as the magma rises directly or not towards the Earth's surface. It was usually assumed that the upper mantle has a uniform composition, and that the other two factors caused the main variation in magma composition. Kuno (1967) took the view that the depth of formation controls the silica saturation of the magma, alkali basalt magma forming between about 200 and 400 km depth and tholeiite forming at shallower depth (Figure 1.2.4). On the other hand, Yoder and Tilley (1962) considered that the primary magma has a picrite basalt composition and the two other types are derived from it through processes of fractional crystallization (Figure 1.2.5).

Nevertheless, the observation of olivine, peridotite, serpentine nodules, found in basalt led people to reconsider the heterogeneity of the upper mantle (Green and Ringwood, 1963; Kuno, 1967). Green and Ringwood (1963) found that pyrolite can crystallize in four different mineral assemblages (amphibolite, plagioclase pyrolite, pyroxene pyrolite, garnet pyrolite) under conditions of temperature, pressure and water-vapour pressure that may occur in the upper mantle. In order to explain low seismic velocity layers, Clark and Ringwood (1964) considered that the primitive pyrolite has differentiated beneath continent, leaving a residual layer of dunite with eclogite pockets (Figure 1.2.7).

The experimental study of Green and Ringwood (1968) on partial melting fields of synthetic high-alumina olivine tholeiite, high-alumina quartz tholeiite, basaltic andesite, andesite, dacite and rhyodacite under dry and wet conditions suggested that the calc-alkaline series may be derived by the



Figure 1.2.7: Petrological model of the upper mantle. Modified after a figure in Clark and Ringwood (1964), from Bott (1971).

partial melting of amphibolite at lower crustal depths under wet conditions, or by the fractional crystallization of a hydrous magma at a similar depths. They suggested two complementary hypotheses, each composed of a two stage igneous process.

- In the first stage, large piles of dry basalt are extruded on the Earth's surface. Under dry conditions and if the magmatic activity stops: the pile of basalt transforms to quartz eclogite, sinks into the mantle and finally undergo partial melting at 100 150 kms depths. This partial melting gives rise to the calc-alkaline magma series leaving a residuum of of clinopyroxene and garnet.
- In the first stage, under wet conditions (produced by the introduction of hydrous rocks in the mantle), piles of basalt are also extruded on the Earth's surface but this basalt is wet. In that case, if the geotherm remains high (because of a constant magmatic activity), partial melting of the basalt may take place near the base of the pile (10 kbars). The formed liquids constitute the calc-alkaline suite and the residual mineralogy is amphibole, pyroxenes and possibly minor garnet and calcic plagioclase.

Petrological model and melting of the subducted oceanic lithosphere

With more results in experimental petrology, it was shown in the late sixties – early seventies, that silica-oversaturated (andesitic) magmas may be produced by partial melting of peridotitic upper mantle under hydrous conditions to depths approaching 100 km (Kushiro et al., 1968; Kushiro, 1969, 1970; Kushiro et al., 1972). The experiments of Nicholls and Ringwood (1972, 1973) demonstrated that silica-saturated tholeiite (even at normative quartz) and olivine tholeiite at high water pressures

can be produced by partial melting of hydrous mantle peridotite at depths of about 70 km -100 km. However, this production is unlikely since the maximum depth at which such liquids may be in equilibrium with olivine (approximately 20 km) represents a crustal rather than a mantle level in many island arcs.

For Nicholls and Ringwood (1972), the combination of the increasing temperature and pressure causes continuous dehydration of water-bearing minerals (such as amphibole, epidote, serpentine, talc, and at greater depths, high-pressure hydroxylated silicates), over a broad depth interval. They proposed that released water creates a viscosity reduction and thus, gravitational instabilites into the overlying mantle. This causes diapirs of hydrous peridotite that undergo partial melting as they raise to a lower depth, and produce silica-oversaturated tholeiitic magmas. Only after their segregation at depths of about 70 km, silica-saturated magmas and quartz tholeiite magmas will fractionate at lower pressures, first crystallizing olivine, then with decreasing temperature and pressure, clinopyroxene, amphibole and plagioclase. The products of this fractionation will be basaltic andesite, andesite and dacites (Green and Ringwood, 1968).

Nicholls and Ringwood (1973) completed their model by taking an interest in the fate of the downgoing oceanic crust and chose an other explanation than fractional crystallization for andesitic melt genesis. At depth of about 100 km, after amphibole destabilisation, the oceanic plate turns into quartz eclogite. The remaining hydrous minerals (serpentine, talc and high-pressure hydroxylated silicates) release their water between 100 and 150 km. When the temperature of the Benioff zone exceeds the quartz eclogite solidus, the downgoing plate melts and produces silica-rich calc-alkali melts (SiO₂ > 65 wt%). Contrary to Green and Ringwood (1968) who proposed a direct rise of acid magmas up to the surface, Nicholls and Ringwood (1973) propounded the idea that calc-alkali melts mostly react with the mantle wedge to form garnet pyroxenites, which inherite some of the geochemical caracteristic of the silicate melts. The last stage of their model is the rise of those garnet pyroxenite in form of diapirs throught the surface and their partial melting to produce andesitic calc-alkali melts.

Wyllie and Sekine (1982) proposed a more complex model for arc magma genesis. In their model (Figure 1.2.8), the slab hydrous fluids originating from the slab dehydration between 70 and 100 km depth (D to E) are too cold to trigger partial melting of the overlying mantle, but the fluids cause the partial melting of the mantle at the root of the crust, through their rise to the surface (black zone above the Moho, Figure 1.2.8). In the M zone, Figure 1.2.8, Wyllie and Sekine (1982) suggested that the slab melting produces hydrous silicate melts, as proposed by Nicholls and Ringwood (1973). Those melts that react with the mantle peridotite (H) creates a layer of phlogopite-pyroxenite. Moving upwards to warmer zones, slab fluids released by hydrous mineral breakdown and the solidification of the phlogopite-pyroxenite layer, causes partial melting of the mantle peridotite (N). The melts hereby

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produced correspond to the calc-alkali magmas of the volcanic front of subduction zones. The remaining phlogopite-pyroxenite layer is dragged downwards by convection. When it reaches appropriate thermal conditions, it melts (R) and generates the undersaturated alkali magmas of the back-arc. To explain the enrichment in potassium of continental intraplate lavas, Wyllie and Sekine (1982) proposed that some phlogopite-pyroxenite diapirs rise through the mantle wedge and are stopped at the density of the root of the continental lithosphere. It provides the source of K for later intraplate magmatism.



Figure 1.2.8: Idealized petrological cross-section through oceanic lithosphere from Wyllie and Sekine (1982), for specific thermal structure with isotherms dominated by cooling of oceanic crust by endothermal dehydration reactions, and warming of mantle wedge by induced convection.

Hydrous phases in the mantle wedge

Several studies showed that the depth of the seismic zone or depth of upper surface of the subducted slab beneath a volcanic front is quite constant (as Isacks and Barazangi, 1977, or reviewed in Gill, 1981). This led Tatsumi et al. to propose that the production of melts is more from a pressure-dependent reaction than a temperature-dependent phenomena, and corresponds to the distribution of the solidus temperature of hydrous peridotite just beneath a volcanic front (Tatsumi, 1986; Tatsumi et al., 1986; Tatsumi, 1989).

All of these studies suggested that the main hydrous phases in the oceanic crust metabasalt are amphibole, epidote and chlorite, which release their water, during the metabasalt metamorphose into amphibolite and then eclogite:

$$Chlorite + \left\{ \begin{array}{c} albite \\ actinolite \\ epidote \end{array} \right\} \rightarrow hornblende + H_2O.$$

 $hornblende \rightarrow garnet + clinopyroxene + H_2O.$

Thereby, the termination of dehydration in a subducted basalt layer is defined by the stability limit of hornblende which occurs around 2.0 - 2.5 GPa in a basalt system. The released water seeps into the overlying mantle, beneath the fore arc region (Figures 1.2.9 and 1.2.10). Following those authors, all hydrous phases in the slab break down before 100 km depth, thus beneath the volcanic arc the subducted oceanic arc is completly anhydrous. During their percolation, fluids react with mantle minerals, following reactions that allows the formation of hydrous peridotite layer (Figure 1.2.9). As the hydrated peridotite is dragged downward with the slab towards higher pressures and temperatures (P - T) region, hydrous mineral assemblages in the peridotite may change according to the following reactions:

$$serpentine \rightarrow olivine + talc + H_2O$$

 $talc + olivine \rightarrow orthopyroxene + H_2O$
 $chlorite + orthopyroxene \rightarrow olivine + garnet + H_2O$
 $amphibole \rightarrow clinopyroxene + garnet + H_2O$

 $phlogopite + orthopyroxene + clinopyroxene \rightarrow$

 $amphibole - like phase + garnet + olivine + K_2O + H_2O.$

Amphibole and chlorite in the dragged hydrated peridotite decompose by pressure- dependent reactions, and the pressure of decomposition is nearly equivalent to the depth at the base of the mantle wedge beneath the volcanic front (about 110 km). The variable depth of the slab beneath a volcanic front (112 \pm 19 km, Tatsumi, 1986) may partially result from differences in the temperature distribution at the base of the mantle wedge in each arc-trench system.



Figure 1.2.9: Hydrous mineral assemblages in the dragged hydrated peridotite layer at the base of the mantle wedge, (after Tatsumi, 1989). SP, serpentine; AM, amphibole; CHL, chlorine; PH, phlogopite; TA, talc. The subducted lithosphere can supply H_2O to the mantle wedge at pressures less than 2.5 GPa as shown by the solid arrows. Serpentine and talc in the dragged hydrated peridotite decompose through temperature-dependent reactions at 600°C and 700°C, respectively. Through the dehydration of serpentine, which is a major hydrous phase in the hydrated peridotite at temperatures below 600°C, a large amount of H_2O must be released. This follows the formation of a hydrous column composed of talc + amphibole + chlorite + phlogopite in the mantle wedge.

When amphibole and chlorite in the dragged hydrated peridotite break down, subduction components held in amphibole and chlorite are then released with H₂O, although part of them (especially K_2O) may be fixed in phlogopite and transported to deeper levels. Beneath the back arc region, the phlogopite in the dragged hydrated peridotite breaks down and releases its water. When the front of H₂O migration from the hydrated peridotite reaches the region with the solidus temperature of hydrous peridotite, partial melting takes place to produce initial magmas (Figure 1.2.10). Successive addition of H₂O to the region expands the partially molten zone upwards and the degree of partial melting increases upwards. From the top of the partially molten zone a mantle diapir starts rising. The mantle diapirs must go through regions with temperatures higher than 1400°C and stop rising to release primary magmas. The depth of magma segregation from a mantle diapir is deeper in the back arc side of a volcanic arc. Beneath the fore arc region, it should be stressed that the solidus temperature of hydrous peridotite (1000°C at depths shallower than 100 km) cannot be reached in a normal subduction zone. It follows that no magma can be produced by partial melting of a hydrous column beneath the fore arc region.



Figure 1.2.10: Model for the migration of H_2O and the generation of basalt magmas in a subduction zone (after Tatsumi, 1989). The hydrated peridotite is formed by the addition of slab-derived mantle H_2O (solid arrows) beneath the forearc region and should be dragged downward with the slab by the subduction of the oceanic lithosphere. Amphibole (AM) and chlorite (CHL) in the dragged hydrated peridotite layer decompose to release H_2O at around 110 km just beneath the volcanic front, and phlogopite (PH) decomposes beneath the back arc side of the volcanic arc.

With this model, partial melting occurs at two different depths beneath the volcanic arc. At the surface, it corresponds to two volcanic chains, parallel to the trench, as observed in numerous island and continental arcs.

In this model, Tatsumi and others (Tatsumi, 1986; Tatsumi et al., 1986; Tatsumi, 1989) did not develop mechanisms of fluid migration and amphibole formation, their model seemed pretty robust to explain the discrete distribution of arc volcanoes, with their subdivision into a front arc, a volcanic arc and a back arc. Nevertheless, several studies (e.g. Pawley and Holloway, 1993; Schmidt and Poli, 1998) have tempted to demonstrated that the subducted oceanic lithosphere dehydrates progressively and continuously down to 250 km depth.

The hydrous flux melting

It turned out that partial melting of peridotite in subduction zones is initiated by an influx of volatiles from the subducted lithosphere. However, contemporary to the Tatsumi model, another much simpler model appeared based on experiments at elevated H₂O pressure. It demonstrated (Grove et al., 1982) that fractional crystallization at $pH_2O > 1$ kbar allows liquids to evolve to compositions that can follow the calc-alkalic trend, if the liquids are moved to a shallow reservoir and allowed to crystallize further under low pressure conditions. Experimental studies (Grove et al., 1982; Grove and Baker, 1983) showed that fractionation assisted by assimilation and magma mixing of basalt and rhyolite also produced compositions that are andesitic and that can fractionate during calc-alkalic differentiation. This idea of simple melting by hydrous flux does not require any hydrous mineral melting or decomposition in the mantle wedge.

Later, Sisson and Layne (1993); Sisson and Grove (1993a); Gaetani et al. (1993) demonstrated that the dissolved H₂O in basaltic melts, so called magmatic H₂O, promotes the development of the calcalkaline differentiation. They found that many aspects of the calc-alkaline differentiation series can be explained if arc basalt or basaltic andesite magmas contain approximately 4 - 6 wt% of H₂O.



Figure 1.2.11: Summary of processes of melt generation and subsequent modification of hydrous magmas produced in the mantle wedge (after Gaetani et al., 2003). An H₂O-rich component ascends into the overlying mantle wedge, where it is modified by reaction with the descending mantle (SiO₂ is stripped from the H₂O-rich component). The modified H₂O-rich component ascends into shallower, hotter part of the mantle wedge by flux melting. As the melt continues its ascent into the cooler shallowest part of the mantle wedge, it becomes SiO₂-rich by dissolving orthopyroxene and precipitating olivine. Finally the magma reaches the overlying crust where assimilation of deep and shallow crust, fractional crystallization, and magma mixing operate to modify most subduction zone magmas.
This model is still currently relevant. Recent studies (Gaetani et al., 2003) reviewed the experimentally determined phase relations for primitive arc lavas and proposed several alternative mechanisms for melt generation in the sub-arc mantle. They concluded that cool, H_2O -rich partial melt generated near the base of the mantle wedge percolates upward through an inverted thermal gradient, assimilating peridotite as it ascends (Figure 1.2.11). This idea is called hydrous flux melting. Nevertheless, it was also suggested that anhydrous adiabatic decompression melting may also occur in many sub-arc environments, to explain near-anhydrous conditions of some melts (e.g. Shasta's melt inclusions are nearly anhydrous, Le Voyer et al., 2010, alkali olivine basalt (AOB) and olivine tholeiite basalt (OTB) from the Northeastern Japan arc, Tatsumi et al., 1983).

A more recent study of Grove et al. (2006) revisited the hydrous flux melting model using new published thermal structure of the mantle wedge (see section 1.2.3), in order to know the melting behavior of the mantle in the presence of an excess H_2O content. They calculated the vertical melting paths from 108 to 55 km above the slab interface. This depth range corresponds to the vapor-saturated melting depths. In this study, they have shown that chlorite is stable and abundant (16 wt% in a near-solidus peridotite assemblage) above the slab at model's P-T conditions, and could hold ~ 2 wt% H₂O. Assuming the melting a chlorite-bearing hydrated mantle above the slab, they modeled the production of a H_2O -rich melt (from 28 wt% at 108 km depth to 20 wt% at 60 km) at the base of the melting region and at low melting rate (2.5 to 5 %). While initial pressure of melting decreases, H_2O content in the melt drops down to 3 to 5 wt% and melt fraction increases (10 - 15 wt%) towards the hotter center of the mantle wedge, ranging from 40 to 63 km depth. Above the hot core of the overlying wedge, the melting occurs at lower temperatures and produces lower melt fraction with higher H_2O contents. Considering that H_2O -rich melt, passing through the hot core to the vaporsaturated solidus area, reacts further with the mantle by converting olivine to orthopyroxene (Grove et al., 2002) and leads to an increase of melt H_2O content. Alternatively, they suggested that melts might ascend as diapirs further causing adiabatic melting processes after pooling and coalescence.

The adakites exception

Since the late seventies, the discovery of arc lavas different from the calc-alkaline series led to the definition of a new magmatism: named adakitic magmatism, by Defant and Drummond (1990) in reference to the first discovery of those lavas on the Adak island (Aleutian, Kay, 1978). Those lavas were later found in the southern Chile (Martin, 1987) and around the Pacific belt (see the review of Defant and Kepezhinskas, 2001). As originally defined (Defant and Drummond, 1990; Maury et al., 1996; Martin, 1999), adakites form suites of intermediate to felsic rocks whose compositions range from hornblende-andesite to dacite and rhyolite; basaltic members are lacking. Martin et al. (2005)

refined the definition, the adakitic lavas differ from the calc-alkaline serie by their high SiO₂ content (> 56 wt%), high Na₂O content (3.5 wt% \leq Na₂O \leq 7.5 wt%), and correlated low K₂O/Na₂O (~ 0.42). Their Fe₂O₃+MgO+MnO+TiO₂ contents are moderately high (~ 7 wt%), with high Mg# (~ 0.51) and high Ni and Cr contents (24 and 36 ppm, respectively). Those lavas do not follow the calc-alkaline trend but the trondhjemitic differentiation trend (Figure 1.2.12).

Noticing that adakites occurrence was in the fore arc that corresponds to 70 - 80 km depth, Defant



Figure 1.2.12: K – Na – Ca triangle (Barker and Arth, 1976) showing adakites plotting on a trondhjemitic differentiation trend (Td) with no affinity for the classical calc-alkaline trend (CA) (after Martin et al., 2005).

and Drummond (1990) assumed adakites arise from the partial melting of a hot and young (< 25 Ma) basaltic oceanic crust, around the depth of 60 to 80 km (2 – 2.5 GPa). Several experiment series (Rapp et al., 1991; Sen and Dunn, 1994; Rapp and Watson, 1995) demonstrated that partial melting (10 to 40 %) of metamophized basalt that had undergone some metamorphism in the amphibolite to eclogite facies, produces silicate melts with major and trace element composition similar to the adakite composition (except lower MgO, Cr and Ni than adakites).

Nevertheless, the thermal model of subduction zones of Peacock et al. (1994) limited the possibility of slab melting (i.e. adakite formation) to 3 conditions:

- 1. fast or slanted subduction that causes high shear stress between plates
- 2. very young (< 5 10 Ma) and abnormaly hot oceanic crust
- 3. first stages of the subduction of a mature and cold subduction.

In fact, adakitic series were described in an old and cold subduction zone. Furthermore, results of experimental work have been interpreted in different ways. Petford and Atherton (1996) suggested adakites arise from the partial melting of basalt, underplated at the base of the continental crust. Others suggested that they arise from the cristallization of an amphibole and garnet cumulate (Prouteau

and Scaillet, 2003; Macpherson et al., 2006). This model was reinforced by experimental results of the crystallization of hydrous basalts and magnesian andesites at 1.2 GPa and 1030 - 1230 °C (Müntener et al., 2001).

The sediment contribution

For most of the subduction zones, the sediment, arriving into the trenches is composed of 76% of terrigenous materials, 7% of calcium carbonate and 17% of hydrous minerals (Plank and Langmuir, 1998). The thickness ranges from 50 - 500 m to several kilometers (Plank and Langmuir, 1998). The sediment contribution, during the dehydration and/or the partial melting of the slab, depends on the thickness of the sediment and on the erosion caused by the subduction. Generally, the sediment contribution is clearly smaller than that of the altered crust of metabasalts. Shimoda et al. (1998) estimated to few percents the sediment contribution in the silicate melt resulting from the partial melting of the subducted oceanic crust, under the Setouchi volcanic arc (Japan). Similarly, results of Sano et al. (2001) from the Japanese volcanic arc indicated that the metasomatic agent in the mantle wedge was composed of only 10% of fluids coming from sediments.

Summary

The current "standard" model for arc magmatism, which is derived from all those suggestions, is described as follows: infiltration of aqueous fluids into the hot region of the mantle wedge radically lowers its solidus and drives partial melting to produce hydrous basalt. This basalt ascends into the over-riding plate, where it differentiates to variable degrees, mixes with both crustal melts and differentiation products of earlier generations of basalt, and produces a characteristic spectrum of intrusive and extrusive igneous rocks, including abundant andesites. The remaining critical point is the origin of this water: is it directly slab-derived (one stage origin) or is it derived from the breakdown and melting of hydrous minerals, previously form by slab-derived fluids (two step origin)? Furthermore, the existence of "exotic lavas", such as adakites, reminds us that this model cannot be applied for all subduction zones. Slab melting was proposed to explain the presence of adakites, which implies different thermal structure than commonly considered in classical subduction zones.

1.2.3 Constraints brought by the thermal structure of the mantle wedge

As it was suggested by the previous discussion, arc magma genesis depends on the thermal structure of subduction zones. For example, the location of melt production is controlled by the specific position of isotherms with respect to the wet solidus of peridotite.

We know that subducting slabs are cool since oceanic lithosphere, the cold upper boundary layer of

Earth's internal convection, descends into the mantle more rapidly than heat conduction warms the slab (Peacock, 2003). Nevertheless, despite subducting slabs being cool compared to the surrounding mantle, almost all subduction zones are distinguished by active arc volcanism, which requires that rocks melt somewhere in the subduction zone system. Early thermal models of subduction zones assumed a priori that arc magmas were derived from direct melts of the subducting slab and these models incorporated high rates of shear heating along the slab-mantle interface in order to supply the required heat (e.g. Oxburgh and Turcotte, 1970; Turcotte and Schubert, 1973). Overtime, this view has evolved and most arc magmas are now thought to represent partial melts of the mantle wedge induced by infiltration of aqueous fluids derived from subducting slab (e.g. Gill, 1981; Hawkesworth et al., 1993). Current thermal models of subduction zones call upon lower rates of shear heating and predict that slab melting only occurs in unusually warm subduction zones characterized by young incoming lithosphere and slow convergence (Peacock et al., 1994).

Studies have identified a number of important parameters that control the thermal structure of a subduction zone (Figure 1.2.13) including: (1) convergence rate, (2) thermal structure of the incoming lithosphere, which is primarily a function of lithospheric age but is also affected by hydrothermal cooling and the thickness of the insulating sediments, (3) geometry of the subducting slab, (4) rate and shear heating (= shear stress \times convergent rate), and (5) vigor and geometry of flow in the mantle wedge (by Peacock, 1996). The first three parameters are relatively well constrained whereas the rate of shear heating and mantle wedge flow are considerably uncertain (Peacock, 2003).



Figure 1.2.13: After Peacock (2003), important parameters which govern the thermal structure of a subduction zone. Red and blue corresponds to hotter and colder regions, respectively.

The thermal structure of subduction zones has been investigated using (1) analytical approximations including various assumptions on the coupling between the subducted crust and the overlying mantle and about the convection in the mantle wedge (e.g. Molnar and England, 1990, 1995; Davies,

1999), (2) purely plate-driven models with uniform viscosity, in which thermal regime is calculated numerically using analytical expressions for the corner flow in the mantle wedge, with parameters including the thickness of the arc "lithosphere" and the depth of coupling between subducting crust and overlying mantle (e.g. Peacock, 1990a,b, 1991; Pearce et al., 1992; Peacock et al., 1994; Ponko and Peacock, 1995; Peacock, 1996; Iwamori, 1997; Peacock and Wang, 1999; Peacock and Hyndman, 1999; Peacock, 2003), and (3) dynamic models in which the mantle flow field as well as the thermal regime are calculated numerically, with parameters such as thermal buoyancy, chemical buoyancy and mantle viscosity (e.g. Davies and Stevenson, 1992; Furukawa, 1993a,b; Kincaid and Sacks, 1997; Furukawa and Tatsumi, 1999; van Keken et al., 2002). These models differ in many respects, but most agree that subduction of a more than 20 million years old oceanic crust, at down-dip rates greater than 20 km/Myr, will not produce temperatures that are high enough to allow fluid-saturated melting of sediments or basalt, above the subducting plate. However, a variety of geochemical and petrological results suggest that partial melting of subducted sediments and/or basalt is common in many arcs (e.g. Kelemen et al., 2003b). Furthermore, water-undersaturated melting at mantle wedge conditions, proved for instance by Tatsumi et al. (1983), requires temperatures higher than 1400°C between 11 and 23 kbars, which is significantly hotter than predicted by the modeled thermal structures using (1) and (2). This discrepancy between petrological observation and geophysical modeling was solved by a model that takes account of the strongly temperature dependant viscosity of the mantle, firstly suggested by Furukawa (1993a,b). Nevertheless, this reconciliation between Tatsumi et al.'s petrological observations and mantle wedge thermal structure was disregarded...The discrepancy between petrological observation and geophysical modelling led to new modelings presented in the following paragraphs.

Some models by Conder et al. (2002); Kelemen et al. (2003b) incorporate only temperature-dependent viscosity. The Kelemen et al.'s model relax also slab-mantle coupling (Kelemen et al., 2003b) . A model by van Keken et al. (2002) incorporates both temperature- and stress-dependent viscosity. All those models show that cooling of material in the mantle wedge causes this material to adhere to the subducting plate, advectively removing part of the thermal boundary layer in the wedge corner. Also, when the asthenospheric viscosity is sufficiently low ($\sim 10^{17}$ Pa.s), a density current carries relatively cold, dense material downward along the slab, further thinning the thermal boundary layer. Entrainment of cold, viscous material with the subducting plate, and convective flow, both drives and enhance return flow of hot material diagonally upward into the wedge corner. The combination of the thinning of the thermal boundary layers and the enhancement of the return flow, raise the temperature at the top of the subducting plate above the fluid-saturated solidus for metabasalt and metasediment. This thinning appears for both : a rigid "lithosphere" layer with a prescribed thickness (Conder et al., 2002; van Keken et al., 2002), or a "lithosphere" with adjustable thickness (Kelemen

et al., 2003b, Figure 1.2.14).

Later studies on slab surface temperature have shown that the slab temperature structure: (i) strongly depends on the slab parameter (convergence rate \times age, e.g. Arcay et al., 2007), but also (ii) is sensitive to the mantle wedge dynamics and the interplate decoupling depth. The interplate decoupling depth corresponds to the depth where the mantle above the subducting lithosphere becomes mechanically coupled to the slab and is carried along with it (Furukawa, 1993a). The coupling between plate tectonics and mantle convection leads to further complicated numerical modeling of thermal structure of subduction zones. This coupling depends on (1) the subduction velocity, (2) the mantle wedge rheology and the overlying plate stiffness, (3) the friction coefficient on the interplate interface, and (4) crustal phase transitions. The (1) and (2) can be discussed (Arcay et al., 2007), while (3) and (4) require more knowledge, for example about dehydration reactions inside the subducted crust and they were until now assumed or simplified.

Modeling strategies significantly affect the final calculated temperatures and flow structure, which partly explains why numerical simulations do not predict whether the subducted crust should melt or not. Nevertheless, a recent paper by van Keken et al. (2008) developed a suite of benchmarks to facilitate the comparison of numerical models for the dynamics and thermal structure of subduction zones. They demonstrated that using simplified governing equations of flow in the wedge, i.e. considering only kinematic velocity of the slab and ignoring thermal buoyancy in the wedge, the thinning of thermal boundary layers remains the most critical point. However, they found that the agreement at high resolution between various codes is quite good, but requires a good implementation of the velocity discontinuity along the seismogenic zone and high resolution in the thermal boundary layer.

In summary, recent advances in numerical modeling showed that slab melting is not impossible, even for subduction zone cases not corresponding to Peacock et al. (1994) criteria, which restricts melting of subducted crust to slow subduction of very young oceanic crust. Kelemen et al. (2003b) obtained models hot enough to allow partial melting of subducted sediment and/or basalt, for subduction of 50 Myr old oceanic crust at 60 km/Myr.

Furthermore, petrological modeling on the fluid transfer from the slab to the wedge brings also thermal constraints on the transfer mechanisms of fluid and devolatilization processes, from microstructural studies of ultramafic massifs (e.g. Padrón-Navarta et al., 2010). It allows to determine for instance that fluids are released from the slab and wedge serpentinite dehydration between 50 and 150 km depth certainly have to cross the cold (680 - 750 °C) chlorite-harzburgite layer before attaining the hotter inner parts of the mantle wedge.

Another constraints on the thermal structure on the mantle wedge is the heat carried by magma



Figure 1.2.14: Plate from Kelemen et al. (2003b), temperature contours, velocity vectors (in white, scaled to subduction velocity of 60 km/Myr), and flow lines (black) for the upper left-hand corner of the model domain in Kelemen et al. (2003b), Plate 2A, after 20 Myr of subduction (left-hand column) and 100 Myr or more (right-hand column). The μ_{∞} and T_{∞} is the asthenospheric viscosity and temperature, respectively. Q is the activation energy of viscosity and R is the molar gas constant. Temperatures are nearly steady state so that temperature distributions are almost identical in the two different columns. Top of subducting plate is indicated by the straight line to which streamlines of wedge flow converge. (A) $\mu_{\infty} = 10^{21}$ Pa.s and $Q/(RT_{\infty}) = 0$ (isoviscous model) (B) $\mu_{\infty} = 10^{21}$ Pa.s and $Q/(RT_{\infty}) = 20$ (isoviscous model). Note horizontal return flow into wedge for the isoviscous model (top), compared to diagonally ascending flow for temperature-dependent viscosity.

rising from the melting region that can modify the thermal structure of the wedge (England and Katz, 2010). England and Katz (2010) demonstrated that melt transport changes the distribution of temperature and melting, by heating the region immediately above that deflects upwards the dry and wet solidi by > 40% of its depth. Their modeling of heat flows in the wedge shows that dynamics of the wedge mainly controls the systematic in the location of the volcanic arcs.

1.3 Geochemical signature of arc magmas

Arc lavas differ from MORB (Mid-Ocean Ridge Basalts) and OIB (Oceanic Island Basalts), among others, by:

- 1. their hydrous and oxidized nature. Their hydrous nature is expressed by the presence of waterrich minerals (such as micas or amphiboles), and also by the high water-content of their quenched glass, which can reach 10 wt% (Grove et al., 2005). Water content explains the oxidized nature of arc magmas and their mantle source. It was measured in Galunggung, Indonesia and Alaska primitive magmas a variation of the oxidation tracer δ^{34} S (e.g. Métrich and Mandeville, 2010) with water content (Mandeville et al., 2010).
- 2. their calc-alkaline differentiation trend (see section 1.1)
- 3. their trace element spectra, (see next section 1.3.1).
- 4. their enrichment, compared to MORB and OIB, in B and in ¹⁰Be (which is a cosmogenic isotope with a short half-life of 1.5 Myr) principally incorporated into oceanic crust sediments (Morris et al., 1990). High content in those element testifies of the slab sediment layer involvement during arc magmas genesis (e.g. Sano et al., 2001).

1.3.1 Trace element signature of arc magmas

When trace element content are normalized to the primitive mantle (Figure 1.3.1), arc lavas present a different spectrum from MORB or OIB. Compared to MORB, arc lavas have high alkali and alkaline earth element (LILE = Large Ion Lithosphere Elements, K, Rb, Ba, Sr, U, Th, Pb, Cs) and are enriched in light elements (B, Be, Li), in light rare earth elements (LREE, e.g. Perfit et al., 1980) compared to heavy rare earth elements (HREE). Unlike MORB and OIB, arc lavas have negative anomalies in high field strength elements (HFSE; Nb, Ta, Ti, Zr, Hf), which correspond to the current consensus defining an "arc signature".

Using synthetic serpentine, Tatsumi et al. (1986) simulated the oceanic lithosphere dehydration (1.2 GPa and 850°C) and have estimated the composition of released fluid. They measured the mo-



Figure 1.3.1: Spiderdiagram modified from Hoffer et al. (2008), showing trace element characteristic of arc lavas (New-Hebrides, Monzier et al., 1997), OIB (Oceanic Island Basalts; Sun and McDonough, 1989; N-MORB (Normal Mid-Ocean Ridge Basalts, Sun and McDonough, 1989); mean HSA and LSA, (Martin et al., 2005). Normalized to the primitive mantle of Sun and McDonough (1989).

bility of trace elements in the fluid phase, which is closely related to their dissolution rate. Their results showed that the bigger the ionic radius of an element is (e.g. Cs, Rb, K, Ba), the more mobile this element is and easily dissolves into the fluid phase (the distribution coefficient $K_{D_{LILE}}^{mineral/fluid}$ < 1, wherein $K_i^{min/melt}$ is the concentration of element *i* in the mineral divided by the concentration the element *i* in the fluid). On the other hand, HFSE are not mobilized by the aqueous phase $(K_{D_{HFSE}}^{mineral/fluid} > 1)$. Consequently, a fluid selectively enriches the magma source in LILE, or even in LREE but not in HFSE (Tatsumi et al., 1986; Maury et al., 1992).

Following Tatsumi et al. (1986), several authors have investigated the processes in the subducted oceanic crust that can retain HFSE to explain their depletion in arc magmas:

1. Measuring trace element contents in amphibole and mica crystals that are included in arc xenoliths, Ionov and Hofmann (1995) noted that those crystals were systematically enriched in Nb and Ta compared to the primitive mantle. Those minerals have $K_{DHFSE}^{mineral/fluid} > 1$, they incorporate those elements, thus their presence leads to a depletion in Nb and Ta. When fluids rise, they can induce partial melting in hot areas of the mantle, or be consumed during

metasomatic reactions with the peridotite, that will later melt. In both cases, the resulting magmatic melts will be depleted in HFSE.

- 2. The depletion of HSFE, particularly Nb and Ta, in arc lavas has been interpreted as due to the presence of a residual titanate phase (e.g. rutile, sphene, ilmenite, perovskite) in their source region (Saunders et al., 1980; Green, 1981; Morris and Hart, 1983; Brophy and Marsh, 1986). The partition coefficient of Nb and Ta between titanate minerals and melt are assumed to be high $(D_{Nb}^{mineral/melt} = 30;$ Green and Pearson, 1987). The possibility of the presence of residual titanate phase of arc mantle was disproved by several studies (Green and Pearson, 1986; Ryerson and Watson, 1987). In fact, TiO₂ is highly soluble in tholeiitic to midly alkaline basaltic melts which prevents the crystallization of a titanate phase in the sub-arc mantle.
- 3. Since basalt/rutile equilibria did not appear to cause the HFSE anomaly in island arc basalt (IAB), several authors decided to test the possible presence of residual rutile during the slab dehydration. For some authors who measured $K_D^{rutile/fluid}$, the presence of rutile is required to impart the high LILE/HSFE ratio to slab-derived fluids (Ayers and Watson, 1993; Brenan et al., 1994, 1995b). Indeed, $K_D^{rutile/fluid}$ is very high (> 100), while it is < 1 for larger ionic radius elements (Brenan et al., 1994, 1995b). The presence of Ti-rich minerals in aqueous brine fluid inclusions in omphacite of eclogitic veins from the Monviso ophiolite implies that Ti-rich minerals were very soluble in saline fluids at the conditions of metamorphism (Philippot and Selverstone, 1991). Nevertheless, Ayers and Watson (1993) concluded that rutile solubility was highly P - Tdependent, while the scale, the timing and the conditions of transport remain uncertain, as does the composition of the metasomatic fluids in metamorphic natural assemblages. However, more recent studies (Audedat and Keppler, 2005; Tropper and Manning, 2005) found significantly lower rutile solubility in pure H₂O (8 – 26 ppm, Audedat and Keppler, 2005) at P - T conditions similar to those explored by Avers and Watson (1993). Despite some remaining discrepancies that may be explained by different experimental approaches, results indicate low rutile solubility in pure H₂O systems under those P - T. The new study by Rapp et al. (2010) shows that rutile is much more soluble in chloride brines $(2 - 4 \text{ times higher than in pure H}_2O)$ and in fluoride brines $(20 - 100 \text{ times higher than in pure H}_2O)$. Their chosen compositions are closer to complex fluid composition in metamorphic rocks. They also suggest that the possible mechanism that explains the rutile precipitation in metamorphic veins (Philippot and Selverstone, 1991) is fluid equilibration with fluorapatite. The resulting decrease of F in the fluid, consequence of fluorapatite precipitation, suppresses rutile solubility, causing rutile precipitation.
- 4. Following (Ayers and Watson, 1993) and (Foley et al., 2000), HFSE fractionation can occur during slab partial melting, in the presence of residual titanate-phases. Gregoire et al. (2001)

arrived to the same conclusion, analyzing trace elements in secondary minerals formed by interaction of hydrous silicate melt and spinel harzburgite. This finding supports experimental data showing that the mobility of LILE and LREE in hydrous melt under mantle conditions are higher than those of HFSE and HREE, respectively (Tatsumi, 1986; Ayers and Eggler, 1995; Brenan et al., 1995b).

5. The last assumption was proposed by Kelemen et al. (1990, 1993). They suggested that trace element fractionation occurs during interactions between the basaltic melt and the mantle peridotite. They demonstrated that partition coefficient between mantle minerals (in particular olivine, orthopyroxene and spinel) and the basaltic melts are much higher for HFSE, particularly for Ti, than LILE or LREE. In summary, they modeled trace element effects during reaction between small-degree melts of the slab and mantle peridotite. For them and others Gill (1974), slab melts are too rich in LREE and other incompatible elements, to be parental to arc magmas.

The consensus tends to be that the calc-alkaline serie geochemical signature derives from element transfer by a metasomatic agent from the slab to the overlying mantle, before this modified mantle melts.

Concerning adakitic lavas, their signature in trace elements differs from the calc-alkaline serie by their depletion in Y(< 18ppm) and in HREE (e.g. Yb < 1.8 ppm), that give extremelly high La/Yb ratio (≥ 20) and Sr/Y ratio (≥ 40 , see Figure 1.3.1). Despite this particularity, those lavas present similar HFSE depletion and isotopic composition (Sr, Nd, Pb) to those of calc-alkaline lavas (Hoffer et al., 2008). Following Rapp et al. (1991) experiments, the residual assemblages producing adakites is made of amphibole, garnet, or even rutile. Thus, without residual plagioclase that retains Sr and Eu, adakites have high Sr and Eu contents. Moreover, garnet and amphibole retain HREE that leads to the depletion of the melt in those elements. Finally, as previously discussed, amphibole or/and rutile in the residue depletes the melt in Ti and HFSE and creates the negative anomalies, observed on Figure 1.3.1.

Experimental works of Kessel et al. (2005) compares of trace element partition coefficients between aqueous fluid (700 – 900°C, 4 GPa), hydrous melt (1000°C, 4 GPa), supercritical fluid (800 – 1200°C, 6 GPa) and eclogitic minerals. It demonstrates that supercritical liquids exhibit in fact an 'adakite-type pattern', with high LREE/HREE, Sr/HREE and Sr/Y, and with excess Th, through a petrological process different from the melting of metabasaltic or metasedimentary eclogite at moderate pressure. This study also proves that supercritical high-pressure liquids at any temperature can produce excess Th over U, thought to be characteristic of slab melting. Slab component in arc magmas may therefore result from supercritical liquids rather than from relatively shallow melts from sediment source.

To conclude this geochemical discussion, trace elements are considered as source tracers of arc lavas, mainly using HFSE depletion. Over the past years, geochemists distinguished subduction zone flux using the large fractionation between fluid mobile elements (Na, Ba, La) and fluid immobile, so-called, high-field strength elements (HFSE; Nb, Ta, Li). The HFSE depletion compared to fluidmobile element was generally attributed to the precipitation of rutile in the dehydrating subducting crust, assuming rutile remained as a residual phase at the dehydration condition of the slab.

1.3.2 New data on rutile saturation in silicate melts

In order for HSFE to be a viable proxy for subducted oceanic crust in the different mantle sources (like OIB, e.g. Weaver et al., 1987; Weaver, 1991; Baksi, 2001; Prytulak and Elliot, 2007; Jackson et al., 2008), the following criteria must be satisfied:

- 1. The HFSE-enriched phase must remain as a residual phase following dehydration and/or partial melting of subducted lithosphere beneath volcanic arcs so that HFSE are retained and transported in the deep mantle.
- 2. This residual phase must be exhausted during partial melting within the plume, releasing the HFSE and creating a geochemically identifiable signature in OIB. Models for rutile saturation in supercritical aqueous fluids and silicate melts can be used to evaluate whether these criteria are met.

As described in the previous section 1.3.1, some disagreements remain about TiO_2 solubility. Nevertheless, recent studies converge towards the idea that rutile is likely to remain as a residual phase following dehydration because only a small amount of TiO_2 will be removed from the subducted oceanic lithosphere by aqueous fluids, that some calls "supercritical", above the first critical point (374°C and 2.2 kbars), (e.g. Ayers and Watson, 1993; Brenan et al., 1994; Foley et al., 2000; Rudnick et al., 2000).

Partial melts of MORB-type eclogite are expected to be siliceous (~ 65 to 71 wt% SiO₂), peraluminous and to contain high concentrations of Na₂O (~ 5 to 7 wt%) and K₂O (~ 1 to 4 wt%) (Rapp et al., 1991; Rapp and Watson, 1995; Klemme et al., 2002). There are currently two models for rutile saturation in silicate melt, neither of which is suitable for evaluating rutile stability during partial melting of eclogite in subduction zones or mantle plumes (Ryerson and Watson, 1987; Hayden and Watson, 2007). The model of Ryerson and Watson (1987) is poorly calibrated for siliceous melt compositions, and predict TiO₂ solubility for these melts that are too large (Hayden and Watson, 2007). The model of Hayden and Watson (2007) is specifically designed for siliceous melt compositions but is only calibrated at a pressure of 10 kbars. The experimental study of Gaetani et al. (2008) examines the solubility of rutile in silicate melts and presents a model for rutile saturation as function of temperature, pressure up to 35 kbars and melt composition. As it was previously shown by other studies (Dickinson and Hess, 1985; Green and Pearson, 1986; Ryerson and Watson, 1987; Green and Adam, 2002; Xiong et al., 2005; Hayden and Watson, 2007), rutile solubility has been shown to (1) increase with the increasing temperature, (2) decrease with the increasing pressure, and (3) decrease with increasing melt polymerization (Figure 1.3.2). The pressure dependence of rutile saturation is expected to be sensitive to composition due to variations in the average coordination number of Ti⁴⁺ in the melt, and to the increase of the partial molar volume of TiO₂ in silicate melts associated with decreasing coordination number (Gaetani et al., 2008).



Figure 1.3.2: From Gaetani et al. (2008), comparison of (a) temperature and (b) pressure dependence of rutile saturation determined experimentally for the model rhyodacire (shaded circles) and haplobasalt (open circles) base melt compositions with the predictions of the model of Ryerson and Watson (1987) (dashed curves). Also shown are predictions from the rutile saturation model developed in Gaetani et al. (2008) (black curves).

The influence of H_2O dissolved in the melt (from anhydrous to 10 wt% dissolved H_2O) is small on rutile saturation (Hayden and Watson, 2007; Gaetani et al., 2008). Nevertheless, for a given pressure and concentration of TiO₂, the addition of H_2O decreases the rutile-saturation temperature. Gaetani et al. (2008) formulate a new model for rutile saturation that incorporates a more extensive set of experimental results into the calibration than the model of Ryerson and Watson (1987) and take a different approach to accounting the influence of melt composition (see Figure 1.3.2). They therefore calculated that rutile is retained as a residual phase following H_2O -saturated partial melting of eclogite in subduction zones, but that the higher solubility of TiO_2 in siliceous melts, during anhydrous partial melting of eclogite within an upwelling plume causes rutile to be exhausted at moderate extents of partial melting. The calculated concentration of TiO_2 in the melt varies between 747 – 423 ppm, over the range of pressure 20 to 40 kbars and over the range of temperature 691 – 768°C, while in the aqueous fluid, TiO_2 concentration varies from 0.2 to 36 ppm (Figure 1.3.3).



Figure 1.3.3: After Gaetani et al. (2008), comparison of TiO₂ concentration in rutile-saturated 1 % partial melts of a MORB-type eclogite formed along the H₂O-saturated basalt solidus (Lambert and Wyllie, 1972) calculated with Gaetani et al. (2008) equations and with TiO₂ concentrations in rutile-saturated aqueous fluids calculated using the models of Ayers and Watson (1993); Audedat and Keppler (2005); Tropper and Manning (2005). Also shown the TiO₂ concentration of the depleted MORB mantle (DMM) from Workman and Hart (2005).

In any cases, rutile remains as a residual phase in the eclogite and the amount of TiO_2 that will be transferred in the mantle wedge will be small, because of the small quantity of TiO_2 dissolved either in the melt, or in the aqueous fluid. For example, :

- Given Workman and Hart (2005) estimate for the concentration of TiO₂ (1195 ppm) and H₂O (110 ppm) in the depleted MORB mantle (DMM), the addition of 3 wt% of a low-degree eclogite partial melt containing 17.3 wt% H₂O will increase the H₂O concentration in the peridotite to 5309 ppm but decrease the concentration of TiO₂ to 1176 ppm (Gaetani et al., 2008).
- The addition of 0.52 wt% of aqueous fluid containing 13.5 ppm of TiO₂ (average of Ayers and Watson, 1993; Audedat and Keppler, 2005; Tropper and Manning, 2005) increases the concentration of H₂O in the peridotite to 5309 ppm and decreases the concentration of TiO₂ in the DMM from 1195 to 1189 ppm.

Therefore, it is not possible to resolve whether the "subduction component" is a hydrous silicate melt or a supercritical aqueous fluid on the basis of TiO_2 concentration in arc basalts.

1.4 New considerations and recent discussions of arc magma genesis

In deciphering the complex geochemical signatures of arc lavas, there is a general agreement about the involvement of a slab component. Disagreements remain on the nature of this component. Many models of subduction zones have been proposed on the basis of, as described in previous sections, 1) thermal structure of subduction zone and, 2) trace element and/or isotopic signature (see e.g. Brown et al. (1982); Tera et al. (1986); Morris et al. (1990) for ¹⁰Be, Kay et al. (1978); Seyfried et al. (1984); Spivack and Edmond (1987); Miller et al. (1994) for B, Sr and Pb isotopic ratios, among others). Recent experimental data presented above challenged well-accepted ideas:

- "idea of cold and old subduction → arc magma genesis by hydrous slab flux, versus young and hot subduction → arc magma genesis by slab melting". This view is no longer correct, since Kelemen et al. (2003b) and others demonstrated that the slab can melt even in a cold and old subduction setting. The question is now if there is enough water to produced fluid-saturated melting in mantle wedge...for cold and old or young and hot subduction zones.
- the idea that arc magmas involving hydrous slab flux or involving slab melting can be distinguished by the presence or absence of the depletion of HSFE in a spidergram is also incorrect (Gaetani et al., 2008).

Furthermore, other studies (England et al., 2004; Syracuse and Abers, 2006) revealed that the depths of intermediate-depth earthquakes underneath volcanic arc, presumably marking the slabwedge interface, vary systematically between ~ 60 and ~ 173 km and correlate with slab dip and convergence rates. On the other hand, water-rich magmas (over $4 - 6 \text{ wt}\% \text{ H}_2\text{O}$) are found in subduction zones with very different subduction parameters, including those with a shallow-dipping slab (north Japan) or steep-dipping slab (Marianas). From these observations, a recent study of Grove et al. (2009) provides a model where the location of arc volcanoes is controlled by a simple combination of geometric parameters of subduction. Melting in the wedge is induced at the overlapping regions in the wedge that are hotter than the solidus of vapour-saturated peridotite and at depths where hydrous minerals both in the wedge mantle and in the slab break down. Their study also provided an independent constraint on the thermal structure of the mantle wedge. As previously presented, England and Katz (2010) successfully modeled the location of volcanic arcs and demonstrated that it is controlled by the dynamics of the wedge, as heat transport and melt flux, and not by the conditions of concentrated release of fluid taking place at the top of the slab. Following their model, the temperature in the wedge may exceed the anhydrous solidus and allows that melt may also be produced as the result of anhydrous decompression melting of upwelling mantle and also both fluid-induced melting in the wedge.

On the other hand, new tools are available and able to supply new information. For example:

• Cosmogenic ¹⁰Be is highly concentrated in young marine sediment that lead to be an outstanding

tracer of sediment subduction and recycling at convergent margins (e.g. Morris et al., 2002). The ¹⁰Be must be extracted from the downgoing slab and transferred through the mantle and to the surface before the signal decays away (¹⁰Be has a short half-life, 1.5 Myr). This tracer is thus used for fast and young subductions (< 4 - 5 Myr). Moreover, the fraction of the subducted ¹⁰Be flux returned to the surface in arc volcanism will be a function of the portion of the sediment column subducted to depth, and the efficiency with which Be is extracted from the subducted sediment and fed to the arc (¹⁰Be recycling efficiency). Reviewing ¹⁰Be signature in several arc, Morris et al. (2002) noticed that ¹⁰Be/⁹Be was higher in rear-arcs. They proposed different scenarios to explain it:

- A single subduction component is derived from the slab and its addition to the mantle creates amphibole and phlogopite (e.g., Davies and Stevenson, 1992; Tatsumi and Eggins, 1995). Dehydrations of mantle amphibole beneath the volcanic front and of mantle phlogopite beneath the rear-arc produce 2 volcanic chains, with different ¹⁰Be signatures.
- 2. Their preferred scenario is that there is a continuous distillation of elements out of the slab as it continues to subduct to higher pressures and temperatures. With increasing pressure and temperature, mineral solubility in the aqueous supercritical fluid increase and the ability of the fluid to transport a wider spectrum of elements increases (e.g. Ryan et al., 1995). Specifically, the subduction component beneath the volcanic front is a fluid enriched in mobile elements such as B, Cs, U and only sparsely enriched in ¹⁰Be. At greater depths slab surface temperatures are hot enough to melt the sediments, leading to a sediment component that is significantly enriched in ¹⁰Be, as well as Ba, K, and Th (Ryan et al., 1995).
- Radiogenic isotope ratios are also used to decipher subduction zone processes, like for example ²³⁸U/²³²Th, ²³⁰Th/²³²Th, ⁸⁷Sr/⁸⁶Sr and ²²⁶Ra/²³⁰Th (Condomines and Allègre, 1980; Dickins, 2005). For instance, ²³⁸U/²³²Th vs. ²³⁰Th/²³²Th ratios are used to discuss the sources and the melting processes of arc magmas (Condomines and Sigmarsson, 1993). The use of ²³⁸U ²³⁰Th desequilibria allowed Sigmarsson et al. (1998) to distinguish arc magmas generated by fluid-induced melting from those generated by slab melting. Most arc magmas generated by fluid-induced melting, display ²³⁸U enrichments or radioactive equilibrium between ²³⁸U and its radiogenic product ²³⁰Th (McDermott and Hawkesworth, 1991; Condomines and Sigmarsson, 1993). Sigmarsson et al. (1998) found in adakites a uniform excess of ²³⁰Th over ²³⁸U. Because U is more compatible than Th in eclogitic garnet, melting of the eclogitic slab enriches Th in the melt. Over time, Th enrichement leads to the observed ²³⁰Th excess in adakites. The ²³⁰Th excess in adakites. The ²³⁰Th

incompatible elements, those tracers depends on the melting rate of the mantle wedge and on their partition coefficients.

• Recently, the growing data set of arc melt inclusion compositions gave new keys for solving the arc magma genesis puzzle. Melt inclusions are little volume of magma trapped in a mineral. They can be found in volcanic or plutonic rocks, regardless of the nature of the mineral. When they are isolated and randomly distributed, they are considered as primary and are formed during the crystallization of the host mineral. Thus, the volume of magma they contain must be primary compared to lavas. While sampled lava composition on the surface is often a result of crustal processes like magma mixing, fractional crystallization, crustal contamination or degassing during their ascent, melt inclusions preserve the composition of the parental magma. Thus, primary inclusions, which are trapped in magnesian olivine (in equilibrium with mantle conditions), allow to retrieve (1) the primitive magma composition and its genesis condition and, (2) the pre-eruptive content of volatile elements. Furthermore, several studies showed that the compositional variation of inclusions from basaltic olivines is broader than the compositional variation of host lavas composition (Sobolev, 1996; Shimizu, 1998; Saal et al., 1998; Schiano, 2003: Saal et al., 2005). Because the magma trapped in melt inclusion represents a moment of the mantle melting, the variability of recorded composition in melt inclusions reflects (spatial or temporal) heterogeneity of mantle sources and/or on a small scale processes.

Rose et al. (2001) measured in melt inclusions from Mount Shasta, and reported (1) B concentrations much lower than in any other arc lavas reported so far and (2) variable δ^{11} B values. Their measured B concentrations in melt inclusions are similar to those in MORB (Chaussidon and Jambon, 1994), suggesting that the source of these melts is depleted in B. However, B is mostly held in the sedimentary cover or the altered oceanic crust (AOC), but not in the mantle wedge (e.g. Clift et al., 2001). Thus, this hypothesis of fluid-induced melting of the mantle wedge is not consistent with the observation of low B concentration. Because B is considered to be preferentially partitioned in the fluid (Chaussidon and Libourel, 1993), fluid-infiltrated mantle should be enriched in B, relatively to DMM. Some δ^{11} B values in melt inclusions are lower than those for AOC and sediments, which argue against melting of previously non-dehydrated materials. It was also shown that B concentration and δ^{11} B composition characteristics derived from dehydration residues, and preserves evidence for dehydration of the slab source. This study concludes that Shasta melt inclusion signature results from fluid-induced melting of the mantle wedge, where the fluid was derived from locally heterogeneous sources as metasedimentary and metabasaltic lithologies.

High pre-eruptive H_2O contents postulated for Mt. Shasta (Grove et al., 2002) disagree with dehydrated slab melting, which is volatile-free melting. Therefore, the slab component in the

Mt. Shasta primitive basaltic and site may be hydrous fluid released after extensive B removal or H_2O -rich slab melt derived from the dehydration residues that has been reequilibrated with the overlying mantle, preserving evidence for progressive dehydration of the slab source in its B characteristics.

Later, among the increasing number of melt inclusion analyses, Le Voyer et al. (2008) attributed the origin of Ecuadorian arc melt inclusions to a mixing between partial melts of amphibolebearing olivine clinopyroxenite lithologies and of peridotitic lithologies, on the basis of major element compositions of melt inclusions. Using trace element and boron isotope compositions, they demonstrated that the slab component that metasomatized the melt inclusion source of their studied volcances (Rucu Pichincha and Pan de Azucar) varies with the increasing slab depth. Their measured B concentrations in those inclusions are much higher than those measured by Rose et al. (2001) in Mt. Shasta melt inclusions. In that case, they are consistent with a fluid-induced melting, but induced by a different component following the melting depth. They made a complex model where at shallower depth, melting involves a heterogeneous fluid derived from both sediments and AOC sources, while at deeper depth, it involves either a heterogeneous aqueous fluid or a silicate melt, both derived from different degrees of dehydration of altered oceanic crust and sediments.

Isotopes, and more particularly isotopes in melt inclusions, are new keys in the understanding of arc magma genesis. They supply information on the source chemistry of the slab component involved in arc magma melting, but neither on element transport processes nor on the lithology of the mantle wedge.

The aim of this PhD work was thus to find new tracers that can supply new information on arc magma genesis.

1.5 Volatile elements in subduction zones

Given that arc magmas are rich in volatile elements, compared to MORB or OIB, information about volatile element contents and volatile element behavior in mantle wedge is becoming a new source of interest. Understanding how arc magma source gets its signature in volatile elements could help to know not only the nature of the slab component, but also the nature of the mantle wedge.

1.5.1 Volatile elements and arc volcanism

Subduction zones volcanoes are the most monitored and studied volcanoes since they are abundant and the most dangerous because of their explosivity. The explosive nature of those volcanoes comes from the mechanisms of their eruptions and the composition of their magmas. As presented before, subduction zone lavas are mostly and esitic, thus viscous and rich in volatile elements: H_2O , CO_2 , SO_2 , H_2S , Cl and F.

Water is the main component in arc magmas and its abundance varies between 0.5 to 8 wt% (Wallace, 2005) and can even possibly reach up to 10 wt% (Grove et al., 2005). The second most abundant volatile specie is CO_2 , which concentration dissolved into magmas may exceed 1 wt% (Wallace, 2005). Sulfure is about with ≤ 4000 ppm (Johnson et al., 2010). In subduction andesites, chlorine and fluorine are concentrated between 100 and 8500 ppm and 100 – 900 ppm, respectively (Aiuppa, 2009). Other elements such as other halogens (bromine, iodine, astatine; Baker and Balcone-Boissard, 2009) or noble gases and nitrogen (Carroll and Webster, 1994) can also be present in very low concentrations in arc magmas.

Those species are dissolved into magmas, but during magma ascent, volatile species solubility decreases and leads to progressive volatile exsolution (e.g. Dixon et al., 1991; Wallace and Anderson, 1998; Blundy and Cashman, 2001; Sparks, 2003). Water exsolution during ascent leads to a increase of the magma viscosity and of the crystallization rate (e.g. Shaw, 1972; Sisson and Grove, 1993a; Richet et al., 1996; Métrich and Rutherford, 1998; Giordano and Dingwell, 2003; Grove et al., 2003; Pichavant and MacDonald, 2007). Exsolution and fragmentation processes create expansion, control the dynamic of magma ascent and constitute the driving force of arc volcanic eruptions (e.g. Anderson, 1975; Sparks, 1978, 2003; Tait et al., 1998; Pinel and Jaupart, 2000; Zhang, 2000).

1.5.2 Volatile elements degassing

For the determination of the nature of the slab component that induces arc magma genesis, the volatile element contents, in particular water, are measured in lavas and more recently, in melt inclusions. For example, variations of water contents could allow the determination of the proportion of hydrous fluid compared to slab melt that induced mantle wedge melting.

- In magmas, from a theoretical point of view, there are two main types of degassing style (e.g. Holloway and Blank, 1994): (1) closed system degassing where vesicles form from the melt and remain in equilibrium with it, (2) open system degassing where vesicles escape continuously from the magma during their formation (e.g. Aubaud et al., 2005). In melt inclusions, while C and H suffer degassing (e.g. Dixon et al., 1995), Cl and F do not experience a degassing event (e.g. Carroll and Webster, 1994).
 - As it was previously suggested, every magma degasses most of its H₂O upon ascent, due to the dramatic decrease in the solubility of H₂O in melt at low pressure. From the pioneering

experimental work of Goranson (1931) it is known that the maximum water solubility in silicate magmas increases rapidly with the increasing total pressure. In geochemical studies covering several decades, water solubility has been measured in many natural and synthetic melt composition over a wide range of pressures and temperatures (see McMillan, 1994 for review). Thus, it is accepted that H_2O degasses early during magma ascent. Thus H_2O content measured in magmas are minimum estimates of primary magmas.

- CO₂ is about an order of magnitude less soluble than H₂O in silicate melts (Lowenstern, 2000). Furthermore, the increase of H₂O content in the melt decreases the solubility of CO₂ (Lowenstern, 2000). Carbon estimates in volcanic submarine glasses, used to constrain the flux of degassing carbon from the mantle (e.g. DesMarais and Moore, 1984; Marty and Jambon, 1987; Javoy and Pineau, 1991; Cartigny et al., 2001; Aubaud et al., 2004, 2005), are thus difficult to obtain due to the degassing processes. Because of its low solubility in basaltic melts (Stolper and Holloway, 1988; Pan et al., 1991; Pawley et al., 1992; Dixon et al., 1995; Jendrzejewski et al., 1997), carbon is responsible for the nucleation and growth of CO₂-rich vesicles (e.g. Pineau et al., 1976) which escape from the magma before reaching the surface. Thus, sampled lavas are depleted in carbon and carbon concentrations in the mantle is studied by vesicles in volcanic glasses (e.g. Aubaud et al., 2005)
- Spilliaert et al. (2006) data in Etna melt inclusions demonstrated that chlorine exsolution begins at $P \leq 100$ MPa. These pressures are one order of magnitude lower than that of sulphur, until 10 MPa. Nevertheless, the high water content of Etna basalt and the high proportion of exsolved gas at 100 MPa ($\sim 40 \%$) may explain why chlorine starts to exsolve at relatively high pressure at Etna. No fluorine loss was detected in most studies of submarine glasses and lavas (see Jambon, 1994 for a review). Substantial F loss (30 – 50 %) was only reported during major subaerial basaltic effusions (Thordarson and Self, 1996; Thordarson et al., 1996). Spilliaert et al. (2006) assess that Etna basalt releases at most 15 % of its fluorine during lateral dyke eruptions. A comparable estimate was derived from summit crater plume emissions (Burton et al., 2003), suggesting a similar behavior of fluorine in the central volcano conduits. The shallower and more restricted exsolution of F than Cl during Etna basalt eruption is consistent with the ionic radius dependency of halogen partitioning between vapour and silicate melts (Schilling et al., 1980; Bureau et al., 2000). Indeed, F and Cl ionic radii ($F^{-}(IV)$ ionic radius is 133 pm and $Cl^{-}(IV)$ ionic radius is 181 pm) are much bigger than S and H (S ionic radii is between 12 pm and 37 pm and H ionic radii is 18 or 38 pm, depending their speciation and coordination number).

Degassing of volatiles is complex because the solubility and vapor-melt partition coefficients of the different volatile components vary with melt and gas composition, temperature, pressure, and in some cases, oxygen fugacity (e.g., Wallace and Carmichael, 1992; Dixon and Stolper, 1995; Webster et al., 1999; Newman and Lowenstern, 2002; Jugo et al., 2005; Alleti et al., 2009). Nevertheless, Spilliaert et al. (2006) shows that F and Cl are the last volatile elements to be exsolved during magma ascent. Thus, Cl and F are the likely elements that retain the information of magma genesis along with other lithophile trace elements (such as REE).

• With recent advances in microanalytical techniques and **melt inclusion** studies, there is a growing body of concentration measurements of volatiles, relatively light-atomic mass elements (H, B, C, S, Cl, F) in primitive melts of subduction zone magmas (Sisson and Layne, 1993; Métrich et al., 1999; Wade et al., 2006; Métrich and Wallace, 2008; Le Voyer et al., 2010). In melt inclusions, several studies suggested that a water loss occur either during a long residence time at high temperature, such as in a magma chamber, or during an extended experimental heating (Sobolev et al., 1989; Massare et al., 2002; Danyushevsky et al., 2002; Hauri, 2002; Severs et al., 2007; Chen et al., 2009). Water loss during inclusion heating is proportional to the heating duration (Massare et al., 2002). Water loss is carried out by hydrogen diffusion out of the inclusion. For example, H⁺ has a high diffusivity in silicate melt and minerals (Mackwell and Kohlstedt, 1990). It can also be carried out by diffusion of hydroxyl group (OH⁻) along dislocations or propagation plan of point defects in hosted crystal (Qin et al., 1992; Massare et al., 2002). Other volatile species CO_2 , F, Cl and S have diffusion speed 5 to 10 times lower than H_2O (Freda et al., 2005; Alletti et al., 2007) in melts. For those species, no loss was evidenced during experimental heating to my knowledge. Le Voyer (2009) showed, by the variations of volatile contents in melt inclusions with saturation pressures, that only F and Cl did not undergo significant degassing before trapping (Figure 1.5.1), while H_2O , CO_2 and S contents in melt inclusions can be used as minimum estimates of primary volatile contents. The correlations of H₂O, CO₂ and S contents in melt with the pressure indicates that melt inclusions suffered a differential degassing before the melt inclusion formation. Figure 1.5.1 shows that Cl, F and Cl/F ratio of inclusions are constant with respect to pressure. This demonstrates that F and Cl are not affected by degassing processes. Balcone Boissard et al. (2008) demonstrated that when the degassing of H_2O -saturated silicate melt is fast, Cl is kept in the silicate melt.

In summary, F and Cl contents, in particular in melt inclusions, are the most reliable volatile contents, that can be used to trace the arc magma source.



Figure 1.5.1: Variations of volatile element concentrations from Mount Shasta, Italy and Ecuador, function saturation pressure in H_2O and CO_2 , modified after Le Voyer (2009). Saturation pressure were calculated using VolatileCalc (Newman and Lowenstern, 2002), using SiO₂, H_2O and CO_2 , and melting temperature of the last daughter mineral (during experimental heating) of each inclusion, except for the vitreous inclusions from La Sommata, where an average temperature of 1208°C was used.

1.5.3 Contribution of fluorine and chlorine to the interpretation of arc magmas genesis

Recently, Le Voyer et al. (2010) measured F and Cl contents and other trace element contents in Mount Shasta melt inclusions, to identify the slab component that induced melting in the mantle wedge beneath Shasta. They investigated the variations of concentration ratios where the fluid-mobile element (here F, Cl, Ba or Sr; Figure 1.5.3) is normalized to fluid-immobile element (here, Y is used because of its small error bars: 10%). They showed that using regular trace elements, as Ba and Sr, Shasta melt inclusion compositions were aligned following one trend. This trend could represent a mixing trend between a MORB mantle component and one H₂O-rich component. However, using F and Cl, melt inclusion compositions, they distinguished two distinct trends following where Shasta melt inclusions are aligned. They thus divided Mount Shasta melt inclusions in two groups, which plot on mixing lines between the depleted source (MORB mantle) and two H₂O-rich components: C1 (95-15 melt inclusions), and C2 (85-1a and 85-47 melt inclusions). These two mixing lines also are detected using B/Y versus Sr/Y ratios (Le Voyer et al., 2010). The imprints of two slab-derived components were also found by using volatile elements only, in particular F and Cl.



Figure 1.5.2: Figure simplified after Le Voyer et al. (2010) showing (a) Ba/Y versus Sr/Y, (b)Cl/Y versus F/Y for the Shasta melt inclusions. Crosses in the bottom right corner of each group represent the typical anlytical error on each ratio. Dashed lines represent mixing between the average HAOT (high alumina basalt) (Le Voyer et al., 2010) melt inclusions compositions and one H₂O-rich component (C1 or C2). On those two graphs, the BA (basaltic andesites) melt inclusions compositions can be reproduced by mixing between a depleted mantle and one of two H₂O-rich component (C1 for the 95-15 melt inclusions and C2 for 85-1a and 85-47 melt inclusions). The modeled compositions of C1 and C2 are given in Le Voyer et al. (2010).

Compiling melt inclusion compositions in volatile and trace elements from three different subduction zones (american, italian and ecuadorian), Le Voyer (2009) showed that their measured melt inclusions can be all divided in two groups with different Cl/F ratios (see Figure 1.5.3). Melt inclusions from Ecuador and the sample 95-15 from Mount Shasta have lower Cl/F ratios (1.2 ± 0.3), while melt inclusions from Italy and samples 85-47 and 85-1a have higher Cl/F ratios. Those two groups appear even with K₂O normalization. This consistent behavior with or without normalization indicates the minor role of melting and crystallization processes on Cl/F ratio variations.



Figure 1.5.3: Figure modified from Le Voyer (2009) showing (a) Variations of Cl versus F concentration in melt inclusions from Mount Shasta, Italy and Ecuador subduction zones. Black lines represent average Cl/F ratios in Pichincha, Pan de Azucar, Mount Shasta 95-15 inclusions (Cl/F ~ 1.2) and in Mount Shasta 85-48, 85-1a and La Sommata inclusions (Cl/F ~ 3.9). For tholeiitic inclusions from (85-38) and MORB, the Cl/F ratio is close to zero. (b) variations of the Cl/K₂O ratio versus the F/K₂O in the studied melt inclusions. Normalization F and Cl values to K₂O allow to be free of melting and crystallization processes (since Cl and K₂O have close incompatibility, Kent et al., 2002), and it minimizes F variations (which is an incompatible element close to intermediate rare earth elements, thus higher than K₂O, Dalou et al., 2009b). The two groups of inclusions with different Cl/F ratios are unchanged on (b). MORB values are from Hofmann (1988); Saal et al. (2002).

Le Voyer (2009) interpreted those two distinct signatures of arc primary magmas by the metasomatism or the influence of two H₂O-rich components in their source: (1) a silicate melt from the dehydrated sediment melting or, (2) an aqueous fluids derived from the dehydration of the oceanic crust.

1.6 Contribution of partition coefficients in melting models in subduction zone

In order to decipher the F and Cl arc magma signature, we need to know the behavior of those element in the mantle wedge. This was the aim of this PhD work. I determined the partition coefficients of F and Cl between main mantle wedge minerals and a basaltic melt with varying water content. The following section explains thermodynamical theories concerning partition coefficients (reviews of previous work using partition coefficient are not given here, but among later chapters) and the use of partition coefficients to trace magma genesis. It outlines the theoretical framework of my dissertation.

1.6.1 Definition of partition coefficients

A partition coefficient of an element is the ratio of its concentration between two phases. The ratios are usually calculated from mass-based values. It is a fruitful variable for studying element distributions. Phases can be minerals, which are not pure chemical compounds but solid solutions, or they can be liquids or gases. This study will be focused on partition coefficients between one mineral phase and one liquid, a silicate melt.

One of the earliest paper devoted to the use of partition coefficient was by Frederickson (1962), who described it, as a 'new tool for studying geological problems'. A partition coefficient is defined, following Beattie et al. (1993) as the ratio of the concentration (c) of a component (i) between two phases (α and β) and written as:

$$D_i^{\beta-\alpha} = \frac{c_i^{\beta}}{c_i^{\alpha}}.$$
(1.6.1)

Here, I assume an equilibrium system at a given pressure (P) and temperature (T), consisting of the two phases α and β , each of which contains dissolved components. For a component *i* the condition for equilibrium partition is that its chemical potential μ be equal in the two phases:

$$\mu_i^\beta = \mu_i^\alpha. \tag{1.6.2}$$

Expressing a for the thermodynamic activity, then this equation can be expanded to:

$$\mu_i^{0\beta} + RT \ln a_i^{\beta} = \mu_i^{0\alpha} + RT \ln a_i^{\alpha}, \qquad (1.6.3)$$

whence

$$ln\frac{a_i^{\beta}}{a_i^{\alpha}} = -\frac{\mu_i^{0\beta} - \mu_i^{0\alpha}}{RT},$$
(1.6.4)

where R is the gas constant, and the term $\mu_i^{0\beta} - \mu_i^{0\alpha}$ is the Gibbs free energy of transfer of 1 mole of the component *i* from the phase β to α , and where a_i is the activity of the component *i*, and its related to the concentration by:

$$a_i = \gamma_i x_i, \tag{1.6.5}$$

where γ_i is called the activity coefficient, and is such that as $x_i \to 1$, $\gamma_i \to 1$. The activity coefficient value can be greater or less than 1. Elements or compounds at a standard state have, by definition, $\gamma = 1$. The coefficient may be *P*- and *T*- dependent, and cannot be considered as a constant event at any given pressure and temperature as it may vary with the concentration of the component. The investigation of the activity-composition relationships is, therefore, an important part of the

study of non-ideal solutions, such as mineral phases. However, for a diluted solution, the activity of a solute component is considered proportional to its mole fraction:

 $a_i = k_h x_i$ as $x_i \to 0$, at constant T and P,

where k_h is a proportionality constant. This relationship is $Henry's \ law$ and k_h is referred to as Henry's law constant, its value being determined from experiment. The concentration range over which Henry's law operates for a particular component is restricted (Figure 1.6.1).



Figure 1.6.1: Possible activity (a_i) – composition relationship of a component, *i*, showing non-ideal solution behavior but obeying Henry's law over of its concentration range, X_i . Ideal behavior (Raoul's law) is shown for comparison.

One consequence of the Henry's law is that we can write:

$$\frac{x_i^\beta}{x_i^\alpha} \alpha \frac{x_i^\beta}{x_i^\alpha} = D_i^{\beta-\alpha}.$$
(1.6.6)

In our study, β is a mineral phase and α is a melt. Here, two cases were considered:

- The first case corresponds to Henry's law. Trace elements in all systems and F and Cl in the dry system were measured at trace levels.
- The second case does not correspond to the Henry's law. In water system, a contamination (see next chapter) led to high F and Cl concentrations. In volatile-rich phases, amphibole and phlogopite, F and Cl were measured at minor, or even major levels. Nevertheless, F or Cl saturation was not achieved since no brine were crystallized.

1.6.2 Thermodynamics of partition coefficient

This section briefly presents the equations that control partition coefficient variations.

Effects of variation of temperature and pressure

The equation (1.6.4.) can be written as:

$$\frac{a_i^\beta}{a_i^\alpha} = D_i^{\beta-\alpha} \star \tag{1.6.7}$$

$$\frac{\mu_i^{0\beta} - \mu_i^{0\alpha}}{RT} = \frac{\Delta G^0}{RT}$$
(1.6.8)

$$lnD_i^{\beta-\alpha} \star = \frac{\Delta G^0}{RT}, \qquad (1.6.9)$$

and this may be used to estimate the effect of change of T or P on the partition coefficient. For example, the effect of temperature is given by the following:

$$\left(\frac{\delta ln D_i^{\beta-\alpha} \star}{\delta T}\right)_P = \frac{\Delta H^0}{RT},\tag{1.6.10}$$

where H^0 is the enthalpy of the reaction and integration of this equation shows that $lnD_i^{\beta-\alpha}$ is inversely proportional to T:

$$ln\left(\frac{D_{i,1}^{\beta-\alpha}\star}{D_{i,2}^{\beta-\alpha}\star}\right)_{P} = -\frac{\Delta H^{0}}{R}\left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right).$$
(1.6.11)

These two equations show that partition coefficient will vary with T. The effect of pressure change is governed by:

$$\left(\frac{\delta ln D_i^{\beta-\alpha} \star}{\delta P}\right)_T = \frac{\Delta V^0}{RT},\tag{1.6.12}$$

which intergrated gives:

$$ln\left(\frac{D_{i,1}^{\beta-\alpha}\star}{D_{i,2}^{\beta-\alpha}\star}\right)_T = -\frac{\Delta V^0}{R} (P_2 - P_1), \qquad (1.6.13)$$

where ΔV^0 is the molar volume change in the mass action equation, showing that $lnD_i^{\beta-\alpha}\star$ is proportional to P. It is seldom important in systems that does not contain gas, which is my case, to consider the pressure dependence, because the ΔV^0 term is negligible.

A little introduction to lattice strain models

There is a functional relationship between the partition coefficient of a cation atom between two phases, and its cationic size. Masuda (1965) was one of the first to record this, for elements partitioned between silicate and melt. Others made similar observations in the following years (Nagasawa, 1966; Onuma et al., 1968; Higuchi and Nagasawa, 1969; Jensen, 1973). The relationship becomes clear if the coefficients $D_i^{mineral/melt}$, between mineral and melt for a series of cations of the same valence are plotted against their radii r_i . Diagrams of this kinds have been referred to as Onuma diagrams (Figure 1.6.2).



Figure 1.6.2: After Shaw (2006), partition coefficients between augite and basalt matrix (from Onuma et al., 1968) vs. ionic radius (Jensen, 1973). The estimated maxima at 0.79 Å and 1.01Å correspond to sites M1 and M2 (chapter 4).

In the nineties, studies using the equation of Brice (1975) superseded the quantitative nature of the $D_i^{mineral/melt}$ vs. r_i relationships of Nagasawa (1966) (e.g. Blundy and Wood, 1994. Partition coefficients measured by those authors are more precise than the earlier values, so their Onuma diagrams show smoother curves. The $D_i^{mineral/melt}$ for the element *i* of a radius r_i at a given pressure and temperature and bulk composition, is expressed following 3 parameters that appear on Onuma diagrams (Figure 1.6.3): r_0 the ideal crystal strain-free radius, E_0 the elastic response of the sites to the elastic strain caused by larger or smaller r_i and D_0 the fictive strain-free partition coefficient for cation with r_0 . These parameters respond to a model called the 'lattice strain model'. The formula is given by Blundy and Wood (1994):

$$D_i^{mineral/melt} = D_0 \, exp\left(\frac{-4\pi E_0 N_A}{RT} \left(\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3\right)\right),$$

where N_A is the Avogadro number, R is the gas constant and T is the temperature in K (see chapter 4 for more details).





This model illustrates the element substitution in mineral structural network. According to their ionic radii and charges, elements are incorporated in different crystal sites. Each site is characterized by the parameters of the lattice strain model (Brice, 1975; Blundy and Wood, 1994). The lattice strain model parameters, especially E_0 and r_0 , quantities the structural changes of mineral following:

- 1. P T conditions,
- 2. Crystal chemistry (the bulk composition of a mineral influences the ease with which a trace element can enter a site),
- 3. The melt structure.

Those effects will be discussed in the chapter 3 and 4 with further details.

Thus the difference, such as an anhydrous or hydrous system, can lead to varying partition coefficient, changing the mineralogy, the mineral composition and the melt structure. This will be the subject of chapters 4 and 5.

The choice of partition coefficient can then have an influence on the melting (or crystallization) models. In the models, it is primordial to select partition coefficient adapted to the conditions and compositions of interests.

1.6.3 Melting models in subduction zones

Partial melting in the upper mantle was investigated for the generation of MORB. Trace element concentrations in the products (residue or melt) has been modeled by element fractionation during partial melting (e.g. Langmuir et al., 1977). Nevertheless, until now, no melting model with F and Cl has been developed for subduction zones. This section will present the melting model and the P -T conditions we choose to be best suited to subduction zones.

It is difficult to have an idea of what occurs in subduction zones, in term of melting, especially because melts that tend to raise up, can also be carry down along the subduction path. In the melting model, I presented in chapter 5, I imagined the melting in subduction zones as the batch melting of Shaw (1970). This model considers two important points for subduction zones:

- When the melting occurs in an area, the melt is extracted and starts to percolate in the mantle. At each melting stage, melts are aggregated, and equilibrated at the point, and this aggregation of melt will rise to the surface.
- 2. It considers a non-modal melting: during melting some minerals are preferentially used and exhausted. Melting can continue with a varying mineralogy, with different phase proportion for each melting stage. This notion is introduced by the P in the following equation. It involves the information of how much of each phase is consumed or created during melting.

The aggregate melting model involves:

 X_i , the mass fraction of mineral *i* in the solid,

 C_0 , the concentration of element in the mantle wedge system before melting,

$$C_0 = \sum_i C_i^0 X_i,$$

 C^L , the concentration of element in the melt,

 D_0 , the whole rock partition coefficient:

$$D_0 = \sum_i D_i^{i/melt} X_i^0,$$

F, the melting rate,

 p_i , the mass fraction of mineral *i* in the melt, and *P*, which is:

$$P = \sum_{i} p_i D^{i/melt},$$

and corresponds to the equation:

$$C^{L} = \frac{C_{0}}{F} \left[1 - \left(1 - \left(\frac{PF}{D_{0}} \right)^{\frac{1}{P}} \right) \right].$$
(1.6.14)

To built those models; p_i were found in the literature and $D^{i/melt}$ were determined in this study for trace elements, F and Cl. The determination of partition coefficient requires a high melt fraction and big crystals to ease the ion probe measurements. In order to have a high melt fraction, I decided to make experiments at P - T conditions of the mantle wedge hotspot. Those conditions were determined using Kelemen et al. (2003b) (Figure 1.6.4).



Figure 1.6.4: Simplified figure after Kelemen et al. (2003b), showing the steady state temperature area (dark grey) in vertical sections, where the top of the subducting plate is at the depth of 100 km. The dark grey area shows the variation of these temperature with the viscosity, the activation energy and the age variations input in Kelemen et al. (2003b) model. The light grey area is the selected depth, which corresponds to the pressure range for my experiments.

I realized experiments between 8 to 25 kbars, which corresponds to 24 to 75 km depths, and between 1040 and 1430°C. As I previously explained partition coefficients can change between anhydrous and hydrous system, I ran experiments in both systems. In the anhydrous system, the associated phases are olivine, orthopyroxene, clinopyroxene \pm plagioclase, \pm spinel or \pm garnet depending of the pressure, in equilibrium with a basaltic melt. In the hydrous system, those phases go with amphibole or phlogopite. After getting the partition coefficient of F, Cl and some other trace elements partition coefficient between those cited minerals and basalt, I use them into a melting model for subduction zones.

This will be presented in the final chapter (Chapter 5).

Chapter 2

Experimental and analytical methods

2.1 Introduction

This chapter presents materials and techniques to determine F and Cl partition coefficients. The first section describes starting material preparation and experimental techniques, with calibration information and experimental procedures. Then I present the different analyses done on the experimental samples. I have performed measurements of major element concentrations by electron microprobe, volatiles (F, Cl, and H₂O) by ion probe and trace elements (including REE, Li, Be, B, U-Th, HSFE, LILE) by ion probe and by ICPMS. I briefly explain the principle of each analytical instrument along with the analytical settings used in this study.

2.2 Experimental techniques

2.2.1 Starting materials

Doped synthetic powders are commonly used to determined partition coefficients of trace elements. Doping allows to control the starting concentration of the element we want to measure, in order to:

- roughly anticipate the final contents in minerals and melt to be above the detection limit of analytical instruments. For highly incompatible elements, their concentration in mantle minerals (especially nominally anhydrous minerals) can be very low and impossible to measure, in natural abundance conditions.
- 2. select and measure only the elements of interest. The measurement of elements with the heaviest mass can be distorted by mass interferences occurring during analysis. For example, in low mass resolution ion probes, ¹⁴⁷Sm mass peak potentially include contributions from ¹³⁵Ba¹²C (e.g. Dalou et al., 2009a). For this study, I doped the experiments with the elements, which do not interfere each other.

One limitation of this strategy is that concentrations in doped materials, minerals and melts after experiments, can not be compared to natural samples' concentration. I imagine this is why, some experimentalists choose to work with a system with natural abundance trace elements, when it is possible (i.e. when trace element concentration enables it).

Our experimental strategy was to approximate the liquidus saturation of mantle phases that are in equilibrium with a high pressure basaltic melt. This is specifically done to increase the melt fraction, and to facilitate the mineral growth, and these are critical criteria for F, Cl and trace element analysis. All desired phases cannot be saturated at the liquidus with the same starting compositions. Some minerals, as volatile-rich minerals (micas or amphiboles) require starting composition richer in water and potassium than the basaltic system for phlogopite. Thereby, each starting composition had to be prepared following the minerals we wanted to have in equilibrium with the melt. During this PhD work, we conducted 3 main projects:

- The main project was the determination of partition coefficients of F, Cl along with trace elements between lherzolite minerals and basaltic melt, at mantle wedge conditions.
- The second point was the determination of the role of water in the partition coefficients of volatile elements. Here, I have studied partition coefficients between lherzolite minerals and hydrous basaltic melt.
- As an exploratory study, and to expand dataset of F and Cl partition coefficients, I have determined F and Cl partition coefficients between volatile-rich minerals, pargasite and phlogopite, and melt.

For each project, different starting materials were prepared. Preparation procedures are described in the following parts..

The compositions were chosen to obtain liquidus saturation of the upper mantle phases (olivine, orthopyroxene, clinopyroxene and aluminous phases: plagioclase, spinel or garnet, depending on the pressure) while maintaining large melt fractions. Therefore, these compositions were prepared to be as close as possible to a basalt-peridotite pair used in the upper mantle liquidus saturation experiments of Gaetani and Grove (1998). As I needed to have another basalt-peridotite pair but MgO-free (as explained in the section 2.2.1), it was more convenient to prepared synthetic gels with the desired compositions. In the same way, liquidus saturation of volatile-rich minerals required hydrated starting compositions, i.e. the preparation of Al_2O_3 -free compositions (as explained in the sections 2.2.1 and 2.2.1). Consequently, all starting materials were chose to be synthetic gels.

Synthetic gels were prepared mostly by J.-L. Devidal and some by myself at the 'Laboratoire Magmas et Volcans' following the procedure of Hamilton and Henderson (1968); those are very homogeneous

mixtures of elemental solutions that are highly reactive (Luth and Ingamells, 1965). After precipitation and drying, each powder was charged in a microgrinder with 12 mL of ethanol and ground during 30 minutes to obtain grain sizes smaller than 10 μ m. Then each powder compositions was checked by ICP-AES at the 'Laboratoire Magmas et Volcan' by Mhammed Benbakkar (Table 2.2.1). Each powder was conditioned for 12 hours at 800°C in a 1 atm gas-mixing furnace, with fO_2 at about 1 log units above the Quartz – Fayalite – Magnetite buffer. We have chosen the oxidation state of sub-arc upper mantle according to Parkinson and Arculus (1999).

After the doping step in F and Cl detailed below, powders were doped to a 100 ppm concentration level with a suite of trace elements that were added to powders using a multi-element solution. Element concentration in the final mixture was approximately 100 ppm (Li, B, Be, As, Sr, Sc, La, Eu, Gd, Ho, Lu, V, Hf, Zr, U, Th), except 1000 ppm for Pb.

Anhydrous experiments

Four synthetic compositions, two basaltic and two peridotitic gel mixtures were used as starting materials for anhydrous experiments (Table 2.2.1). Basalt and peridotite compositions were prepared to be as close as possible to a basalt-peridotite pair used by Gaetani and Grove (1998). The second basalt and peridotite mixtures were created without MgO to allow the addition of MgCl₂ and MgF₂ powders.

The starting material was weighed to the desired proportions of synthetic basalt and peridotite (70:30 % respectively) and was ground in an agate mortar with ethanol for 45 min. The bulk Cl and F abundances were controlled by adding the Cl- or F- bearing basalt powder and, in certain cases, by adding the Cl- or F- bearing peridotite powder (for particularly high concentration Cl and F) to the halogen-free mix. More than twenty powders covering a broad range of different volatile contents were prepared: from 100 ppm to 15 wt% of Cl or F. For anhydrous experiments, except for two 25 kbars experiments, we made separately Cl- bearing and F- bearing mixtures. For the 25 kbars experiments, we used powder with 400 ppm of Cl and 400 ppm of F.

Before weighting out, each powder was dried in a oven (110°C) for several hours. This was done to minimize absorption of moisture from the air. This procedure caused a secondary problem. We noticed after measuring F and Cl in our samples that we had a Cl contamination of the powder, because the NaCl cylinders (used for piston-cylinder experiments) were stocked in the same drying oven.

Two series of anhydrous experiments were run; one without and one with the addition of cpx seeds, whose composition is presented in Table 2.2.1. Cpx seeds were added to promote the growth of smaller number of bigger cpx grains, instead of larger number of smaller grains, in the recovered samples.

Hydrous experiments

In addition to anhydrous powders, two Al-free gel mixtures were prepared: one Al-free basalt and one Al-free peridotite. Water-bearing basalt and peridotite powders were created by adding $Al(OH)_3$ to Al-free powders in order to complete their Al_2O_3 contents. As for anhydrous powder, we weighted out 70% of basalt and 30% of peridotite that are then ground in an agate mortar with ethanol for 45 min. The bulk H₂O abundance of each was adjusted by adding the H₂O-bearing basalt powder and, in certain cases, the H₂O-bearing peridotite powder (for particularly high water concentrations). We made three series of hydrous powders: with 3, 5.4 and 6.1wt% of H₂O. Nevertheless, not all initial water doping was recovered in samples. Up to 0.5 wt% of water loss was noted. This loss likely have happened during welding.

Several Cl or F doping level were chosen for each of those powders: 400, 1000 and 4000 ppm. $MgCl_2$ and MgF_2 powders were directly added into the mixtures. The increase of MgO due to the doping of 4000 ppm volatiles is negligible (less than 0.26 wt%).

We choose $Al(OH)_3$ (or gibbsite) to add water in the system, instead of $Mg(OH)_2$ (brucite) which is commonly used. A recent study (Béarat et al., 2002) demonstrated that brucite is easily carbonated. After several non-conclusive trials to make fresh brucite, notably using a gas pressure vessel (supervised by Nicolas Cluzel, at the 'Laboratoire Magmas et Volcans'), we decided to used gibbsite. No significant CO_2 addition were measured in our samples. Three samples (F1#3b, CC1#16kb and H5V4p) were double-polished and analysed by the FTIR of the 'Laboratoire Magmas et Volcans'. In hydrous experiments, less than 100 ppm was measured. In anhydrous samples, surrounded by graphite, less than 900 ppm was measured.

Pargasite – melt experiments

In the same way than hydrous basalt and peridotite were prepared, hydrous mixtures of andesite and peridotite, were prepared in the proportion 50:50 and 70:30. Andesite composition is presented in Table 2.2.1. It was synthesized in order to be as close as possible to the basaltic andesite B715 (Médard and Schmidt, 2008). We first used the B715 basaltic andesite, supplied by Etienne Médard ('Laboratoire Magmas et Volcans'), but textures of the recovered samples suggested that the powder had absorbed CO_2 over years. Our first preliminary samples had carbon-rich minerals, even though experiments were ran with welded metallic capsules. Therefore, we prepared Al-bearing and Al-free andesite in order to add 6wt% of water in the system andesite – peridotite. MgCl₂ and MgF₂ powders were directly added into the mixtures to get 400 ppm or 1000ppm of Cl₂ and F₂ in the final mixture.

Table 2.2.1: Composition of starting materials. Analyzes were done by ICP-AES on the basalt and peridotite powders and by electron microprobe on the cpx seeds. Analyzes were done before F, Cl and trace element doping stage. Mg-free and Al-free powder compositions are not presented. MgCl₂ or MgF₂ and Al(OH)₃ were added after so as to complete the MgO and Al₂O₃ contents of compositions presented here.

	Basalt	Peridotite	Cpx seeds	Basaltic andesite	Shoshonite
SiO_2	47.70(47)	45.97(45)	53.20(60)	58.86(58)	46.20(45)
TiO_2	0.62(1)	0.18(0.2)	0.57(6)	1.01(3)	1.06(3)
Al_2O_3	19.05(19)	4.06(4)	5.62(30)	22.05(24)	12.01(13)
$\mathrm{Cr}_2\mathrm{O}_3$	0.12(0)	0.47(0)	1.07(20)	ND	ND
FeO^*	7.82(18)	7.54(17)	3.12(11)	3.07(3)	9.89(10)
MnO	0.15(0.3)	0.13(0.3)	0.07(6)	ND	0.16(0.2)
MgO	10.49(31)	37.79(112)	15.60(30)	4.13(1)	10.00(3)
CaO	11.75(35)	3.21(10)	19.20(40)	5.85(13)	11.50(26)
Na_2O	2.35(5)	0.33(0.1)	ND	4.56(10)	3.10(7)
K_2O	0.08(0.3)	0.03(0.1)	2.11(13)	0.43(1)	4.14(12)
P_2O_5	0.01(0.02)	0.03(0.1)	ND	0.04(0.1)	1.22(3)
Total	100.13	99.99	100.56	99.99	99.28

Units in parentheses represent one standard deviation. ND: not determined. Standard deviations were determined from analytical error compared to the standard BHVO-1.

(FeO* is total Fe as FeO).

Phlogopite – melt experiments

A shoshonite was synthesized to be close to the composition of the sample B883 of Holbig and Grove (2008). MgCl₂ and MgF₂ powders were directly added into the mixtures to get 1000 ppm of Cl and F. No Al-free powder was prepared.

To perform hydrous experiment, we just added water as liquid distilled water with a micropipette. I estimate that about 5 μ L entered into the capsule (less than 10% of a 35 μ L water drop). Nevertheless, I assumed that a part of this liquid water could have been evaporated, and the heating during the welding could have destabilized a part of gibbsite.

2.2.2 Piston-cylinder experiments

Experiments were performed at pressure between 8 and 25 kbars in piston-cylinder apparatus 3/4" and 1/2". The 3/4" and 1/2" notation corresponds to piston diameter in inch, namely 19.1 and 12.7 mm, respectively. A piston-cylinder is a solid-medium pressure apparatus, as opposed to gas-medium pressure apparatus enclosed in a vessel. In piston-cylinder, a solid assembly surrounding a sample
is pressurized by a tungsten carbide piston. Hereafter I describe the experimental assemblies and procedures.

Capsules and assemblies

From the outside to the inside, assemblies consist of a NaCl cell wrapped in a lead foil, a Pyrex cylinder, a graphite furnace and inner pieces of crushable MgO. The sample is in the center of those crushable MgO pieces composed of: a MgO cylinder inside which the thermocouple sleeve passes, a MgO stopper (that prevents reaction between graphite and the thermocouple), a MgO ring, the sample capsule and a MgO bar (see the scaled drawing, Figure 2.2.3). For water-bearing experiments, we used hexagonal boron nitride (hBN) pieces instead of MgO crushable pieces, and the MgO stopper is replaced by a corundum slice. The hBN is a soft material that provides pseudo-hydrostatic conditions and promotes homogeneous temperature inside the cell because of its good thermal conductivity (Perrillat, 2008).

Before each experiment, the assembly was dried at least 12 hours at 300°C and the MgO pieces about 6h at 1000°C.

For high-pressure and high-temperature experiments, the sample container has to be inert and gasproof to perfectly retain the sample composition and to be stable at high-temperature. Depending on whether experiments were water-free or water bearing, we used different capsules, as described below:

• Capsules for anhydrous experiments

For anhydrous experiments for oxygen fugacity corresponding the upper mantle (FMQ-4 – FMQ-1 (Woodland and Koch, 2003), graphite is the suitable container material.

For this series of experiments, we performed multi-capsule experiments, using a graphite slice with four holes (Figure 2.2.1) to put different volatile-doping composition of dry or nearly dry powders. No sealed metallic capsule was used outside of graphite. A thin graphite lid and a thin MgO disc were placed between the sample graphite slice and the thermocouple.

When an experiment was terminated, we recovered the graphite slice, each sample is identified from the asymetric positioning of the holes (Figure 2.2.1). The graphite slice was then cut by a diamond-tipped saw and samples were individually put into the epoxy resin for polishing.

• Capsules for water-bearing experiments

In the presence of water, graphite container cannot be used, since water causes graphite oxyda-



Figure 2.2.1: Scaled schematic sketch of the top view on the left and 3D side view on the right, of the holed graphite slice.

tion. Consequently water can chemically erode the graphite container via chemical reaction:

$$C + O_2 = CO_2$$

Furthermore, this reaction may induce reduction reactions:

$$2Fe_2O_3 = 2FeO + O_2$$

$$2H_2O = 2H_2 + O_2.$$

Those reactions are quantified in Médard (2004). In the extreme case where all the Fe²⁺ was converted in Fe³⁺, he estimated a dissolved CO₂ content of 0.4 wt% for high melting rates, similar to what we have.

I chose, as an alternative, gold – palladium (AuPd) capsules. Nevertheless, those capsules are known to form an alloy with Fe, that leads to the reduction of the Fe of the sample (Jaques and Green, 1980; Kawamoto and Hirose, 1994). In order to prevent the Fe loss, AuPd capsules were pre-saturated in Fe before experiments as described in Gaetani and Grove (1998). Conditioning $Au_{80}Pd_{20}$ inner an outer capsules for experiments was done by packing capsules with the basalt used in high-pressure experiment mixtures. Capsules were placed into a pyrophyllite support, and suspended in the hotspot of a vertical gas-mixing furnace by Pt wire. The pre-saturation was done at 1250°C, with fO_2 controlled at 1 log unit below the FMQ buffer, for 72 hours.

To prevent damages to the capsules, I decided not to extract the silicate glass mechanically. Instead, I washed the capsules in a HF bath during 48 hours on a heating plate at 90°C and then in distilled water agitated in an ultrasonic bath. Finally, capsules were cleaned in a 22% concentrated HNO₃ solution at 60° C to dissolve any remaining oxide and fluoride precipitates, and again rinsed with distilled water. The capsules were dried in an oven at 110°C. Every capsule is inspected under a binocular before use.

This procedure allows the perfect removal of basaltic melt, but F analyses done a few months later revealed that an appreciable amount of F (up to 9 wt%, calculated afterwards by mass balance) remained on the metallic capsules and during the experiments added more F in the sample than initially designed. As presented on the Figure 2.2.2, an outer capsule, filled up with dried and ground olivine (San Carlos, $\sim 10 \ \mu$ m), surrounds the inner capsule, which contained the sample. Olivine was chosen to prevent water loss, since water is highly incompatible in olivine. Before each experiment, capsules were heated with a spark until reddening.



Figure 2.2.2: Non scaled schematic sketch of the double capsule, used for water-bearing experiments.

To attest the success of my pre-saturated capsules, I checked 1) the efficiency of the Fe-saturation of my capsules by the Fe loss estimation (Table 2.2.2), and 2) the water seal.

- 1. By mass balance, I check if the recovered samples gained or lost Fe compared to the starting compositions presented in Table 2.2.1. As explained later in section 2.3.4, our mass balances often failed to converge, which means that my calculated Fe loss and gain are just rough estimations. In the following table, we can see that most of the gain or loss are less than 2 wt%, and two samples have extreme values: +2.00 for SHO1 and +1.64 for SHO4. Those former values are high, likely because something, such as a bad setting of the fO_2 , has happened during the pre-saturation. Nevertheless, as presented in Tables and of the Chapter 4, all those samples have the expected phases with the right stoichiometry.
- 2. Mass balance calculation is not appropriate to check the water leak of the capsule, because I

Experiment	Р	Т	Duration	H_2O^a	Run products	Phase proportions	r^2	Fe
	(kbars)	$(^{\circ}C)$	(days)	(wt%)		(wt%)	(%)	$exchange^b$
H3V04	12	1240	5	2.6	Gl, Cpx, Opx, Ol	15.5:51.2:20.0:13.3	28.6	+ 0.32
H4V4p	12	1180	5	4.3	Gl, Amp, Opx	45.0:33.5:21.5	1.9	-0.01
H5V4p	12	1190	5.5	4.9	Gl, Cpx, Opx	$64.4{:}21.4{:}14.2$	2.4	-0.02
H6V04	12	1200	4	5.9	Gl, Amp, Opx	66.5:18.2:15.3	4.9	+ 0.60
Grt3V4p	25	1370	4.5	1.6	Gl, Grt, Cpx, Opx	7.8:22.2:55.5:14.5	-	-
SHO1	12	1300	4.5	4.3	Gl, Phlo, Ol	91.6:3.2:5.2	5.52	+ 2.00
SHO4	12	1230	6	4.9	Gl, Phlo, Amp	69.6:26.1:4.3	6.5	+ 1.64

Table 2.2.2: Experimental conditions and phase assemblages.

Abbreviations used: Gl, quenched basaltic melt; Cpx, clinopyroxene; Opx, orthopyroxene; Ol, olivine; Amp, pargasitic amphibole; Grt, garnet; Phl, phlogopite.

Calculated phase proportions are in wt%; r^2 is the sum of weighted squared residuals from phase proportion calculations, modified after Albarède and Provost (1977). The calculation had to take account of F, Cl and H₂O addition to the starting materials (that diluted the initial element concentrations). The uncertainties linked to the doping processes explain the high r^2 .

 a Concentration of H₂O dissolved in the melt, measured by the SIMS 1280 of WHOI.

 b Fe exchange is the difference between the FeO content of the bulk composition used in the starting material and the FeO in the sample bulk composition as determined by the mass balance calculation, in relative weight percent. Positive value indicates apparent Fe gain, while negative value indicates apparent Fe loss.

was never sure of how much water I managed to put in the starting powder. Water was added by Al(OH)₃ or water drop and under those two forms, it can undergo evaporation during spark welding, because of the heat. Thus, to control water seal, we measured by ion probe the water abundance in the outer capsule olivine, after the experiment. We measured 238 ± 1 ppm of water content in the outer olivine of the sample H3V04. Typical water content in mantle olivine is 50 ppm maximum Bell and Rossman (1992). Thus the measured 238 ppm of water content was acquired by the olivine during the experiment, but the total water mass in the outer capsule is considered as negligible compared to the percents water in the sample powder.

Piston-cylinder principles

Once the assembly is ready, it is put into a cylindrical chamber in tungsten carbide. To generate the pressure, the assembly is compressed between a base plug and a piston, both in tungsten carbide (Figures 2.2.4 and 2.2.5). Therefore, pressure is uniaxial and non-isotropic. The NaCl external cell is extremely ductile at high temperature, which reduces the uniaxial strain and creates a quasihydrostatic (isotropic) stress field. The nominal pressure in the cylinder, P_{sample} is expected to be equal to the product of the oil pressure exerted by the oil pump, P_{oil} , multiplied by the ratio of the ram surface to the piston surface, S_{ram}/S_{piston} :

$$P_{sample} = P_{oil}.S_{ram}/S_{piston}.$$
(2.2.1)

The conductive graphite furnace heats the sample by Joule effect, with large electric current (300 - 400)A, 4-5 V). The electric isolation of the assembly is provided by a pyrex cylinder between the NaCl cell and the furnace. The temperature is measured by a couple of tungsten 95% – rhenium 5% and tungsten 74% – rhenium 26% thermocouple wires (W95Re5 – W74Re26). Because of the significant thermal gradient (see section 2.2.2), the thermocouple must be placed at reproducible location with respect to the sample, ideally at the same place relative to the sample. However, to avoid reaction with the graphite, in the case of dry experiment, as described before, a MgO slice is placed between the thermocouple and the graphite multi-capsule. In the case of hydrous experiment, a corundum slice is used to separate the metallic capsule and the thermocouple. To avoid the oxidation of the W-Re wires (we used to run 5 days – experiments), argon gas is continuously sent along the thermocouple wire. A photophic slice (see Figure 2.2.3) is put between the base stopper (1, on Figure 2.2.3) and the base plug (2, on Figure 2.2.3). This is to isolate from short-circuits the base and the top of the cylinder linked to the graphite furnace, (at the top by graphite slices (3), and at the base by the base stopper (inox)(1). In this work, I used two types of piston-cylinder apparatuses: the piston-cylinder 3/4" (Figure 2.2.4) which is without end-load (Holloway and Wood, 1988) for experiments from 0.8 to 16 kbars, and the piston-cylinder 1/2" (Figure 2.2.5) which is with end-load (Boyd and England, 1960) for experiments at 25 kbars and some experiments at 12 kbars. Details of all experiments are presented in the Table "Appendix B" (page 263). End-loaded pressure apparatus allows to support higher internal pressure by partially compensating the high pressure enclosure (see Figure 2.2.5) with compression by an external (end-load) ram.

Pressure and temperature control

• Pressure control:

Pressure is measured with the hydraulic oil circuit, by a metallic dipstick pressure sensor. As we mentioned, the ratio between the solid pressure applied to the assembly and oil pressure is equal to the ratio of the jack and the piston surfaces (equation 2.2.1). Frictions between the piston and the carbide cylinder inner surface can create a pressure loss that requires a calibration of the experimental assembly. Nevertheless, usually, the use of NaCl surrounded by a Pb foil as pressure transducer leads to negligible frictions, that do not require pressure corrections (Johannes et al., 1971; McDade et al., 2002). In addition, to make the piston slide easier, the tungsten carbide core is coated with a lubricant paste (MOLIKOTE® G – Rapid Plus) before each experiment.

For the 3/4" experiments, taking into account the daily variations of pressure, we estimate that the accuracy of our pressure measurement is ± 0.5 kbars. For the 1/2" experiments, this value a)

b)



Figure 2.2.3: Scaled schematic sketch of 3/4" (19.1mm) assembly (a) and 1/2" (12.7 mm) assembly (b). The function of parts (1), (2) and (3) of assemblies are described in the text, in the subsection 2.2.2.





Figure 2.2.4: Captioned picture (a) and non-scaled drawing (b) of one piston-cylinder 3/4" without end-load of the 'Laboratoire Magmas et Volcans' (modified from Lambart, 2009). Assembly is in the tungsten carbide cylinder. Pressure is applied to the assembly between the piston and the base plan.



Figure 2.2.5: Captioned picture (a) and non-scaled drawing (b) of one piston-cylinder 1/2" with back pressure of the 'Laboratoire Magmas et Volcans' (modified from Lambart, 2009). Big arrows represent the pressure applied by the internal ram on the piston. Little arrows represent the end-load applied by the external ram on the tungsten carbide cylinder.

is higher, around $\pm 1 - 2$ kbars (considering preliminary work on quartz-coesite transition), but this was not really well calibrated.

• Temperature control:

Temperature is measured with an accuracy of $\pm 1^{\circ}$ C with a type C thermocouple (W74Re26 – W95Re5). The accuracy on temperature measurements can be distorted by two main causes:

- an uncertainty related to the thermocouple calibration and to the electronic controller.
 This uncertainty is likely low, of the order of a few degrees (2 3°C maximum), given that the W Re wires are calibrated. Effect of pressure to emf (electromotive force) is assumed to be negligible (e.g. Liebermann and Wang, 1992).
- Some errors are related to thermal gradients in the experimental assemblies. They will be described in details in the section 2.2.2. Generally, the presence of a temperature gradient will create two types of errors :
 - * a systematic error due to the distance between the thermocouple and the sample, because they cannot be at the same temperature. This can be minimized because of a calibrated assembly, and a posteriori correction.
 - * an uncertainty related to the thermal gradient inside the experimental sample: when the capsule size is important, the sample will not be at an homogeneous temperature.

The gradient in our capsules can reach 15°C.

Pressurization and heating

Pressurization and heating paths are illustrated by Figure 2.2.6, for experiments without end-load and Figure 2.2.8 for experiments with end-load.

For experiments without end-load, pressure under cold conditions is applied to 3 - 3.5 kbars, and the temperature increase is programmed at 50° C/min, until the pyrex starts to deform. At 650° C, a plateau is maintained from 6 to 8 minutes to reach the desired pressure (8 to 16 kbars). Then the heating starts again to the target temperature, at 50° C/min.

In order to promote clinopyroxene (cpx) growth in our samples, some experiments at 8 and 12 kbars on 3/4" piston-cylinder (detailed in Table 'Appendix B') were done with a temperature variation. After the temperature ramp, (steps 1, 2 and 3 on Figure 2.2.7), a first heating pause was maintained during 6h at 10 or 15° C above the final temperature (step 4). Then, temperature decreased by 0.01° C/min over about one day, (step 5), to reach the final temperature until the end of the experiment, (step 6).

This strategy succeeded in growing cpx, but may have caused two subsequent issues: 1) the growth



Figure 2.2.6: Pressurization (in red) and heating (in black) procedure for experiments on the piston-cylinder 3/4", without back pressure. Case for an experiment at 16 kbars – 1355°C.

of non-equilibrated cpx, and thus 2) the failure of some mass balance. Those equilibrium issues are discussed in the section 2.2.3.



Figure 2.2.7: Schematic diagram of each heating steps for experiments with temperature variations. Case of an experiment at 8 kbars with a temperature variation from 1280 to 1265°C. Steps are detailed in the text.

On the piston-cylinder with end-load, 2 series of experiments were realized: one at low pressure (12 kbars) and one at high pressure (25 kbars). In both cases, the end-load is applied once at cold conditions, to 4500 psi (psi: Pound per Square Inch, 1 psi = 6894.8 Pa), then 3 - 3.5 kbars are manually reach by the internal ram and then heated at 650°C. While at this temperature, the pressure is raised to 12 kbars over approximately 15 min. To reach 25 kbars, the end-load is first loaded to 4000 psi at cold conditions and the to 8500 psi during the 650°C plateau (step 2, Figure 2.2.7), to minimize the variation of the ratio of sample pressure/ end-load pressure. Then, we increase

Figure 2.2.8: Pressurization and heating procedure for experiments on the piston-cylinder 1/2", without back pressure. Pressure (P) on the sample is reprenseted by the solid red line. Back pressure (BP) is represented in dashed red line and is expressed in psi. Solid black line represents the heating step. Case for an experiment at 25 kbars – 1430°C. Back pressure stage were done to keep the ratio P/BP constant during pressurization.



the pressure to 25 kbars, and the heating starts again (Figure 2.2.8).

During the experiments, a Eurotherm controller automatically controls temperature. Pressure is manually adjusted at least twice per day, more often during the first day of an experiment. Experiments were run during 4 to 7 days. The experiment is terminated by cutting electric current supplied to the assembly, resulting into a brutal decrease of the temperature, i.e. a quench. The water circuit accelerates the cooling of the assembly. When the assembly is sufficiently cold (less than 70° C), the pressure (and if necessary, the back pressure) is slowly decreased (around 0.01 kbars/s) down to the atmospheric pressure.

Thermal structure of assembly and temperature gradient evaluation

In piston-cylinder, temperature distribution is characterized by horizontal and vertical gradients. Watson et al. (2002) showed that the temperature is slightly higher closer to the furnace than in the center. The lateral gradient is considered as low: temperature variation inside the furnace is about 30° C between the wall of the furnace and the middle of the furnace, for 3/4" assemblies (see Figure 2.2.9). The 1/2" assemblies are narrower; consequently they are less sensitive to lateral gradient. This gradient is not significant for 3 mm capsules, used in hydrous experiments, because they are perfectly centered thanks to the other pieces of the assemblies. On the other hand, in graphite capsules, because sample holes are spread on the 6 mm diameter graphite disc, this lateral gradient can be observed in the sample texture.

Concerning the longitudinal gradient, they are much more significant: longitudinal profiles have a parabolic shape; the parabola maximum defines the hot spot.



Figure 2.2.9: Temperature variation inside the graphite furnace in 3/4" assemblies. Case of an experiment nominally ran at 1400 °C.

Temperature decreases by about ~ 200°C over 1 cm on both side of the hot spot in the middle of the furnace (Watson et al., 2002). Consequently, sample must be located at the same level in the graphite furnace and in the 'useful' zone of 5 to 10 mm in which temperature variations are less than 20° C, to secure the reproducibility of the temperature for each experiment. In our study, we chose the calibrations of Médard (2004) and Laporte et al. (2004). In the 1/2" experiment, the use of a thicker furnace reduces considerably the temperature gradient. Thermal profiles of the Figure 2.2.10 are used to estimate temperature variations inside experimental capsules. For example, in our experiment, we can see Figure 2.2.10 that:

- in 3/4" assemblies, thermal gradient inside the sample is about 5°C and about 1°C for 1/2" assemblies.
- the nominal thermocouple temperature is slightly lower than the sample temperature (0 to 10°C) in the 3/4" assemblies and is the same temperature to the degree in the 1/2" assemblies.



Figure 2.2.10: Comparison of temperature profiles in 19.1 mm (black line) and in 12.7 mm (grey line) assemblies. Measurements (filled points) were done at 900°C – 10 kbars on the 3/4" (black points, Laporte et al., 2004) and at 1000° C – 10 kbars on the 1/2" (grey points, Laporte, personal communication) and are expressed by *D*T, the temperature difference to the measured temperature to the base of the assemblies (at 14.8 mm in the 3/4" and at 13.1 mm in the 1/2"). With a quadratic equation (black and grey lines) adjusted on Laporte et al.'s measurements, we estimated temperature variations inside our experiments: circles 1 correspond to the thermocouple tip, circles 2 correspond to the sample base and circles 3 correspond to the sample top. Positions of points 1, 2, 3 are from Laporte et al. (2004) and are directly applicable to our experiments since our capsules have the same size.

General processes limiting equilibrium achievement

A system is at the equilibrium when its intensive variables (temperature, pressure and chemical activities) are homogeneous in all the system and stay constant with time. Concretely, it means that at equilibrium, no reaction occurs in the system. In the case of my experiments, which are crystallization experiments, several processes can limit the achievement of equilibrium, linked to 1) the heterogeneity of the starting composition, 2) P-T conditions, 3) thermal gradient in the capsule, 4) duration of the experiments, and 5) enclosure of the system.

1. Heterogeneity of the starting composition:

- We used in our experiments synthetic gels that are homogeneous chemically. ground gels are amorphous but, they are heterogeneous texturally, since they are formed by different micrograins. Nevertheless, to start piston-cylinder experiments, as explained before, we attained the high temperature (650°C) at low pressure (3 kbars). At that time, we can imagine that atoms start to move fast. Some parts of the sample can be at the liquid state while in other places, atoms start to be arranged and form nuclei. Then, at experimental conditions, because my experiments are liquidus experiments and have a high melt fraction, we can imagine that the melt convects inside. Here I can say that my material is homogeneous texturally and chemically, but not uniform. During the duration of the experiment, crystals grow and the system tries to reach its equilibrium state. The achievement of equilibrium and the solid phase homogeneization in those experiments will be controlled mostly by dissolution – crystallization processes and by diffusion. Note that dissolution – crystallization processes are the fastest and most efficient processes to reach the equilibrium.
- This is more complex when we add crystals in the starting materials. Since gels are amorphous, they present no nucleation sites to grow crystals. To grow crystals, it is easier to work with natural materials, which are ground crystals, because they act as nucleation sites. Nevertheless, the use of those ground crystals favors crystal zonations. In my experiments, I could not manage to grow cpx as big as I wanted. I only obtained reactional cpx as rims around opx, (Figure 2.2.11).



Figure 2.2.11: Representative anhydrous experiment (12 kbars – 1360°C) with automorph opx with polygonal shape (equilibrated shape), surrounded by quench cpx (QuCpx) that can form thin lighter rims around opx.

In order to improve cpx growth, I decided to add cpx seeds, ground down to 10 to 15 μ m diameter, in the starting composition. Those seeds are relatively stable in my experimental conditions, although not inert. This implies that those crystals will need more time to be in equilibrium with the system. In that case since seeds are already crystallized, the process that will control the achievement of equilibrium of those seeds is the diffusion. Diffusion is a slow process, looking at the diffusivity of some major elements (compiled in Médard, 2004 from Freer et al., 1982; Zhang and Stolper, 1991; Chakraborty, 1995; Kohlstedt and Mackwell, 1998), especially in minerals ($\sim 10^{-15} \text{ m}^2 \text{.s}^{-1}$ in olivine and $\sim 10^{-18} \text{ m}^2 \text{.s}^{-1}$ in clinopyroxene compared to 10^{-9} to 10^{-12} m².s⁻¹ in silicate melt, for the same element). Experimental duration had to be long (e.g. Falloon et al., 1999; Pickering-Witter and Johnston, 2000; Schwab and Johnston, 2001), in the order of some months for a cpx crystal of 10 μ m diameter to reach equilibrium. This explains why some cpx in some of my samples (maybe depending on the seeds quantity I added) are zoned. Those cpx did not just act as nuclei in my system. As I said they are not inert, some chemical components from the seeds were also exchanged with the rest of the sample, like Fe and Mg that diffuse fast. During mass balance calculations, I took special care to take in account the most equilibrated cpx, thus not the cpx "seeds", as described in section 2.3.4. Because of Fe – Mg exchange, the mass balance did not work. This will be discussed later in section 2.3.4. It means that my system is out of the global complete equilibrium. However, remaining liquid and the interface of cpx "seed" crystal can be at equilibrium. For example, my cpx (from seeds) have a Ca-rich core with Ca-poor interface. The Ca inside the cpx tends to diffuse slowly out the cpx to attain homogeneous crystal, so Ca at the interface and in the basalt will increase. So at every given time t, the interface is locally at the equilibrium but with time,

its composition is changing to reach equilibrium. Since I observed zoned crystals, at the moment I stopped my experiment, all my system is not globally equilibrated.

2. P - T conditions:

Variations of P - T during the experiment can disturb the achievement of equilibrium. A crystal starts to grow in some conditions tempting the reach equilibrium conditions and then when those conditions change, it continues its crystallization tempting to reach these new equilibrium conditions. Thus, we can observe zonation. At the same time, diffusive exchange inside the crystal and between the crystal and the melt will tend to re-equilibrate the compositions.

I already mentioned that in a piston-cylinder P and T variations are negligible. Although in the order to grow cpx as I presented, I ran experiments with a temperature decrease. In those experiments, I took a special care to decrease the temperature (by 15 °C) really slowly $(0.01^{\circ}C/min)$ and then the final temperature is maintained during 3 days. Here, the time scale and the range of temperature variations are very important. The lower the range of T is, the smaller the compositional difference between core and crystal's rim will be and therefore the faster to reequilibrate by diffusion.

Nevertheless, I noted that mass balance calculation, which is one criterion to check the equilibrium state, failed mostly in the case of experiments with temperature decrease, i.e. at 8 and 12 kbars. For the same experiment at 16 kbars, without temperature decrease but with the addition of cpx seeds, mass balance worked. I cannot be sure of what causes the mass balance calculation to fail, cpx seeds addition or temperature variation.

3. Thermal gradient:

If there is a significant thermal gradient in the capsule, crystals will form at different local equilibrium. Thus, the compositions of mineral at the top and bottom of the capsule will be different. In my experiments, this process is negligible. Because in my experiments, I have a large quantity of liquid, which convects during the experiment and this may constantly move the crystal and help homogenize the melt chemistry. This creates a pseudo-local equilibrium. I have measured the same mineral composition, for example in opx at the top or at the bottom, or everywhere in the capsule. Moreover, my melt compositions are perfectly homogeneous (variations are within the analytical error bars). Therefore, there is no compositional stratification of my sample due to the thermal gradient.

Nevertheless, I observed a textural stratification that can be explained by a thermal gradient. Many experiments, especially multicapsule experiments, show a zonation where crystals and melt are separated on each sides of the capsule (see Figure 2.2.12 a and b). This phenomenon cannot be explained by gravity, because crystal density is higher than melt density. This phe-



Figure 2.2.12: Crystals-melt segregation due to thermal gradient, for multicapsule experimental sample, runned in 3/4" piston-cylinder, a) without cpx seeds addition and b) with cpx seed addition. Thermal gradient is maximum $10 - 15^{\circ}$ C. From the sample texture, we localised thermal structure by + and -, indicating hotter and colder areas.

nomena can be explained by a thermal migration, that is internal differentiation of an initially homogeneous system under temperature gradient effect (Lesher and Walker, 1988). In this case, the thermal migration occurs even for low temperature gradient, such as what we have $(10^{\circ}\text{C.mm}^{-1})$ or even lower.

To summarize, this effect favors the crystallization in some colder parts of the capsule, but it does not create compositional stratification because of the large quantity of melt of my experiments. In my experiment this phenomenon was advantageous because it promotes melt segregation and big melt surface were created that eased melt analyzes.

4. Duration of experiments

Theorically, duration of experiments is important because it gives time for elements to diffuse and reach an equilibrium state. But diffusion is a slow process. Typical REE diffusivity at my T conditions is at the range from 10^{-20} to 10^{-18} m².s⁻¹, which corresponds for my crystal sizes, to a range of 2 to 200 years of experiments! In crystallization experiments, crystals tend to equilibrium by dissolution-crystallization. Thus, for my experiments, time is more critical for growing big crystals. After several test experiments, we saw that 3 days of experiment, in my anhydrous system, were not sufficient to grow crystal bigger than 20 μ m diameter, which is too small for trace elements and F and Cl analyses. After 5 – 6 days, some crystals were bigger than 50 μ m diameter. I decided that 5 – 6 days of experiment was a good compromise to grow sufficiently big crystals and without abusing piston-cylinders usage.

5. Enclosure of the system

The enclosure of a system is fundamental for this system to attain the equilibrium. As for P

and T conditions, if the composition of the system changes with time, it will be more difficult, nearly impossible, to reach equilibrium state. For example, a crystal starts to grow in some bulk system composition, if the bulk composition changes, the crystal continues its growth with a different composition. The crystal is zoned. Consider the same previous example of the cpx, with Ca-rich core and Ca-poor interface. I said the Ca of the cpx core tends to diffuse slowly out the cpx to attain Ca homogeneity in the crystal. Given that the diffusivity of elements are several order of magnitude slower in minerals than in the liquid, if the liquid is loosing its Ca (relatively fast), the Ca in the crystal will never attain equilibrium.

In high-pressure experiments, it implies the sealing of the capsule. Even if special care is taken to weld the capsules, experimentalists can never really be sure of the closure of their sample system, except by proving by mass balance.

For my experiments, this is critical for H, leaking out of the capsule in hydrous experiments, because H has a fast diffusivity in melt and crystals. As I explained, I cannot be sure of how much H_2O I put under the form of $Al(OH)_3$ and/or liquid water, thus mass balances of hydrous samples cannot be conclusive. The only way I checked water leak is by analyzing water in olivines in the outer capsule. In spite of the fact I found more water in those olivines than in natural mantle olivines, the 200 ppm measured H_2O content is assumed to be negligible. The enclosure of capsules is considered secured.

2.2.4 Criteria to judge the equilibrium

There are 4 strict criteria to assure us of the equilibrium state of an experiment:

- 1. Minerals compositions are homogeneous within and among the grains. Liquid composition is constant through out the charge.
- 2. The mass-balance calculation determines phase proportion and shows no loss or gain of oxides.
- 3. (1) and (2) does not change with time.
- 4. The reversal experiment gives the same (1) and (2)

(1) and (2) demonstrate that the system is closed. (3) shows the system reached steady state. (4) demonstrates the "path-independent" attainment of an identical steady state. The failure of any of these prevents the achievement of global equilibrium.

(1) and (2) can be tested using measurements in minerals and melt, done by the different analytical techniques (section 2.3), but it just demonstrates that the system is closed.

(3) will be difficult to detect given the slow diffusity of trace element.

(4) is nearly impossible for partitioning experiments. In the case of my experiments, it implies the

running of the experiments with F, Cl and TE-rich minerals with F, Cl and TE-free basalt, to control if we obtain the same F, Cl and TE concentrations in the final products. This was technically inconceivable.

To conclude, I cannot assess the perfect achievement of equilibrium of my experiments. What is sure is that my experiments were **close** to the equilibrium state, sufficiently close to guarantee the accuracy of my results. To do that, petrologists use different criteria.

• I know that a system achieved its thermodynamical equilibrium when constituting phases are homogeneous and the chemical potential of an element is identical in every phases. For one given chemical element, we control the steadiness of the chemical potential among phases using concentration ratio of this element between phases. This relation is expressed by the partition coefficient D of the element i between the phase A and the phase B:

$$D_i = X_i^A / X_i^B.$$

Ford et al. (1983) and Libourel (1999) experimentally determined that Fe, Mg, and Ca partition coefficients between olivine and melt correlated perfectly (0.993 for Fe and 0.996 for Mg) with temperature, pressure and melt composition. If olivine crystals achieved equilibrium, the calculated parameters such as pressure and temperature have to correspond to experimental conditions (within the errors bars).



Figure 2.2.13: Comparison between experimental temperature and calculated temperature, using Ford et al. (1983) geothermometer, modified by Etienne Médard ('Laboratoire Magmas et Volcans') from Médard and Grove (2008). This takes into account water content in the sample, and that diluted in the melt. Grey tinted area corresponds to $\pm 15^{\circ}$ C. In that figure, we put samples containing olivine and for which we had water analyzes (20% of our samples). Δ T corresponds to the samples which have gone through temperature stages (see Figure 2.2.7). Figure 2.2.13 shows that our samples are in good agreement $(\pm 15^{\circ}C)$ with Ford et al. (1983) and Médard and Grove (2008) models, both for anhydrous and hydrous experiments, in the basaltic system.

Another test of thermodynamical equilibrium, is the distribution coefficient of Fe (Fe²⁺) and Mg between olivine and melt called Kd:

$$Kd_{Fe/Mg}^{olivine/melt} = D_{Fe}^{olivine/melt} / D_{Mg}^{olivine/melt} = (FeO_{olivine} \cdot MgO_{melt}) / (FeO_{melt} \cdot MgO_{olivine}).$$

For olivine, this coefficient is not very temperature sensitive (Roeder and Emslie, 1970; Ulmer, 1989), but is pressure and melt composition sensitive. Even if the dominant effect is still debated (Longhi et al., 1978; Ulmer, 1989; Kushiro and Walter, 1998; Kushiro and Mysen, 2002), the equilibrium Kd value varies between 0.27 and 0.36 in basaltic systems (Hirose and Kushiro, 1993; Kogiso and Hirschmann, 2001; Wasylenski et al., 2003; Laporte et al., 2004). Samples out of this small variation are considered to be out of the thermodynamical equilibrium state. Our samples of the basaltic systems have a Kd from 0.301 to 0.347. Among our samples, those out of the accepted equilibrium Kd range are those that suffered experimental problems.

Toplis (2005) developped a predictive model for $Kd_{Fe/Mg}^{olivine/melt}$, which can be used to test equilibrium in mantle melting experimental studies. In experiments where olivine is present, I tested the Toplis model 2005. This is illustrated on Figure 2.2.14, where Kds values measured in my experiments are compared to values predicted by the Toplis model.



Figure 2.2.14: Comparison between the exchange Mg-Fe coefficients between olivine and melt of my experiments (Kd^{mes}) and the calculated coefficients (Kd^{Th}) with the Toplis model 2005. Symbols are the same than in figure 2.2.13.

This Figure 2.2.14 shows that the Toplis model 2005 cannot explain the measured values. The measured values are up to 40% higher than the measured values, which is significant. This can be attributed to Cl concentrations in samples that tends to increase Kds (Filiberto et al., 2010).

There is not yet quantification of Cl effect over Kds, but this is a work in progress, in a paper in preparation by Filiberto et al. (2010).

Because olivine is not a systematic solid phase in our experiment, thermodynamic equilibrium had to be tested using cpx composition in olivine-free samples. We compared our $D_{Al_2O_3}^{Cpx/melt}$ and $D_{CaO}^{Cpx/melt}$ with those of Gaetani and Grove (1998), to evaluate the thermodynamic equilibrium. The $D_{Al_2O_3}^{Cpx/melt}$ in our Cpx is systematically lower (from 0.26 to 0.38 in anhydrous experiments and in average 0.41 in hydrous experiments) than Gaetani and Grove (1998) samples (from 0.44 to 0.51 in anhydrous experiments at comparable conditions and from 0.35 to 0.46 in hydrous experiments). This systematic could reflect the incomplete equilibration of cpx due to the seeds in our experiments, which are richer in Al₂O₃ and lower in CaO than those used by Gaetani and Grove (1998). Concerning $D_{CaO}^{Cpx/melt}$, my range of data (from 1.24 to 1.28 – and 1.63 in one sample CC01#8kb4 – in anhydrous samples and in hydrous samples 1.69 and 2.11) are comparable to Gaetani and Grove (1998) range (from 1.19 to 1.40 in anhydrous samples and in hydrous samples 1.61 and 2.17).

• We argue in petrology that polyhedral form is an indication of equilibrium. Polyhedral form occurs when the rate of crystal growth is sufficiently slow at near equilibrium condition. Note that crystal would not grow at equilibrium. Thus it is just an indicator of near equilibrium condition. This is the case in my experiments, see Figure 2.2.11, especially for anhydrous experiments.

Nevertheless, sometimes I could observe samples showing crystals out of equilibrium growth. In order to preserve high temperature equilibrium, quench process had to be instantaneous. Quenched speeds are 50° C.s⁻¹ for 3/4" assemblies and 200° C.s⁻¹ for 1/2" assemblies, in piston-cylinder. Such speeds are not sufficient to avoid quench-crystals growth, especially quench-cpx (QuCpx) growth (Figures 2.2.11 and 2.2.15). This crystal growth is ultra-rapid and is in desequilibrium with the melt (partition coefficient equal to 1, Gamble and Taylor, 1980). Quench cpx growth is favored by the fast crystal growth speeds of cpx 100 – 200 μ m/s (Kirkpatrick et al., 1976). This phenomenon does not exist for other crystals like olivine and opx in anhydrous samples. Moreover, in hydrous samples, we could observe big cpx dendrites in reactional areas between crystallized part and melt (Figure 2.2.15). Water decreasing melt viscosity, it should promote fast dendrites growth. Those reactional or dendritic crystals were not taking into account in mass balance calculations.



Figure 2.2.15: Crystals formed by rapid growth during quench. Hydrous experiment with 2.6 wt% of water. We can observed cpx dendrites in overgrowth on automorph opx, but also big isolated cpx dendrites, "christmas tree" shape.

2.2.5 What kind of information can be extracted from my experiments?

What I demonstrated is that my experiments were not at the global equilibrium but close to the equilibrium. To know that I succeeded to grow equilibrium crystals, so that measurements I made in crystals can be used, I calculated the Peclet number of elements of interest: F and Cl.

The Peclet number is a dimensionless number relevant in the study of transport phenomena by advection – diffusion in fluid flows. It is the ratio of the advection rate of a physical quantity by the flow over the rate of diffusion of the same quantity driven by an appropriate gradient. Applied in our case, it represents the competition between crystal's moving (during crystal growth boundaries) and the diffusivity of an element. Knowing the time of experiments t, considered as the reaction time, and deducing the growth speed of crystals present in experiment v, we calculated x_b the distance grain boundary moves during each experiments, following:

$$x_b = v \cdot t.$$

The distance an element i can move during the same time is defined by:

$$x_d = \sqrt{D_i \cdot t},$$

where D_i is the diffusion rate of the element *i*. When $\sqrt{D_i \cdot t} < vt$, this means that the diffusion of the element *i* is faster than the grain growth and we considered that element *i* is equilibrated in the system. This can be expressed by the relation:

$$v^2 t / D_i < 1.$$

that is called the mass transfer Peclet number. We estimated that mass transfer Peclet number for F and Cl in our 5 days experiments is of the order of 10^{-6} (calculated for opx and olivine), that is the F and Cl diffusion rates are faster than crystal growth rate. Thus, I conclude that it is possible to

grow an equilibrium mineral grains in these experimental conditions and considered that measured F and Cl partition coefficients in fact represent equilibrium values.

2.3 Analytical techniques

2.3.1 Procedure for the analyzes of the experimental samples

Chemical analyses of samples were carried out in the following order to maximize the amount of data on small experimental charges.

- Texture and phase assemblies of each sample were inspected by scanning electron microscopy (SEM). I look if the sample has: (i) an equilibrated texture (as discussed in above section 2.2.3), (ii) grains were larger than 20-30 μ m, and (iii) sufficiently large quenched melt pools were present, separated from the crystallized part (approximately > 20% melt fraction favors such condition).
- For the selected samples, a chemical mapping is acquired to locate the different phases in the sample. This step has provided critical maps for locating phases during SIMS and LA-ICPMS analyses.
- The sample is then analyzed in major and minor elements (and F and Cl for amphibole and phlogopite samples), by electron microprobe.
- The bigger crystal grains and the quenched melt, of the selected samples are mounted in indium, and analyzed for H₂O, F and Cl by the SIMS Cameca 1280 of Woods Hole Oceanographic Institution (WHOI). Three analysis sessions were carried out (see Table 2.3.1).
- When the size of the remaining grains enables it, trace element analyzes were done in crystals and quenched melt by the SIMS Cameca 3f of WHOI and SIMS Cameca IMS5f of the 'Laboratoire Géosciences' of Montpellier (noted GM). Five measurement sessions were carried out (see Table 2.3.1).
- At this point, samples were cleaned and analyzed by Raman spectroscopy.
- To finish, because it is the most destructive technique, we analyzed all the samples with LA-ICPMS. Three sessions were carried out (see Table 2.3.2).
- At the end of all this analysis series, SIMS pit and LA-ICPMS crater localization was done by SEM.

In the following parts, procedures and set-ups of each analytical technique are detailed.

Session	Dates	Apparatus	Elements	Analyze number	Sample number	Samples
1	sept-2 to $sept-4-2008$	1280 WHOI	$\mathrm{F,Cl,H_2O}$	113	16	
	sept-5 to sept-9-2008		REE	102		anhydrous samples (12 kbars – 1360°C)
	$\substack{\text{sept}-10 \text{ to}\\ \text{sept}-16-2008}$	3f WHOI	light TE	97	14	(
	sept-17 to sept-21-2008		Sc	101		
2	feb-23 to feb-27-2009	$5f~\mathrm{GM}$	F, Cl (try) + TE	47	6	anhydrous samples (big zoned crystals)
3	aug-2 to aug-7-2009	1280 WHOI	F,Cl,H_2O	130	16	anhydrous samples
	aug-5 to aug-10-2008	3f WHOI	REE	76	7	(from 8 to 16 kbars)
4	feb-22 to feb-26-2010	$5f~\mathrm{GM}$	TE	49	11	anhydrous samples + amp, phl
	march-23 to march-26-2010	1280 WHOI	F,Cl,H_2O	133	8	hudnesse commilee
5	march–27 to april–1–2010	3f WHOI	REE	102		+ amp, phl + 25kb
	april–2 to april–4–2010		light TE	62	51	

Table 2.3.1: Summary of SIMS sessions. Details of different set-ups are described in the text in the SIMS section (section 2.3.6)

Amp, Phl and 25kb are respectively for amphibole-, phlogopite-, garnet-bearing samples.

Table $2.3.2$:	Summary	of LA-ICPMS	sessions.	Details of	differents	set-ups	are	described	in	the
text in the l	LA-ICPMS	section (section	on 2.3.8).							

Session	Dates	Apparatus	Elements	Analyze number	Sample number	Samples
1	july-2-2009	femto LMTG	TE	116	16	anhydrous samples no used
2	june-7-2010	LMV	TE	139	10	anhydrous samples (12 kbars–1360°C)
3	june-14-2010	LMV	TE	52	4	anhydrous samples (from 8 to 16 kbars)
4	sept-13-2010	LMV	TE	89	4	hydrous samples (from 12 to 25 kbars)

TE is for trace elements. When it is put without any notes, it means that all the elements cited in the text were analyzed in the same series. We did not use the first session results because the instrumental background was too high. This was attributed to a leak in the sample chamber.

2.3.2 Samples preparation

After each experiment, the recovered sample was embedded in an epoxy mount. Samples were then leveled by polishing using silicon carbide grinding paper (from 200 to 2400) then diamond polishing discs (6, 3 and $1/4 \ \mu m$), for SEM and electron microprobe analyses.

Before SIMS analyses, each sample was removed from the epoxy mount using a sharp tipped soldering iron, and put in an aluminum-mount of 1 inch (2.54 cm) diameter, filled with high-purity indium (Figure 2.3.1). Indium used is 99.99 wt% pure and melts at ~ 150°C in the mount. After some minutes of cooling, indium remains soft and the polished sample can be organized on the indium. This method is described in Aubaud et al. (2007).



Figure 2.3.1: Picture of the indium mount prepared for the last SIMS session. The alumina mount is 1 inch (2.54 cm) diameter, filled with high-purity indium.

When the mount is full, the samples are pressed into indium with a large vice over several hours to assure the flow on indium metal, and as a consequence, the polished sample surfaces aligned themselves to be parallel to the mount surface. The indium mount is then washed in ultrasonic bath with ethanol followed by distilled water and dried in an oven at 120°C, before gold coating. During this PhD, four mounts were prepared; each contained between 8 to 16 samples. To ease SIMS analyses, the three last mounts were repolished a few seconds with 1/4 micron alumina grinding paper, to emphasize the relief of grains compared to the quenched melt. This is usually not advised for electron microprobe analyzes, but this can help locating minerals during SIMS analyses of multiphases texture of experimental samples.

After SIMS analyses, to be analyzed by LA-ICPMS (last step of our sample analysis series) and by Raman spectroscopy, samples were repolished several minutes to remove the metallic coating.

2.3.3 Scanning electron microscopy (SEM)

I used the JEOL 519LV of 'the Laboratoire Magmas et Volcans'. It is equipped with an energy dispersive spectrometer (EDS).

An primary beam of incident electron exited the sample surface. Detectors collect either the secondary or backscattered electrons (imagery mode), or photons (analysis mode). The use of secondary electrons emitted by the sample surface provides an image of the surface topography (Secondary Electron Imaging, SEI). The backscattered electrons (Back Scattered Electrons Imaging, BSEI) are emitted from the effect of the primary beam penetration deeper in the sample, and their energy depends on the average atomic numbers of the elements it came across. The produced image roughly illustrates chemical contrast between different phases, or phase zoning in the sample: with the increasing average atomic number, the image becomes brighter. Using the analytical mode, photons emitted by the EDS detector are retrieved and picked up by a receptor. We get an energy spectrum that allows qualitative phase identifications. The comparison of the peak intensity on this spectrum identifies phases.

2.3.4 Electron microprobe

Principle of the analysis

I used the electron microprobe a CAMECA SX 100 of the 'Laboratoire Magmas et Volcan' (LMV). One session was done on the JEOL 733 of the Massachusetts Institute of Technology (MIT). Electron microscopy is an in situ non-destructive analytical technique, used to measure major and minor element concentrations (and F and Cl concentrations in phlogopite, amphibole and their associated melts) in my experimental samples.

The electron microprobe is composed of one electron gun and four wavelength dispersive spectrometers (WDS, see Figure 2.3.2). The sample, in a vacuum chamber, is bombarded by primary beam of electrons accelerated by a 15 kV potential, focused by several electromagnetic lenses. The absorbed electrons excite the electron orbits of atoms that emitted X rays of characteristic wavelength of the element present in the sample, and of intensity proportional to the element concentration. The emitted waves are reflected into a detector by a specifically orientated monochromatic single crystal, characterized by their reticular distance. A photoelectrical detector measures the intensity for each wavelength. Comparing the wavelengths and the intensity of X rays that the sample emitted with those of the standards, taking into account matrix effects, we can therefore quantitatively determine element concentrations in the sample.



Figure 2.3.2: Captioned drawing (on the left) and picture (on the right) of the electron microprobe CAMECA SX 100 of the 'Laboratoire Magmas et Volcans'. The microprobe is about 1 m³. The captioned drawing was modified after http://barrande.nm.cz/images/5/2.jpg

Analytical conditions

For anhydrous experiments, we measured only major elements by electron microprobe. For crystals, an accelerating voltage of 15 kV and a beam current of 15 nA with a focused beam were used. For quenched melt, an 8 nA beam current and a 5 to 20 μ m defocused beam, depending on the quenched melt area, were used. Reproducibility difference between the CAMECA SX 100 of the LMV and the JEOL 733 of the MIT is better than the analytical precision of the two methods. This has been tested by repeated analyses of F2p#2a sample melt, olivine and orthopyroxene.

Generally, analytical totals were between 98 to 100 wt%, except for hydrous experiments melts and highly volatile-rich concentrated melts. Counting time was 10 s for all elements, but 20 s for chromium, nickel and titanium; backgrounds were measured for the same times. Calibration was done using: albite (Na, Si), olivine (Mg), orthose (K), wollatonite (Ca), MnTiO₃ (Ti, Mn), Fe₂O₃ (Fe), Al₂O₃ (Al), Cr₂O₃(Cr) and NiO (Ni).

For amphibole-bearing and phlogopite-bearing experiments, we measured F and Cl in melt, phlogopite and amphibole. An accelerating voltage of 15 kV and a beam current of 40 nA were used with a 2 to 10 μ m defocused beam in crystals and a 20 μ m defocused beam. Counting time for F and Cl analyses was 60 s. For phlogopite analyses, we increased the FeO counting to 20 s.

Data reduction and mass balance calculation

During phase analyses, care was taken to avoid analysis of quenched rims of crystals (like quench cpx), or zoned crystals. Some criteria have been applied to keep only equilibrated or the most equilibrated pyroxenes. We considered that compositions of the most equilibrated clinopyroxenes have the lowest calcium concentrations and the most equilibrated orthopyroxene have the highest calcium concentration (Schwab and Johnston, 2001). For all anhydrous mineral phases, we kept only analyses with a total of 100 wt% \pm 1 wt%. For quenched melt, when it was possible (i.e. except for highly volatile concentrated melts), we discarded analyses with a total <97wt%.

When F and Cl were measured, a correction had to be applied on the data. Analytical totals exceeded 100 wt%. When the microprobe recalculated oxides from atom measurements, it doesn't take into account that F and Cl replace oxygen O in the structures and it creates an excess of O. To correct for that, we needed to substract half of the fluorine atom number and half of the chlorine atom number to the oxygen total atom number: n(O)-(n(F)/2)-(n(Cl)/2). We needed to divide volatile atom number (O^{2-} and F^- , Cl^-). This correction is done to respect electroneutrality, given that F and Cl are linked to cations in crystals. In melt, this depends on the complexation state of F and Cl. It was showed by NMR studies on Cl in silicate and alumino-silicate melt that Cl and F are not free, but bonded to Al, Ca, and Na (Sandland et al., 2004; Zimova and Webb, 2007). Thus, this same electroneutrality correction was done in melt analyses. Then, the new oxygen atom number is redistributed to calculated oxides. The new oxide total has to be 100 wt%.

Errors presented in tables and on Figures for major elements are one standard deviation calculated for each phase on the selected analyses.

Mass balance calculations for each experiments were done using a program developed by Ariel Provost (Albarède and Provost, 1977), using the chemical composition of each phase and of the starting composition. The robustness of this program comes from the fact it takes into account the standard deviations of the compositions.

In these mass balance calculations, dentritic crystals in the hydrous quenches were not taken into account. Since dendritic growth is very fast, and so non equilibrated, it doesn't change the melt composition (partition coefficients tend to be 1 for major elements, Gamble and Taylor, 1980), particularly in the case of high melting experiments.

As discussed previously, for some anhydrous experiments samples, the achievement of equilibrium was not complete. This led to the non-convergence of the mass balance program. Removing sometimes CaO, sometimes Al_2O_3 from the compositional matrix, the mass balance converged. This confirmed the non-complete equilibrium of some of our experiments. This can be also attributed to the fact that F and Cl are not taken into account into the mass balance (see Table 4.5.2, Chapter 4).

Thus, phase proportions presented further have been given only for indication.



Figure 2.3.3: Pictures of SIMS a) Cameca 3f (about 1 m²) and b) Cameca 1280 (about 5 m²) of WHOI

2.3.5 Ionic microprobe

General presentation

The ion probe or secondary ion mass spectrometer (SIMS) is an in-situ hardly destructive analytical method. Only a few angstrom (Å) of the sample surface are removed. SIMS analyses were done at the 'Laboratoire Géosciences' of Montpellier, France (noted GM in the following pages) on the Cameca IMS 5f, and at Woods Hole Oceanographic Institution (WHOI) in Woods Hole, U.S. on the Cameca IMS 3f (Figure 2.3.3a) and IMS 1280 (Figure 2.3.3b).

All SIMS have the same principle (Shimizu and Hart, 1982; Valley et al., 1998): primary ions (positive cesium or negative oxygen) are generated by a gas source. In contrast to an electron microprobe, which uses an electron beam to bombard a solid sample and analyses intensities of characteristic X-rays of chemical elements, a SIMS analytical system (ion microprobe) uses a finely focused beam of primary ions (usually these are Cs^+ , O^+ , O^{2+} , O^- and O^{2-}) directed onto a sample. In the primary sector, ions are accelerated in the primary column (Figure 2.3.4) and focused on the sample that is under vacuum. The impact removes ion from a focused part on the sample due to collision cascade reactions: particles are tore off and ejected, ionized to form the secondary ion beam. Between the sample and the first transfer lenses, the beam is accelerated by an electric field. At this point, ions are sent in the secondary sector, the spectrometer part of the machine. Secondary ions are separated following the initial energy by the electrostatic sector. The spectrometer lenses refocus them. Then the magnetic sector separates the ions following their mass/charge ratio. Selected ions are then collected in the counting system.

In the following part, the primary sector and the spectrometer will be described with more details.

Sector description

• The primary sector:

The primary sector is composed of the gas source and the primary column (see Figure 2.3.4). The 3f SIMS (WHOI) has a duoplasmatron source, that produces oxygen ions, and the 1280 (WHOI) and the 5f SIMS (GM) have both a duoplasmatron, a cesium source and an electron gun.



Figure 2.3.4: Captioned drawing of the principle of an ion probe, that shows the main lenses, diaphrams and optical ways of the primary and secondary beams. The captioned drawing was modified from Valley et al. (1998)

The duoplasmatron operates as follows: a cathode filament emits electrons into a vacuum chamber. A gas such as argon is introduced in very small quantities into the chamber, where it becomes charged or ionized through interactions with the free electrons from the cathode, forming an oxygen plasma. Following the plasma position, positive (at the center of the plasma) or negative (at the edge of the plasma) ions are extracted. The plasma is then accelerated through a series of at least two highly charged grids, and becomes an ion beam, moving at fairly high speed through the aperture of the device.

The cesium source is coupled to an electron gun. The heating of a cesium carbonate reservoir produces cesium vapor. Getting in contact with a high temperature $(1100^{\circ}C)$ tungsten plate, this cesium vapor is ionized. Ions are then extracted and accelerated through an electric field applied between the plate and the extraction lenses.

The colinear electron gun allows to neutralize the electric charges that can be developed in some conditions on the sample, by adding electrons.

The primary column contains a series of electrostatic lenses, deflectors and removable diaphragms that accelerate the primary beam, regulate its intensity, limit its aperture and focusses it at 45° of the sample surface (Figure 2.3.4). The interaction of primary ions with sample surface causes three major effects:

- 1. Mixing of the upper layers of the sample that results in an amorphization of the material structure,
- 2. Implantation of the primary ion beam atoms in the sample, and
- 3. Ejection of particles (atoms or small molecules) from the sample surface, which can be electrically neutral, as well as positively and negatively charged.

The charged particles of one polarity called "secondary ions" extracted and accelerated by electrostatic field form a secondary ion beam focused at the spectrometer entrance by transfer lenses.

• The secondary sector:

The secondary sector contains the system of optic treatment, the electrostatic sector and the magnetic sector (Figure 2.3.4). The combination of an electrostatic and a magnetic sector allows reducing the aberrations produced by energy dispersion of the ions. It allows a triple focus: in image, in energy and in mass.

- The optic treatment system is composed of a series of lenses and diaphragms that enable the display and that focuses the secondary ion beam in a image plan or focal plan at different levels along the ion path (Figure 2.3.4). The contrast diaphragm is located in a focal plan and is used to eliminate secondary ions with too high a lateral energy. Entry, energy and exit slits of the electrostatic sector and the counting system are also located in a focal plan. The field diaphragm is located in the image plan and is used to delineate the size of the analyzed zone. The display of different plans on a screen is used to adjust the focus of the secondary beam.

- The electrostatic sector is located between the entry slit and the energy slit (Figure 2.3.4). It is made of two hemispheric plates between which a potential difference is applied. Ions are deflected following a curve which radius depends on the initial energy and the voltage putted between plates. This sector separates ions according to their energy to let only desired ions entering in the magnetic sector. The energy slit is centered on the optical axis of the machine, which corresponds to the average energy of the secondary ions. Shifting the slit towards higher energy decreases polyatomic interferences. This filtering is put by shifting the voltage applied on the sample. This is what is called the offset. In those conditions, the energy slit let cross only ions with an energy sufficient to offset the shift. For instance, applying an offset of 75 V on the accelerated voltage of secondary ions, ⁷⁵As can be measured at only less than 10% of its maximal value, but it will reduce to a negligible contribution the mass interference of ²⁹Si³⁰Si¹⁶O.
- The magnetic sector deflects ions according to a curve which radius depends on their energy and their mass/charge ratio. This sector is used to separate ions of different mass that will be focused on different spot at the exit of the sector. The double focusing, in energy and in mass, is used to adjust the mass resolution power (MRP). Entry and exit slits adjust the mass resolution. A high mass resolution power (MRP) improves the separation of two closest masses, however it leads to sensitivity loss. Mass interferences are solved with higher MRP. The number of impacts received per mass is measured by a monocollection detector, composed by either a Faraday cup, or an electron multiplier (Figure 2.3.4). Faraday cup measures the ion current hitting a metal cup. With an electron multiplier, an impact of a single ion starts off an electron cascade, resulting in a pulse of 108 electrons which is recorded directly.

2.3.6 Volatile analyzes

Volatile elements (H_2O , F and Cl) were analyzed with the SIMS 1280 in WHOI, using the cesium source. One of the main problem during volatile analysis is the background intensity. Organic matter traces, water in the epoxy resin or carbon coat residue are potential sources of pollution that increase the background intensity. This is why we use very pure indium mount to analyze volatiles. The mount is placed under vacuum to degas during the night prior to its analysis. To clean the sample surface, removing surface contaminations, a presputtering (thin surface abrasion) is applied during 180 seconds before each analysis start. The scan uses a current of 1.5 nA. The raster beam scans a $30 \times 30 \ \mu\text{m}^2$ area, then a centered $15 \times 15 \ \mu\text{m}^2$ projected beam size was used for the analysis, which lasted about 350 s.

Settings (presented in 3.5.2.) unable a mass resolution of 6660, allowing the discrimination of mass interferences on the analyzed peaks: ¹⁷O over ¹⁶O¹H, ¹⁸O¹H over ¹⁹F, ²⁹Si¹H over ³⁰Si and ³⁴S¹H over ³⁵Cl. The mass interference over ³⁵Cl is resolved by a mass resolution power of 5120 and the other mass interferences are resolved with lower mass resolution.

Standard use and data reduction

Physical principle of particules ablation and ionisation is a complex process. Measured concentration have to be calculated against a certified standard we measured several times during the analytical sessions. Concentration of an element is calculated normalizing the counts (directly received by the machine detector and given as output files by the related computer) to counts of one element taken as reference, for which concentration was measured by another machine (such as electron microprobe). This element is called the internal standard. In this study, we mostly used different Si isotopes. To have comparable matrix effect, standard composition has to be close to the sample composition. For volatile analyses, calibration is done using a set of 7 basalt samples as certified glasses (Rose-Koga et al., 2010), that cover the compositions of our basaltic quench glasses. Volatile concentrations are known for those glasses and presented in Table 2.3.3.

Table 2.3.3: Composition of the set of basalt samples, used as stardards to build working curves for H_2O , F and Cl (Rose-Koga et al., 2008, 2010). DL is for below detection limit.

Standard	SiO_2 (%)	$H_2O~(\%)$	F (ppm)	Cl (ppm)
Gl03–D51–3	49.5	0.443	299	182
AlV519-4-1	48.8	0.17	124	45
EN113-46D-2	49.5	0.112	90	45
D20–3	± 50	0.05	DL	DL
$\rm JD17H$	± 50	2.49	DL	DL
ALV1654–3	56.7	1	997	2914
Gl03-D52-5	48.6	1	431	322

Theorically, measured intensity must be corrected by a factor that takes into account the silica content difference between standard and samples. In practice, concentration of an element, F for example, correlates with the measured intensities ${}^{19}\text{F}/{}^{30}\text{Si}$ ratio. This correlation forms a calibration

line, called working curve. Working curves were calculated for each measured volatile element (Figure 2.3.5). The slope and Y-intercept of these working curves were used to determine the volatile concentrations in the sample phases.



Figure 2.3.5: Working curves obtained for volatile element analysis by the SIMS Cameca 1280 in WHOI. Working curves are calculated at the beginning at each analytical session. Those presented here correspond to the 3rd session in WHOI (see Table 2.3.1). Errors on standard composition is equal or less than 10% (Le Voyer, 2009). Errors on intensities ratio are within the symbols.

Table 2.3.4 presents the variation of working curves for each analytical session on the SIMS 1280 of WHOI. The maximum difference between working curve slopes is 30%. This difference must depend on the intensity of the current, the background (depending on the vacuum quality or the cleanliness of the sample), primary sector settings and focus of the primary beam for the concentration of ions, secondary sector settings (can increase the percentage of ions on the detector), detector quality.... Observed difference on the Y-intercept mainly depends to background quality during each session.

Figure 2.3.6 shows that working curves, especially the one of Cl working curves, obtained by SIMS are different following glass compositions. It underlines that it becomes really important to calibrate volatile element analyses using standards with compositions as close as possible as the sample compositions. Nevertheless, during this PhD, I didn't analyze and showshonitic standards glasses.

Using the working curves, we do not take into account the differences of Si abundance of the


Figure 2.3.6: Comparison of F and Cl measurements on the SIMS IMS 1280 (WHOI) and on the SIMS IMS 5f (GM). Solid diamond and empty squares are data on my experimental samples in basaltic melts, while grey triangles are different glass compositions (KL2-G : basaltic glass, Jochum and Stoll, 2003, KE12: peralkaline rhyolitic glass, Devine et al., 1995, ATHO-G: rhyolitic glass, Borisova et al., 2010). It shows that following composition of glasses, calibration curves are changing.

Element	Session	a	b
	1	0.424	-0.084
$\rm H_2O$	2	0.480	-0.069
	3	0.374	-0.147
	1	420	-31
F	2	377.6	-1.43
	3	416.8	-58.926
	1	647	17
Cl	2	761.4	-0.162
	3	594.4	5.986

Table 2.3.4: Comparison of working curves coefficients a and b obtained for each SIMS session on the 1280 of WHOI

phases. The Si abundance correction is thus done during the partition coefficient D_i (here *i* is H₂O, F or Cl) calculation, following the equation:

$$D_i^{crystal/melt} = rac{C_i^{crystal} \cdot C_{Si}^{melt}}{C_i^{melt} \cdot C_{Si}^{crystal}}.$$

No mineral standard exists for volatile analyses. Reliability of basalt glass standards for mineral analyzes has been tested in two ways:

- 1. Elactic Recoil Detection analyzes (ERDA) were done on the set of basalts by Estelle Rose-Koga (Rose-Koga et al., 2010) at ETH Zurich, in the Ion Beam Physics laboratory of the Paul Scherrer Institut. This technique is a nuclear technique, commonly used to have elemental concentration depth profiles. It measures elastic nuclear interaction of a focused ion beam, in the case of F and Cl analysis it was ¹²⁷I ions, with the atoms of the sample. Consequently, in that case, measurements are absolute and physical, which implies that measured concentrations do not depend on the sample composition. Rose-Koga et al. (2010) used this technique to measure F and Cl absolute concentration in the set of basaltic glasses.
- 2. Electron probe measurements of F and Cl were compared to ion probe results for a set of samples (Figure 2.3.7). This effort was made as part of a project of inter-calibration of volatile element analyzes (Cl, F and S) between electron probe and SIMS (Rose-Koga et al., 2008). This project was completed by Marion Le Voyer for higher volatiles concentrations (Le Voyer, 2009). For our range of low concentrations, there is a very good agreement between the two techniques both for crystals and basaltic melt glasses. Figure 2.3.7 shows that correlations worsens when we get close to or under the detection limit of the electron microprobe. Moreover, analytical errors on those elements are much higher for electron microprobe, especially for F, see Table 2.3.5.



Figure 2.3.7: Variations of F (a) and Cl (b) contents, in quench melt glass, opx and cpx of our anhydrous experimental samples, measured by the electron microprobe of the 'Laboratoire Magmas et Volcans' versus contents measured by SIMS 1280 of WHOI.

Table 2.3.5: Comparison of mean detection limits (ppm) and mean errors (relative %) of F and Cl electron microprobe and SIMS analyses.

	Electron	ı probe	SIN	4S
	Detection limit	Relative error	Detection limit	Relative error
F	200	26	20	5
Cl	40	6	30	10

Summary of analytical conditions

For each analysis, optimum setting represent a compromise between :

- 1. an ionic output high enough to have sufficient intensity on the secondary beam.
- 2. a sufficient filtering to discriminate interferences on selected masses.

Those two actions are opposed. Narrowing slits to increase the MRP, we reduce the beam intensity and therefore the counts.

Similarly with the sample texture we have (with grain size seldom bigger than 50 μ m, like in Figure 2.2.11), the beam has to be well-centered and small (we reached $15 \times 15 \ \mu\text{m}^2$ to $10 \times 10 \ \mu\text{m}^2$ on the SIMS 1280). Nevertheless, we cannot reduce too much the beam size, to keep sufficient beam intensity signal. For crystal analysis with very low concentrations like in olivine, if the beam is too focused (too small), signal is too weak to be measured. This is true for volatile and trace element measurements, both on SIMS and LA-ICPMS.

The H_2O , F, and Cl contents were measured during the same procedure in a single analysis. The primary beam intensity was adjusted between 520 pA and 1.43 nA for the following phases: 1.43 nA

was generally used for anhydrous samples and only 520 pA was used for amphibole and phlogopite, much richer in volatile elements. The electron gun was used to compensate the charging of the sample surface.

The aperture of slits and diaphragms was set to (Figure 2.3.4): 81 μ m for the entrance slit, 400 μ m for the constrast diaphragm, 805 μ m for the field aperture, 9 μ m for the energy slit and 30 μ m for the exit slit.

Ten cycles of acquisition were done for each mass. Counting times were of 10 s for volatile elements and 5 s for 30 Si. Waiting times between each mass was 2 s before 19 F, 30 Si and 35 Cl and 3.04 s before 16 O¹H.

For mineral analysis, a raster $30 \times 30 \ \mu m^2$ was used to clean the analysis area and after 180 s the pre-sputtering was turned off and then a $15 \times 15 \ \mu m^2$ projected beam size was used for the analysis, which lasted about 350 s. For the basaltic melt analysis, the $30 \times 30 \ \mu m^2$ raster was used through out the analysis.

2.3.7 Trace element analyzes

For trace elements, secondary ionic mass spectrometry analyses were carried out on a Cameca IMS3f (Woods Hole Oceanographic Institution, WHOI, USA) and on a Cameca IMS5f ('Laboratoire Géosciences' Montpellier, GM, France). Session details are presented in table 2.3.1. A primary O^- ion beam of 6 nA was accelerated to 10 kV before hitting the sample.

The following masses were analyzed in three different series on WHOI SIMS: ⁷Li, ¹¹B, ²⁸Si, ⁵¹V, ⁵²Cr, ⁸⁸Sr, ⁹⁰Zr for the first series; ²³Na, ²⁸Si, ¹³⁹La, ¹⁵³Eu, ¹⁵⁹Tb, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb and ²³⁸U for REE element series and ⁴⁵Sc was analyzed separately to pay specific attention to mass interferences, during the first session. On GM SIMS, the following masses were analyzed in two different series: ⁷Li, ⁹Be, ¹¹B, ³⁰Si, ⁵²Cr, ⁵⁹Co, ⁷⁵As for the first serie and mass 25, ³⁰Si, ⁴⁵Sc, ⁵¹V, ⁸⁸Sr, ⁹⁰Zr, ¹³⁹La, ¹⁵³Eu, ¹⁵⁹Tb, ¹⁶⁰Gd, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁸⁰Hf, ²⁰⁸Pb and ²³²Th, for the second serie.

To reduce mass interference by molecular ion species, the energy filtering method was used. Secondary ions were subject to a 4500 V accelerating voltage with a -70 V offset for REE series and -90 V offset for other trace elements, with a ± 25 eV energy window for WHOI SIMS and with an -80 V offset for the two series with ± 30 eV energy window for GM SIMS (Shimizu and Hart, 1982). The size of the primary beam was set to 20 μ m (critical focusing) on WHOI SIMS and to 40 μ m (Kohler illumination) on GM SIMS. On WHOI SIMS, counting time for each mass was chosen to attain a minimum of 1000 counts per second for 500 ppm concentration, and are 20 to 30 s for each mass, except 3 to 5 s for 28 Si. On GM SIMS, counting time for each mass was chosen between 2 and 30 s, following each phase, during mass calibration to attain a minimum a hundreds of counts per second for tens of ppm concentration.

The trace element abundances were determined by taking ratios of each mass over ²⁸Si (WHOI) and ³⁰Si (GM), and the ratio was multiplied by a calibration factor after correcting for isotopic abundance. The calibration factor was determined from the measurement of NIST 610 and of NIST 612 (Reed, 1992; Pearce et al., 1997; Gagnon et al., 2008) at the beginning and the end of each analytical session. Geostandard KL2-G (Jochum and Stoll, 2003) was used as a secondary external standard to estimate the accuracy and precision of our measurements..

2.3.8 LA-ICPMS

General presentation

The Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) is an in-situ destructive method. Several μ m of samples are destroyed by laser ablation. That is why this method was the last to be used on our samples. During this work, we used the LA-ICPMS Agilent 7500 cs ICPMS coupled to a 193 nm Excimer Resonetics M-50E laser ablation system, of the 'Laboratoire Magmas et Volcans' (LMV) in Clermont-Ferrand and the LA-ICPMS an Agilent 7500 quadrupole ICPMS coupled to a Ti: sapphire femtosecond laser ablation (Pulsar-10, Amplitude Technologies) of the 'Laboratoire des Mécanismes et Transferts en Géologie' (LMTG) in Toulouse.

In LA-ICPMS the sample is directly analyzed by ablating with a pulsed laser beam. Within an ablation cell, an amount of matter is extracted from the sample by focusing the laser beam on its surface. The energy provided by the laser is absorbed by the sample resulting in vaporization and generation of aerosol. The aerosols (analyte atoms) are transported by a 'carrier gas', here argon, into the core of inductively coupled argon plasma (ICP-torch), which generates temperature in the order of 6000 - 10000° K.

The produced ions are extracted from the plasma into the spectrometer region, which is held at high vacuum (typically 10^{-4} Pa). Ions are then separated and collected according to their mass to charge ratios.

Analysis of samples by LA-ICPMS can be divided in three steps, which will be described in the following parts: ablation – nebulization, ionization – mass separation and detection.

• The ablation-nebulization:

We focus on the sample surface a pulsed laser beam of ultraviolet to infrared wavelength. At the point of impact (some μ m to some tens of μ m), the coherent light disintegrates the matter



Figure 2.3.8: Non scaled, captioned drawing of the working process of the LA-ICPMS of the 'Laboratoire Magmas et Volcans' that shows the 3 main steps, by color, presented in the text. The drawing was built following the advices of Jean-Luc Devidal. Pictures of the ablation part of the LA-ICPMS of the 'Laboratoire Magmas et Volcans' are presented in Figure 2.3.9

and sublimates it to a very thin aerosol of nanoparticules. With high wavelength, a melting zone appears that fractionate elements following their volatility. When the pulse lasts long, a coupling plasma forms that absorbs the incident energy, resulting in efficiency fall of the ablation.

Lasers with shorter wavelength are excimer source laser with 193 or 157 nm (no melting phenomena). This 193 nm laser is the one used at the 'Laboratoire Magmas et Volcans'. Some generates pulse of the order of femtoseconds (10^{-15} s) , which prevents coupling plasma ignition by run out of time. This femtosecond laser is the one used at the 'LMTG' in Toulouse. Lasers deliver energies in the order of millijoules but beam concentration on a microscopic point gets to reach energy density required for ablation, i.e. several megajoules per cm⁻².

The impact energy is integrated into the sample in some nano-, pico- or femtoseconds. This energy is suddenly changed into heat. This leads to a 'microexplosion' under the surface with vapor ejection, tiny droplets and solid bits, called aerosols in the following explanations.

• The ICPMS:

- Sample Introduction:

The aerosol then passes into a spray chamber where larger droplets are removed via a drain (Jarvis and Jarvis, 1992). Typically, only 2% of the original mist passes through the spray chamber (Olesik and Dziewatkoski, 1996). This process is necessary to produce droplets small enough to be vaporized in the plasma torch (see Figure 2.3.8).

– Argon Plasma/ sample ionization:

Passing through the nebulizer, the aerosol moves into the torch body where it is mixed with more argon gas. A coupling coil is used to transmit radio frequency to the heated argon gas, producing an argon plasma "flame" located at the torch (Jarvis and Jarvis, 1992). The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. In addition to being ionized, sample atoms are excited in the hot plasma, a phenomenon, which is used in ICP – atomic emission spectroscopy. The aerosol moves into the bottom of the torch body.

- ICP-MS interface:

Because atomization/ionization occurs at atmospheric pressure, the interface between the ICP and MS components becomes crucial in creating a vacuum environment for the mass spectrometer (MS) system. Ions flow through a small orifice, approximately 1 millimeter in

diameter, into a pumped vacuum system. Here a supersonic jet forms and the sample ions are passed into the MS system at high speeds, expanding in the vacuum system (Jarvis and Jarvis, 1992). The entire mass spectrometer must be kept in a vacuum so that the ions are free to move without collisions with air molecules.

– Mass Spectrometer (MS):

In the first stage of the mass spectrometer ions are removed from the plasma by a pumped extraction system. An ion beam is produced and focused further into the actual unit. There are several different types of mass analyzers, which can be employed to separate isotopes based on their mass to charge ratio. The one used in Clermont-Ferrand is a quadrupole analyzers. The quadrupole mass filter is made up of four metal rods aligned in a parallel diamond pattern. A combined direct current (DC) and alternative (AC) electrical potential is applied to the rods with opposite rods having a net negative or positive potential. Ions enter into the path between all the rods. When the DC and AC voltages are set to certain values only one particular ion is able to continue on the path between the rods and the others are forced out of this path. This ion will have a specific m/z ratio. Many combinations of voltages are chosen which allows an array of different m/z ratio ions to be detected. In the plan formed by the positive pairs (Figure 2.3.8) light ions are too much deviated and are brought into contact with the rods. Desired ions and those with higher mass remain between rods. The quadripole plays the part of high-pass filter. In the negative pair, high ions are deviated, which is equivalent to a low-pass filter. Combining both filters, only ions with desired m/z ratio pass completely through the quadrupole rod array and into the detector.

• The detector:

The fundamental purpose of the detector is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. The ion detector of the LA-ICPMS of the LMV is a channeltron electron multiplier. It uses a high negative voltage on the front surface of the detector to attract the positively charged ions to the detector. Once the ion hits the active surface of the detector, a number of electrons is released which then strike the next surface of the detector, amplifying the signal.



Figure 2.3.9: Captioned picture of the ablation part of the LA-ICPMS of the 'Laboratoire Magmas et Volcans'.

Summary of analytical conditions

In this section, we presented settings for analyses achieved at the Laboratoire Magmas et Volcans, Clermont-Ferrand. Analytical conditions used at LMTG, Toulouse are available in Dalou et al. (2009a) in the appendix. No results from the LA-ICPMS of the LMTG will be presented in this work (see Table 2.3.2).

The ICPMS of the 'Laboratoire Magmas et Volcans', Clermont-Ferrand is an Agilent 7500 cs ICP-MS coupled to a 193 nm Resonetics M-50E laser ablation system. The laser wavelength was 193 nm with maximum output energy of 8 mJ. We used a laser pulse frequency of 2 Hz with a 5 ns pulse.

The beam diameter was between 15 and 20 μ m. Seventeen masses were collected with an integration time of 30 ms per mass: ⁷Li, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁸⁸Sr, ⁹⁰Zr, ¹³⁹La, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb, ²³²Th, ²³⁸U, except 10 ms for ²⁸Si and ⁴⁴Ca.

Silica abundance measured on electron microprobe was used as internal standard. A typical signal acquisition started by collecting a background signal for 30 s, and then, depending on crystal size, laser firing lasted from 30 to 70 s. The NIST 610 glass was used as an external standard (Reed, 1992; Pearce et al., 1997; Gagnon et al., 2008).

The glasses NIST 612 and BCR-2G (Wilson, 1997) were analyzed also to check analyses accuracy and precision.

2.3.9 Comparison between LA-ICPMS and SIMS trace element measurement, modified from Dalou et al. (2009a), see in Appendix A

Our measurements on basalt standards BCR-2G, KL2-G and SRM NIST 612 (Figure 2.3.10) provide a first order comparison of uncertainty and accuracy between the LA-ICPMS and SIMS measurement series. Because a LA-ICPMS measurement takes less than 3 minutes, we have managed to analyze several basalt standards throughout the course of the analytical session. On the contrary, the total analytical duration for a SIMS measurement over 18 elements takes nearly one hour; therefore fewer basalt standards were measured during these sessions. Therefore, the uncertainty of BCR-2G measurements (LA-ICPMS) is given by the one standard deviation of the distribution of 4 measurements for LMTG session (Dalou et al., 2009a), and of 8 measurements for LMV session 2 (Table 2.3.1). The uncertainty on SRM NIST 612 measurements is given by the one standard deviation of the distribution of 12 measurements for LMV session 2 (Table 2.3.1). The uncertainty of KL2-G measurement by SIMS is approximately 20% relative for most of the elements. This conservative estimates are based on the counting statistics of a typical counting rate (in average between 100 for Lu and 500,000 for Si).

The analyses obtained by fs LA-ICPMS measurements (LMTG) are accurate to within 10% (except to within 17% for U) when compared with recommended concentrations of BCR-2G (Figure 2.3.10). The concentrations obtained agree with the recommended values of BCR-2G (Figure 2.3.10). The one standard deviation is approximately less than 4% relative for heavy REE, Hf, U, and Th, while less than 3% for the other elements.

The accuracy of the SIMS results is less than previously reported values with the same instruments (5% relative for diopside PHN2661, Shimizu and Le Roex (1986); with the IMS 3f at WHOI). Because of low counts, the offsets of Th and U are within the uncertainty based on the counting statistics (Figure 2.3.10). This is most likely explained by the mass interferences since measurements of Sc, and mid to heavy REE (especially Eu) are notoriously prone to mass interferences. For example, there exists an interference with ²⁹Si¹⁶O⁺ molecule at mass of ⁴⁵Sc⁺ (Steele et al., 1981; Weinbruch et al., 1993). In Dalou et al. (2009a), we suspected interferences with ¹³⁵Ba¹²C, and ¹³⁴Ba¹³C, since the samples had carbon coating prior to SIMS analyses. That is why we choose not to dope our powders in Ba. Therefore, as we used the same isotopes for most of the element analyzed by LA-ICPMS and SIMS, the offset of accuracy between LA-ICPMS and SIMS is due to instrumental characteristics rather than the choice of mass peaks. This instrumental difference is, as a first order, the total count achieved by each technique, thus precision. The LA-ICPMS both for LMTG (see BCR2-G on Figure 2.3.10) and for LMV (see srm NIST 612 on Figure 2.3.10) provide equivalent to more precise measurements than those of SIMS, due to its higher counting statistics. For instance, because of the



Figure 2.3.10: Measurements of trace element compositions of external samples divided by their certified values. Circles are LA-ICPMS data using BCR-2G and SRM NIST 612. White and black circles are data from the LA-ICPMS of the session 2 in LMV (see Table 2.3.2) and grey circle are data from Dalou et al. (2009a) at the LMTG. Diamonds are SIMS data using KL2-G. White diamonds are data of the second session in GM (see Table 2.3.1) and grey diamonds are data from Dalou et al. (2009a) on the SIMS 3f of WHOI. Error bars are one standard deviation. The grey field represents $\pm 20\%$ relative deviation of the standard values. BCR-2G analyzes in the LMV are systematically out of the 20% of the standard value, suggesting severe matrix effect (e.g. oxide mass interference), than do not occur for srm NIST 612.

higher counts, the LA-ICPMS is more suitable to measure U, and Th in natural glasses than the SIMS. BCR-2G analyzes in the LMV are systematically out by 20% compare to the standard value. We suggest that it is due to severe matrix effect (e.g. oxide mass interference, Jean-Luc Devidal, personal communication). For SIMS, Th and U in KL2-G (1.0 and 0.55 ppm respectively) give about 55 and 50 counts total, respectively. In contrast, for LA-ICPMS, these counts on BCR-2G (Th = 5.9 and U = 1.7ppm) give about 1000 and 2300 counts total, respectively (total duration of analysis, approximately 2 minutes). For SIMS, Pb in KL2-G (2.07 ppm) give about 30 counts per cycle, while for LA-ICPMS, Pb in NIST 612 (38.96 ppm) give thousands of counts. For Be, in KL2-G measured by the 5f SIMS, data have to be considered with caution since we detected an interference, during SIMS mass calibration, likely of ${}^{18}\text{O}^{2-}$. For ${}^{52}\text{Cr}$, we suggested an interference with ${}^{36}\text{Cl}{}^{16}\text{O}$. On the other hand, to explain Co discrepancy between LA-ICPMS measurements in BCR-2G and its certified value, we suggest the interference of ${}^{41}\text{Ca}{}^{18}\text{O}$.

Despite these limitations, we presented SIMS measurements in this study since the partition coefficients by SIMS and LA-ICPMS show a good agreement. The calculation of the partition coefficient appears to cancel out the molecular interferences by SIMS that are identical for minerals and liquid, except for Cr and Pb, for which we choose the more accurate values.

The first session of trace element measurements on the SIMS 3f of WHOI is not presented in this work. On this machine, mass calibration is hand made, by programming the SIMS magnet on each position of isotope masses. Mass positions are detected finding the maximum intensity peaks for each measured mass. For some isotopes, maximum intensity peaks are not obvious to find manually. A little shift of every mass position was introduced at the beginning of the first SIMS session. This explain why recovered concentrations were too low to be presented here: only 30% to 40% of the initial concentration was recovered.

Another factor that differentiates SIMS and LA-ICPMS measurements is the ablation process itself. Both SIMS and LA-ICPMS beams could be focused down to $15 \times 15 \ \mu m^2$. However, while the ablation depth is few angstroems by SIMS, it is several μm for LA-ICPMS. This is illustrated by the Figure 2.3.11. This justifies why LA-ICPMS analyzes had to be done lastly during this work.



Figure 2.3.11: Back-scattered electron image of the sample CC4#7b, where SIMS and LA-ICPMS pits are visible. Repolishing was done between SIMS and LA-ICPMS analyzes, which explains the small size of SIMS craters (< than 20 μ m). Abbreviations used: Opx, orthopyroxene; Cpx, clinopyroxene; Melt, quenched basaltic melt.

2.3.10 Raman spectrometry

Working process

In order to study if F and Cl had consequences on crystal networks, our samples were analyzed by Raman spectroscopy at the 'Laboratoire des Materiaux Inorganiques' (LMI) in Clermont-Ferrand. This technique is a spectroscopic non-destructive technique, used to characterize molecular composition and structure of a material. Analysis is done by material excitation. A powerful light source (as source of electromagnetic monochromatic wave), a laser in that case, sends energy to the material, that produce radiation collected and analyzed by a suitable detector. When the laser light passes through the sample material, most of the photons exits from the sample with no change (elastic diffusion), but a small fraction is scattered and interacts with the sample atoms. This type of scattering (inelastic diffusion) is known as Raman scattering, while elastic light scattering with no change in energy is known as Rayleigh scattering. In Raman spectroscopy, the energy of the scattered light is analyzed using a spectrometer, and Raman lines appear as weak peaks shifted in energy from the Rayleigh line (which has the energy of the incident beam). Individual peaks in the spectrum correspond to energies of vibrational transitions within the sample, or in more common terminology, to the frequencies of vibration modes. The positions of these Raman peaks relative to the incident laser line correspond to the frequencies of Raman-active vibrations in the sample. To calibrate the Raman spectrometer, at the beginning of each session, the energy of the Rayleigh line is measured using a pure silica glass.

Since a vibrational Raman spectrum is dependent on the interatomic forces in a particular sample, it is a sensitive probe of the microscopic structure and bonding within the material. In crystals, the vibration of each atom is influenced by the vibrational motion of its neighbors. Since the atoms are arranged in a periodic pattern, the vibrational modes take the form of displacement waves traveling through the crystal. These are known as lattice vibrations.

Raman peak resolution strongly depends on mineral crystallinity. Amorphe glass analysis produces large bands while well crystallized minerals produce narrow peaks. Moreover, following the crystal orientation, peak intensity (not the wavelength) can change. In the following work, only wavelengths of the maximum peak intensity, called vibration modes, will be discussed.

Summary of analytical conditions

Before Raman analyses, samples, in indium mounts, were cleaned by 1 minutes of polishing on alumina polishing disc and by a 30 minutes ethanol bath under ultrason.

Raman spectra were recorded on a Jobin-Yvon Horiba Model T64000 spectrometer that was equipped with a liquid-nitrogen cooled CCD detector. The excitation beam is provided by the 514.5 nm line of an argon-ion laser (Spectra Physics, Model 2017). The laser beam $(\pm 1 \ \mu m^2)$ is focussed on the sample through an Olympus confocal microscope with ×100 magnification. In that study, it was necessary to put the laser to its maximum, 1.6 W. A motorized three-axis stage and direct imaging allowed zones to be selected easily.

Raman spectra have been recorded in olivine, orthopyroxene, clinopyroxene between 180 and 800 cm⁻¹ and some in basaltic melt between 800 and 1200 cm⁻¹ of our anhydrous samples. As we said, the intensity of the modes varies with the orientation of the single crystal under investigation, whereas the wavenumber of the modes remains the same. Therefore, for each mineral, several crystals (2 to 3 by samples, thus with different orientations) were attempted and an average in the peak position was taken for each vibration mode. The spectral resolution for each mode is on the order of ± 1 cm⁻¹. Spectra were acquired by 4 scans of 60 s. The spectra have been corrected using rubberband correction and peak positions were determined by the PeakFit program.

Chapter 3

F and Cl incorporation in mantle minerals

This chapter introduces the first results of F and Cl partitioning between mantle nominally anhydrous minerals and basaltic melt. Those results are presented in the form of a paper accepted in May 2011 to *Contribution to Mineralogy and Petrology*.

In that study, I present:

- 1. the incorporation mechanisms of F and Cl in mantle minerals, particularly in pyroxenes,
- 2. the effects that can control F and Cl partition coefficients, as crystal-chemistry and melt structure and,
- 3. I illustrate the consequence of F and Cl incorporation on the pyroxene crystal-network.

Those results are the outcome of the interpretation of relations between F and Cl partition coefficients with mineral chemistry and with the melt viscosity, of lattice strain models, but also of the realization of Raman measurements in minerals with different F and Cl concentrations.

This study was made in collaboration with Nobumichi Shimizu as an expert of SIMS measurements, with Julien Boulon who built the mathematical fitting program able to carry out the 'lattice strain model' for the two pyroxene octaedral sites and, Jean-Luc Devidal, who significantly helped during LA-ICP measurements.

Experimental determination of F and Cl partitioning between lherzolite and basaltic melt

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3.1 Abstract

We experimentally determined F and Cl partition coefficients together with that of 19 trace elements (including REE, U-Th, HFSE and LILE) between basaltic melt and lherzolite minerals: olivine, orthopyroxene, clinopyroxene, plagioclase and garnet. Under conditions from 8 to 25 kbars and from 1265 to 1430°C, compatibilities of F and Cl are globally ordered as $D^{Cpx/melt} > D^{Opx/melt} > D^{Grt/melt} > D^{Ol/melt} > D^{Plag/melt}$, and $D_F^{mineral/melt}$ is larger than $D_{Cl}^{mineral/melt}$. Four other major results were brought to light. (i) Chlorine partition coefficients positively correlate with the jadeite component in orthopyroxene, and increase of the CaTs component promotes Cl incorporation in clinopyroxene. (ii) Variations of fluorine partition coefficients correlate strongly with melt viscosity. (iii) F and Cl partition coefficients correlate with the Young's modulus (E_0) of pyroxene octahedral sites (M sites), and with Raman vibrational modes of pyroxenes. This demonstrates a fundamental interaction between the M site of pyroxenes and the incorporation of F and Cl. (iv) We also determined the parameters of the lattice strain model applied to 3+ cation trace elements for the two M sites in orthopyroxene and clinopyroxene: D_0^{M1} , D_0^{M2} , r_0^{M1} , r_0^{M2} , E_0^{M1} and E_0^{M2} .

3.2 Introduction

Volatiles, such as H_2O , CO_2 , S, Cl and F, play a crucial role in subduction zone magmatism. They trigger mantle wedge melting (Gill, 1981; Tatsumi and Eggins, 1995) and influence on the eruption dynamics (Wilson, 1980; Eichelberger and Westrich, 1981; Kokelaar, 1986; Roggensack et al., 1997; Cashman, 2004). With recent advances of microanalytical techniques and the soaring of melt inclusion studies, there is a growing body of concentration measurements of relatively volatile, light-atomicmass elements (H, B, C, S, Cl, F) in primitive melts of subduction zone magmas (e.g. Sisson and Layne, 1993; Sobolev, 1996; Métrich et al., 1999; Wade et al., 2006; see also references in Wallace, 2005). Water, carbon and sulfur in magma are likely to suffer variable degassing (Dixon et al., 1995; Wallace, 2005), but the high solubilities of F and Cl cause them to remain dissolved in the melt during magmatic degassing (Carroll and Webster, 1994; Spilliaert et al., 2006; Le Voyer et al., 2010). Spilliaert et al. (2006) shows that Cl and F are the last volatile elements to be exsolved during magma ascent (Cl at 100 MPa and F at < 20 MPa). Consequently, F and Cl contents in melt inclusions are certainly less affected by degassing than H₂O, CO₂ and S. Thus, Cl and F are the volatile elements that best retain the information of magma genesis along with lithophile trace elements.

There are an increasing number of experimental studies of the solubility (e.g. Holtz et al., 1993; Webster and Rebbert, 1998; Tamic et al., 2001) and viscosity of volatile-bearing (H₂O, CO₂, Cl and F) silicate melts (e.g. Dingwell, 1987; Dingwell and Webb, 1992; Richet et al., 1996; Schulze et al., 1996; Dingwell and Hess, 1998; Bourgue and Richet, 2001; Romano et al., 2001; Whittington et al., 2001; Giordano et al., 2004; Zimova and Webb, 2006, 2007). However, F and Cl partition coefficients between solid mantle and silicate melt at high pressure conditions are scarcely documented (some preliminary measurements have been reported on natural mantle minerals, Hervig and Bell, 2005; Bromiley and Kohn, 2007). Furthermore, since F and Cl are anions of the halogen group, their incorporation mechanism in minerals is poorly understood and is studied only for volatile-rich minerals as amphibole (reviewed in Oberti et al., 2007), micas (Noda and Roy, 1956; Stormer and Carmichael, 1971; Muñoz and Ludington, 1977; Volfinger et al., 1985; Icenhower and London, 1997) or apatite (Mathez and Webster, 2005).

Our study reports the first F and Cl partition coefficients along with that of 19 trace elements (Li, Be, B, Sc, V, Cr, Co, As, Sr, Zr, La, Eu, Gd, Ho, Lu, Hf, Pb, Th and U) between mantle minerals and basaltic melt for pressures and temperatures relevant to subduction zone setting, i.e. from 8 kbars to 25 kbars and from 1265°C to 1430°C. A combination of SIMS (Cameca IMS 1280 ion probe and Cameca IMS5f) and LA-ICPMS (Agilent 7500 cs ICP-MS) was used to analyze F, Cl and trace elements in silicate phases. Similarly to lithophile element incorporations (e.g. Onuma et al., 1968; Brice, 1975; Nielsen, 1985; Blundy and Wood, 1991, 1994; Gaetani and Grove, 1995; Schosnig and Hoffer, 1998; Hill et al., 2000; Gaetani, 2004), Cl and F partition coefficients are affected by factors including pressure, temperature, mineral composition and melt composition. In this paper, we determine anion partitioning systemetics by examining correlations between F and Cl partition coefficients and these factors.

3.3 Materials and Methods

3.3.1 Starting materials and experimental procedure

Four synthetic gel mixtures, two basaltic and two peridotitic compositions (following the procedure of Hamilton and Henderson, 1968), were used as starting materials for this study (Table 3.3.1). The first set of basaltic and peridotitic mixtures was made without F and Cl. The compositions were chosen

to obtain liquidus saturation of the upper mantle phases while maintaining a large melt fraction. Therefore these compositions were prepared to be as close as possible to a basalt-peridotite pair used by the upper mantle liquidus saturation experiments of Gaetani and Grove (1998). The second basalt and peridotite mixtures were created without MgO to allow the addition of MgCl₂, MgF₂. All the gels were conditioned for 12 hours at 800°C in a 1atm gas-mixing furnace, with fO_2 approximately 1 log unit above the Fayalite – Magnetite – Quartz buffer (FMQ+1). Note that this oxidation state is considerably less oxidized than that of Gaetani and Grove (1998); we have chosen the oxidation state of sub-arc upper mantle according to Parkinson and Arculus (1999).

The starting material was weighed into the desired proportions of synthetic basalt and peridotite (70 and 30 wt% respectively) and was ground in an agate mortar with ethanol for 45 min. The bulk Cl_2 and F_2 abundance was controlled by adding Cl- or F-bearing basalt powder and, in certain cases, Cl- or F-bearing peridotite powder (for particularly high concentrations of Cl and F) to the halogenfree mix. Before weighing, every powder was oven-dried for several hours. The desired quantity of basalt and peridotite mixtures were doped to the 100 ppm concentration level with a suite of trace elements that were added as a multi-element solution (1000 ppm in 0.5M HNO₃⁻ solution). Element concentration in the final mixture was approximately 100 ppm (Li, B, Be, As, Sr, Sc, La, Eu, Gd, Ho, Lu, V, Hf, Zr, U and Th), except 1000 ppm for Pb. Trace elements have been chosen to minimize molecular and isotopic mass interferences during LA-ICPMS and SIMS analyses.

	Basalt	Peridotite	Cpx seeds
SiO_2	47.70(47)	45.97(45)	53.20(60)
TiO_2	0.62(1)	0.18(0.2)	0.57(6)
Al_2O_3	19.05(19)	4.06(4)	5.62(30)
$\mathrm{Cr}_2\mathrm{O}_3$	0.12(0)	0.47(0)	1.07(20)
FeO^*	7.82(18)	7.54(17)	3.12(11)
MnO	0.15(0.3)	0.13(0.3)	0.07(6)
MgO	10.49(31)	37.79(112)	15.60(30)
CaO	11.75(35)	3.21(10)	19.20(40)
Na_2O	2.35(5)	0.33(0.1)	ND
K_2O	0.08(0.3)	0.03(0.1)	2.11(13)
Total	100.13	99.99	100.56

Table 3.3.1: Composition of starting materials in wt%.

Units in parentheses represent one standard deviation. Analyses were done by ICP-AES on basalt and peridotite powders and on electron microprobe for cpx seeds. FeO* indicates total Fe as FeO. ND: not determined.

Two series of experiments were conducted: with and without the addition of natural clinopyroxene

seed crystals. Composition of cpx seeds is presented in Table 3.3.1. The contribution of cpx seeds represents, on average, 1% of the trace element abundance of the starting material (Supplementary Table 1). For the experimental series with the addition of cpx seeds, powders were dried at least 24 hours in a drying oven at 110°C. Before loading capsules, some pellets of compacted starting powders were analyzed by infrared absorption spectroscopy. In these powders, water and carbon concentrations were less than 900 ppm and 100 ppm, respectively. Experiments were conducted at conditions ranging from 8 kbars to 25 kbars and from 1265° C to 1430° C using 3/4 and 1/2 inch piston-cylinder apparatus, for durations between 5 to 7 days. From the outside to the inside, concentric cylindrical assemblies consist of a lead foil wrapped around a NaCl cell, a Pyrex cylinder, a graphite furnace, and inner pieces of crushable MgO. The 3/4 inch assembly is described in the scaled drawing shown in Fig. 3.3.1. Multi-capsule experiments were performed using a graphite cylinder with four holes that served as sample capsules for nearly dry, volatile-doped powders. No metallic capsule was used outside of the graphite. Under our P-T conditions, a thin graphite lid and a thin MgO disc were placed between the sample and the thermocouples. Before each experiment, the assembly was dried for at least 12 hours at 300°C. Run temperature was controlled to within $\sim 1^{\circ}$ C of the set point using W95Re5/W74Re26 thermocouples. To ensure no temperature drift, power output was monitored during the runs. Before

rapidly (~50°C/s). The recovered samples were mounted in epoxy resin and polished for analyses by an electron microprobe. Before volatile and trace element analyses by ion probes, samples were taken out of the epoxy mounts using a soldering iron, and were pressed into high-purity indium metal mounts. The indium mounts were then washed in ultrasonic baths with ethanol followed by distilled water and

decompression, the power applied to the furnace was shut down and the experiment was quenched

3.3.2 Analytical procedure

dried overnight in an oven at 120°C before gold coating.

Major element composition of the samples were analyzed with the CAMECA SX100 electron microprobe at the Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand, France) and a JEOL 733 electron microprobe at the Massachussets Institute of Technology (MIT, USA). For crystals, an accelerating voltage of 15 kV and a beam current of 15 nA with a focused beam were used. An 8 nA beam current and a 5 μ m defocused beam were used for quenched melt analyses. Repeated analyses of F2p#2a sample melt, olivine and orthopyroxene, show that the reproducibility of the sample between the two electron microprobes is better than the analytical precision.

Fluorine, chlorine and water abundances were determined at Woods Hole Oceanographic Institution (WHOI, USA) with a Cameca IMS 1280 ion probe, using a Cs^+ primary beam, of ~1.5 nA intensity; an electron gun was used to avoid the charging of the sample surface. A mass resolution of 6660

Samples	Т	Duration	Run	Phase proportions	$\sum R^{2*}$
	$(^{\circ}C)$	(days)	products	(wt%)	
F2p#2b	1360	5	Gl, Opx, Ol	88(2):11(1):1(2)	1.46
F4p#3a	1360	5	Gl, Opx	89(5):11(5)	0.28
F1#3b	1360	5	Gl, Opx	81(2):19(1)	1.00
F5#3b	1360	5	Gl, Opx	90(0.7):10(0.7)	0.40
C4p#2b	1360	5	Gl, Opx, Ol	78(3):4(5):18(2)	0.06
C8p#2b	1360	5	Gl, Opx, Ol	79(1):2(2):18(1)	0.13
C04#3a	1360	5	Gl, Opx, Ol, Sp	79(1):8(1):12(2):1(0.3)	0.01
C4#4a	1360	5	Gl, Opx	74(1):26(1)	2.19
CC01#8kb4 † ^a	1265	6	Gl, Opx, Cpx, Ol, Plag	56(8):1(4):34(4):8(2):1(2)	0.08
CF1#8kb5 † ^a	1265	7	Gl, Opx, Cpx, Ol	64(1):11(6):4(5):21(2)	0.08
CC4#7b \dagger^{**}	1310	6	Gl, Opx, Cpx	68(32):16(2):16(19)	0.82
CF5#7c †**	1310	6	Gl, Opx, Cpx	81(6):12(2):7(8)	0.58
CF01#16kb1 \dagger^b	1350	5	Gl, Opx, Cpx	60(1):13(1):27(1)	0.63
${\rm C4p}\#25{\rm kb}^c$	1430	5	Gl, Opx, Cpx, Grt	28(2):4(1):40(1):28(2)	0.64

Table 3.3.2: Experimental conditions and resulting phase assemblages.

All experiments were conducted at 12 kbars, except for those noted by ${}^{a}8$, ${}^{b}16$, and ${}^{c}25$ kbars. Abbreviations are as follow: Glass = quenched silicate melt, Opx = orthopyroxene, Cpx = clinopyroxene, QuCpx = quench-cpx, Ol = olivine, Plag = plagioclase, Sp = spinel, Grt= garnet. \dagger represents cases where cpx seeds were added in the starting material.

 $^*\sum R^2$ is the mean of squared residuals from phase proportions calculations, modified from Albarède and Provost (1977). The calculation takes into account the uncertainties on the mixing between basalt and peridotite, and cpx seed addition to the starting materials. These uncertainties increase the $\sum R^2$. ** Mass balance calculations predicted more than 15% of cpx seeds. For those samples, errors of phase proportions are bigger.



Figure 3.3.1: sketch of the of the 3/4 inch assembly.

allowed the discrimation of interferences (¹⁷O over ¹⁶O¹H, ¹⁸O¹H over ¹⁹F and ³⁴S¹H over ³⁵Cl). A monocollection ion counting mode was used to measure the intensity of ¹⁶O¹H⁻, ¹⁹F⁻, ³⁰Si⁻⁻ and ³⁵Cl⁻ masses. Ten cycles were acquired for each mass. For olivine, orthopyroxene, clinopyroxene, garnet and plagioclase analysis, a $30 \times 30 \ \mu\text{m}$ raster was used to clean the analysis area, pre-sputtering was turned off after 180 s, and a $15 \times 15 \ \mu\text{m}$ projected beam size was used for analysis, which lasted about 350 s. For the analysis of basaltic melt, the raster ($30 \times 30 \ \mu\text{m}$) was maintained for the duration of the analysis.

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Sample	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	Cr2O3	FeO*	MnO	MgO	CaO	Na ₂ O	K20	Total	F(ppm)	Cl (ppm)	H_2O (ppm)
F2p#2a	Melt [3]	48.50(33)	0.60(9)	16.39(13)	0.17(2)	8.29(19)	0.15(4)	13.21(14)	9.66(23)	1.79(9)	0.13(0.4)	98.89(46)	2775(5)	2009(4)	2904(10)
	Opx [3]	53.71(13)	0.07(1)	6.53(29)	0.78(6)	6.08(19)	0.11(3)	31.60(31)	1.39(8)	0.02(1)	0.01(1)	100.32(59)	119(7)	26(2)	172(21)
F4p#3a	Ot [9] Melt [3]	40.32(39) 47.62(10)	0.63(2)	17.45(7)	0.10(2) 0.06(2)	8.49(4)	0.15(3)	$\frac{40.92(29)}{11.24(10)}$	10.46(7)	2.45(19)	0.16(1)	98.93(26)	4807(14)	1560(4)	4524(22)
-	Opx [3]	52.07(42)	0.12(1)	9.11(27)	0.63(9)	7.17(10)	0.14(3)	29.45(40)	1.72(7)	0.07(3)	ND	100.50(19)	268(2)	15(2)	348(2)
F1#3b	Melt [4]	47.41(25)	0.56(6)	16.14(16)	0.14(4)	8.25(9)	0.13(3)	13.30(13)	10.01(17)	1.76(4)	0.15(2)	97.85(42)	11985(16)	1939(3)	3661(34)
	Opx [8]	53.65(57)	0.06(4)	6.19(62)	0.76(8)	6.34(9)	0.11(2)	31.12(29)	1.27(5)	0.12(18)	0.01(1)	99.67(60)	558(3)	29(2)	ND
F'5#3D	Melt [5] Ony [6]	48.11(32) 53 03(17)	0.62(7)	16.61(14) 5 79(33)	0.11(3) 0.74(7)	8.30(8) 6.49(10)	0.15(6)	12.69(21)	1 40(9)	1.69(6)	0.19(3)	98.69(33) 100 36(53)	6721(400) 336(1)	1537(19U) 43(1)	4577(1264) ND
C4n#2b	Welt [5]	48.22(9)	0.57(6)	16,69(5)	0.18(3)	8.19(20)	0.16(3)	12.90(7)	10.00(22)	1.90(8)	0.10(4)	98.92(21)	41(0.2)	$\frac{1}{2362(8)}$	2778(24)
	Opx [5]	53.48(10)	0.08(3)	7.10(33)	0.86(10)	6.08(12)	0.11(1)	31.40(24)	1.45(11)	0.05(1)	(0.00(0))	100.66(39)	ND	40(9)	ND
	0i [4]	40.79(39)	0.04(4)	0.13(2)	0.04(4)	10.12(12)	0.13(1)	48.57(30)	0.23(1)	0.03(2)	0.00(0)	100.34(72)	ND	ND ND	ND
C8p#2b	Melt [3]	48.11(7)	0.57(4)	16.54(6)	0.21(3)	8.41(12)	0.18(2)	13.18(16)	9.21(23)	1.79(13)	0.15(1)	99.22(63)	38(1)	3102(12)	2526(16)
	Opx [3]	53.49(2)	0.12(2)	6.77(26)	0.79(6)	6.09(11)	0.12(2)	31.16(21)	1.39(3)	0.03(3)	QN	99.97(24)	2(0.06)	43(2)(2)	QN
0	01 [3]	40.75(25)	0.01(1)	0.11(0)	0.13(1)	9.76(35)	0.12(3)	48.37(4)	0.20(0)	0.15(1)	ND	99.45(13)	ND	ND	ND
C04#3a	Melt [3]	46.64(10)	0.53(5)	17.22(6)	0.15(4)	7.70(1)	0.17(3)	11.99(12)	11.26(7)	2.39(5)	0.20(1)	98.57(4)	54(1)	1352(5)	4981(33)
	Opx [2]	02.83(29) 40 e1 (90)	(T)T0.0	(.88(28)	(0)10.0	0.03(4/) 10 99/1E)	(1)7(1)	30.27(19)	2.00(17)	(e)eT.U		100.48(1.7)	0(7.0)e	39(1) NTD	2338(131) ND
	5 5 5	40.51(20)	(T)TOLO	0.11(2) 69 14(33)	U.U((2) 7 55(33)	8 01(5) 8 01(5)	0.14(1) 0 11(3)	46.11(32) 2285(41)	(1)62.0			100.42(12) 101.05(45)			
$C4 \pm 4a$	Melt [4]	49.25(48)	0.61(6)	16.64(66)	0.11(6)	8.12(51)	0.14(7)	10.63(32)	10.47(8)	2.04(2)	0.15(2)	98.17(110)	35(1)	4965(27)	3043(15)
	Opx [5]	52.24(39)	0.11(15)	8.11(59)	0.15(2)	7.40(13)	0.15(2)	29.25(18)	1.78(6)	0.07(1)	0.00(0)	99.92(41)	QN	148(7)	ND
CC01#8kb4	Melt [2]	49.28(12)	0.59(4)	16.78(5)	0.17(5)	7.63(5)	0.11(4)	9.60(26)	11.73(10)	2.11(9)	0.18(1)	98.16(33)	152(1)	$203\hat{5}(29)$	2127(32)
	Opx [4]	53.54(32)	0.13(1)	5.82(18)	1.03(7)	6.82(13)	0.14(4)	29.90(31)	2.09(26)	0.05(3)	0.00(0)	99.54(33)	31(1)	4(1)	973(54)
	Cpx [5]	52.95(55)	0.58(2)	5.29(24)	1.06(3)	3.40(11)	0.08(5)	16.41(33)	19.17(31)	1.10(5)	0.02(2)	100.78(33)	16(4)	26(16)	318(8)
	01 [4]	40.44(22)	0.01(1)	0.07(2)	0.15(2)	11.67(19)	0.15(7)	46.83(44)	0.29(1)	0.01(2)	0.01(1)	99.67(56)	15(1)	2(0.1)	1697(87)
	Plag [3]	49.64(19)	0.02(3)	31.02(12)	0.04(3)	0.23(5)	0.00(0)	0.26(2)	15.13(4)	2.84(7)	0.04(2)	99.21(27)	15(1)	3(1)	745(24)
CF1#8kb5	Melt [3]	49.49(17)	0.64(4)	16.26(19)	0.18(7)	7.18(17)	0.20(10)	10.84(18)	12.41(9)	2.10(7)	0.16(3)	99.46(69) 100 46/41)	6011(29)	1860(10)	1807(6) 1906(88)
	Chx [0]	53.61(19)	0.10(1)	4.29(20)	1.09(32) 0.86(5)	(67)(20)	0.14(5) 0.14(4)	20.65(2)	2.00(31)	0.02(1) 0.33(4)	0.00(0)	100.40(41) 100.60(14)	472(2)	$\frac{4}{37(2)}$	1290(00) 89(5)
	01 [3]	40.42(16)	0.04(3)	0.08(2)	0.22(7)	11.06(9)	0.19(2)	48.04(12)	0.29(3)	ND	ND	100.39(30)	ND	ND	ND
CC4#7b	Melt [4]	49.58(27)	0.67(7)	15.85(12)	0.15(1)	8.03(11)	0.13(7)	10.46(10)	11.80(21)	2.11(4)	0.15(3)	98.93(40)	101(1)	8515(57)	1712(29)
	Opx [3]	54.04(7)	0.08(4)	5.93(46)	0.94(11)	6.73(7)	0.15(7)	30.51(8)	2.14(2)	0.08(5)	0.03(2)	100.60(22)	14(0.3)	19(3)	1039(78)
	Cpx [5]	52.26(46)	0.20(6)	5.96(56)	1.09(6)	4.80(24)	0.13(2)	20.33(54)	14.78(92)	0.42(3)	0.01(2)	99.97(21)	16(0.3)	77(4)	550(3)
CF5#7c	Melt [3]	49.01(8)	0.61(8)	16.04(20)	0.16(2)	7.76(14)	0.13(4)	11.24(25)	11.82(3)	1.97(12)	0.13(2)	98.86(36)	5336(21)	2386(10)	2222(25)
	Opx [4]	54.33(29)	0.11(4)	5.97(26)	0.96(5)	6.69(14)	0.13(5)	30.44(0.3)	2.20(7)	0.10(3)	0.01(2)	100.93(17)	520(29)	5(1)	1351(126)
CE01 #161-P1	Cpx [9]	02.03(08) 40.10(4)	0.14(0.1)	0.10(44) 17 66/10)	1.10(10)	4.93(U) 0.07(96)	(T)01.0	20.04(7) 10.02(94)	14.74(9) 10.09/19)	0.40(4)	(2)2(2)	100.54(55)	020(28)	12(1) 9509(90)	UN 1009/94)
	Onx [3]	49.10(4) 52.66(18)	0.72(6)	8.31(38)	0.72(6)	7.29(18)	0.17(3)	28.91(5)	2.33(15)	2.32(3)	0.13(2)	39.37(31)	24(1)	5(1)	1902(24) ND
	Cpx [3]	50.46(24)	0.72(2)	9.73(45)	0.71(2)	5.36(18)	0.16(2)	18.96(13)	14.09(5)	0.59(3)	0.1(1)	100.35(41)	28(0.4)	2(0.2)	QN
C4p#25kb	Melt [4]	45.76(6)	1.08(8)	13.88(13)	0.08(3)	9.25(32)	0.09(4)	11.24(19)	8.70(14)	4.32(11)	0.35(3)	94.75(41)	6406(122)	4772(93)	7938(227)
	Opx [8]	54.10(36)	0.09(2)	6.74(35)	0.26(5)	7.32(39)	0.11(3)	29.28(43)	1.97(16)	0.43(7)	0.01(2)	100.32(41)	121(4)	13(1)	4856(91)
	Cpx [9]	53.38(33)	0.17(3)	8.23(30)	0.13(3)	6.52(22)	0.13(3)	21.24(41)	8.76(41)	1.64(7)	0.01(1)	100.40(42)	319(4)	10(0.4)	3936(152)
	Grt[11]	41.99(31)	0.28(12)	23.88(27)	0.49(10)	8.32(51)	0.19(4)	20.37(62)	4.55(50)	ND	ND	100.07(36)	73(1)	13(0.3)	4674(127)

Numbers in brackets indicate number of individual electron microprobe analyses included on average. (FeO* total Fe as FeO) Numbers in parentheses represents one standard deviation in terms of least units cited. ND : not determined. For trace elements, secondary ionic mass spectrometry analyses were carried out on a Cameca IMS5f (Laboratoire Géosciences Montpellier, GM, France). A primary O⁻ ion beam of 6 nA was accelerated to 10 kV before hitting the sample. The following masses were analyzed in two series: ⁷Li, ⁹Be, ¹¹B, ³⁰Si, ⁵²Cr, ⁵⁹Co, ⁷⁵As in the first series and ³⁰Si, ⁴⁵Sc, ⁵¹V, ⁸⁸Sr, ⁹⁰Zr, ¹³⁹La, ¹⁵³Eu, ¹⁵⁹Tb, ¹⁶⁰Gd, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁸⁰Hf, ²⁰⁸Pb and ²³²Th, in the second series. To reduce mass interference by molecular ion species, we applied a -80V offset to the secondary ions accelerating voltage of 4500V for the two series with \pm 30 eV energy windows (Shimizu and Hart, 1982). The size of the primary beam was set to 40 μ m (Köhler illumination). For the mass calibration, the counting time for each mass was chosen between 2 and 30 s, depending on the analyzed phase, to attain a minimum of hundreds of counts per cycle for tens of ppm concentration.

Water, F, Cl and trace element abundances were determined by taking ratios of each mass over ³⁰Si (1280, WHOI and 5f, GM), and the ratio was multiplied by a calibration factor after correcting for isotopic abundance. The calibration factor was determined by measuring a set of natural glasses of known compositions (D51-3, 46D-2, 1649-3, D20-3, JD17H, 1654-3, 519-4-1 and D52-5 for ¹⁶O¹H, ¹⁹F and ³⁵Cl; Rose-Koga et al., 2008; and NIST 610 and NIST 612 for trace elements, Gagnon et al., 2008), at the beginning and the end of the same session and under the same analytical conditions. For trace element measurements, geostandard KL2-G (Jochum and Stoll, 2003) was used as a secondary external standard to assess accuracy.

Trace element analyses on ICPMS were achieved at the LMV with an Agilent 7500 cs ICPMS coupled to a 193 nm Excimer Resonetics M-50E laser ablation system with a maximum output energy of 6 mJ. Analyses were made with a laser pulse frequency of 2 Hz. The beam diameter ranged from 15 to 20 μ m. Seventeen masses were collected with an integration time of 30 ms per mass: ⁷Li, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁸⁸Sr, ⁹⁰Zr, ¹³⁹La, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb, ²³²Th, ²³⁸U, except 10 ms for ²⁸Si and ⁴⁴Ca. Silica abundance measured on electron microprobe was used as internal standard. A typical signal acquisition started by collecting a background signal for 30s, and followed by a laser firing of 70 s. The NIST 610 glass was used as an external standard (Gagnon et al., 2008). The glasses NIST 612 and BCR-2G (Gao et al., 2002) were also analyzed to check the accuracy and precision of analyses. Assessments on accuracy, uncertainties, advantages and disadvantages, and interferences on trace element analyses by laser ablation ICPMS and SIMS can be found in Dalou et al. (2009a). Posteriori examinations of every ion probe and laser pit, using scanning electron microscopy (SEM) imaging, assure the quality of analyses and identify the poorly placed pits (Fig. 3.3.2). Signal stability was also carefully monitored for every analysis to identify the presence of foreign material in analyses.



Figure 3.3.2: Back-scattered electron image of CC4#7b sample. Abbreviations used: Opx, orthopyroxene; Cpx, clinopyroxene; Melt, quenched basaltic melt. (a) Overview of the experimental samples (CC4#7b). (b) SIMS and LA-ICPMS pits are visible. Repolishing was done between SIMS and LA-ICPMS analyses, which explains reduced the size of SIMS craters ($< 20 \ \mu m$).

3.4 Results

3.4.1 Experimental samples

In the first part of Table 3.3.2, we present the samples annealed at 12 kbars and 1360°C. In these runs, the experimental products consist of approximately 10 to 30% orthopyroxene (opx), 0 to 20% olivine, some quench-cpx (< 5 μ m, forming a reaction rim around opx) which were excluded from the mass balance, 0 to 5% spinel and 70% to 90% quenched basaltic melt. The remaining samples in Table 3.3.2are those with cpx seeds. In these run products, mineral assemblages depend on the pressure (P), temperature (T) and volatile element abundance. All the experiments with cpx seeds were saturated with opx and cpx (0 to 30% each), except for high-volatile-concentrated samples that are saturated only with opx. At 8 kbars, the experiments are saturated with olivine (5 to 20%) and plagioclase (1%), in addition to opx saturation and cpx saturation. The 25 kbars experiment is saturated with garnet $(\sim 30\%)$, in addition to opx saturation and cpx saturation. All the experiments contain more than 25%of basaltic melt. Mineral assemblages are consistent with those obtained by Gaetani and Grove (1998) for the same starting composition and run conditions. Normally, sample texture is appropriate for microanalysis since the liquid phase segregates from grains. Grain sizes are generally less than 40 μ m, making their analyses difficult, however possible (Fig.3.3.2 a and b). Occasionally, crystal sizes exceed $80 \ \mu m$, notably for plagioclase and olivine. In samples with cpx seeds, cpx are systematically located at the bottom of the capsule, opposite from the thermocouples' position, indicating the presence of a thermal gradient. On the basis of previous work done in the petrology group of the LMV (Médard, 2004; Laporte et al., 2004), the thermal gradient is approximately less than 10° C/mm for a maximum 2 mm capsule length.

Major element compositions of all experimentally produced phases are reported in Table 3. Silicate melts have a basaltic composition (on average: SiO₂ 48.4 wt%, Na₂O + K₂O 2.13 wt%, Mg# = Mg/(Mg+Fe) in mole 0.71), similar to the melts' composition of Gaetani and Grove (1998) (samples B292, B394 and B302). We infer that the liquid compositions of our experiments are close analogues of primary basaltic magma, which can exist in the upper mantle. The estimated oxygen fugacity in samples ranges from FMQ+1 to FMQ-2 (Médard and Grove, 2008). Calculated from its spinel composition (Fe²⁺/Fe³⁺ ratio), the oxygen fugacity of sample C04#3a is FMQ+0.8. Fluorine and chlorine contents dissolved in the melt range from 60 ppm to 1.2 wt% and from about 1000 to 8000 ppm, respectively (Table 3). Water contents dissolved in the melt range from 240 to 4000 ppm (Table 3). Mineral compositions are similar to those found in natural peridotite. The Fo content of the olivine is 0.88 to 0.90, and the Mg# of the Opx is 0.88 to 0.90. The Cpx have Mg# of 0.87 to 0.89, and a CaO content of 13.8 to 19.2 wt% (increasing with decreasing pressure). Plagioclase in sample CC01#8kb4 has a herzolitic anorthite content [An = Ca/(Ca+Na)] of 0.746. Garnet composition

 $(Py_{72}Gr_{10}Alm_{17}Uv_{01})$ is within the compositional variation of fertile garnet peridotites occurring in kimberlites, peridotites, alkali basalts and pyroclastic rocks (Mottona, 1986).

3.4.2 Assessment of equilibrium

We have conducted more than 40 experiments between 8 and 25 kbars. Among all the samples obtained, only 14 have textures and grain sizes suitable for volatile and trace element analyses; the others are not presented. In these 14 samples, mineral textures show polygonal shapes of crystals that suggest equilibrium growth (Fig. 3.3.2b), no detectable compositional zoning in crystals, and a compositional homogeneity of melt (see standard deviations on replicate analyses, Table 3). These observations indicate that a run duration of 5 days is sufficient to reach, at least, local equilibrium. Moreover, the large melt fraction obtained in all samples promotes equilibration and crystal growth. Minerals must nucleate and grow from starting materials in synthetic gels. However, in experiments where cpx seeds were added, cpx reequilibrates through exchange between melt and cpx via dissolution and growth. Clinopyroxene compositions are different from that of cpx seeds (with the exception of cpx in sample CC01#8kb4) and no cpx-core has a composition similar to the starting cpx seeds, even in large clinopyroxenes. This indicates that in all samples with cpx seeds, element exchange rates were fast enough to reequilibrate the cores of cpx grains in 5 days. It should be noted that sample CC01#8kb4 did not reach a complete equilibrium.

The attainment of chemical equilibrium is assessed by the Fe-Mg exchange coefficient between olivine and melt, ${}^{Ol/Melt}K_D^{Fe/Mg} = ({}^{Ol}\text{Fe}^{2+}.{}^{Melt}\text{Mg}) / ({}^{Melt}\text{Fe}^{2+}.{}^{Ol}\text{Mg})$. Our $K_D^{Fe/Mg}$ are compared with those of Gaetani and Grove (1998) and with experimentally calibrated values (Roeder and Emslie, 1970; Toplis, 2005). The $K_D^{Fe/Mg}$ values for olivine in our experiments vary from 0.32 to 0.35, which is close to the expected values (0.32 to 0.34, model prediction; 0.32, Gaetani and Grove, 1998). We also compared the Fe-Mg exchange coefficients of orthopyroxene and clinopyroxene against melt to those obtained by Gaetani and Grove (1998). The $K_D^{Fe/Mg}$ values (0.29 to 0.33) are similar to those of Gaetani and Grove (1998) (0.30 to 0.31) for orthopyroxene, and they vary from 0.31 to 0.37 (except 0.26 for sample CC01#8kb4) for clinopyroxene, while Gaetani and Grove (1998) values vary from 0.32 to 0.35.

Another approach to assess chemical equilibrium is to run mass-balance calculations using major element abundances (Albarède and Provost, 1977), because the experimental system must be closed to attain chemical equilibrium. To converge, mass balance calculations take into account an uncertainty on the mixing proportions of basalt and peridotite and on the amount of cpx-seeds. The average sums of squared residuals ($\sum R^2$ in Table 3.3.2) range between 0.01 and 2.09. Considering uncertainties in mixing of several powders, these residuals are expected and probably acceptable.

Lastly, F and Cl are relatively homogeneous in minerals and melt among all the experiments. The

mean standard deviation is 8% relative for F and 18% relative for Cl in opx, is 7% relative for F and 19% relative for Cl in cpx, is 13% relative for F and 26% relative for Cl in olivine, is 5% relative for F and 37% relative for Cl in plagioclase, is lower than 2% relative for F and Cl in garnet and is 1% relative for F and for Cl in the melt. These relative standard deviations are either the same or smaller than the internal analytical uncertainties. Moreover, given that F and Cl have diffusivities on the order of 10^{-10} m²s⁻¹ in basaltic melt (at the temperatures of our experiments, Alletti et al., 2007), the equilibration time of halogens in the basaltic melt is expected to be six hours at the scale of our samples. Because of the lack of halogen diffusion data, the equilibration time in minerals is unknown. Considering their ionic radii (equivalent to oxygen or larger), diffusivities of F and Cl in minerals are probably slower than most cations. Unless crystals grow in near equilibrium manner, we assume that it is impossible to equilibrate F and Cl abundance in minerals via diffusion. Therefore, we estimate the time t necessary to satisfy the mass transfer Peclet number (= v^2t/D) to be less than one. Assuming a linear growth of radius, r, for a time period, t, the relation is expressed as r^2 / (t* D_i <1. When the mass transfer Peclet relation is true, the element diffusion rate is faster than crystal growth rate. For the grain growth of 15 μ m in a melt with $D_{halogens} = 10^{-10} \text{ m}^2 \text{s}^{-1}$, a time (t) on the order of few seconds satisfies the relation. This suggests that even if the majority of crystal growth takes place within the first few hours of annealing, near-equilibrium F and Cl abundances are incorporated into the crystal. As presented in the following section, the lithophile trace element partition coefficients are in agreement with previous data at similar experimental conditions. We conclude that the experiments achieved near equilibrium conditions including for F, Cl and trace element partitioning.

3.4.3 Analytical results

Fluorine and chlorine partition coefficients (wherein $D_i^{min/melt}$ is the concentration of element *i* in the mineral divided by the concentration of the element *i* in the melt) are presented in Table 4.5.4. Trace element partition coefficients are compared to literature data in Figure 3.4.1 and the values are available in supplementary material.

In order to check the accuracy of SIMS or LA-ICPMS measurements for all trace elements, we have compared the sum of initial trace element abundances (100 ppm for all elements and 1000 ppm for Pb) with the sum based on the phase proportion of the charges (Table 3.3.2). For 5f SIMS and LA-ICPMS measurements, nearly all elements converge within 40% relative standard deviation from the initial. Considering the analytical precision, uncertainty on phase proportions, and doping quality of starting powders, this somewhat large relative deviation is expected and is an acceptable demonstration of the system closure. The exceptions are Li and Pb, for which between 50 to 90% of the initial concentrations were not recovered both for SIMS and LA-ICPMS analyses. This cannot be explained by analytical odd effects, because secondary standard values were consistent with certified values (NIST 612, BCR-2G and KL2-G). We assume that Li and Pb were inadvertently lost into the graphite capsule during the drying procedure or during initial heating of the experiments. Nevertheless, as described in the following sections, Li and Pb partition coefficients are consistent with literature data.



Figure 3.4.1: Crystal-melt partition coefficients for a) orthopyroxenes, b) clinopyroxenes, c) olivines and d) garnet, for all samples. Grey fields are literature data, discussed in the text.

3.4.4 Orthopyroxene

We report in F and Cl partition coefficients between dry silicate minerals and basaltic melt (Table 4.5.4). We can observe that F is less incompatible in those minerals than Cl. This incompatibility difference can reach two orders of magnitude for orthopyroxene. Fluorine and chlorine partition coefficients for opx vary by a factor of 3 for D_F and 10 for D_{Cl} . We observe these variations in D_F and D_{Cl} while P and T are constant, therfore D_F and D_{Cl} changes must be related to other thermodynamic parameters, such as phase compositions. Nevertheless, we note that, for the experimental series at 12 kbars – 1360°C, D_F and D_{Cl} vary within a factor of 2 (0.0429 – 0.0556) and 3 (0.0117 – 0.0280), respectively. In the second series, P - T conditions vary, D_F changes by one order of magnitude and

Run	D_F	D_{Cl}	Run	D_F	D_{Cl}
Ort	hopyroxene		Clir	opyroxene	
F2p#2a	0.0429(26)	0.0117(26)	CC01#8kb4	0.098(8)	0.012(1)
F4p#3a	0.0557(5)	0.0188(4)	CF1#8kb5	0.0725(7)	0.021(4)
F1#3b	0.0465(3)	0.0151(9)	CC4#7b	0.153(4)	0.0086(5)
F5#3b	0.0500(31)	0.0193(39)	CF5#7c	0.109(6)	0.0048(5)
C4p#2b	ND	0.0171(37)	C4p#25kb	0.0428(16)	0.0017(1)
C8p#2b	0.0495(25)	0.0125(8)			
C04#3a	ND	0.0278(6)		Olivine	
C4#4a	ND	0.0280(15)	CC01#8kb4	0.1164(63)	0.0012(1)
CC01#8kb4	0.1841(89))	0.0018(6)			
CF1#8kb5	0.0850(13)	0.0017(3)]	Plagioclase	
CC4#7b	0.1233(41)	0.0021(4)	CC01#8kb4	0.0980(44)	0.0014(7)
CF5#7c	0.0875(58)	0.0017(5)			
CF01#16kb1	0.0976(68)	0.0018(3)		Garnet	
C4p#25kb	0.0158(11)	0.0022(2)	C4p#25kb	0.0123(4)	0.0029(1)

Table 3.4.1: Fluorine and chlorine partition coefficients between mineral and melt: $D_i^{mineral-melt} = c_i^{mineral} / c_i^{melt}$ in run products.

Numbers in parentheses represent one standard deviation in terms of least units cited. ND : not determined.

 D_{Cl} by less than a factor of 2, but the values do not correlate with pressure or temperature. Our results of trace element partition coefficients between opx and melt generally agree with literature data (Fig. 3.4.1a; van Kan Parker et al., 2010; Frei et al., 2009; McDade et al., 2003b,a). Our higher partition coefficients for V (Frei et al., 2009; McDade et al., 2003b,a) can be explained if we consider that our experiments were run at higher oxidation state (Canil and Fedortchouk, 2001). The discrepancy for partition coefficient for LREE are notable. The *Ds* between opx and melt are highly variable. They increase systematically with P - T conditions (Frei et al., 2009). Also, at constant P - T conditions, trace element partition coefficients among samples are variable (Fig. 3.4.1a and 3.4.2). Figure 3.4.2 shows that, even though partitioning patterns look globally alike, differences in partitioning values are significant. Those differences are larger for LREE (around 250% of variation) than HREE (42% of variation). These variations are likely caused by various quantities of doped volatiles in the melt and crystal compositions.

3.4.5 Clinopyroxene

Fluorine and chlorine partition coefficients between cpx and basaltic melt also vary by a factor of about 4 for D_F and D_{Cl} . We observe no systematic D_F variation with respect to P - T conditions. As a first order observation, D_{Cl} is higher at 8 kbars – 1265°C (0.021± 0.004) than at 16 kbars – 1430°C (0.0017± 0.0001).



Figure 3.4.2: Othopyroxene-melt partitioning values for REE of samples of the same P - T conditions. Note that variation of partition coefficients between samples is higher for LREE than MREE and HREE.

Figure 3.4.1b shows that, even though partitioning patterns are similar to literature data (Gaetani, 2004; McDade et al., 2003b; Johnson, 1998; Hauri et al., 1994; Hart and Dunn, 1994), our data are systematically, although not significantly, lower. Our REE data agree within less than 30% difference for MREE and HREE, and less than 50% difference for LREE with Wood and Blundy's model (1997). These differences are within or close to the error bars of our experimental data. The Mg# of our melts is generally lower than previous studies (Gaetani, 2004; McDade et al., 2003b; Johnson, 1998; Hauri et al., 1994; Hart and Dunn, 1994), and this difference in melt composition most likely contributes to the observed disparities.

3.4.6 Olivine

Due to the complexe texture of our samples, successful in situ analyses were difficult to achieve. Here, we only report one sample (CC01#8kb4) for which reproducibility of olivine analyses (standard deviation of 8%, 3 measurements) gave acceptable accuracies for $D_F^{Ol/melt}$ and $D_{Cl}^{Ol/melt}$.

The distribution of our trace element partition coefficients overlaps with that of the literature (Fig.3.4.1c; Zanetti et al., 2004; McDade et al., 2003b; Salters et al., 2002; Taura et al., 1998). Our $D_i^{Ol/melt}$ at 8 kbars are generally smaller than those annealed at higher pressures (between 10 kbars and 140 kbars; Zanetti et al., 2004; McDade et al., 2003b; Salters et al., 2002; Taura et al., 1998). This positive pressure dependancy of olivine-melt partition coefficients was described previously (Taura et al., 1998).

3.4.7 Plagioclase

Because of the analytical difficulties, only F and Cl were measured in plagioclases from one sample (CC01#8kb4). This datum is the mean of 3 measurements (standard deviation of 3%). Fluorine has

the same compatibility in plagioclase as in cpx, but it is more incompatible in opx and olivine than in plagioclase. Chlorine is more incompatible in opx, and less incompatible in cpx and olivine, than in plagioclase.

3.4.8 Garnet

One set of $D_F^{garnet/melt}$ and $D_{Cl}^{garnet/melt}$ shows that F and Cl are more incompatible into garnet than clinopyroxene. $D_F^{garnet/melt}$ and $D_{Cl}^{garnet/melt}$ are within the broad range of $D_F^{opx/melt}$ and $D_{Cl}^{opx/melt}$. At 25 kbars (Table 4.5.4), $D_F^{cpx/melt} > D_F^{garnet/melt} > D_F^{opx/melt}$ and $D_{Cl}^{cpx/melt} > D_{Cl}^{garnet/melt} \approx D_{Cl}^{opx/melt}$. Our trace element partition coefficients are generally consistent with garnet-melt partition coefficients of the literature (Gaetani, 2004; Salters et al., 2002; van Westrenen et al., 2000, 1999; Hauri et al., 1994) and with predictive models (van Westrenen and Draper, 2007; Supplementary Fig. 4). The discrepancies observed for partition coefficients of large cations such as La, Pb or Sr (all lower than in previous studies) can be explained by the Py fraction and the experimental conditions (ranging between 16 and 34 kbars and between 1230 and 1565°C). In fact, partition coefficients of large cations such as LREE and U, Th, Pb and Sr increase with the decreasing Py fraction and with decreasing T at a given Py fraction (van Westrenen et al., 1999).

3.5 Discussion

3.5.1 Crystal chemical controls on F and Cl incorporation in pyroxenes

Cation incorporation into a crystal is generally controlled by the size and the charge of the hosting crystallographic site. Since anions are not substituted in the same sites as cations, the control of anion incorporation may be different than that of cation. We examine the anion incorporation mechanisms using our pyroxene data. Given the negative charge and the ionic radii of F and Cl, they are expected to be substituted into oxygen sites. While no specific correlation between D_F and end-member components of opx is found, we observe a positive correlation between D_{Cl} and the mole fraction of the jadeite component (Fig. 3.5.1a). While they are annealed at the same P - T conditions, the proportion of the jadeite component decreases when the total volatile abundance in the melt increases (i.e. $(H_2O + F)$ varies from 0.26 to 1.6 wt%, Supplementary Fig. 1). The initial $(H_2O + F)$ in the starting materials ranges from 0.2 to 1.3 wt%.

The increase of D_{Cl} in the samples may be caused by compositional variation of opx and melt. The result of this compositional variation is that Cl becomes less incompatible with increasing jadeite content in opx. The jadeite component involves the coupled substitution of (i) Na⁺ for Mg²⁺ in the M2 site and (ii) Al³⁺ for Mg²⁺ in the M1 site, to balance the charge. Because this coupled substitution appears to promote the incorporation of Cl in opx, we propose the following substitution equation for Cl incorporation in opx using the Kröger-Vink notation (Kröger and Vink, 1956):

$$Na'_{Mg} + Al^{\bullet}_{Mg} + Si^{\times}_{Si} + O^{\times}_{O} + Cl^{\times}_{melt} + 2MgO^{\times}_{melt} = Na^{\times}_{melt} + Al'_{Si} + SiO^{\times}_{2\ melt} + O^{\times}_{melt} + Cl^{\bullet}_{O} + 2Mg^{\times}_{Mg}$$

$$(3.5.1)$$

where superscript symbols are the charge states of the lattice: \times indicates neutral, ' negatively and • positively charged lattice. Subscripts indicate the locations (melt or lattice site in crystal) where the species are. This equation shows that Cl⁻ substitution into the O²⁻ site is balanced by Al³⁺ substitution into Si⁴⁺ sites. The higher the abundance of jadeite component in opx, the reaction progresses from left to right. The Gibbs free energy given by the equation 3.5.1 can be written as,

$$\Delta G = -RT \ln \left(\frac{a_{Na}^{melt} a_{SiO2}^{melt} a_{Cl}^{opx} a_{Al}^{opx} a_{Enstatite}^{opx}}{a_{Jadeite}^{opx} a_{Cl}^{melt} a_{MgO}^{melt 2}} \right).$$
(3.5.2)

Here, the activities of oxygen and Si in opx, and oxygen in melt, are considered as unity. Therefore, the Cl partition coefficient can be expressed as,

$$D_{Cl}^{opx/melt} = \frac{[Cl]^{opx}}{[Cl]^{melt}} \propto \frac{a_{Cl}^{opx}}{a_{Cl}^{melt}},$$

$$D_{Cl}^{opx/melt} \propto \frac{a_{Jadeite}^{opx} a_{MgO}^{melt 2}}{a_{Na}^{melt} a_{SOO}^{opx} a_{A}^{opx} a_{Enetatite}^{opx}} \exp\left(-\frac{\Delta G}{RT}\right).$$
(3.5.3)

Assuming that the ratio of activity coefficients $(\gamma_{Cl}^{opx}/\gamma_{Cl}^{melt})$ is constant over the ranges of experimental parameters, equation 3.5.3 shows that $D_{Cl}^{opx/liq}$ is correlated positively with $a_{Jadeite}^{opx}$ and negatively with $a_{Enstatite}^{opx}$. Because of the constant P - T and the small variation of jadeite and enstatite, $X_{Jadeite}^{opx}$ is proportional to $a_{Jadeite}^{opx}$, and $X_{Enstatite}^{opx}$ is proportional to $a_{Enstatite}^{opx}$ (see supplementary Table 2 for the variations of pyroxene components).

In clinopyroxene, we observe a positive correlation between D_{Cl} and the mole fraction of the CaTs component of the cpx (Fig. 3.5.1b). The CaTs component substitutes Al³⁺ for Mg²⁺ in the M1 site, and Al³⁺ for Si⁴⁺ in the tetrahedral site (or T). The incorporation of Cl appears to be promoted by Al substitution in the Si site. Using similar reasoning as for opx, we propose the following Cl incorporation reaction in cpx:

$$Al_{Mg}^{\bullet} + O_O^{\times} + Cl_{melt}^{\times} + Mg_{melt}^{\times} = Al_{melt}^{\times} + O_{melt}^{\times} + Cl_O^{\bullet} + Mg_{Mg}^{\times}.$$
(3.5.4)

The substitution of Cl^- into the O^{2-} site balances the Al^{3+} incorporation into the Si^{4+} site. Since $[Cl] \ll [Al]$, the incorporation of Al^{3+} into the Si^{4+} site is also charge-compensated by the Al^{3+}



Figure 3.5.1: Variation of Cl partition coefficient in different samples with pyroxenes composition variation of samples. a) Increase of D_{Cl} between opx and melt with the jadeite content (in %) of opx among samples obtained at the same P - T i.e. without cpx seeds. b) Increase of D_{Cl} between cpx and melt with increasing CaTs content (in %) in cpx from seeded experiments.

substitution into the Mg^{2+} site, following the Tschermak substitution. The equation 3.5.4 can be expressed as,

$$D_{Cl}^{cpx/melt} \propto \frac{a_{Cl}^{cpx}}{a_{Cl}^{melt}} = \frac{a_{Al}^{cpx} a_{Mg}^{melt}}{a_{Al}^{melt} a_{Mg}^{melt}} \exp\left(-\frac{\Delta G}{RT}\right)$$
(3.5.5)

Here, given $a_{CaTs}^{cpx} \propto a_{Al}^{cpx}$, equation 5 explains the correlation in Fig. 3.5.1b between CaTs abundance and $D_{Cl}^{cpx/melt}$.

3.5.2 Relationship between anion partitioning and cation site deformations

Cation partitioning between solid and liquid is often dominantly controlled by crystal chemistry (e.g. Blundy and Wood, 1994, 2003). According to their ionic radius and charge, elements are incorporated into different crystal sites. Each site is characterized by the parameters of the lattice strain model (Brice, 1975; Blundy and Wood, 1994). This lattice strain model is built on the observation that the logarithms of the D_i , for an isovalent series of elements, *i*, substituted into a particular crystal lattice site, describe a pseudo parabolic function of trace element radius, r_i (Nagasawa, 1966; Onuma et al., 1968; Brice, 1975).

Here, we present a lattice-strain model for the partitioning of 3+ cations, (Al, Cr, Sc, Lu, Ho, Gd, Eu, and La), between orthopyroxene, clinopyroxene and basaltic melt. Orthopyroxene and clinopyroxene have two octahedral sites, M1 and M2. Following Frei et al. (2009), $D_i^{crystal/melt}$ regression to the lattice strain model is expressed as,

$$D_i^{px/melt} = D_0^{M1} \exp\left(\frac{-4\pi E_0^{M1} Na}{RT} \left(\frac{r_0^{M1}}{2} (r_i - r_0^{M1})^2 + \frac{1}{3} (r_i - r_0^{M1})^3\right)\right) + D_0^{M2} \exp\left(\frac{-4\pi E_0^{M2} Na}{RT} \left(\frac{r_0^{M2}}{2} (r_i - r_0^{M2})^2 + \frac{1}{3} (r_i - r_0^{M2})^3\right)\right).$$

For cations that enter into the crystal site M1 or M2, the partition coefficient (D_i) is described by six parameters: r_0^{M1} and r_0^{M2} , the ideal crystal strain-free radii of M1 and M2 sites; E_0^{M1} and E_0^{M2} , the elastic response of the sites to the elastic strain caused by larger or smaller r_i than r_0^{M1} and r_0^{M2} ; and D_0^{M1} and D_0^{M1} , the fictive strain-free partition coefficient for cations with r_0^{M1} and r_0^{M2} , respectively. Here, N_A is the Avogadro number; R is the gas constant and T is the temperature in K. For the case in which r_0^{M1} and r_0^{M2} are sufficiently different, the model fit can be performed on two independent parabolas, as it has been done for cpx in many previous studies (e.g. Blundy and Wood, 1994). The trivalent cations were fitted by the differential evolution constrained algorithm (Storn and Price, 1997). We minimized the cost function using the Nash criterion (> 0.9995) and the root mean square error (RMSE < 0.04). The optimization procedure was constrained with realistic boundary values for each parameter (6, 3 per site) according to the accuracy of the measured data. The parameter space was defined as large as possible to avoid a priori determination (e.g. $E_0^{M2} \in [100; 1000]$ GPa). For divalent and tetravalent cations, the number of experimental data is less than that of model parameters and we did not run the lattice strain model on those data.

The best-fit values for r_0^{M1} , r_0^{M2} , E_0^{M1} , E_0^{M2} , D_0^{M1} and D_0^{M2} are presented in Table 3.5.1. Fig. 3.5.2 shows selected model fits. There appear to be no systematic variations of r_0^{M1} , r_0^{M2} , E_0^{M1} , E_0^{M2} , D_0^{M1} and D_0^{M2} with respect to increases of P and T (Fig. 3.5.2a and c). This was also previously noted by Frei et al. (2009). Figure 3.5.2b shows a variation of Onuma diagram for opx formed under identical P - T conditions.

We find negative correlations between D_F and E_0^{M1} and between D_{Cl} and E_0^{M2} in opx (Fig. 3.5.3a and b). Variations of E_0 and D_0 for both sites show no correlation with pyroxene components in opx. Because, for the jadeite substitution observed in opx, the ionic radius of Na⁺ is comparable to that of Mg²⁺, no significant site deformation is expected. Thus, the observed variations of the lattice strain parameters, especially E_0 and D_0 , cannot be entirely explained by the variation of either the pyroxene components alone, or the P - T conditions alone (Fig 3.5.2b). Therefore, we suggest that cation substitution energetics also influences anion substitution, and there are two potential explanations:

• When E_0 is higher, the substitution of larger or smaller size ions, even anions, requires higher strain energy for the deformation of anion-cation sites. The incorporation of F and Cl in

Run	D_0^{M1}	$E_0^{M1}(\text{GPa})$	$r_0^{M1}(\text{\AA})$	D_0^{M2}	$E_0^{M2}(\text{GPa})$	$r_0^{M2}(\mathrm{\AA})$
			Orthop	yroxene		
F2p#2b	7(2)	1190(220)	0.650(4)	0.222(22)	539(58)	0.849(11)
F4p#3a	9(2)	1265(115)	0.646(2)	0.251(18)	378(48)	0.843(10)
F1#3b	6.0(3)	1144(57)	0.651(2)	0.190(22)	454(128)	0.842(14)
F5#3b	9(1)	1382(78)	0.649(2)	0.223(30)	413(50)	0.849(15)
C4p#2b	8(1)	1179(195)	0.651(2)	0.206(50)	454(10)	0.884(28)
C8p#2b	6(1)	1187(124)	0.648(2)	0.247(82)	501(89)	0.840(26)
C04#3a	8(3)	1195(245)	0.648(4)	0.211(24)	224(48)	0.849(18)
C4#4a	8(3)	1206(207)	0.649(4)	0.288(55)	173(53)	0.827(22)
CC01#8kb4	2.3(1)	663(59)	0.660(2)	0.234(11)	387(15)	0.824(4)
CF1#8kb5	4.7(6)	1169(78)	0.651(2)	0.133(19)	512(83)	0.823(6)
CC4#7b	7.1(2)	1255(31)	0.647(1)	0.190(6)	414(10)	0.821(1)
CF5#7c	8.5(1)	1330(19)	0.648(1)	0.184(7)	463(10)	0.821(1)
$\rm CF01\#16kb1$	7.77(8)	1275(16)	0.646(1)	0.203(5)	455(14)	0.821(2)
C4p#25kb	4.8(6)	1275(68)	0.638(1)	0.081(11)	464(35)	0.825(6)
			Clinopy	roxene		
CC01#8kb4	6.9(6)	809(173)	0.654(2)	0.558(36)	448(57)	1.010(2)
CF1#8kb5	6.5(2)	1050(24)	0.661(0.1)	0.441(42)	430(37)	1.012(2)
CC4#7b	8.36(18)	1163(54)	0.649(1)	0.470(6)	408(23)	1.009(11)
CF5#7c	9.25	1221	0.649	0.354	462	1.016
C4p#25kb	6.35(44)	1175(38)	0.643(1)	0.217(22)	475(39)	1.007(3)

Table 3.5.1: Best-fit values fit to D_0 , E_0 and r_0 for M1 and M2 site of pyroxenes for trivalent cations.

The r_i , the ionic radii of cation elements, were originally from Shannon (1976). For orthopyroxenes, ionic radii were chosen as 6-fold coordination for both M sites and for clinopyroxenes, as 6-fold coordination in the M1 site (Al, Cr, Sc) and 8-fold coordination in the M2 site (REE).

The uncertainties on parameters are determined the Monte Carlo simulation accounting for the errors on the partition coefficients.


Figure 3.5.2: Lattice strain models (Brice, 1975; Blundy and Wood, 1994) applied to orthopyroxene (a and b), clinopyroxene (c) -basaltic melt partition coefficients for trivalent cations. Solid lines represent fits of the lattice strain model to $D_i^{px/melt}$, i.e. the sum of $D_i^{M1/melt}$ (stippled parabola) and $D_i^{M2/melt}$ (dashed parabola). Circles represent measured $D_i^{px/melt}$ presented in Table 4.5.4. In (a) and (c), models were presented for samples CC4#7b (12 kbars-1310 $^{\circ}\mathrm{C})$ CC01#8kb4 (8 kbars-1265°C), and C4p#25kb (25 kbars-1430°C). Figure (b) shows data for 12 kbars-1360°C samples. Note that we have no systematic change of the fit geometries according to variations of P - T conditions. For the same P - T conditions in (b), there are notable changes in the partition coefficients of large radii cations.



Figure 3.5.3: Variation of the calculated E_0^{M1} with the measured D_F among all samples (a) and E_0^{M2} with D_{Cl} for the same P - T conditions (b).

the pyroxene structure is therefore more difficult with high E_0 , and hence F and Cl are less compatible.

 Charge deficiency caused by F⁻ and Cl⁻ substitution into the O²⁻ site involves a lengthening of the cation-anion distance, which relaxes the strain energy (demonstrated for cation partitioning by Hill et al., 2000). The more F and Cl substitution, the smaller E₀ becomes.

In cpx, we found a positive correlation between pyroxene component and r_0 (Supplementary Fig. 5). However, we did not observe any correlation between E_0 and pyroxene component, in spite of the demonstration that E_0 and D_0 for M1 and M2 sites increase with an increase of CaTs in clinopyroxene (Hill et al., 2000). The CaTs content in cpx correlates with r_0^{M1} resulting from the substitution of the small ionic radius of Al³⁺ relative to Mg²⁺ that leads to the shortening of M1-O bonds (Cameron and Papike, 1981; Gaetani and Grove, 1995). The r_0^{M2} is linearly correlated with the diopside content of the cpx (Supplementary Fig. 5), resulting from the large radius of Ca²⁺ relative to Mg²⁺. Therefore, r_0^{M1} and r_0^{M2} changes among cpx are relevant to crystal composition variations, while E_0 variations have to be related to another variable, such as F and Cl incorporation. Because of the variable P - T in these experiments, we are incapable of demonstrating cation-anion interaction observed in opx.

3.5.3 Correlations between melt viscosity and F and Cl partition coefficients

It has been demonstrated that melt polymerization contributes to variations of the D_0 (Gaetani, 2004). Our data also show that the variation of D_0 correlates weakly with the melt viscosity (η) . Here, changes in volatile element concentrations dissolved in the melt are responsible for the viscosity variations at given P - T conditions. The partitioning of F in opx shows strong correlations with the viscosity, suggesting a coupling of the melt polymerization and D_F . On the contrary, the partitioning of Cl in opx shows no correlation with the viscosity (Fig. 3.5.4). We have argued that opx crystal chemistry controls D_{Cl} variation (Fig. 3.5.1), but D_F does not correlate with any parameter related to opx crystal chemistry. Instead, the variation of D_F is apparently influenced by melt structure.

F and Cl are equally charged, but their ionic radii are different; $F^-(IV)$ ionic radius is 133 pm and Cl⁻(IV) ionic radius is 181 pm. In comparison, O^{2-} is 140 pm. For cations, smaller ions are more sensitive to melt depolymerization, as D_i of smaller cations varies significantly with melt depolymerization (Gaetani, 2004). Anions seem to follow the same tendency. The smaller anion F concentrates into more depolymerized melt, while such systematics does not show up for larger Cl. Contrasting effects of crystal chemistry and melt composition/structure on D_F and D_{Cl} are found. (1) Melt structure appears more influential on D_F relative to crystal chemistry. (2) D_{Cl} is more strongly influenced by crystal chemistry relative to melt structure.



Figure 3.5.4: Variation of D_i in opx with the melt viscosity. a) D_F among all samples, and b) D_{Cl} among samples of the same P - T. The same Y-axis range is kept for comparison. Note the D_F is strongly correlated with the viscosity of the melt, while D_{Cl} shows no relation with the viscosity.

3.5.4 Deciphering the anion environment in anhydrous silicate minerals

Orthopyroxene

We have acquired a set of Raman spectra of the experimentally synthesized opx (Fig. 3.5.5). From the shifts of vibration modes, and their correlation with cation and halogen concentrations, it is possible to infer the specific sites where F and Cl were incorporated. Of the several vibration modes, we have observed significant shifts in the wavenumbers around 380, 407, 522, and 577 cm⁻¹. These peaks are generally attributed to 1) M-site cation-anion stretching modes (380 and 407 cm⁻¹), and 2) O-Si-O

bending modes (522 and 577 cm^{-1} ; Huang et al., 2000). For the following discussion, all the vibration modes are identified using Huang et al. (2000).



Figure 3.5.5: Representative Raman spectroscopic patterns for four opx from four different samples. Dark grey band underlines change of peak wavenumbers that can be related to F and Cl concentration in opx. Letters refer to Fig. 3.5.6.

Vibrational modes in opx (between 200 and 1100 cm⁻¹, except for around 870 cm⁻¹ and 940 cm⁻¹) decrease in wavenumber with increase of the average O-M1 interatomic distance, when the Fe content increase (Huang et al., 2000). For the series of experiments synthesized at identical pressure and temperature conditions, we have found clear negative correlations between abundances of F or Cl in opx and certain vibration modes. These tendencies may be interpreted in two manners (Fig. 3.5.6):

1) These correlations are the consequences of site distortions due to the slight variation of cation abundances. Note that the experiments are conducted at the same P - T conditions, and abundances of volatiles are systematically changed, which resulted in a variation of opx compositions. However, so far, we have not found a straightforward correlation between vibrational frequencies and chemical composition of pyroxenes.

2) Alternatively, variable abundances of F and Cl in opx are the primary cause of distorting the cation-anion bond lengths. The distortion is observed as the changes in vibration frequency. Vibrational frequency of a molecule is defined by the oscillator harmonics equation, $\nu \propto \sqrt{k/\mu}$, where μ is the reduced mass defined by $\mu = m_1 m_2/(m_1 + m_2)$, where k is a force constant and m_i are atomic weights of bonding atoms. Based on this relation, the replacement of O by F gives insignificant change of the reduced masses. On the contrary, the replacement of O by Cl would lead to approximately 20% reduction in vibrational frequency, assuming constant k. This may explain the observed anti-correlation between the anion-Si-anion vibration mode and Cl concentration in pyroxenes (Fig. 3.5.6d) but does not explain the positive correlations of the anion-cation vibration modes with Cl concentration (Fig. 3.5.6b).

From the Coulomb law, the bond strength between two charged atoms depends on each atom's charge over the squared distance between those atoms $(k \propto (q_1q_2)/r^2$ where q_1 and q_2 are the charges of the atoms and r is the distance between the two charges). Considering that F and O have similar ionic radii, when F⁻ replaces O²⁻ in its site, the charge difference between those two anions causes a decrease of the bonding force between anion and cation, and reduces the vibrational frequency. This potentially explains the negative correlation between F concentration in opx and the vibrational frequency modes (Fig. 3.5.6 a and c).

Regardless of the cause of the observed correlations, it demonstrates that F and Cl incorporation is strongly associated with the local environment of the adjacent M1 or M2 site. This is consistent with the correlations observed between D_F and E_0^{M1} , and between D_{Cl} and E_0^{M2} (Fig. 3.5.3), where Eis a Young's Modulus describing cation incorporation environment. Furthermore, the anion-Si-anion vibration modes are also affected by F and Cl incorporation into opx (Fig. 3.5.6c and d). From these observations, because Cl incorporation is mainly associated with M2 sites and tetrahedral Si sites, we infer that Cl is substituted into O3 sites. The O3 site is the larger O site coordinated with two octahedral M2 and two tetrahedral (T) cations (Cameron and Papike, 1981). The incorporation of F is mainly related to M1 sites (D_F correlates with E_0^{M1}) and Si sites, hence we suggest that F is substituted into O1 sites, which are the smaller O sites coordinated with two M1, one M2 and one T cations. It should be noted that these halogen substitution processes have been inferred from the opx with 100 ppm-level halogen abundances, not the end-member pyroxene with maximum replacement of halogen in oxygen sites. This substitution hypothesis needs to be verified in the future.



Figure 3.5.6: Variation of the wavenumber position of raman spectra peaks of opx (a to d) and cpx (e and f) for different samples. Raman spectra were corrected from the baseline using a rubberband correction and peak positions were determined using the PeakFit software. Samples of the same P - T conditions are presented here, except for C4#4a.

Clinopyroxene

Among the cpx synthesized in our experiments and despite the limited number of samples, there are two sets of linear correlations: 1) between F concentration and the shift of the Ca-anion stretch vibration mode (Fig 3.5.6e), and 2) between Cl concentration and the shift of the Mg-anion stretch vibration mode (Fig. 3.5.6f). In cpx, Ca enters M2 sites and Mg enters M1 sites. The increase of F content leads to a decreased M2-anion stretch vibration mode. Therefore, F is likely substituted into the O3 site associated with the M2 site. Given that the O3 site is the biggest O site, we guess that it is the easiest site for F substitution and to substitute F in any other smaller oxygen site (O1 and O2) will require more effort. Because F incorporation shows no clear correlation with pyroxene chemistry, our inference remains inconclusive. On the contrary, the increase of Cl content leads to a distortion of the pyroxene network that shortens M-O bond distances. Furthermore, our Cl substitution model (equation 3.5.4) also shows that Cl incorporation is associated with Al^{3+} substituted in T sites, and promoted by CaTs component. Consequently, Cl is more likely substituted into O1 or O2 sites in cpx.

Olivine and garnet

Current F and Cl data of olivine are insufficient to resolve F and Cl substitution mechanisms. In our samples, less than 50 ppm of F and Cl enters olivine (Table 3). Nevertheless, we anticipate two possible substitution mechanisms: 1) Cl may enter the larger O site (O3) and F the smaller O sites (O1 or O2), and they will be coordinated with M site cations, or 2) the clinohumite defects in olivine may accomodate halogens, because it was described as one of the OH incorporation site (Hermann et al., 2007). It should be noted, however, that the planar clinohumite defect occurs at temperatures below 1000°C (Hermann et al., 2007; Weiss, 1997). Alternatively, F-bearing humite is stable at higher temperatures than OH humite (Engi and Lindsley, 1980). The substitution mechanism in olivine remains inconclusive.

There is 0.76 wt% F in metamorphic garnet from Adirondack calc-silicates (Valley et al., 1983). This is equivalent to 1.5 mol% substitution of fluorine for oxygen. The authors suggested the occurrence of two coupled substitutions that we can write in Kröger-Vink notation as:

$$Si_{Si}^{\times} + 4NaF_{melt} + 4O_{O}^{\times} = V_{Si}^{\prime\prime\prime\prime\prime} + 4F_{O}^{\bullet} + SiO_{2melt} + 2Na_{2}O_{melt},$$

 $2Al_{Al}^{\times} + 2O_{O}^{\times} + 2NaF_{melt} + 2MeO_{melt} = 2Me_{Al}^{\prime} + 2F_{O}^{\bullet} + Al_{2}O_{3melt} + Na_{2}O_{melt},$

wherein $Me = Mg^{2+}$, Fe^{2+} .

These coupled substitutions can also describe Cl substitution in garnet. In our study, only 0.02 wt% of F and Cl are substituted into garnet. The substitution equation implies that F and Cl bond with Y-site cations (i.e. Mg, Fe) in garnet (Heinemann et al., 1997).

3.6 Conclusion

We reported F and Cl partition coefficients among orthopyroxene, clinopyroxene, olivine, garnet, plagioclase and basaltic melt for P - T conditions ranging from 8 to 25 kbars and 1265 to 1430°C, respectively. We demonstrated that Cl incorporation into minerals strongly depends on crystal chemistry because of its large ionic radius (30% larger than O). In orthopyroxene, the increase of the jadeite component promotes the Cl incorporation, while in clinopyroxene, the increase of CaTs eases Cl incorporation. It appears that the F substitution process mostly depends on melt viscosity and not on crystal structural parameters. From the Raman spectra and compositional correlations, we propose that Cl enters into the larger O3 site and F into the smaller O1 site of opx. In cpx, Cl is mainly coordinated with the M1 site, and F is coordinated with the M2 site.

Lattice strain models performed on trace elements between pyroxenes and melt indicate that F and Cl incorporations correlate with the lattice strain energy needed to deform cation sites (E_0) . For instance in opx, given constant D_0 and r_0 parameter and constant P - T conditions, a range of E_0^{M2} from 170 GPa to 450 GPa corresponds to a variation of D_{Cl} of a factor of 2. At the same time, this variation coincide with a range of jadeite content from 0.2 to 0.4. Lastly, this E_0^{M2} variation leads to a change in D_{LREE} of almost 75% and D_{HREE} of less than 1%.

Melt structure changes F and trace element partition coefficients (D_0) . Here, a viscosity increase by a factor of 5, increases F partition coefficients by one order of magnitude and trace element partition coefficients by a factor of 3.6 (calculated from D_0).

Primary magmas of subduction zones contain a wide range of volatile concentrations (e.g. Le Voyer et al., 2010). We have shown that trace element fractionation are influenced by variable melt viscosity and crystal chemistry. Therefore, any change of volatile abundances in the source of these magmas could produce non-negligible variations of trace element signatures in arc magmas. We expect that further observations on F, Cl and REE abundances in arc primitive magmas should help us determine the role of slab-fluid/melt.

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3.7 Supplementary material

This supplementary section reports several aspects of the reported data, as well as data themselves. Section 3.7.1 reports all trace element data acquired in the study, as well as the trace element Ds that are not reported in the main section. Section 3.7.2 reports pyroxene end member fractions in mol%. In a serie of the reported experiments, pyroxene composition varies significantly while the P - Tconditions are kept constant. This was unexpected since our major element composition was kept constant except for the quantity of total volatile elements in the system. In Section 3.7.3, weak correlations between pyroxene compositions and total volatile contents show a relationship between these parameters when the P - T conditions are kept constant. Section 3.7.4 discusses the comparisons of trivalent trace element lattice strain models for opx, cpx, and garnet. Section 3.7.5 shows wellestablished correlations between pyroxene end-member components and the optimal cite radius for trace element partitioning (see Wood and Blundy, 1997). This demonstrates that our trace element partitioning data are coherent with previously reported studies.

3.7.1 Trace element data : concentrations and partition coefficients

Trace element concentrations in the cpx seeds:

Table 3.7.1: Trace element composition of cpx seeds (in ppm).

Element	V	\mathbf{Cr}	\mathbf{Sr}	Υ	\mathbf{Zr}	La	Ce	Nd	Sm	Eu	Gd	Dy	\mathbf{Er}	Yb
Cpx seeds	314	6145	74	3.3	28	5.2	5.3	7.2	7.3	8.6	4.8	2.6	1.5	1.8

Trace element abundances of clinopyroxene seed crystals are given in Table 3.7.1. The concentration was determined by SIMS 3f (WHOI) measurements (on average of 3 points in several grains from a natural lherzolite). It illustrates that the addition of trace elements by the cpx seeds are negligible to the total quantity of the dope.

Trace element concentrations are shown in Tables 2 and 3 for LA-ICPMS measurements and Table 4 for SIMS measurements. Trace element partition coefficients (wherein $D_i^{min/melt}$ is the concentration of element *i* in the mineral divided by the concentration of the element *i* in the melt) are presented in Tables 5 (orthopyroxene) and 6 (other minerals: clinopyroxene, olivine, plagioclase and garnet). Beryllium and boron data presented were measured by 5f SIMS (Montpellier). Beryllium partition coefficients are presented as maximum values, because of a likely interference of ¹⁸O²⁻, which is detected during SIMS mass calibration. In order to check the accuracy of SIMS or LA-ICPMS measurements, and verify the closure of experimental charge, we have compared the sum of initial trace element masses for all trace elements (100 ppm for all elements and 1000 ppm for Pb) with the sum based on the phase proportion of the charges.

	F2p#2a			F4p#3a		F1#3b		F5#3b		C4p#2b		C8p#2b		
	Melt [3]	O1 [4]	Opx [3]	Melt [2]	Opx [7]	Melt [4]	Opx [5]	Melt [5]	Opx [5]	Melt [2]	Opx [3]	Melt [2]	OI [3]	Opx [4]
Li	47(2)	14.3(9)	8.0(2)	20.5(6)	4.7(1)	25.8(8)	5.4(5)	24.5(4)	3.8(5)	46.6(7)	8.2(1)	47(2)	13.8(8)	7.7(1)
$\mathbf{S}_{\mathbf{C}}$	81(1)	17(1)	79(1)	78(1)	82(2)	78(2)	(2)62	86.3(9)	83(3)	71.9(5)	82(4)	79.6(8)	17.4(9)	75(1)
>	70(1)	21(1)	177(4)	57.0(5)	147(5)	57(1)	107(17)	63.4(2)	173(8)	66(1)	173(9)	73(3)	24(1)	170(2)
\mathbf{Cr}	1075(15)	855(38)	3222(42)	506(4)	3622(88)	854(14)	4765(534)	777(7)	4723(178)	896(2)	5270(150)	991(96)	882(93)	5084(84)
Co	60(1)	167(12)	87(1)	58.6(5)	94(4)	58(1)	87(3)	59(1)	104(9)	62.4(5)	91(1)	61(3)	162(8)	84(1)
\mathbf{Sr}	85.6(1)	0.003(1)	0.2(1)	96.0(6)	0.8(2)	91.2(8)	1.9(9)	116(1)	0.136(3)	75(1)	0.18(2)	89(4)	0.05(2)	0.4(3)
\mathbf{Zr}	97(1)	0.06(3)	3.1(1)	114(2)	5.1(6)	91.5(7)	3.6(4)	107.2(5)	3(1)	94.8(6)	2.8(5)	96(4)	0.12(4)	2.8(3)
\mathbf{La}	96(1)	0.006(1)	0.2(4)	118(2)	1.4(2)	94.6(9)	0.3(2)	111.0(7)	0.9(10)	87.6(4)	0.1(2)	97(4)	0.04(2)	0.3(2)
Еu	109(1)	0.03(2)	1.9(6)	133(1)	8.1(3)	108(1)	6(2)	125(1)	4(1)	100.035(7)	2.1(2)	112(5)	0.13(3)	4.6(2)
Gd	89.1(8)	0.10(7)	3.1(3)	108(2)	11.4(5)	83(3)	7(2)	101(2)	5(1)	81(2)	3.7(4)	88(3)	0.25(9)	7.06(2)
Но	92.9(6)	0.56(5)	8.2(7)	110(2)	13.7(3)	88(2)	11(1)	100(9)	11(1)	85(1)	9.3(7)	95(4)	0.65(5)	13.97(3)
Lu	90.1(8)	2.6(2)	17.0(7)	104(2)	24(5)	85(2)	15.6(8)	96(2)	20(1)	83(1)	19(1)	88(4)	2.8(2)	15.96(2)
Ηf	87(1)	0.08(4)	5.3(5)	104(1)	7.76(4)	84(1)	0.88(7)	99(5)	5.0(8)	80.9(7)	5.0(5)	86(4)	0.15(5)	4.60(1)
$\mathbf{P}\mathbf{b}$	114(4)	0.21(4)	1.4(2)	145(1)	0.9(5)	115(1)	0.1(1)	129(2)	0.015(2)	111.4(5)	0.7(4)	111(5)	0.10(6)	0.47(56)
$\mathbf{T}\mathbf{h}$	96(1)	0.005(18)	0.25(19)	115(2)	0.8(3)	91(1)	0.2(1)	105.9(6)	0.06(1)	89(1)	0.4(2)	92(5)	0.02(3)	0.2(2)
D	102(2)	0.006(19)	0.4(3)	126(3)	0.9(4)	95(1)	0.6(4)	118(1)	0.14(3)	98.5(6)	0.1(3)	101(5)	0.03(2)	0.3(3)

Table 2: Trace element concentrations (in ppm) of run products measured by LA-ICPMS (Laboratoire Magmas et Volcans).

	C04#3a			C4#4a		CC01#8	kb4			CF1#8kl	J 5		
	Melt [2]	OI [4]	Opx [3]	Melt [2]	Opx [3]	Melt [3]	OI [3]	Opx [2]	Cpx [2]	Melt [2]	OI [1]	Opx [2]	Cpx [2]
Гi	16.5(3)	4.8(3)	2.5(2)	14(5)	3.5(1)	58(2)	12.5(6)	7.6(7)	10.3(5)	78.6(8)	17(1)	10.4(3)	16.3(1)
$\mathbf{S}_{\mathbf{C}}$	79(1)	16(1)	81(2)	80(2)	93(3)	55(1)	10.7(5)	53(6)	83(2)	83.1(4)	12.7(9)	63(6)	130(3)
>	60.9(4)	13.9(9)	134(5)	57.5(9)	171(6)	48.5(9)	20(1)	181(13)	233(10)	71(1)	43(3)	234.2(3)	438(3)
\mathbf{Cr}	611(8)	500(85)	3791(214)	735(76)	4470(76)	917(9)	1017(211)	5376(570)	6484(420)	1570(3)	1259(73)	5868(394)	7211(317)
Co	41.7(6)	129(9)	80(5)	63.9(8)	128(9)	34.80(7)	105(1)	55(5)	33(1)	43(1)	131(10)	81(7)	64(18)
$\mathbf{S}_{\mathbf{r}}$	97(1)	0.06(1)	0.4(1)	99(4)	0.1(1)	86(1)	0.06(2)	0.10(2)	4(1)	110.5(3)	0.02(3)	0.22(3)	4.9(5)
\mathbf{Zr}	131(3)	0.10(2)	4.2(4)	108(2)	4(1)	76.8(6)	0.13(3)	2.3(3)	8(1)	136.2(9)	0.07(5)	1.9(3)	9(2)
\mathbf{La}	107(2)	0.05(2)	1.5(5)	114(2)	0.2(10)	84(2)	0.054	0.075(3)	2.7(8)	116(1)	d.l.	0.05(6)	3.2(6)
Еu	118(2)	0.10(2)	4.6(7)	127(3)	2.6(20)	72(3)	0.18(8)	1.3(1)	14.2(9)	119(1)	0.003(46)	1.3(4)	14(1)
Gd	98(2)	0.12(6)	5.5(5)	105(1)	3.6(13)	67(2)	0.2(2)	2.8(5)	28(3)	95(2)	0.04(14)	2.6(1)	29(6)
но	100(2)	0.52(4)	12.4(6)	106(3)	12(1)	69(2)	0.7(2)	7.3(9)	37(2)	95.0(1)	0.32(5)	5.9(6)	39(5)
Lu	95(2)	2.4(2)	21.7(7)	102(2)	23(1)	66(2)	2.2(1)	13(2)	34.6(2)	89.7(1)	1.9(2)	12(1)	38(2)
Ηf	96(2)	0.05(4)	6.5(7)	99.5(5)	6.4(5)	71(2)	0.3(1)	4.5(6)	12(3)	97(2)	0.04(9)	3.1(2)	12(4)
$^{\mathrm{Pb}}$	136.195(7)	0.109(1)	0.4(3)	134(4)	0.2(1)	765(41)	0.3(1)	0.15(6)	3(2)	140(3)	0.19(9)	0.2(2)	0.7(8)
$\mathbf{T}\mathbf{h}$	109(2)	0.04(2)	0.1(7)	115.2(9)	0.21(9)	73(3)	0.03(2)	0.031(5)	0.7(1)	99(2)	d.l.	0.06(5)	0.4(3)
D	121(1)	0.04(2)	0.3(7)	131.0(9)	0.25(7)	78(4)	0.074	0.09(2)	0.9(2)	100(2)	0.04(4)	0.20(6)	0.75(31)
Numbe	rs in parenthe	ses represe	nt one standard	deviations in	terms of least	t units cited.							

Table 3: Continued.

Numbers in square brackets are numbers of LA-ICPMS analyses.

Abbreviations used: Melt, quenched basaltic melt; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene.

	CC01#8]	kb4		CF1#8kl	55		CC4#7b			CF5#7c			CF01#16	ikb1
	Melt [2]	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx
Li	30.8(2)	12.98(6)	9.72(7)	43.0(3)	20.1(1)	9.89(7)	19.91(6)	4.98(9)	7.0(1)	22.85(8)	3.97(8)	10.67(7)	36.7(1)	13.32(3)
\mathbf{Be}	63.8(2)	6.04(6)	6.00(2)	102.0(4)	9.4(1)	6.10(1)	107.1(2)	9.32(6)	15.9(1)	103.3(2)	2.48(3)	28.2(1)	94.9(1)	14.75(6)
в	586(2)	21.0(3)	10.9(1)	268(2)	32.5(4)	11.1(1)	330.2(5)	31.0(1)	51.5(4)	196.0(4)	3.24(9)	56.4(4)	156(5)	24.2(2)
$\mathbf{S}_{\mathbf{C}}$	59.1(3)	61.8(3)	119.9(9)	85.2(3)	33.4(3)	122.1(9)	89.9(6)	79.0(4)	110(1)	90.1(6)	82.4(7)	110.3(6)	72.0(4)	66.5(4)
>	53.2(4)	93.3(7)	284(2)	76.2(4)	58.8(5)	289(2)	87.1(6)	181.9(6)	242(2)	87.3(6)	190(1)	220(1)	75.3(5)	149.9(9)
$\mathbf{C}_{\mathbf{r}}$	887(7)	1296(3)	6165(52)	1492(19)	2009(5)	6275(53)	1035(1)	5811(37)	6773(12)	976(1)	6371(41)	6536(8)	603(9)	3784(3)
Co	53(1)	158(1)	79(1)	94(1)	246(2)	80(1)	126(2)	155(2)	114(1)	130.1(1)	161(2)	126(1)	77.5(5)	98.9(5)
$\mathbf{S}_{\mathbf{r}}$	66.5(5)	3.1(2)	7.0(2)	85.8(7)	8.0(2)	7.1(2)	89.0(8)	6.1(1)	14.4(4)	104(1)	0.43(2)	27.6(7)	84.0(6)	13.3(4)
\mathbf{Zr}	72.9(8)	5.5(1)	12.6(2)	126(1)	11.9(3)	12.8(2)	111(1)	10.8(2)	18.2(4)	109.4(8)	3.02(6)	31.1(7)	84.5(6)	15.1(3)
La	77.2(4)	3.13(9)	6.6(2)	106.2(7)	9.2(3)	6.7(2)	109.3(6)	7.4(1)	14.4(3)	110.4(7)	0.16(1)	25.2(4)	91(1)	14.2(2)
Еu	68.0(5)	3.98(6)	15.6(2)	108.1(6)	8.9(1)	15.9(2)	117(1)	9.0(1)	31.2(4)	116(1)	2.28(8)	43.9(7)	86.5(9)	15.3(2)
Gd	50.9(5)	3.87(7)	23.9(3)	72(1)	5.9(2)	24.3(3)	78.3(7)	7.8(2)	29.4(3)	82(1)	3.10(9)	37.5(3)	65(1)	12.6(2)
но	68.6(5)	9.2(1)	39.4(4)	93.0(7)	8.1(1)	40.1(4)	103.3(7)	15.5(2)	48.2(4)	103.8(8)	9.4(2)	58.4(3)	85(7)	19.5(1)
Lu	61.6(6)	14.0(2)	33.8(1)	82.7(6)	9.1(1)	34.4(1)	91.4(8)	20.0(3)	42.3(4)	92.1(6)	16.5(3)	51.5(3)	76(6)	22.4(3)
Ηf	62.5(7)	6.4(2)	13.8(1)	83(1)	7.5(2)	14.1(1)	91.5(8)	10.3(2)	18.9(4)	90(1)	4.3(1)	30.7(7)	90(1)	17.9(4)
$^{\mathrm{Pb}}$	1851(22)	76(2)	11.2(9)	296(6)	23(2)	11(1)	339(3)	19.8(8)	40(2)	310(3)	0.5(1)	68(2)	2219(24)	305(9)
$^{\mathrm{T}\mathrm{p}}$	66.2(4)	2.63(5)	3.7(2)	88.8(4)	7.8(1)	3.8(2)	100.5(4)	6.9(1)	10.8(4)	100.8(8)	0.074(6)	21.6(6)	83.8(6)	13.3(1)
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Table 4: Trace element concentrations (in ppm) of run products measured by IMS 5f SIMS (Géosciences Montpellier).

Numbers in parentheses represent one standard deviations in terms of least units cited.

Numbers in square brackets are numbers of SIMS analyses. However, most of the analyses represent one measurement.

Abbreviations used are the same as in Table 3.

\mathbf{Run}	F2p#2a	F4p#3a	F1#3b	F5#3b	C4p#2b	C8p#2b	C04#3a	C4#4a	CC01#8kb4	CF1#8kb5	CC4#7b	CF5#7c	CF01#16kb1	C4p#25kb
P(kbars)	12	12	12	12	12	12	12	12	×	×	12	12	16	25
$T(^{\circ}C)$	1360	1360	1360	1360	1360	1360	1360	1360	1265	1265	1310	1310	1350	1430
Li	0.169(11)	0.229(14)	0.208(26)	0.155(21)	0.177(7)	0.162(9)	0.154(16)	0.246(17)	0.131(16)	0.132(5)	0.270(34)	0.171(17)	0.212(6)	0.319(25)
\mathbf{Be}	ND	ND	ND	ND	ND	ND	ND	ND	< 0.094	< 0.093	<0.087	< 0.024	<0.16	< 0.36
В	ND	ND	ND	ND	ND	ND	ND	ND	0.0357(6)	<0.12	< 0.094	0.0165(5)	<0.15	< 0.24
\mathbf{Sc}	0.978(49)	1.053(36)	1.021(107)	0.969(47)	1.133(65)	0.941(25)	1.031(15)	1.16(12)	0.97(13)	0.71(8)	0.87(4)	0.82(3)	0.77(3)	0.44(3)
^	2.52(9)	2.58(10)	1.87(33)	2.73(13)	2.63(21)	2.33(13)	2.21(10)	2.97(26)	3.73(33)	3.29(6)	1.93(9)	1.86(13)	2.08(16)	1.106(14)
\mathbf{Cr}	5.2(1)	7.2(2)	5.6(7)	6.1(3)	5.9(2)	5.1(6)	6.2(4)	6.1(8)	3.5(3)	3.5(4)	4.6(2)	6.52(5)	6.76(75)	4.37(53)
Co	1.46(5)	1.61(8)	1.50(10)	1.75(19)	1.46(3)	1.37(9)	1.92(14)	2.00(17)	1.57(14)	1.91(21)	1.10(4)	1.32(11)	1.35(6)	1.14(8)
\mathbf{Sr}	0.0029(15)	0.0083(28)	0.0042(23)	0.0012(0.4)	0.0024(3)	0.0041(31)	0.0037(16)	0.0014(12)	0.0009(3)	0.0020(3)	0.0028(8)	0.0021(5)	0.0024(2)	0.0023(1)
\mathbf{Zr}	0.032(8)	0.045(7)	0.021(11)	0.027(10)	0.030(6)	0.029(4)	0.032(4)	0.037(12)	0.030(4)	0.011(2)	0.025(5)	0.021(2)	0.021(3)	0.015(0.3)
La	0.0033(7)	0.0115(22)	0.0031(20)	0.0081(20)	0.028(20)	0.0035(6)	0.039(11)	0.054(25)	0.0009(4)	0.0008(4)	0.0012(2)	0.0014(8)	0.0016(2)	0.0102(2)
Eu	0.063(3)	0.093(4)	0.058(5)	0.089(25)	0.079(31)	0.041(2)	0.118(29)	0.153(11)	0.046(1)	0.011(2)	0.026(1)	0.020(6)	0.026(1)	0.015(2)
Gd	0.106(5)	0.108(5)	0.082(9)	0.114(8)	0.134(60)	0.082(5)	0.131(24)	0.180(12)	0.059(2)	0.027(5)	0.047(1)	0.035(8)	0.035(2)	0.021(3)
Но	0.156(8)	0.188(6)	0.120(9)	0.149(39)	0.149(35)	0.147(7)	0.167(22)	0.212(96)	0.132(3)	0.062(7)	0.102(2)	0.087(24)	0.072(4)	0.045(5)
Lu	0.222(15)	0.244(13)	0.185(17)	0.212(16)	0.225(21)	0.257(94)	0.225(19)	0.268(40)	0.223(6)	0.119(13)	0.186(4)	0.158(16)	0.141(4)	0.079(9)
Ηf	0.060(7)	0.0075(1)	0.01(2)	0.051(9)	0.062(7)	0.053(3)	0.068(9)	0.0064(6)	0.063(9)	0.032(2)	0.039(2)	0.044(12)	0.060(7)	0.0075(1)
\mathbf{Pb}	0.005(2)	0.007(3)	0.0009(1)	0.0012(2)	0.006(4)	0.004(5)	0.003(2)	0.002(1)	0.0002(1)	0.001(1)	0.002(0.04)	0.0014(2)	0.005(2)	0.007(3)
$^{\mathrm{Th}}$	0.001(2)	0.007(3)	0.002(1)	0.0006(1)	0.005(2)	0.004(5)	0.001(2)	0.007(3)	0.0004(1)	0.0006(6)	0.0012(1)	0.0011(5)	0.001(2)	0.007(3)
n	0.003(3)	0.008(3)	0.006(4)	0.0012(2)	0.001(3)	0.003(3)	0.001(7)	0.002(1)	0.0012(3)	0.002(1)	0.001(0.004)	0.0015(8)	0.003(3)	0.008(3)

Table 5: Orthopyroxene-melt partition coefficients $D_i^{orthopyroxene-melt} = c_i^{orthopyroxene}/c_i^{melt}$, of trace elements in run products.

Numbers in parentheses represent one standard deviation in terms of least units cited. ND : not determined.

	$D_i^{Cpx-melt}$					$D_i^{Ol-melt}$		$D_i^{Plag-melt}$	$D_i^{Grt-melt}$
\mathbf{Run}	CC01#8kb4	CF1#8kb5	CC4#7b	CF5#7c	C4p#25kb	CC01#8kb4	CF1#8kb5	CC01#8kb4	C4p#25kb
P(kbars)	×	×	12	12	25	×	×	∞	25
$T(^{\circ}C)$	1265	1265	1310	1310	1430	1265	1265	1265	1430
Li	0.178(13)	0.207(4)	0.271(3)	0.289(44)	0.661(82)	0.215(16)	0.212(25)	ND	0.015(8)
\mathbf{Be}	< 0.094	< 0.060	<0.148	< 0.273	ND	ND	ND	ND	ND
в	0.0186(3)	< 0.042	< 0.155	<0.287	ND	ND	ND	ND	ND
\mathbf{Sc}	1.52(8)	1.57(5)	1.16(4)	1.17(1)	0.77(1)	0.196(13)	0.152(12)	ND	6.81(16)
>	4.8(3)	6.2(2)	3.31(6)	3.2(3)	1.98(9)	0.415(36)	0.604(64)	ND	2.13(18)
\mathbf{Cr}	5.32(7)	4.22(9)	6.54(2)	7.0(7)	5.6(4)	1.1(2)	0.80(8)	ND	10.6(11)
Co	0.95(4)	1.52(46)	0.84(2)	0.88(6)	1.29(9)	3.00(4)	3.08(36)	ND	1.24(9)
\mathbf{Sr}	0.057(5)	0.102(8)	0.083(37)	0.098(37)	0.033(3)	0.0007(3)	0.0002(3)	ND	0.0009(3)
\mathbf{Zr}	0.045(17)	0.064(7)	0.095(23)	0.093(54)	0.050(4)	0.0017(3)	0.0005(4)	ND	0.33(3)
La	0.031(10)	0.054(2)	0.054(18)	0.033(60)	0.011(2)	0.0006(4)	ND	ND	0.0007(3)
Eu	0.228(19)	0.144(3)	0.273(6)	0.249(71)	0.117(13)	0.003(1)	0.00002(40)	ND	0.29(2)
Gd	0.410(57)	0.334(9)	0.322(27)	0.309(50)	0.161(17)	0.006(3)	0.0004(15)	ND	0.57(5)
Но	0.535(44)	0.429(7)	0.467(6)	0.397(68)	0.224(21)	0.013(4)	0.003(1)	ND	2.37(20)
Lu	0.524(15)	0.416(4)	0.461(9)	0.369(57)	0.234(53)	0.033(4)	0.021(2)	ND	5.9(5)
Ηf	0.17(4)	0.12(4)	0.15(5)	0.13(6)	0.094(7)	0.004(2)	0.0004(10)	ND	0.031(3)
$\mathbf{P}\mathbf{b}$	0.004(3)	0.005(6)	0.002(1)	0.01(6)	0.0048(5)	0.0004(2)	0.0014(7)	ND	0.0001(1)
$\mathbf{T}\mathbf{h}$	0.008(2)	0.004(3)	0.03(6)	0.008(66)	0.0022(5)	0.0004(3)	ND	ND	0.0006(4)
U	0.010(3)	0.008(3)	0.03(6)	0.012(68)	0.0027(8)	0.0009(6)	0.0004(40)	ND	0.008(1)

Numbers in parentheses represent one standard deviation in terms of least units cited. ND : not determined.

Table 6: Mineral-melt partition coefficients $D_i^{mineral-melt} = c_i^{mineral}/c_i^{melt}$, of trace elements in run products.

3.7.2 Components of pyroxenes

To calculate pyroxene components, we used the method of recalculation of pyroxene end-members of Cawthorn and Collerson (1974). With this method, the jadeite component is calculated first, then tschermak end-members (here Ca-tschermak or CaTs), wollastonite, enstatite and finally ferrosilite. In this study, orthopyroxene was calculated just with jadeite, CaTs, enstatite and ferrosilite, and for clinopyroxenes, we replaced wollastonite by diopside. The procedure was as follows for clinopyroxene: 1) Na + K go into jadeite (NaAl^{VI}Si₂O₆),

2) The amount of Al used in jadeite is deducted from total Al content. The remaining Al is calculated as the CaTs component (CaAl₂SiO₆).

3) The Ca in the CaTs component is deduced from total Ca and the remaining Ca is calculated as diopside (CaMgSi₂O₆).

4) The Mg in diopside is deduced from total Mg, and the remaining Mg (+Ni) is calculated as enstatite $(Mg_2Si_2O_6)$,

5) Fe (+Mn) is calculated as ferrosilite (Fel₂Si₂O₆).

Table 7 presents the pyroxene end-members for orthopyroxene and clinopyroxene of samples of this study.

Run		Ort	hopyroxene				Clinopyro	xene	
	Jadeite	CaTs	Enstatite	Ferrosilite	Jadeite	Ca-Ts	Diopside	Enstatite	Ferrosilite
F2p#2a	0.09	7.32	88.09	4.50					
F4p#3a	0.24	9.86	84.57	5.33					
F1#3b	0.23	6.99	88.01	4.77					
F5#3b	0.16	6.65	88.30	4.88					
C4p#2b	0.17	7.88	87.48	4.47					
C8p#2b	0.10	7.62	87.74	4.54					
C04#3a	0.42	8.42	86.47	4.69					
C4#4a	0.35	8.61	85.37	5.67					
CC01#8kb4	0.22	6.49	87.82	5.47	1.62	10.23	33.36	49.25	5.54
CF1#8kb5	0.07	5.22	89.53	5.18	1.79	11.65	42.26	39.01	5.29
CC4#7b	0.32	6.54	87.92	5.22	2.24	9.64	33.54	49.10	5.48
CF5#7c	0.34	7.02	87.40	5.24	2.54	9.50	35.10	47.49	5.37
CF01#16kb1	0.46	9.37	84.52	5.65					
C4p#25kb	1.61	6.93	85.66	5.80	7.79	8.23	14.63	62.69	6.65

Table 3.7.2: Pyroxene components, in mol%.

3.7.3 Relation between mineral chemistry and volatile content

We noticed that mineral chemistry varies among samples annealed under the same P - T condition. The only parameter that varies significantly among samples is the total quantity of doped volatile elements. We noted, as illustrated in Supplementary Figure 3.7.1, that jadeite and CaTs components in orthopyroxene vary with the F+H₂O content dissolved in the melt.



Figure 3.7.1: Relation between orthopyroxene components and $F+H_2O$ content dissolved in the melt. On the left, we distinguished samples with $[F]>[H_2O]$ (diamonds) from $[H_2O]>[F]$ (squares).

3.7.4 Lattice strain models of opx, cpx and garnet compared to literature data or predictive models

Orthopyroxene

As we noted in the main text, our trace element data are consistent with Frei et al. (2009). We represented in Supplementary Fig. 4.5.17 the results of lattice strain model fits of our data and those of Frei et al. (2009) (grey fields). While there exist the main differences (notably for D_0^{M1}), the agreements are reasonable for the low volatile samples (light gray lines). The observed differences for the M1-site are explained by the disparity of D_{Cr} between the two studies. The D_{Cr} is related to the melt fraction (Johnston and Schwab, 2004). Johnston and Schwab (2004) show that D_{Cr} decreases with the decreasing melt fraction.



Figure 3.7.2: Results of lattice strain modeling of trivalent cations partition coefficients between the M1 and M2 sites of orthopyroxene and basaltic melt. Our fits on experimental data are compared to those of Frei et al. (2009) (grey field) for samples 1101-12-06 (11 kbars – 1230° C), 6617-12-06 (20 kbars – 1330° C) and 2303-04-02 (23 kbars – 1440° C).

Clinopyroxene

Supplementary Figure 3.7.3 shows the comparison of our results plotted with the lattice strain model and the predictive model of Wood and Blundy (1997). For samples of 12 and 8 kbars, our models show a very good agreement with the predictive model. Slight disparities in Supplementary Figure 3.7.3a and b are attributed to the difference of fitting processes (one site vs. two sites, and the formulation of the weighted residual error function) between the two models. The predictive model is in disagreement with the experimental data for the sample of 25 kbars. This is most likely due to the high volatile content (F + Cl + H₂O = 1.9 wt% dissolved in the melt) in this sample, which is not accounted for in the Wood and Blundy (1997) predictive model.



Figure 3.7.3: Fit results of the lattice strain model of trivalent cations partition coefficients between the M1 and M2 sites of clinopyroxene and basaltic melt. The experimental data (circles) are compared to the predictive model of Wood and Blundy (1997) (bold grey curves). In this model, lattice strain parameters are predicted from cpx and melt composition in major elements. We plotted predicted lattice strain parameters for samples CC01#8kb4, CC4#7b and C4p#25kb (grey curves).

Garnet

Our fits of the lattice strain model on our experimental data are in a good agreement with the van Westrenen and Draper (2007) and Draper and van Westrenen (2007) predictive models for garnet-melt partitioning (Supplementary Fig. 3.7.4).

3.7.5 Relation between components of pyroxenes and their r_0 size.

We observe a positive correlation between r_0^{M1} and the CaTs component of cpx (Supplementary Fig. 3.7.5a). This correlation results from the substitution of Al³⁺ to Mg²⁺. We found also an increase





Figure 3.7.4: Results of lattice strain modeling of partitioning of trivalent cations between the X-site of garnet and basaltic melt. The experimental data (white squares) of this study are compared to the predictive models from van Westrenen and Draper (2007), and Draper and van Westrenen (2007). The upper boundary was calculated using the thermodynamical prediction of van Westrenen and Draper (2007) and the lower one using the statistical prediction Draper and van Westrenen (2007).

of r_0^{M2} with the diopside component in clinopyroxenes (Supplementary Fig. 3.7.5b). This correlation results from the large ionic radius Ca²⁺ relative to Mg²⁺ in the M2 site.



Figure 3.7.5: Relation between cpx component a) CaTs and b) Diopside in wt% and r_0 size in Å. In a), because of Al substitution in to the Mg site, CaTs component is linerally related to r_0^{M1} . In b), because of Ca incorporation into the M2 site, r_0^{M2} increase with the increasing diopside component.

Chapter 4

The role of water molecule on F and Cl behavior in magmas

In this chapter, I investigate the variation of F and Cl partition coefficients with respect to temperature and water content. The aim of the chapter is to start to demonstrate why geochemists find more variation of F and Cl signatures than in trace element signatures, in primitive arc magmas.

This chapter begins with general descriptions of the samples obtained from hydrous experiments. Data of trace elements and fluorine and chlorine partition coefficients are presented and trace elements data are compared to literature data, in order to assess the accuracy of measurements both for trace and volatile elements. The equilibrium state of samples is also discussed.

The results show that F partition coefficient decreases linearly with water content of the melt $(D_F^{Opx/melt} \text{ from } 0.123 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O} \text{ to } 0.021 \text{ with } 5.9 \text{ wt\% } \text{H}_2\text{O}; D_F^{Cpx/melt} \text{ from } 0.153 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O})$, while Cl partition coefficient increases linearly $(D_{Cl}^{Opx/melt} \text{ from } 0.002 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O})$, while Cl partition coefficient increases linearly $(D_{Cl}^{Opx/melt} \text{ from } 0.002 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O})$, while Cl partition coefficient increases linearly $(D_{Cl}^{Opx/melt} \text{ from } 0.002 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O})$ to $0.069 \text{ with } 5.9 \text{ wt\% } \text{H}_2\text{O}; D_{Cl}^{Cpx/melt} \text{ from } 0.008 \text{ with } 0.2 \text{ wt\% } \text{H}_2\text{O} \text{ to } 0.015 \text{ with } 4.9 \text{ wt\% } \text{H}_2\text{O})$. Here, high H₂O runs were conducted at 150 °C lower temperature than low H₂O runs. This counter intuitive increase of D_{Cl} with water content of samples is assumed to be the result of crystal-chemistry changes resulting from temperature and water content variations. We also show that F is compatible in phlogopite (> 1.2) while it is incompatible in pargasite (from 0.36 to 0.63 with increasing water content from 4.3 to 5.9 wt% H₂O). On the contrary, Cl is more incompatible in phlogopite (in average 0.09 ± 0.02), than in pargasite (from 0.12 to 0.38 with increasing water content from 4.3 to 5.9 wt% H₂O).

At this end of this chapter, a paper in preparation, from this chapter, is presented. In this paper, we discuss the influence of water on F, Cl and trace element partition coefficients.

4.1 Introduction

Trace element study of subduction-related volcanic rocks and more recently of arc melt inclusions plays a fundamental role in the understanding of melt generation in the sub-arc mantle. Their trace element abundance pattern, enriched in large ion lithophile elements (LILE; e.g. Sr, K, Ba, U, Th) and depleted in high field strength elements (HFSE, e.g. Ti, Zr, Nb, Hf), is most likely the results of a metasomatism of sub-arc peridotite, by an H₂O-rich component derived from the subducting oceanic lithosphere (e.g. Perfit et al. (1980); Arculus and Johnson (1981); Maury et al. (1992)). A recent study of Mt Shasta melt inclusions shows that fractionation of F and Cl may fingerprint the signature of two different slab-derived components (Le Voyer et al., 2010), which are indistinguishable by commonly used trace elements (Sr, Ba, K₂O). They also show that these signature may reflect the presence of hydrous minerals, amphibole and phlogopite, which are formed by infiltration of fluids from the subducted slab.

The development of element fractionation models to describe the behavior of F and Cl in the mantle wedge requires experimental determinations of F and Cl partition coefficients between lherzolite minerals (olivine, orthopyroxene, clinopyroxene and garnet), and also hydrous minerals (mantle high pressure mica and amphibole, phlogopite and pargasite, respectively) and hydrous silicate melt, at temperature and pressure comparable to those in the sub-arc mantle. Here, I present new experimental determinations of Cl and F partition coefficients between hydrous basaltic or hydrous shoshonitic melt and mantle minerals: such as olivine, orthopyroxene, clinopyroxene, garnet and also pargasite and phlogopite. The values were compiled from more than 150 measurements in 9 hydrous melting experiments, conducted at 12 and at 25 kbars and between 1180 and 1370°C. Hydrous experiments were run with 0.2, 2.6, 4.3, 4.9 and 5.9 wt% of H₂O dissolved in the melt. The low-abundance F, Cl measurements in minerals were done by Cameca IMS 1280 at WHOI using negative secondary ion mode. For volatile-rich minerals as phlogopite and pargasite, measurements were done by both electron microprobe and ion probe.

The results show that F and Cl partition coefficients vary with the water content of the melt and the temperature of experiments. These variations are attributed to crystal-chemistry changes of minerals and melt structure influence. We show that those changes affect more F and Cl partition coefficients than other trace elements.

4.2 Experimental results of hydrous melting

4.2.1 Sample description

Experiments were run on piston-cylinder apparatuses following the experimental procedure described in the Chapter 2, and the composition of starting material is also given in the chapter (Table 2.2.1) The Figure 4.5.1 and 4.2.2 shows the back scattered electron images of samples that representative of my hydrous experiments in the basaltic system and the shoshonitic system respectively.

The degree of crystallization in runs varies from 26.9 to 92.2%. Generally crystals accumulate in one side of the capsule, while quenched melt segregates from grains and forms a separated volume. In all runs melt forms a homogeneous quenched surface. Size of grains varies from run to run. All runs produce quenched melt and in the basaltic system, all runs produce orthopyroxene, while in the shoshonitic system, all runs produce mica. All crystals forms polyhedral grains, but we observe clinopyroxene (cpx) that are sometimes intergrown with other phases, as reactional cpx around orthopyroxene crystals or dendrites at the boundary between crystallized part and quenched melt part. This growth zoning of cpx is systematic among our hydrous samples. It implies that those experiments are not globally equilibrated (equilibrium of samples will be later discussed). Consequently, I had to take a special care to select most equilibrated cpx (lowest calcium concentration, Schwab and Johnston, 2001) and to analyze them by SIMS and LA-ICPMS. Furthermore, dendritic cpx compositions were not taking into account in mass balances presented Table 4.5.2. Most experiments produce crystals large enough (with minimum size > 50 μ m) to be analysed by SIMS and LA-ICPMS, except H5V4p and Grt3V4p, in which crystals are mostly 30 μ m, verily less (see Figure 4.5.1).

Olivine crystallizes only at pressures lower than 25 kbars, as in Adam and Green (2006) experimental series of hydrous experiments from a primitive nepheline basanite composition. At 12 kbars, olivine is the liquidus phase in H₂O-poorer samples, in the basaltic system and the shoshonitic system. It forms big (> 50 μ m) euhedral crystals and it is concentrated at the opposite edge of the capsule, from quenched melt. Clinopyroxenes crystallizes in samples, where temperature and/or water content were too high to stabilized amphibole. In my samples, cpx are both euhedral and anhedral with variable sizes. They crystallize at the opposite part of the capsule, from quenched melt, or in the middle of the capsule. Garnet crystallizes at 25 kbars, forming crystals, all over the capsule, of 30 μ m maximum diameter, by easily identifiable by their high relief.

Amphibole crystallizes at unexpected conditions (at 1180, 1200 $^{\circ}$ C in the basaltic system and 1230 $^{\circ}$ C in the shoshonitic system), likely stabilized by F. It was discussed in previous experimental

work that F in magma extends the stability of alkali amphibole to higher temperatures (Ferguson, 1978), and maybe to higher pressure. It forms huge euhedral crystals (> 100 μ m) in the crystallized part of the capsule; sometimes, it forms anhedral crystals of 20 – 30 μ m, in the middle of the melt, likely formed during by the quench. In my experiments, phlogopite stability is enhanced to higher pressure (12 kbars) than in Holbig and Grove (2008) where Holbig and Grove (2008), no phlogopite was crystallized at pressure > 10 kbars. As in the case for amphibole, F increases phlogopite stability to higher *P*–*T* conditions (Harlow, 2002). In my samples, phlogopite crystals are layered, and sometimes contain lamellar structure, as shown in figure 4.2.2.

Run	Р	Т	Duration	H_2O^a	Run proc	ducts (v	vt%)					r^2	Fe
	(kbars)	$(^{\circ}C)$	(days)	(wt%)	Olivine	Opx	Cpx	Garnet	Amp	Mica	Melt	(%)	$\operatorname{exchange}^{b}$
CC4#7b	12	1310	6		0.2		35.5	53.5				12.0	+ 1.76
H3V04	12	1240	5	2.6	13.3	20.0	51.2				15.5	28.6	+ 0.32
H4V4p	12	1180	5	4.3		21.5			33.5		45.0	1.9	-0.01
H5V4p	12	1190	5.5	4.9		21.4	14.2				64.4	2.4	-0.02
H6V04	12	1200	4	5.9		18.2			15.3		66.5	4.9	+ 0.60
C4p#25kb	25	1430	5		0.8		2.0	43.7	32.8		13.4	0.01	0.9
Grt3V4p	25	1370	4.5	1.6		14.5	55.5	22.2			7.8	_ c	-
SHO1	12	1300	4.5	4.3	5.2					3.2	91.6	5.52	+ 2.0
SHO4	12	1230	6	4.9					4.3	26.1	69.6	6.5	+ 1.64

Table 4.2.1: Experimental conditions and phase assemblages.

Abbreviations used: Opx, orthopyroxene; Cpx, clinopyroxene Amp, amphibole; Melt, quenched basaltic melt.

Calculated phase proportions are in wt%; r^2 is the sum of weighted squared residuals from phase proportions calculations, modified from Albarède and Provost (1977). The calculation had to take account of F, Cl and H₂O addition to the starting materials (that diluted the initial element concentrations). The uncertainties linked to doping processes increase the r^2 .

 a Concentration of $\mathrm{H_2O}$ dissolved in the melt, measured by the SIMS 1280 of WHOI.

 b Fe exchange is the difference between the FeO content of the bulk composition used in the starting material and the FeO in the sample bulk composition as determined by the mass balance calculation, in relative weight percent. Positive value indicates apparent Fe gain, while negative value indicates apparent Fe loss.

 c Mass balance of sample Grt3V4p failed to converge, apparently because of clinopyroxene composition. I assumed that the measured clinopyroxenes compositions were far from the equilibrium. Clinopyroxenes of this sample are too small to be analyzed with SIMS or LA-ICPMS.



Figure 4.2.1: Back-scattered electron images of hydrous samples in the basaltic system, with experimental temperature conditions and water content dissolved in the melt indicated above each image. From the top to the bottom, sample names are H3V04, H5V4p and H6V04. Abbreviations used: Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Ca-Cpx, calcic clinopyroxene; QuCpx, quench clinopyroxene; Amp, amphibole; and Melt, quenched melt. White part is the capsule noted as Fe-AuPd, *i.e.* in AuPd pre-saturated in iron. In the outer capsule, recrystallized olivine is visible. Mineral phases on these images have $> 30 \ \mu$ m diameter, which is appropriated for SIMS and LA-ICPMS measurements. This Figure shows the variation of sample textures with the increasing water content in samples.

15kU

X55 200µn



Figure 4.2.2: Back-scattered electron image of SHO4 sample. Abbreviations are the same as those used in Figure 4.5.1, Phlo, is phlogoite mica (its stoichiometry reported in Table 4.5.7). Phlogopites are the tabular crystals, while amphibole have a polygonal shape.

4.2.2 Analytical results

Analyses of major and minor elements in crystals and quenched melts from experiments are presented in Table 4.5.3. As mentioned in the Methods chapter 2, a correction scheme was applied to the measured cation, F, Cl abundance by taking account for the presence of F and Cl in the O site. Because the oxygen was not measured, the microprobe determines oxygen abundance from the charge balance of every cation measured. For a given abundance of Si, it calculates for SiO₂, instead of SiO_xF_{2(1-x)} by accounting for anions other than O. By charge balance between O²⁻ and F⁻ or Cl⁻, (2F⁻, 2Cl⁻)=O²⁻, the correction balances the O excess in atomic % basis. In an anhydrous or nearly anhydrous system, this correction step is accurate. In such case, the stoichiometry of phases is respected. Nevertheless, it is impossible to recalculated concentration in oxide weight%, without excess O and total, because calculation of oxide abundance forces to create fictitious oxide. To corrected for this excess of high F and Cl concentration, I subtracted from the total (including major element oxides and, F and Cl measured by SIMS, see the footnotes of Table 4.5.3 for a factor calculated from:

$$F \times MO_2/MF_2 + Cl \times MO_2/MCl_2 = F \times 0.42 + Cl \times 0.23,$$

where F and Cl are the concentration measured by the microprobe, and M(i) is an element *i*. This subtraction allow to correct the mass excess produced by heavier F and Cl than O and for anhydrous or nearly anhydrous phases, a total of about 100 wt% is recovered.

Concerning hydrous samples, it is more complicated. Because the microprobe only balances with measured cations, it creates an O deficit for halogen, water bearing sample. When the computer recalculates atomic proportion of major elements, to be 100%, the water is included and its oxygens

are redistributed among major elements. That is why in table 4.5.3, the total after correction of the equation 4.2.2 is close to 100 wt%, even samples contain 2 to 6 wt% of water. Thus, just in order to appreciate the most accurate total, I subtract the water abundance measured by SIMS to the previously calculated total. This will create the total significantly lower than 100.

Concentrations measured by LA-ICPMS in crystals and melt and derived mineral/melt partition coefficients are given in Tables 4.2.3 and 4.2.4. The precision and the accuracy of analyses varied depending upon absolute concentration, crystal size and the presence or absence of other included phases. In order to evaluate the possibility of some of the mineral analyses by small melt pools, mass-balances allowed to filter data for which recovered total concentration was higher than the 100 ppm initial trace element concentrations. The presence of even very minor analytical contamination are made obvious by plotting data on Onuma diagram, on top of other data verification tests (Chapter 3). Horizontal digressions from parabolic trends usually indicate analytical contamination. Such analyses are not used. Despite that trace elements in all those samples were also measured by SIMS, for reasons explained in the previous chapter (Section 3.4.3), I choose to present here only LA-ICPMS measurements.

Measured concentrations of water, F, Cl and partition coefficients for F and Cl are presented in Table 4.2.6. To come to high precision on water, F and Cl concentrations, I filtered data by several processes:

- I made between 3 to 10 spots of each phases, in order to have a good statistic and in the time to be sure of my data, since melt contamination can occurred.
- Then, I select data for which signal was very stable (less than 20% signal variation). This reduced the error on the analysis, since it is calculated on the standard deviation on the signal stability.

It provides the first F and Cl partition coefficients between olivine, orthopyroxene, clinopyroxene, garnet and silicate melt. The F and Cl concentrations in the samples presented in this chapter are measured both by SIMS (1280, WHOI) and electron microprobe (LMV). A significant difference of measured concentrations for F exists between the two techniques and illustrated on the Figure 4.2.3, which concerns only high F measured concentrations (> 1 wt%). This can be likely explained by the change of the calibration curves (used to calculate concentrations from SIMS measurements) with high F concentrations. It should be noted that high concentration data are represented by kaersutite amphibole, phlogopite and volatile-rich basalts. Some the Cl and F measurements in high concentrated F and

1	15	6

Table 4.2.2: Electron microprobe analyzes of experimental run products.

H_2O^d																							F	x
Total –		,			94.99		98.69	90.86	'	'	92.19	,	95.30	93.43		,		93.06	96.90	'	92.78	94.24	-	
$Total^{c}$,	ı	,	99.29		96.96	95.76			98.07	,	99.70	95.02	,			97.37	100.00		97.59	98.44	98.95	
$-O \equiv F, Cl^b$		ı			3.40	ı	1.78	0.56	ı	ı	2.89		1.62	0.42	ı	ı	ı	3.59	3.51	ı	2.81	3.43	1.88	
Total $(+F,Cl)^a$	96.52(57)	100.26(21)	100.30(39)	100.47(49)	102.69(44)	100.03(29)	101.74(53)	96.32(52)	100.15(32)	99.73(42)	100.97(39)	100.34(42)	101.31(29)	95.44(41)	99.53(39)	99.79(31)	100.10(22)	100.95(24)	103.51(63)	100.42(49)	100.40(28)	101.87(13)	100.64(37)	
CI					0.0190(4)	0.003(5)	0.002(6)	0.22(1)	0.003(3)	0.003(3)	0.036(6)	0.01(1)	0.005(5)	0.44(2)	,	0.001(1)	0.003(3)	2.88(31)	0.24(1)	,	0.98(2)	0.072(5)	0.017(1)	
Ĺц					8.06(9)	0.18(5)	4.2(1)	1.21(4)	0.04(2)	0.07(1)	6.8(1)	0.10(4)	3.84(6)	0.77(2)	,	0.008(7)	0.045(4)	6.97(8)	8.20(8)		6.15(5)	8.10(6)	4.35(10)	
K_2O	0.13(2)	0.01(1)	0.001(2)	0.003(5)	0.09(3)	0.01(1)	0.10(2)	0.17(3)	0.005(9)	0.01(2)	0.09(3)	0.007(6)	0.12(2)	0.51(5)	ND	0.01(1)	0.002(4)	2.35(17)	10.36(10)	0.04(4)	0.86(6)	9.09(23)	0.77(13)	
Na_2O	2.69(10)	0.07(1)	0.62(3)	0.003(6)	1.46(8)	0.11(2)	2.79(8)	2.79(10)	0.08(2)	0.88(4)	1.81(9)	0.05(1)	3.09(6)	3.51(15)	ND	0.40(1)	1.66(6)	2.30(9)	0.59(2)	0.01(1)	2.61(10)	1.53(6)	2.92(24)	
CaO	10.94(4)	1.74(10)	18.57(24)	0.24(2)	13.35(25)	1.87(19)	8.52(33)	9.56(11)	1.29(23)	20.16(19)	12.65(16)	1.25(8)	9.40(18)	7.46(34)	4.80(57)	1.71(7)	8.90(22)	10.30(23)	0.05(4)	0.14(3)	12.71(14)	0.17(3)	9.89(19)	
MgO	10.28(12)	30.78(22)	17.30(6)	45.78(42)	12.75(13)	27.65(20)	21.10(14)	9.30(12)	34.41(19)	15.72(17)	14.84(13)	31.03(45)	21.61(23)	6.77(4)	19.45(48)	28.25(11)	19.35(40)	19.37(23)	26.96(28)	49.84(28)	15.55(12)	25.60(18)	18.47(57)	
MnO	0.14(3)	0.16(4)	0.14(3)	0.16(1)	0.18(4)	0.24(3)	0.15(3)	0.14(7)	0.18(4)	0.14(3)	0.13(4)	0.21(2)	0.10(3)	0.11(5)	0.23(3)	0.14(3)	0.15(5)	0.98(2)	0.00(0)	0.20(4)	0.15(5)	0.02(2)	0.16(4)	
FeO*	10.13(12)	7.50(19)	5.07(27)	13.58(9)	7.87(16)	12.16(36)	6.84(11)	6.73(17)	4.53(11)	6.80(36)	7.71(14)	8.42(11)	5.04(13)	6.51(11)	9.92(25)	8.64(19)	7.31(4)	6.56(15)	1.54(5)	8.72(9)	9.30(15)	2.69(11)	8.12(14)	
Cr_2O_3	0.04(5)	0.86(5)	0.94(2)	0.04(3)	0.04(2)	0.49(5)	0.63(11)	0.04(4)	0.23(8)	0.30(6)	0.11(3)	0.89(17)	0.98(12)	0.04(3)	0.37(9)	0.36(6)	0.31(8)	ND	ND	0.02(1)	0.03(4)	0.06(2)	0.02(1)	
Al_2O_3	15.56(20)	5.25(27)	6.36(36)	0.09(2)	13.35(10)	3.70(66)	10.38(47)	14.63(22)	4.93(34)	6.01(32)	12.44(12)	3.83(62)	11.12(22)	15.01(24)	23.04(70)	6.32(42)	9.23(52)	10.03(8)	12.75(19)	0.07(2)	10.02(14)	12.48(10)	10.22(8)	
TiO_2	0.71(7)	0.11(3)	0.22(3)	(0)00.0	0.58(7)	0.08(5)	0.20(7)	0.60(4)	0.06(2)	0.20(4)	0.59(6)	0.05(3)	0.21(4)	1.28(6)	0.39(18)	0.10(5)	0.24(2)	0.05(6)	0.48(4)	0.03(3)	1.12(5)	0.48(3)	1.24(5)	
SiO_2	45.88(42)	53.74(11)	51.04(16)	40.36(16)	44.95(23)	53.52(83)	46.78(22)	50.92(16)	54.39(34)	49.43(34)	43.69(19)	54.58(61)	45.79(20)	53.04(44)	41.24(35)	53.87(45)	52.91(26)	38.78(33)	42.36(51)	41.37(22)	40.93(10)	41.60(9)	44.25(20)	
Phase	Melt [4]	Opx [7]	Cpx [5]	OI [5]	Melt [6]	Opx [6]	Amp [5]	Melt [5]	Opx [7]	Cpx [8]	Melt [7]	Opx [10]	Amp [8]	Melt [5]	Grt [12]	Opx [4]	Cpx [4]	Melt [4]	Phlo [8]	O1 [6]	Melt [5]	Phlo [2]	Amp [3]	
\mathbf{Sample}	H3V04				H4V4p			H5V4p			H6V04			Grt3V4p				SHO1			SHO4			

Numbers in brackets indicate number of individual electron microprobe analyses included in average.

(FeO* total Fe as FeO)

Numbers in parentheses represents one standard deviation in terms of least units cited. ND : not determined.

 $^a\,$ Total of major elements oxides and F and Cl measured by electron microprobe.

 b Factor calculated by the following equation: F * M(O₂) / M(F₂) + Cl * M(O₂) / M(Cl₂) = F * 0.42 + Cl * 0.23, where F and Cl are concentrations measured by SIMS.

 d Total^c – H₂O^d measured by SIMS. ^c New total: total^a – the factor^b.

l hydrous basaltic melt.	2
a lherzolite minerals and	
on coefficients, betwee	
d trace element partit	ſ
n) of run products and	
concentrations (in ppn	
le 4.2.3: Trace element	
Tab	

	H3V04							H4V4p			H5V4p				
	Melt [2]	Ol [4]	Opx [3]	Cpx [3]	$D^{Ol/Melt}$	$D^{Opx/Melt}$	$D^{Cpx/Melt}$	Melt [2]	Amp [2]	$D^{Amp/Melt}$	Melt [2]	Opx [4]	Cpx [2]	$D^{Opx/Melt}$	$D^{Cpx/Melt}$
Li	100(2)	20.8(2)	15(1)	13(1)	0.207(6)	0.136(16)	0.145(13)	25.11(5)	10.3(8)	0.41(3)	48.1(2)	9.6(6)	12.6(1)	0.20(1)	0.265(3)
$\mathbf{S}^{\mathbf{C}}$	29.5(8)	6.3(8)	24(4)	37(6)	0.21(3)	0.83(14)	1.27(26)	39.0(4)	18(5)	0.5(1)	34.054(6)	22(2)	42.1(7)	0.65(7)	1.24(2)
>	61(2)	3(2)	9(2)	43(9)	0.05(3)	0.16(4)	0.71(16)	38.2(2)	41(8)	1.1(2)	83.2(5)	2.9(3)	7.0(7)	0.131(4)	0.084(9)
C.	167(6)	112(76)	2029(448)	2091(250)	0.67(0.48)	12(3)	12(1)	212(2)	2174(581)	10(3)	209(8)	810(88)	721(46)	3.87(59)	3.45(35)
Co	25(1)	2.8(1)	34.2(3)	14(1)	2.8(1)	1.34(7)	0.55(6)	15.5(2)	31(9)	2.0(6)	29.9(3)	54(3)	23(1)	1.8(1)	0.76(4)
\mathbf{Sr}	106(3)	0.1(1)	1.6(8)	15(4)	0.001(1)	0.015(7)	0.14(4)	32.39(5)	9.0(7)	0.28(2)	59.70(4)	0.8(4)	6.9(3)	0.114(7)	0.116(4)
$\mathbf{Z}\mathbf{r}$	40(1)	0.2(1)	1.5(6)	6(1)	0.005(2)	0.04(1)	0.15(3)	52.48(4)	3(3)	0.05(5)	58.4(4)	1.58(5)	9.2(4)	0.027(2)	0.157(8)
La	52(1)	0.10(7)	0.96(5)	2.53(9)	0.002(1)	0.005(9)	0.049(2)	57.8(2)	0.7(36)	0.012(63)	83.4(7)	1.1(3)	7.9(5)	0.013(1)	0.094(8)
Еu	46.0(5)	0.2(2)	2.3(7)	14(2)	0.033(4)	0.05(2)	0.31(4)	51.9(7)	6(1)	0.12(3)	67.2(3)	1.9(6)	27.6(3)	0.029(9)	0.411(7)
Gd	39.3(7)	0.6(3)	2.0(5)	14(2)	0.033(4)	0.06(1)	0.36(5)	45.36(9)	5.7(10)	0.13(2)	56.2(4)	2.2(3)	24.7(3)	0.038(7)	0.443(8)
но	41.4(3)	0.2(3)	4(1)	16(2)	0.051(7)	0.10(2)	0.46(6)	46.94(3)	7.9(4)	0.17(1)	58.3(9)	3.4(14)	27.7(3)	0.06(3)	0.49(1)
Γn	40.9(2)	(6)6.0	6(2)	16(2)	0.08(2)	0.15(4)	0.40(4)	46.6(4)	7.7(6)	0.17(1)	59(1)	6.2(9)	23.7(1)	0.10(2)	0.41(1)
Ηf	41.15(5)	0.40(16)	3(1)	7.5(7)	0.01(0.4)	0.07(3)	0.18(2)	46.1(5)	5(2)	0.10(4)	60(1)	2.4(5)	15(1)	0.04(1)	0.25(2)
$^{\mathrm{Pb}}$	5.84(8)	0.3(2)	0.7(1)	2.12(9)	0.05(4)	0.12(2)	0.36(2)	5.8(1)	2(2)	0.3(3)	926(14)	94(9)	44(6)	0.102(1)	0.048(8)
чт	50.0(5)	0.22(5)	0.3(5)	0.71(9)	0.004(1)	0.007(9)	0.014(2)	54.5(5)	0.2(35)	0.004(66)	80(1)	1.1(2)	5.3(5)	0.013(5)	0.068(7)
n	58.0(3)	0.22(4)	0.4(5)	0.66(3)	0.0037(6)	0.007(9)	0.0113(6)	55(1)	0.3(38)	0.005(71)	87(2)	1.3(4)	5.0(8)	0.015(7)	0.060(11)
Numbe	rs in parent	heses repres	ents one stan	dard deviations	in terms of least	t digits cited.									
Numbe	rs in square	· brackets ar	e numbers of	LA-ICPMS anal	yses.										
A b b rev	riations used	i: Melt, que	nched basalti	c melt; Ol, olivin	le; Opx, orthopy	roxene; Cpx, cl	inopyroxene; Amp	, pargasitic a	mphibole; Grt, g	garnet; Phl, mica ph	logopite.				

	H6V04					Grt3V4I				
	Melt [2]	Opx [4]	Amp [3]	$D^{Opx/Melt}$	$D^{Amp/Melt}$	Melt [5]	Opx [2]	Grt[4]	$D^{Opx/Melt}$	$D^{Grt/Melt}$
Γi	25.9(8)	6.57(7)	7.4(4)	0.25(1)	0.29(4)	53(3)	19(1)	2.9(4)	0.35(3)	0.055(7)
$\mathbf{S}_{\mathbf{C}}$	27.6(6)	17.7(1)	21(1)	0.64(2)	0.75(5)	17.7(6)	8.8(4)	43(1)	0.49(2)	2.41(8)
>	37(1)	18.4(9)	27(1)	0.50(4)	0.74(5)	39(1)	23(1)	20(3)	0.58(3)	0.50(5)
\mathbf{Cr}	317(2)	3517(383)	3156(9)	11(1)	9.96(3)	127(9)	700(40)	526(12)	5.5(5)	4.1(3)
Co	21.3(8)	41.36(4)	17(1)	1.94(3)	0.81(9)	26(2)	35.5(8)	24(3)	1.34(6)	0.92(12)
$\mathbf{S}_{\mathbf{r}}$	29.8(8)	0.58(28)	10.8(9)	0.02(4)	0.36(6)	158(8)	0.32(1)	1.8(10)	0.00204(8)	0.012(5)
\mathbf{Zr}	32.8(9)	0.63(12)	1.57(98)	0.019(5)	0.05(8)	89(5)	0.90(5)	10.6(18)	0.0101(5)	0.119(14)
La	32.4(4)	0.14(2)	0.54(43)	0.0044(8)	0.017(52)	228(13)	0.29(8)	2.7(1.1)	0.0013(3)	0.012(3)
Eu	30.4(5)	0.67(13)	5.0(8)	0.022(7)	0.16(4)	139(6)	1.138(5)	23(2)	0.0082(2)	0.163(13)
Вd	26.5(5)	0. 95(10)	4.8(11)	0.036(7)	0.18(5)	94(4)	1.83(6)	24(2)	0.0196(7)	0.260(2)
но	27.7(5)	1.3(1)	6(1)	0.047(9)	0.22(4)	40(2)	1.12(5)	40.2(2)	0.028(1)	1.00(2)
$\mathbf{L}\mathbf{u}$	27.4(3)	2.29(3)	5.56(91)	0.083(3)	0.20(4)	17.0(8)	1.15(4)	41(4)	0.068(3)	2.43(2)
Ηf	34.0(4)	1.3(4)	3.3(12)	0.04(1)	0.10(4)	109(4)	1.5(1)	12(2)	0.014(1)	0.106(13)
$^{\mathrm{Pb}}$	4.7(1)	0.388(7)	0.61(11)	0.083(5)	0.13(4)	60(4)	0.578(3)	1.4(5)	0.0096(3)	0.024(7)
\mathbf{Th}	31.4(8)	0.18(2)	0.16(1)	0.0058(9)	0.005(17)	221(9)	0.37(6)	2.8(15)	0.0096(2)	0.024(5)
D	30.7(3)	0.19(2)	0.2(3)	0.0061(8)	0.007(17)	242(10)	0.55(21)	4.2(23)	0.0023(6)	0.017(7)
Numbe	ers in parer	theses repres	sents one stan	dard deviations	in terms of least	units cited.				

Table 4.2.4: continued

Numbers in square brackets are numbers of LA-ICPMS analyses.

Abbreviations used: Melt, quenched basaltic melt; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Amp, pargasitic amphibole; Grt, garnet; Phl, mica phlogopite.

SHO1 SHO4 $D^{Ol/Melt}$ $D^{Phlo/Melt}$ $D^{Phlo/Melt}$ Melt [2]O1 [2] Phlo [2] Melt [2]Phlo[3] \mathbf{Li} 27.0(2)4.7(8)0.230(9)6.2(2)0.18(3)12.9(1)2.4(3)0.19(3) \mathbf{Sc} 36.1(5)8.5(4)5.7(3)0.24(1)0.16(1)49.8(1)4.82(2)0.097(6) \mathbf{V} 39.6(9)21.8(6)0.11(1)4.6(6)0.12(2)0.55(3)59.0(2)6.6(6) \mathbf{Cr} 107.8(5)93.8(9)200(5)0.87(12)1.85(5)91.0(9)156(5)1.71(7) \mathbf{Co} 19.4(4)65(3)6.5(1)3.42(7)0.34(1)30.2(2)15(2)0.51(6) \mathbf{Sr} 36.1(4)0.079(8)12.3(6)0.0022(3)0.34(2)27.11(8)6.7(3)0.25(1) \mathbf{Zr} 30.6(7)0.16(1)0.6(2)0.0053(6)0.020(7)41.2(1)0.250(9)0.0061(2)42(1)0.083(4)0.07(2)0.0013(4) \mathbf{La} 0.11(3)0.0020(1)0.0027(7)59.3(3)0.0121(5) $\mathbf{E}\mathbf{u}$ 41(1)0.10(3)3.1(2)0.0023(8)0.072(9)70.582(5)0.86(3) \mathbf{Gd} 36.4(7)0.30(5)0.37(4)0.008(2)0.010(1)62.3(4)0.34(4)0.0055(7)Ho 39.2(8)0.20(1)0.07(2)0.0053(4)0.0018(5)68.8(2)0.02(3)0.0018(5) $\mathbf{L}\mathbf{u}$ 38.0(9)0.84(6)0.09(2)0.022(2)0.0024(6)69.7(3)0.14(4)0.0021(6)Hf 31.8(8)0.20(4)0.9(3)0.006(2)0.028(9)47.62(8)0.39(2)0.0082(4) \mathbf{Pb} 1.42(3)0.17(3)0.30(4)0.12(3)0.21(3)14.03(5)1(2)0.1(1) \mathbf{Th} 0.0039(9)37(1)0.122(9)0.1182(2)0.0033(4)0.0031(1)55.1(3)0.22(5)U 39(1)3(2)0.182(7)0.08(5)0.0047(3)73(1)0.22(7)0.003(1)

Table 4.2.5: Trace element concentrations (in ppm) of run products and trace element partition coefficients, between minerals and hydrous shoshonitic melt.

Numbers in parentheses represents one standard deviations in terms of least units cited.

Numbers in square brackets are numbers of LA-ICPMS analyses.

Abbreviations used: Melt, quenched basaltic melt; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Amp, pargasitic amphibole; Grt, garnet; Phl, mica phlogopite.

Cl glass standards. This is part of an ongoing PhD project of Guggino and Hervig (AGU Fall meeting 2010, V51C-2209). The concentration in melts and anhydrous minerals (olivine, opx, cpx and garnet) are calculated by a single working curve based on natural basalts. As recent test (Shimizu personal communication, done on WHOI IMS1280) found variable working curves among kaersutite amphibole. K-richterite phlogopite and volatile-rich basalts. The working curve built from kaersutite amphibole and K-richterite phlogopite standards was used to calculate F concentrations in hydrous minerals. Curiously, the partition coefficients determined by SIMS using the two different working curves (built from basalt or built from hydrous minerals) disagrees with those determined by electron microprobe, while partition coefficients determined by electron microprobe and SIMS using only basalt working curve show good agreement (opened diamonds on Figure 4.2.4). It appears to cancel out the matrix-dependant calibration shift. I choose not to adapt working curve slopes measured from hydrous minerals, because disparities between electron microprobe and ion probe concentration data were reduced for partition coefficient data. I interpreted that influence of the matrix dependent calibration curve for SIMS is minor for the determination of partition coefficients. Nevertheless, this leads me to suspect that the working curves for very highly F concentrated phases are sensitive to matrix-dependent ion emissivity. Certainly, a further systematic study is needed to address this phenomenon. For Cl, there is a good agreement between the two methods (Figure 4.2.4). Nevertheless, for low-Cl concentrations, the detection limit of electron microprobe contributes to the deterioration of SIMS-EPMA correlation below 100 ppm. This also explains a significant, non-zero, Y-intercept of the working curve (Figure 4.2.4). The same argument can be said for the Y-intercept of the F working curve. In the following part of this chapter, I will present the SIMS measured concentrations - because of its low-concentration sensitivity - and partition coefficients for F and Cl, determined using only the basalt working curve.



Figure 4.2.3: Plot of measured concentrations in crystals and melts of my hydrous samples by electron microprobe (EPMA) versus ion probe (SIMS, 1280 WHOI). I present F measurement on the left by and Cl measurement on the right. Closed diamonds are melt data and opened squares are crystal data. The perfect consistency between the two techniques implies diamond alignment on a line y = x. For F, there is almost a factor of 2 between the measured concentrations in melts by the two methods and a factor 0.5 between the measured concentrations in minerals. (Phlo: phlogopite; Amp: amphibole) by the two methods. For Cl, the measured concentrations by the two methods are in good agreement, regarding at the regression line equation. The Y-intercept is likely created by the low concentration measurements. As presented in the Methods chapter, the detection limit of the EPMA is much higher than the detection limit of the SIMS (1280). This is illustrated by the zoom of the low concentration measurements of Cl, at the bottom right.

Samples		Fluorine	1	Chlorine		Water	$D_F^{Min/Melt}$	$D_{Cl}^{Min/Melt}$
		EPMA	SIMS	EPMA	SIMS	SIMS		
CC4#7b	Melt [3]	ND	0.010(0.1)	ND	0.852(6)	0.171(3)		
	Opx [3]	ND	0.0014(0.3)	ND	0.0019(3)	0.104(8)	0.123(4)	0.0021(4)
	Cpx [4]	ND	0.0016(0.3)	ND	0.0077(4)	0.550(3)	0.153(4)	0.0086(5)
H3V04	Melt $[3]$	ND	1.824(6)	ND	0.349(1)	2.59(1)		
	Ol [8]	ND	0.0073(2)	ND	0.0013(1)	0.1(2)	0.0045(1)	0.0043(4)
	Opx [5]	ND	0.120(4)	ND	0.0083(2)	0.203(7)	0.563(3)	0.0203(6)
	Cpx [3]	ND	0.232(2)	ND	0.0044(3)	0.211(2)	0.114(2)	0.0113(9)
H4V4p	Melt $[3]$	8.06(9)	14.7(17)	0.0190(4)	0.0405(7)	4.3(4)		
	Opx [3]	0.18(5)	0.49(2)	0.003(5)	0.0027(1)	0.95(5)	0.028(6)	0.056(14)
	Amp $[4]$	4.2(1)	6.2(2)	0.002(6)	0.0057(8)	1.27(2)	0.36(7)	0.12(4)
H5V4p	Melt $[3]$	1.21(4)	1.47(4)	0.003(3)	0.249(1)	4.89(2)		
	Opx [2]	0.04(2)	0.067(4)	0.003(3)	0.0099(3)	0.49(1)	0.042(4)	0.037(2)
	Cpx [3]	0.07(2)	0.118(2)	0.003(4)	0.0035(2)	0.54(1)	0.083(4)	0.0145(8)
H6V04	Melt $[2]$	6.8(1)	11.9(11)	0.036(6)	0.06(7)	5.9(3)		
	Opx [3]	0.10(4)	0.200(2)	0.01(1)	0.0035(3)	1.2(2)	0.021(2)	0.07(1)
	Amp $[3]$	3.84(6)	6.3(5)	0.005(5)	0.020(3)	4.4(1)	0.63(9)	0.38(8)
m C4p#25kb	Melt $[3]$	ND	0.64(1)	ND	0.477(9)	0.79(2)		
	Opx [3]	ND	0.0121(4)	ND	0.0013(1)	0.486(9)	0.0158(11)	0.0022(2)
	Cpx [4]	ND	0.0319(4)	ND	0.0010(0.4)	0.394(15)	0.043(2)	0.0017(1)
	Grt $[5]$	ND	0.0073(1)	ND	0.013(0.3)	0.47(1)	0.0123(4)	0.0029(1)
Grt3V4p	Melt $[2]$	0.77(2)	0.765(4)	0.44(2)	0.338(1)	1.582(8)		
	Opx [5]	0.008(7)	0.0352(5)	0.001(1)	0.0022(2)	0.45(1)	0.0462(9)	0.0064(5)
	Cpx [4]	0.045(4)	0.0536(6)	0.003(3)	0.0011(1)	0.385(9)	0.070(6)	0.003(4)
	Grt [4]	ND	0.099(1)	ND	0.023(1)	0.52(2)	0.166(2)	0.087(4)
SHO1	Melt $[2]$	6.97(8)	11.3(4)	2.9(3)	2.81(9)	4.31(3)		
	Ol [3]	ND	0.194(6)	ND	0.020(2)	6.0(1)	0.016(1)	0.007(1)
	Phl[2]	8.20(8)	14.9(9)	0.239(7)	0.31(3)	3.1(2)	1.2(1)	0.10(1)
SHO4	Melt $[2]$	6.15(5)	12(1)	0.98(2)	1.3(1)	4.8(2)		
	Phl [3]	8.10(6)	16(1)	0.072(5)	0.11(1)	4.2(2)	1.3(2)	0.08(2)

Table 4.2.6: Fluorine, chlorine and water concentrations in run products (in %), and F and Cl partition coefficients.

Numbers in parentheses represents one standard deviations in terms of least units cited.

Numbers in square brackets are numbers of SIMS analyses.

Abbreviations are the same used in Table 4.5.2. ND, not determined.



Figure 4.2.4: Plot of F partition coefficients calculated from electron microprobe (EPMA) measurements versus those calculated by ion probe (SIMS, 1280 WHOI). Closed diamonds were calculated from the two working curves: the one determined from the basalt set and the one determined from kaersutite amphibole and K-richterite phlogopite standards. Opened diamonds were calculated from the basalt set. The alignment of the diamonds on a regression line having a factor close to 1 and a Y-intercept ~ 0 shows that the agreement between the two set of data is very good.

Olivine

Olivines synthesized in the experiments are Fo₈₅ in the basaltic system and Fo₉₀ in the shoshonitic system. In the basaltic system, the synthesized olivines show a close similarity to those of Gaetani and Grove (1998). Some variations, richer in FeO (an average of 13.6 wt% instead of 11.4 wt%) and poorer in MgO (an average 45.8 wt% instead of 48.4 wt%) for the runs with a similar starting composition, can be attributed to difference in water content of the system and some variations of P– T conditions due to inter-laboratory bias. In the shoshonitic system, I obtained olivines with higher forsterite-content than Holbig and Grove (2008) for the runs with a similar starting composition for similar P - T conditions, but their experiments are in anhydrous system. All olivines are stoichiometrically balanced (Table 4.5.6).

Literature data report wide range of partition coefficients between olivine and melt, explained by the strong pressure dependence of trace element partition coefficients (Taura et al., 1998). On Figure 4.5.2, I compare my data with recent literature data from Beattie (1994); Taura et al. (1998); Salters et al. (2002); McDade et al. (2003b); Zanetti et al. (2004). My data are in agreement with literature data for the elements studied: general patterns of trace elements partition coefficients are similar. Nevertheless, Th and U are significantly more compatible in my study than in the literature. These elements are very difficult to analyze, and the large error bars are due to the poor ion counts for both SIMS and LA-ICPMS on these elements. Consequently, the partition coefficients of these elements (as Pb, Th, and U) have to be considered as potential partition coefficients. In literature, these partition coefficients show a broad range of variation (approximately factor of 20 or more in opx and cpx,




Figure 4.2.5: Olivine/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses. Data of U and Th come only from McDade et al. (2003b); the large field is created by error bars. Detection limits of the LA-ICPMS are presented in Appendix F.

In the olivine synthesized in the sample SHO1, I measured a huge amount of water $(6.0 \pm 0.1 \text{ wt\%})$. While the abundance of water is measured by SIMS (with a constant OH signal during analysis), the electron microprobe data did not yield a total less than 100 wt%. From this ground, it is unlikely that there is a secondary humite structure within this olivine. Whatever the cause of this anomaly, I will exclude the data obtained from this olivine for the rest of discussions.

Orthopyroxene

The orthopyroxene from experiments are aluminous orthopyroxenes with variable concentrations of enstatite (from 0.85 to 0.91), ferrosilite (from 0.03 to 0.08), and jadeite (from 0.002 to 0.02) as major components, with some Ca-tschermaks for 12 kbars orthopyroxenes (0.05 to 0.07) and diopside for 25 kbars orthopyroxene (0.05). Their compositions vary with changes of temperature, pressure and water content of experiments and are closed to those of Gaetani and Grove (1998). Their Mg numbers (Mg# = 100 Mg/(Mg + total Fe)) are presented in the Table 4.5.6, the values can be lower than those of Gaetani and Grove (1998), varying from 87.6 to 91.6. The orthopyroxenes, especially ones in H4V4p, are more ferreous than those of Gaetani and Grove (1998). While majority of orthopyroxenes have a good stoichiometry (Table 4.5.6), the orthopyroxenes of H4V4p and Grt3V4p have stoichiometric sum of the cations < 4. These data will be excluded from the rest of the discussion. It appears that my data are in an agreement with literature data (Figure 4.5.3; McDade et al., 2003b,a; Adam and Green, 2006; Frei et al., 2009; van Kan Parker et al., 2010). Note some elements are variable depending on

the samples, this can be explained by changes in experimental conditions. Also note that F and Cl are also changing and more significantly than other cation trace elements between samples.



Figure 4.2.6: Orthopyroxene/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Dashed part of the grey field was extrapolated from Gd from Adam and Green (2006) and Ho from McDade et al. (2003a). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Clinopyroxene

Clinopyroxene from the experiments are the ferreous and aluminous clinopyroxenes with variable concentrations of diopside (from 0.33 to 0.56), enstatite (from 0.17 to 0.49), ferrosilite (from 0.05 to 0.10), Ca-tschermaks (from 0.04 to 0.10), jadeite (from 0.01 to 0.06) and eskola (0.001 to 0.06). Their compositions vary with changes of temperature, pressure and water content of the experiments, and are closed to those of Gaetani and Grove (1998). However, H5V4p sample is poorer in SiO₂ and more ferreous, thus lower Mg# (Table 4.5.3) than clinopyroxenes of Gaetani and Grove (1998). Our clinpyroxene Mg# is rather closer to those of Adam and Green (2003)conducted experiments in the hydrous basanitic system. Majority of clinopyroxene oxide compositions are consistent with pyroxene stoichiometry (Table 4.5.6). As in the case for orthopyroxene, clinopyroxenes of Grt3V4p has questionable stoichiometry (the sum of cations < 4, maybe due to Ca-Eskola component that lowers sum of cations due to its stoichiometry Ca_{0.5} $\Box_{0.5}$ AlSi₂O₆) and the mass balance of this sample failed to converge. Thus, again, the clinopyroxene data of Grt3V4p are excluded from the rest of the discussions.

Compared with recent literature data as Gaetani et al. (2003); McDade et al. (2003b,a); Adam and Green (2006), my clinopyroxene/melt partition coefficients are in a good agreement with literature data. For all phases and most of the samples, Pb partition coefficients have to be consider as auxiliary, because trace element concentrations did no add up to recover the initial Pb abundance by mass balance. Except for sample H5V4p, for which about 1000 ppm were recover after mass balance, the recovery is only about 10% of the starting Pb composition. Therefore, Pb partition coefficients for some samples are in disagreement with previous work. As shown by Figures 4.5.3 and 4.5.4, Pb partition coefficients between pyroxenes and melt vary between samples. It is not clear if D_{Pb} variation was due to real phenomena provoked to water content or temperature, or just due to an analytical issue. Moreover, standard deviations on Pb data were significant, meaning that measured Pb contents in samples were not homogeneous. For more safety, I decided not to discuss Pb data.

Water abundance measurements in pyroxenes found high concentrations in pyroxenes, especially in orthopyroxenes: from thousands of ppm to 1.2 wt% in the orthopyroxene of sample H6V04. This unusually high concentration cannot be attributed to an analytical issue since the 3 carried out measurements were reproducible within less 2000 ppm variation. As far as I know, there are no published work studied water solubility in orthopyroxene in a natural system, such as mine. Nevertheless, the review by Mierdel et al. (2007) shows that water content in orthopyroxene at pressure of 10 to 35 kbars commonly reach thousands of ppm, even more than 8000 ppm (Bell et al., 1995). Furthermore, they suggested that water solubility increases with Al content of orthopyroxene. In the same time, the thermodynamic models suggest that water solubility increases with the decreasing



Figure 4.2.7: Clinopyroxene/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

temperature (Mierdel and Keppler, 2004; Mierdel, 2006; Keppler and Bolfan Casanova, 2006). Those models even reach water solubility of about 2 wt% in 'Al-saturated enstatite' that refers to enstatite in equilibrium with forsterite and the stable aluminous phase, i.e. MgAl₂O₄ spinel or pyrope, at temperature of 700°C, and at pressure between 10 and 20 kbars. Those models can be applied to my pyroxenes since the decreasing relation between Al₂O₃ and temperature is observed between studied pyroxenes.

With regards to those studies, it appears that from 1000 to 6000 ppm of water content that I found in orthopyroxene and clinopyroxene is also commonly found in pyroxenes. Concerning the measured 1.2 wt% of water in orthopyroxene, this value can be plausible. Nevertheless, the high water abundance is equally possibly due to amphibole lamellae and/or inclusions in these pyroxenes. However, the mineral stoechiometry shows that there can not be significant amphibole component; CaO and Al_2O_3 are too low, while SiO₂, MgO and FeO are too high to accommodate amphibole stoichiometry.

Garnet

The synthesized garnet is a mixture of three dominant component: pyrope, grossular and almandine $(Py_{67}Gr_{11}Alm_{20}Uv_{01})$. This garnet is less calcic and more ferrous and magnesian than garnets obtained by Gaetani et al. (2003) and Green et al. (2000), but these are formed at lower temperature (between 1200 and 1230 °C than the one in my experiment (1370°C). The stoichiometry of the synthesized garnet is balanced (Table 4.5.7).

Literature provides a broad range of garnet/melt partition coefficients (Figure 4.5.5). The garnet data are in good agreement with literature data (Hauri et al., 1994; Johnson, 1998; Gaetani et al., 2003; Pertermann et al., 2004; Adam and Green, 2006). However, it appears that D_{REE} are less compatible that the range of data provided by the literature. Given the literature REE data corresponding to those elements are those of Green et al. (2000), which experimental conditions are at

	Oliv	ine			С	rthopyrox	ene		(Clinopyrox	ene
run	H3V04	SHO1		H3V04	H4V4p	H5V4p	H6V04	Grt3V4p	H3V04	H5V4p	Grt3V4p
Si	1.000	1.001	Si	1.869	1.906	1.867	1.901	1.884	1.849	1.829	1.874
Al^{IV}	0.003	0.002	Al^{IV}	0.131	0.094	0.133	0.099	0.116	0.151	0.171	0.126
sum T	1.003	1.003	sum T	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Ti	0.000	0.001	Ti	0.003	0.002	0.002	0.001	0.003	0.006	0.006	0.006
Al^{VI}	0.000	0.000	Al^{VI}	0.085	0.061	0.067	0.058	0.145	0.121	0.091	0.259
\mathbf{Cr}	0.001	0.000	\mathbf{Cr}	0.024	0.014	0.006	0.025	0.010	0.027	0.009	0.009
Fe^{3+}	0.028	0.018	Fe^{3+}	0.022	0.036	0.013	0.025	0.025	0.015	0.021	0.022
Fe^{2+}	0.253	0.159	Fe^{2+}	0.196	0.326	0.117	0.221	0.227	0.138	0.189	0.195
Mg	1.690	1.798	Mg	1.596	1.468	1.761	1.611	1.473	0.934	0.867	1.022
sum M	1.972	1.976	sum $M1$	1.925	1.907	1.966	1.967	1.883	1.241	1.184	1.513
			Mn	0.005	0.007	0.005	0.006	0.004	0.004	0.004	0.005
			Ca	0.065	0.071	0.047	0.047	0.064	0.721	0.799	0.338
			Na	0.005	0.008	0.005	0.003	0.027	0.044	0.063	0.114
			sum $M2$	0.074	0.086	0.058	0.056	0.095	0.769	0.867	0.456
Total cations	2.985	2.985		4.000	3.993	4.024	3.997	3.979	4.010	4.051	3.969
Mg#	87.7	85.7		88.0	80.2	93.1	86.8	85.4	85.9	80.5	82.5

Table 4.2.7: Olivine, orthopyroxene and clinopyroxene structural formulae.

 $Mg\# = Mg/(Mg + \sum Fe)$

The ${\rm Fe}^{3+}$ was calculated assuming ${\rm Fe}^{3+}/$ ${\rm \Sigma}{\rm Fe}$ = 0.11

Olivine stoichiometry was calculated assuming 3 cations per 4 oxygens. Orthopyroxene and clinopyroxene stoichiometries were calculated assuming 4 cations per 6 oxygens.

T is for tetrahedral site, and M (1 or 2) is for octahedral site. The site allocations are those used to calculate parameters fro the lattice-strain model (section 4.5.6).

lower temperature, and higher pressure (between 3 and 7.5 GPa) than mine. In consequence, garnet compositions are different. Because experimental conditions and garnet compositions have a strong influence on REE partitioning (van Westrenen et al., 1999), the disparity appeared here is rather expected. Discrepancies could also be explained by water content differences between experiments.



Figure 4.2.8: Garnet/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Amphiboles

The amphiboles are fluor-pargasitic hornblende, following the nomenclature of calcic amphibole of (Leake, 1978, F > 2wt%). In the basaltic system, they show relatively little compositional variation, while the amphibole crystallized in the shoshonitic system has higher Ti, Fe²⁺, Na, K and lower Cr, Mg than that of basalt (see Table 4.5.7). Amphibole is a trace-element accommodating mineral, including REE, HSFE, LILE (e.g. Adam and Green, 2006) and volatile elements. Partition coefficients of these elements are higher than those of other commonly occurring igneous minerals, except for F, which is more compatible in micas than in amphiboles. Most of measured partition coefficients between amphibole and basaltic melt are in agreement with literature data (Figure 4.5.6, comparing with Brenan et al., 1995a; Adam and Green, 2003, 2006). Some disparity can be noticed for Li, Sc, V, HSFE as Zr, Hf and REE, for which my values are lower. One possible explanation for this discrepancy may be the amount of Mg in the M4-site (considered to house REE) of amphibole, which is absent from the amphibole of earlier study (Brenan et al., 1995a; Adam and Green, 2003, 2006). Furthermore, my amphibole contains a lower amount of Ca in the M4-site, and a lower amount of Ti in the M1–3 sites (assumed to house Hf and Zr) compared to those of previous work (Brenan et al., 1995a; Adam and Green, 2003, 2006). Such compositional differences contribute to a distortion of the amphibole structure, and the M4 and M1-3 sites are smaller than those in previous studies (Mg ionic radius < Ca ionic radius). In consequence, the M4 and M1–3 sites accommodates REE, and Zr, Hf, in my study than the others. Alternatively, some differences of partition coefficient values could be

attributed to changes in activity coefficients of these elements in association with the changes in the degree of melt polymerization. As it was demonstrated in the previous Chapter 3, and in Dalou et al. (2009a), for example, the decreasing degree of melt polymerization decreases partition coefficients of some elements. Here, I compared my partition coefficients in basaltic system with data obtained from more polymerized melts: andesitic system Brenan et al. (1995a) and basanitic system Adam and Green (2003, 2006).



Figure 4.2.9: Amphibole/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Micas

The micas from experiments are all tri-octahedral phlogopites, with only limited substitutions of dioctahedral components. In tri-octahedral characterization, cations occupy the three octahedra, while di-octahedral characterization means that cations occupy only two octahedra. For the phlogoite of this study, nearly all the three octahedra are occupied, since the sum of cations in octahedral sites is closed to 6 (5.9, see Table 4.5.7). The phlogopites synthesized in my two experiments are closed in composition.

Phlogopite easily accommodates Sr, Pb (assumed to be substituted in the interlayer), with partition coefficients of the same order of magnitude as for amphiboles, while other elements, especially REE (assumed to be substituted in the octahedral site), are highly incompatible in phlogopite. Note that Eu and even Gd partition coefficient is anomalously high compared to other REE, by a factor 2 to 30 above La partition coefficient values. This cannot be attributed to an analytical odd effect, since Eu measurements are well reproducible within 8% of maximum variation. Also note that F is compatible and Cl is incompatible in the phlogopite. On the contrary, F was less compatible than Cl in the amphibole. Most of measured partition coefficients between phlogopite and basaltic melt are globally in agreement with literature data (Figure 4.5.7, with Green et al., 2000; Adam and Green, 2006). Here, contrary to amphibole case, my data are higher that Adam and Green (2006) data. As it is the case for amphibole, the discrepancy among pholgopite partitioning data can be the result of the

	Garnet		1	Amphibole	1		Mi	ica
run	Grt3V4p		H4V4p	H6V04	SHO4		SHO1	SHO4
Si (Z-site)	2.962	Si	6.623	6.478	6.475	Si	5.945	5.940
		Al^{IV}	1.377	1.522	1.525	Al^{IV}	2.055	2.060
Al	1.946	sum T	8.000	8.000	8.000	sum T	8.000	8.000
Fe^{3+}	0.059							
\mathbf{Cr}	0.021	Ti	0.021	0.022	0.137	Mg	5.640	5.449
Ti	0.021	Al^{VI}	0.356	0.332	0.238	Al^{VI}	0.054	0.041
sum Y	2.077	\mathbf{Cr}	0.071	0.110	0.002	Fe^{2+}	0.163	0.289
		Fe^{3+}	0.081	0.060	0.099	Fe^{3+}	0.018	0.032
Ca	0.369	Fe^{2+}	0.729	0.537	0.894	Ti	0.051	0.052
Mn	0.014	Mg	3.743	3.940	3.630	\mathbf{Cr}	0.000	0.007
Fe^{2+}	0.535	sum M1–3	5.000	5.000	5.000	Mn	0.000	0.002
Mg	2.077					sum M	5.926	5.872
sum X	2.995	Mn	0.018	0.012	0.020			
		Ca	1.293	1.425	1.551	Κ	1.855	1.656
		Na	0.000	0.284	0.429	Na	0.161	0.424
		Mg	0.711	0.617	0.399	Ca	0.008	0.026
		sum M4	2.021	2.000	2.000	sum I	2.023	2.106
		Na	0.766	0.563	0.429			
		Κ	0.018	0.022	0.144			
		sum A	0.784	0.585	0.573			
Total cations	8.004		15.805	15.923	15.942		15.949	15.978
Mg#	77.8		84.6	88.4	80.2		96.9	94.4

Table 4.2.8: Garnet, amphibole and phlogopite structural formulae.

 $Mg\# = Mg/(Mg + \sum Fe)$

The ${\rm Fe}^{3+}$ was calculated assuming ${\rm Fe}^{3+}/$ ${\rm \Sigma}{\rm Fe}$ = 0.11

Garnet stoichiometry was calculated assuming 8 cations per 12 oxygens. Pargasite and phlogopite stoichiometry were determined excluding (OH)-site, assuming that 2 $OH^- = 1 O^{2-}$. Pargasite pfu were calculated with 22 O and phlogopite with 23 O, both assuming 16 cations.

Z is for the tetrahedral site, Y, the octahedral site and X, the dodecahedral site in garnet. T is for tetrahedral site, and M (1 or 2) is for octahedral site. I is for the interlayer in micas. The site allocations are those used to calculate parameters for the lattice-strain model (section 4.5.6).

higher amount of Mg (bigger cation) and the lower amount of small cations as Al, Ti, Cr and Mn in the octahedral site of my phlogopite compared to those of Adam and Green (2006). Thus, in my experiments, phlogopite better accommodates trace elements, such as REE. However, there are no potential model explaining why Sc, V, Cr and Co partition coefficients of my phlogopite are lower than those of Adam and Green (2006). Hypotheses based neither on crystal structure nor the degree of melt polymerization provides coherent explanations. The small number of partitioning studies of phlogopite and melt does not allow me to perfectly understand all differences between my data and data from previous work.



Figure 4.2.10: Phlogopite/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, Adam and Green, 2006). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Water measurements in hydrous minerals are presented in Table 4.2.6. The measured water content in the amphibole (sample H4V4p, 1.27 wt%) is in a good agreement with the water measured in the amphibole of (La Tourette et al., 1995, 1.63 wt% H₂O). For both studies, water dissolved in the melt is at both 4.3 wt% H₂O. The water content measured in the phlogopite (sample SHO1 and SHO4, 4.3, 4.2 wt% H₂O, respectively) is also in an agreement with the water content in the phlogopite of (La Tourette et al., 1995, 4.6 wt% H₂O), for a comparable amount of water dissolved in the melt (4.3, 4.8 and 3.3 wt% H₂O for SHO1, SHO4, and La Tourette et al., 1995, respectively).

4.2.3 Equilibrium considerations

In the previous section 4.2.2, I argued that compositions of olivine, orthopyroxene and clinopyroxene are believed to be close to equilibrium, because conditions and phase compositions are close to an earlier work where equilibrium was examined via reversal experiments (Gaetani and Grove, 1998). Remaining differences between previous studies can be attributed to different water contents and temperature differences. The equilibrium textures (polygonal shapes of the crystals, see Figures 4.5.1 and 4.2.2), the lack of detectable compositional zoning in crystals and the homogeneity of produced melt

(judging from the small standard deviations of replicate analyses of glasses (see Table 4.5.3) indicate that a run duration of 4 to 5 days is sufficient to reach, at least, local equilibrium. As explained in the Methods chapter 2, I cannot prove whether my experiments achieved complete chemical equilibrium or not, because that would require reversal experiments for all the runs. However for the reasons outline below, I conclude that the experiments approached equilibrium sufficiently that they can be used to determine partition coefficients of F, Cl and trace elements.

The attainment of chemical equilibrium can also be inferred from evaluation of the well-established Fe-Mg exchange coefficient between olivine and melt, $O^{Ol/Melt} K_{DFe-Mg} = (O^{Ol} Fe^{2+}.Melt Mg) / (Melt Fe^{2+}.O^{Ol} Mg)$ Roeder and Emslie, 1970). In most basaltic melts, K_{DFe-Mg} values are around 0.3 (Roeder and Emslie, 1970; Takahashi, 1978; Jones, 1984; Ulmer, 1989; Beattie et al., 1991; Hirschmann and Ghiorso, 1994; Fallon et al., 1997). The K_{DFe-Mg} value of the H3V04 sample is 0.30. For SHO1 sample, the K_{DFe-Mg} value is 0.51, which can be explained either by preferential Fe loss from melt during the experiment, or by high F and water content in the sample. The Fe-Mg exchange coefficient can be also calculated for orthopyroxene or clinopyroxene and melt, and be compared to those obtained by Gaetani and Grove (1998). For the volatile-poor experiments (H3V04 and Grt3V4p, 0.25 and (0.32), K_Ds are similar to those of (Gaetani and Grove, 1998, 0.28 to 0.35) for orthopyroxene, and 0.29 and 0.39 versus 0.28 to 0.35 variation for clinopyroxene. Nevertheless, for volatile-rich samples (containing more than more than 6 wt% of volatile total (F + Cl+ H_2O)), K_Ds values are highly variable (between 0.18 and 0.71). The effect of F and Cl on Fe-Mg exchange must be also considered. Filiberto et al. (2010) observed that K_D increase with increasing F content of the melt. Therefore, they infer that F complexes with Mg in the melt and thus increases the silica activity of the melt. depresses the liquidus, and changes the composition of the crystallizing minerals.

Fluorine and chlorine are relatively homogeneous in minerals and melt among all the experiments, with a mean standard deviation of 5% relative for F and 7% relative for Cl in opx, of 2% relative for F and 10% relative for Cl in cpx, of 3% relative for F and 12% for Cl in olivine, of 8% relative for F and 15% relative for Cl in amphibole, 1% relative for F and 6% relative for Cl in garnet, 6% relative for F and 9% relative for Cl in phlogopite and of 12% relative for F and 17% relative for Cl in the melt. These relative standard deviations are either the same or smaller than the internal analytical uncertainties.

To conclude, the large amounts of melt present, the consistent partitioning and major and minor element composition of solid phases observed in my experiments indicate that the experimental phases are close enough to equilibrium to aid in the understanding of F, Cl and trace element partitioning.

4.3 Discussion

As shown in the different parts of previous sections, significant variations of phase assemblages, mineral compositions and element partitioning between samples are found. Those variations cannot be completely explained neither by pressure effect since all samples except Grt3V4p are from 12 kbars experiments, nor by temperature effect since 3 samples (H4V4p, H5V4p and H6V04) have only 10°C to 20°C of experimental temperature differences. Water abundance in samples, described by water content dissolved in melt, is the main variable component between samples that may contribute to samples disparity. In the following sections, I will focus on the water effect on mineral composition variation and its direct or indirect effect on trace elements partitioning and finally on F and Cl partitioning.

4.3.1 Effect of water on element partitioning

Effect of water on assemblies and composition of phases

In my experiments, the calcic (and sodic) fraction in the clinopyroxenes increases at nearly constant CaTs (\pm Esk), as illustrated on Figure 4.3.1 by sample CC4#7b (12 kbars – 1310°C and 0.2 wt% H₂O, Table 4.5.6), sample H3V04 (12 kbars – 1240°C and 2.6 wt% H₂O) to sample H5V4p (12 kbars – 1190°C and 4.9 wt% H₂O). The orthopyroxene becomes more magnesian and ferreous from sample CC4#7b, sample H3V04, sample H5V4p and sample H6V04 (12 kbars – 1200°C and 5.9 wt% H₂O).



Figure 4.3.1: Ternary diagram showing experimentally produced clinopyroxene (on the left) and orthopyroxene (on the right) compositions recalculated into $En+Fs = enstatite + ferrosilite (Mg_2Si_2O_6 + Fe_2^{2+}Si_2O_6)$, Diop + Jad = diopside + jadeite (CaMgSi_2O_6 + NaAlSi_2O_6) and CaTs + Esk = Ca-Tschermak and Ca-Eskola (CaAlAlSiO_6 + Ca_{0.5}\Box_{0.5}AlSi_2O_6) for clinopyroxenes and recalculated into $En+Fs = enstatite + ferrosilite (Mg_2Si_2O_6 + Fe_2^{2+}Si_2O_6)$, Jad and Ts = (Mg, Ca, Cr)Tschermak ((Mg,Ca,Cr)AlAlSiO_6). Here, $\sum Fe$ was considered to make ferrosilite.

This pyroxene composition evolution is generally attributed to temperature. When temperature decreases, orthopyroxene becomes richer in enstatite and clinopyroxenes become more diopsidic (Fig-

ure 4.3.2). Nevertheless, these pyroxene chemistry difference are observed between samples with only 10° C of temperature difference (samples H5V4p and H6V04). Figure 4.3.2 reports orthopyroxene and clinopyroxene compositions and shows that samples repartition does not correspond to experimental temperature repartition. This discrepancy could be explained by water content. Observed tendencies were also compared using MELTS calculator (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995), in which melting of a basalt-peridotite mixture (70:30 as used in my experiments) with 0.5, 3 and 5 wt% H₂O was modeled. It showed for clinopyroxenes that 1) MgO decreases while Al₂O₃ and CaO increase with the decreasing temperature and 2) as well, MgO decreases while Al₂O₃ and CaO increase with the increase of bulk water content at the same temperature. It is difficult to dissociate effects of water from temperature, since they produce the same compositional evolution in pyroxenes. Nevertheless, in my study, given the small temperature difference (~10°C) between some samples, the significant compositional difference is caused by the variation of water abundance in melt.



Figure 4.3.2: Isobaric phase diagram from the quadrilateral redrawn after Lindsey (1980), showing that orthopyroxene composition get richer in enstatite with the decreasing temperature, here between 1200 and 810°C (downward arrow), while clinopyroxene composition get richer in diopside with the decreasing temperature (upward arrow). On this diagram are reported pyroxene (opx in grey and cpx in orange-red) compositions, following the same symbols of the Figure 4.3.1.

The increase of the calcic character of clinopyroxene is previously observed by hydrous experiments, but it was attributed to temperature effect, because hydrous experiments are performed at lower temperature than dry experiments (Parman et al., 1997; Gaetani et al., 1993, *e.g.*). In my case, variation of composition between samples can be, at least partly, explained by the difference of water content (as H₂O content dissolved in the melt). Water content of melt changes the composition of melt by dilution and also the change of activity of the Si (a_{Si}^{Melt}) . The increase of water dissolved in the melt increases the a_{Si}^{Melt} (Gaetani and Grove, 1998). In Gaetani and Grove (1998), the authors explains that a_{Si}^{Melt} is linked to the Mg-Fe ratio between melt and olivine. It is perfectly understandable that a_{Si}^{Melt} variation, thus melt water content here, changes the composition of my crystals.

Olivines from sample CC01#8kb4 (see chapter 4, 8 kbars – $1265^{\circ}C$ – 0.21 wt% H₂O) and sample H3V04 (12 kbars – $1240^{\circ}C$ – 2.59 wt% H₂O) becomes more ferreous (from 0.241 Fe²⁺ + Fe³⁺ pfu to

2.281) and less magnesian (from 1.727 Mg pfu to 1.690). Concerning garnet, from sample C4p#25kb (25 kbars – 1430°C – 0.8 wt% H₂O) to sample Grt3V4p (25 kbars – 1370°C – 1.6 wt% H₂O), garnet composition becomes more grossular (Ca₃Al₂Si₃O₁₂) and almandine (Fe₃Al₂Si₃O₁₂) and less pyrope (Mg₃Al₂Si₃O₁₂); thus garnet are enriched in the calcic endmember and depleted in magnesic endmember. Although this tendency is consistent with clinopyroxene evolution with water content, in those two garnet-bearing experiments, temperature effect cannot be negligible since there is 60°C of temperature difference between the two samples.

As well as for clinopyroxenes, pargasites are more magnesian, calcic and less sodic in H6V04 and in H4V4p (12 kbars – 1180°C and 4.3 wt% H₂O). Concerning phlogopites, they are more sodic in SHO4 than in SHO1. Nevertheless, in those minerals, compositional variations can be related to H₂O incorporation and abundance in its site.

Modelling $D_i^{mineral/metl}$ with the lattice strain models: crystal-chemistry control on trace element partition coefficients

In order to better constrain water effect on partitioning, resulting structural changes in mineral networks is studied using lattice strain models. As explained in the previous chapter 3, trace element partition coefficients with the same valence state substitute toa single lattice site vary systematically as a function of cationic radius (Onuma et al., 1968). This systematics results from the contribution of strain energy, due to the misfit between a substituting cation and the lattice site, to the free energy change for incorporating a cation which fits exactly onto the site (Nagasawa, 1966; Brice, 1975; Beattie, 1994; Blundy and Wood, 1994). As the misfit between optimum radius for the lattice site (r_0) and the radius of the substituting cation (r_i) increases, the mineral/melt partition coefficient ($D_i^{mineral/metl}$) decreases according to the equation:

$$D_i^{mineral/melt} = D_0 \, exp\left(\frac{-4\pi E_0 Na}{RT} \left(\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3\right)\right),$$

where D_0 is the mineral/melt partition coefficient for the strain-free substitution, E_0 is the effective Young's modulus for the lattice site, N_A is the Avogadro's number, R is the gas constant, and T is temperature (Brice, 1975; Blundy and Wood, 1994; Wood and Blundy, 1997).

Data of my experiments in the basaltic system were fitted to the equation ?? for olivine, garnet, and amphibole / melt partition coefficients. This model simultaneously fits two cation sites in pyroxenes, due to quantitatively evaluation of the response of changing water content, to crystals chemistry, and pressure and temperature, affects trace element partitioning (Figures 4.3.3, 4.3.5, 4.3.6, 4.3.7). Fits were made only for trivalent cations using the procedure described in the previous chapter (Chapter 3, section 3.5.2) for pyroxenes and the procedure described in Dalou et al. (2009a) for garnet, olivine

and amphibole. The r_i , the ionic radii of cation elements, were originally from Shannon (1976), and were chosen as 6-fold coordination in olivine and pyroxenes and, and 8-fold coordination in garnet and pargasite. For divalent and tetravalent cations, experimental data points are less than the number of model parameters. It was not relevant to run the lattice strain model on those data. The derived best-fit values for r_0 , E_0 and D_0 for garnet, olivine and amphibole and r_0^{M1} , r_0^{M2} , E_0^{M1} , E_0^{M2} , D_0^{M1} and D_0^{M2} for pyroxenes are presented in Table 4.5.8.

		Orthopy	roxene			Cli	nopyroxen	e
runs	$CC4\#7b^*$	H3V04	H5V4p	H6V04		CC4#7b	H3V04	H5V4p
		M1 s	ite				M1 site	
D_0	8.31	6.24	7.00	6.48		8.65	17.38	4.53
r_0	0.647	0.649	0.650	0.650		0.650	0.651	0.655
E_0	1278	1232	1353	1248		1214	1579	881
		M2 s	ite				M2 site	
D_0	0.185	0.214	0.237	0.250		0.426	0.444	0.470
r_0	0.827	0.881	0.870	0.866		1.012	1.011	1.027
E_0	324	466	522	509		552	333	362
	Olivir	ne	_	Garı	net		Ampl	nibole
runs	$\rm CC01\#8kb4$	H3V04		C4p#25kb	Grt3V4p		H4V4p	H6V04
	M sit	e	_	X si	te		M2	site
D_0	0.164(13)	0.156(3)		9.6(3)	2.8(8)		0.17(4)	0.22(9)
r_0	0.765(5)	0.790(2)		0.920(1)	0.91(1)		1.00(1)	1.01(1)
E_0	474(3)	311(1)		642(0.5)	365(4)		389(3)	427(6)

Table 4.3.1: Site parameters for lattice strain models for trivalent cations.

 r_0 values are in angstroms, E_0 values are in GPa.

* available in the last chapter.

Fitted curves presented in Figure 4.3.6, 4.3.7 agreed well with the data, with the exception of the lattice strain model of the olivine from the sample CC01#8kb4. This is caused by La, which concentration in olivine is < 0.1 ppm, thus difficult to measure. Because my data are reproduced by the fitted model based on the lattice strain theory, it shows that the mineral – basaltic melt partitioning is mainly controlled by the mineral's crystal structure. A systematic variation of D_0 and E_0 between samples that can be related to both to crystal chemistry and melt structure, which includes both temperature and water content dissolved in the melt. A r_0 variation is significant for pyroxenes and olivine. For garnet and amphibole, this variation is within the error bars.

Orthopyroxene

According to Frei et al. (2009), the $r_0^{M2(3+)}$ is function of Al^{tot} and Ca of orthopyroxene and can be described by:

$$r_0^{M2(3+)} = 0.753 + 0.118Al^{tot} + 0.114Ca_2$$

with Al^{tot} and Ca being the number of cations per formula unit on the basis of 4 cations. The estimated error of this correlation is ± 0.012 Å. For orthopyroxenes of my experiments, the above equation results in $r_0^{M2(3+)}$ is in average 0.78 Å, with the variation among the samples included in the error. The poor agreement of this predicted value and my results suggest that the equation is invalid for hydrous experiments. The fitted $r_0^{M2(3+)}$ for the dry sample CC4#7b (0.83 \pm 0.02 (assessed from the different model runs with worse RMSE) Table 4.5.8) is in a merginal agreement with the prediction (0.79 \pm 0.01). Among hydrous samples of my experiments, $r_0^{M2(3+)}$ increases with the increasing tschermak component.



Figure 4.3.3: Lattice strain models (Brice, 1975; Blundy and Wood, 1994) applied to orthopyroxene – hydrous (grey to black curves) – nearly dry (light grey curve) basaltic melt partition coefficients for trivalent cations. Solid hyperbola represent fits of the lattice strain model to $D_i^{cpx/melt}$, this represents the sum of the resulting fits for $D_i^{M1/melt}$ (stippled parabola) and for $D_i^{M2/melt}$ (dashed parabola). For more clarity, measured $D_i^{Opx/Melt}$ are not presented on this figure. Lattice strain models with measured $D_i^{Opx/Melt}$ are available in Appendix E. As it is the case for $r_0^{M2(3+)}$, E_0^{M2} in orthopyroxenes varies among the samples. It appears that E_0^{M2} increases with the increasing enstatite and ferrosilite content in orthopyroxene and decreases with the increasing (Mg, Ca, Cr) tschermak content (Figure 4.3.4). The tschermak component involves the substitution of Al³⁺ for Mg²⁺ in the M1 site charge balanced by substituting Al³⁺ for Si⁴⁺ in the tetrahedral (or T) site. This substitution seems to increase M2 site, showed by $r_0^{M2(3+)}$ increases. This correlation does not appear on E_0^{M1} . likely since M1 lattice strain parameters highly depends on Cr partition coefficients, it self highly dependant of temperature conditions and melting rate of samples. As previously noted in the previous chapter, Hill et al. (2000) already observed for clinopyroxenes that E_0 for M1 and M2 sites can increase with the CaTs increase in cpx. The authors suggested that the substitution of the 'wrong' charge into a site appears to require deformation of the cation – O bond, leading to much higher strain energy and hence higher E_0 . This argument can suggest that the substitution of a more charged ions at the place of a less charged ions (Al³⁺ for Mg²⁺ and Ca²⁺) could cause the decrease of $E_0^{M2(3+)}$ observed on the Figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the Figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the Figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the Figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the Figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure 4.3.4b) and the increase of $E_0^{M2(3+)}$ observed on the figure



Figure 4.3.4: Relation between calculated orthopyroxene components and $E_0^{M2(3+)}$ derived from the fitting of my data into the lattice strain model. a) presents the variation of the enstatite + ferrosilite component, as the magnesian and ferreous component, with $E_0^{M2(3+)}$ and b) presents the variation of the tschermak component, as the aluminous component, with $E_0^{M2(3+)}$. As explained in the previous chapter 3, no error is calculated on fit parameters, but evaluated from the calculated optimization criteria, Nash criterion and RMSE, to be > 0.9997 and < 0.04, respectively. Correlation coefficients are > 0.97.

Clinopyroxene

According to Wood and Blundy (2003), the $r_0^{M2(3+)}$ is function of Al^{M1} (the Al entering in the M1 site) and Ca of clinopyroxene and can be described by:

$$r_0^{M2(3+)} = 0.974 + 0.067Al^{M1} + 0.114Ca.$$

For clinopyroxenes of my experiments, the above equation results in $r_0^{M2(3+)}$ is 1.00 for sample CC4#7b, 1.04 for sample H3V04 and 1.04 for sample H5V4p, which shows that as for orthopyroxene the equation is invalid for hydrous experiments. It also demonstrates that $r_0^{M2(3+)}$ increases with the calcic composition of clinopyroxenes, which observed for my hydrous samples results.



Figure 4.3.5: Lattice strain models applied to clinopyroxene – hydrous (grey to black curves) and nearly dry (light grey curve) – basaltic melt partition coefficients for trivalent cations. Solid hyperbola represent fits of the lattice strain model to $D_i^{cpx/melt}$, this represents the sum of the resulting fits for $D_i^{M1/melt}$ (stippled parabola) and for $D_i^{M2/melt}$ (dashed parabola). For more clarity, measured $D_i^{Opx/Melt}$ are not presented on this figure. Lattice strain models with measured $D_i^{Opx/Melt}$ are available in Appendix E.

Unlike orthopyroxene, I found no relation between $E_0^{M2(3+)}$ and clinopyroxene components. It implies that crystal chemistry is not the dominant effect that can explain the change of lattice strain parameters.

Olivine

In Table 4.5.8 comparing olivines of sample CC01#8kb4 obtained at 8 kbars and sample H3V04 obtained at 12 kbars, a decrease of all parameters is observed. Changes of lattice strain parameters for olivine are mainly attributed to pressure variation (Taura et al., 1998). In this case, D_0 , E_0 and r_0 are lower at higher pressure. This is perfectly consistent with Taura et al. (1998), who observed the same tendency between an olivine synthetized at 3 GPa and an olivine synthetized at 14.4 GPa.



Figure 4.3.6: Lattice strain models applied to olivine (a) and garnet (b) – hydrous (black curve) and nearly dry (grey curve) – basaltic melt partition coefficients for trivalent cations. Diamonds and squares represent measured $D_i^{Mineral/Melt}$ for P - T conditions shown in the legend. The gray dashed boundary indicates the plot region of other Onuma diagrams.

Garnet

Garnet lattice strain parameters were calculated using the predictive model of Draper and van Westrenen (2007) and van Westrenen and Draper (2007), to be compared with parameters from the data fitting. The predicted value of E_0 for C4p#25kb (595 GPa) is significantly lower than the E_0 fitted from my data (642 GPa), while the predicted value of E_0 for Grt3#V4p (588 GPa) is significantly higher than the E_0 modeled from my data (365 GPa). The predictive model takes in the account of the chemistry of garnets and the temperature (pressure is the same for the two samples). Thus it reproduces the E_0 decrease between the two samples, linked to temperature and compositional differences. The difference between E_0 modeled from my data could be explained by water or total volatile (H₂O, F and Cl) content difference of the two samples. Generally, E_0 and r_0 are parameters considered to be related with crystal-chemistry only. Thus, when volatile content is mentioned to explain E_0 changes, it must mean volatiles content in crystals. Even water content in the two garnet is close (0.46 and 0.52 wt% H₂O for C4p#25kb and Grt3#V4p, respectively), F and Cl concentration is different (86 and 1215 ppm F + Cl for C4p#25kb and Grt3#V4p, respectively). As I previously I suggested in the previous chapter 3, F and Cl are substituted into O site, described by two coupled substitution. This substitution implies that F and Cl would be incorporated to bond with Y – site (octahedral) of the garnet (Heinemann et al., 1997), where Mg and Fe are assigned. To understand fluorine substitution in fluorine-bearing garnets, Valley et al. (1983) suggested that it requires that Mg is placed in the octathedral site instead of the dodecahedral site of garnet, to maximize F substitution. This rearrangement could lower the E_0 of the dodecahedral site (X – site) of the volatile-richer garnet, since one major cation Mg²⁺ is removed from it (I infer that creates the site relaxation, thus a E decrease).

Amphibole

The E_0 increases in amphiboles of sample H4V4p and sample H6V04 (Table 4.5.8). The r_0 also increases from H4V4p to H6V04 by the change within the error bar. Significant changes of lattice strain parameters are reported with respect to pressure variation (Adam and Green, 2003), but the two samples here were synthesized at the same pressure. There is an increase of Ca²⁺ and Na⁺. Since they are two major anions of the M4 sites, r_0 is expected to increase with Ca and Na content. This Ca and Na increase could also have an effect on E_0 parameter.



Figure 4.3.7: Lattice strain models applied to pargasite – hydrous basaltic melt partition coefficients for trivalent cations (grey to black curves). Squares represent measured $D_i^{Amp/Melt}$ for conditions detailed in the legend.

Melt structure effect on D_0

It has been known that the predicted D_0 parameter (Wood and Blundy, 1997, e.g.) is consistent with the experiments for restricted range of compositions. To explain disparity between predicted and empirically fit D_0 parameters of hydrous silicate melts, Gaetani et al. (2003) explored compatibility change on the basis of the changes in melt polymerization. It suggests that H₂O content dissolved in the melt significantly change melt polymerization. An addition of 6.26 wt% H₂O in melt produces ~ 17 mol% hydroxyl groups and decreases viscosity by ~ 98% relative to an anhydrous melt at the same temperature (Gaetani et al., 2003). In my experiments, with temperature and water content dissolved in the melt (up to 5.9 wt% H₂O), variation of D_0 with respect to water abundance is expected. The water abundance and D_0^{M2} are positively correlated for orthopyroxenes (Figure 4.3.8a), and for clinopyroxene (Figure 4.3.8b). The Wood and Blundy's parameterization applied to sample H3V04 predicts a D_0^{M2} of 0.688. In order to evaluate the influence of melt structure on D_0^{M2} , the melt structure correction (Gaetani et al., 2003) is applied to D_0^{M2} and obtain 0.343. Although the calculation does not exactly predict my predicted D_0^{M2} parameter from experimental data for this sample (0.444), it does indicate that the discrepancy with Wood and Blundy's parameterized D_0^{M2} is consistent a melt polymerization effect.



Figure 4.3.8: Relation between water content dissolved in the melt and D_0^{M2} calculated from lattice strain fits (a) for orthopyroxene and (b) clinopyroxene, with experimental temperature of each samples. The evolution of D_0^{M2} with water content and temperature is reversed between orthopyroxene and clinopyroxene. Note that if water content or temperature were the major effect that control D_0^{M2} , the same tendency of D_0^{M2} evolution with water or temperature would appear.

4.3.2 F and Cl behavior change in hydrous experiments

F and Cl substitution mechanisms in pyroxenes:

The role of crystal-chemistry:

The previous chapter (Chapter 3) concludes that crystal chemistry in minerals likely controls Cl partition coefficients, while F partition coefficients are mainly controlled by melt structure. The substitution mechanism of Cl in orthopyroxene is deduced from correlations between Cl partition coefficients and the jadeite and enstatite component. Similarly, the substitution mechanism of Cl in clinopyroxene is deduced from correlation between Cl partition coefficient and CaTs content of clinopyroxene. Here, as I previously mentioned, presence of water causes significant variations of pyroxenes chemistry, and such variation improve the correlation due to Cl and F substitution mechanisms in minerals.

Figures 4.3.9 and 4.3.10 show a set of binary correlations between the partition coefficients $D_{F,Cl}^{Mineral/Melt}$ and end-member pyroxene components of ortho- and clinopyroxenes. Naturally, some correlations are reversed because of exchanging relationships, for example enstatite + ferrosilite and tschermak (Figure 4.3.9) and enstatite + ferrosilite and diopside + jadeite (Figure 4.3.10). Comparing Figure 4.3.9 with Figure 3.5.1 of the Chapter 3 (section 3.5.1), some data are incomparable, because the data on Figure 3.5.1 represents a variation of pyroxene composition at constant pressure, temperature, and composition except for volatile abundance, while the data on Figure 4.3.9 represents the variation with a constant pressure and composition, but varying temperature and volatile abundance. It should be stressed that $D_{F,Cl}^{Mineral/Melt}$ varies over factor of 6 for F and more than 10 for Cl.

Studies of pyroxenes have suggested that volume of polyhedra, as well as Si – O, M1 – O and M2 – O distances, can change with temperature and mostly with pyroxene compositions (Cameron and Papike, 1981; Boffa Ballaran et al., 1998). For instance, Boffa Ballaran et al. (1998) measured that Si – O and M1 – O distances decrease with the increase of the jadeite component of clinopyroxene. This was explained by the disorder created by the substitution of ions of different sizes into octahedral sites and the Al content tetrahedral site since: $r_{Si} < r_{Al}$ and $r_{Al} < r_{Mg} < r_{Ca} < r_{Na}$, generated by the jadeite coupled substitution: Ca²⁺ + Mg²⁺ (Fe²⁺) \rightarrow Na⁺ + Al³⁺ (Fe³⁺). Thus it can be interpreted that F and Cl incorporations are promoted or hindered by changes in these Si – O, M1 – O and M2 – O distances. In the previous chapter study I have inferred that F is incorporated into the O3 in orthopyroxene, and F goes into the O3 site and Cl into the O1 or O2 sites in clinopyroxene (Chapter 3, section 3.5.4). Furthermore, deciphering the coupled



Figure 4.3.9: Diagrams showing the relation between F partition coefficients (a, b and c) and Cl partition coefficients (d, e and f) with the orthopyroxene endmembers used in the Figure 4.3.1: (Mg, Ca, Cr)Tschermak (a and d), jadeite (b and e) and Ens + Fs (c and f), in the same samples presented in Figure 4.3.1 and described in the text above.



Figure 4.3.10: Diagrams showing the relation between F partition coefficients (a and b) and Cl partition coefficients (d and e) with the clinopyroxene endmembers used in the Figure 4.3.1: diopide + jadeite (b and e) and Ens + Fs (c and f) that are opposite components, in the same samples presented in Figure 4.3.1 and described in the text above.

substitution, it assumes that Cl⁻ was bonded with Na⁺, thus with the M2 site in orthopyroxenes:

$$Mg_{Mg}^{\times} + O_O^{\times} + NaCl_{melt} = Na'_{Mg} + Cl_O^{\bullet} + MgO_{melt}$$

and that Cl⁻ was bonded with Al³⁺, thus with the T and/or the M1 sites in clinopyroxenes:

$$Mg_{Mg}^{\times} + Si_{Si}^{\times} + O_{O}^{\times} + Cl_{melt} + Al_2O_{3melt} = Al_{Si}' + Al_{Mg}^{\bullet} + Cl_{O}^{\bullet} + SiO_{2melt} + MgO_{melt}$$

In addition, Rossi et al. (1983) suggests that M2 - O3 distance decreases with the increase of jadeite component in clinopyroxenes, while average M1 - O and even M1 - O1 and M1 - O2 distances increases with the increase of Mg and Fe content in the pyroxene. Without interpreting exact nature of mechanism, this allows to explain the correlations observed in Figures 4.3.9 and 4.3.10:

- In orthopyroxenes: Mg²⁺ and Fe²⁺ are the major cations. Increase of the enstatite and ferrosilite component determines and increases the M1 O1 and M1 O2 distance, while its opposite components as jadeite increases the M2 O3 distance. The lengthening of M2 O3 promotes the Cl incorporation, which will have more space in orthopyroxene structure. Regarding F, it seems to be retained with more difficulties into O1 while M1 O1 distance increases.
- In clinopyroxenes: the O1 M1 distance increases with the increase of calcic component, *i.e.* the diopside component (Cameron and Papike, 1981; Rossi et al., 1983). This should promote

Cl incorporation into O1 site, as illustrated on Figure 4.3.10d. Consequently, Figure 4.3.10e shows that the increase of enstatite and ferrosilite component shortens the O1 – M1 and hinders the Cl incorporation. The smaller F^- is substituted into the O3 site in clinopyroxene. As it is already shown for orthopyroxene, it seems that F decreases in O3 when O3 – M2 distance increases.

The role of water molecule:

The previous chapter (Chapter 3, section 4.5.10) has shown that F is highly influenced by the melt structure and tends to become more incompatible when the melt is more depolymerized. This is illustrated by Figure 4.3.11a and Figure 4.3.12a. Figures 4.3.11b and 4.3.12b show that Cl has the inverse behavior compared to F.



Figure 4.3.11: Diagrams showing the relation between F (a) and Cl (b) partition coefficients between orthopyroxene and basaltic melt and the water content dissolved into the basaltic melt.

As shown by Figure 4.3.8, water content dissolved in the melt has an influence on trace element partition coefficients. Consequently, it is expected that it has also a direct influence on F and Cl partition coefficients. Moreover, Smyth et al. (2007) demonstrates that nearest neighbor distances (M - O) and coordination parameters (as polyhedral volume) change between a hydrous aluminous orthopyroxene and an anhydrous pure Mg orthoenstatite. Those changes are induced by the disorder of the H⁺ proton. The modification of pyroxene structure caused by the protonation can promote or inhibit F or Cl incorporation. Nevertheless, changes caused by protonation versus changes caused by major element composition variation are apriori not quantified. As a first approximation, I calculated that variation of jadeite and acmite component in clinopyroxene after Boffa Ballaran et al. (1998) between 0 and 1 change the M – O distance of 7%, while there is 3.5% difference between the hydrous



orthopyroxene and the anhydrous orthoenstatite of Smyth et al. (2007).

Figure 4.3.12: Diagrams showing the relation between F (a) and Cl (b) partition coefficients between clinopyroxene and basaltic melt and the water content dissolved into the basaltic melt.

It is thus possible to explain correlations between pyroxene components, that highly variable in hydrous system, and F and Cl partition coefficients without prosing a different incorporation mechanisms of anions with the presence water molecule. Furthermore, the recent study of O'Leary et al. (2010) demonstrates the F incorporation, with different water contents. F partition coefficients are linked with the IV Al (see Figure 4.3.13). This tendency is perfectly in agreement with the substitution mechanism inferred for Cl in clinopyroxene: Si⁴⁺. O²⁻ \leftrightarrow Al³⁺. Cl⁻. Thus it seems that F is incorporated into clinopyroxene just like Cl. O'Leary et al. (2010) observes the variation of IV Al³⁺ in clinopyroxene caused by variation of the bulk water in the experiments at constant T. Because of the assumed substitution mechanism of F, related to IV Al³⁺ increase, the D^{Cpx/Melt}_F increases. Figure 4.3.13 shows that my data, close diamonds, are in disagreement with O'Leary et al. (2010) data trend.



Figure 4.3.13: Fluorine partition coefficient variation with ${}^{IV}\text{Al}^{3+}$ in clinopyroxenes, calculated in atom per formula unit (apfu). Close diamonds are data from this study, with variable T (temperature) and H₂O dissolved in the melt. Open diamonds are O'Leary et al. (2010) data, with H₂O dissolved in the melt (from 0.2 to 4.9 wt%H₂O) at 1275°C.

This disagreement is not explained by difference of major element composition between the two studies. It appears on Figure 4.3.14 that O'Leary et al.'s F partition coefficients decrease with the bulk water in the experiments, as well as in my study. This trend could signify that, by melt depolymerization, the water content dissolved in the melt control F partitioning between clinopyroxene and melt. On this Figure, however, the observed decrease of F partition coefficients of O'Leary et al. (2010) is less significant than the decrease of my F partition coefficients. Moreover, my F partition coefficients are higher than O'Leary et al.'s F partition coefficients.



Figure 4.3.14: Fluorine partition coefficient variation with water content dissolved in the melt. Close diamonds are data from this study, with variable T(temperature) and H₂O dissolved in the melt. Open diamonds are O'Leary et al. (2010) data, with H₂O dissolved in the melt (from 0.2 to 4.9 wt%H₂O) at 1275°C.

These discrepancies can be explained by the following reasoning: in my experiments, the combination of water and temperature variation caused high variation of the calcic component of clinopyroxene, which, as previously presented, could induce the dilatation of the site for F and reduces its incorporation. It causes, therefore, the significant decrease of my F partition coefficients with water content than those of O'Leary et al. (Figure 4.3.14).

Using this reasoning, I infer that correlations of Figures 4.3.9 and DCpx are not the results of sub-

stitution mechanisms from those suggested in the previous chapter (Chapter 3, section 3.5.1), but rather reflect that the presence of water is the main cause for the changes on crystal-chemistry and F and Cl partition coefficients.

Substitution of F and Cl in other anhydrous minerals:

Given that I do not infer a substitution mechanism of F and Cl incorporation into the olivine with the two olivines (anhydrous: CC01#8kb4 and hydrous: H3V04) I measured. Nevertheless, it could be noted that from anhydrous to hydrous olivine, F becomes more incompatible while Cl become less incompatible, as it was the case for pyroxene. This trend could be related to water content of the sample or to previously noted crystal-chemistry variation between the two olivines. It has been noted that hydrous olivine was enriched in Fe and depleted in Mg compared to the anhydrous olivine, now Fe^{2+} or Fe^{3+} is a smaller cation than Mg^{2+} . Thus between anhydrous to hydrous olivine, an increase of the M – O distance is expected, which should explain F and Cl partition coefficients difference between the two samples.

In garnet, both F and Cl partition coefficients increase from anhydrous (C4p#25kb) to hydrous (Grt3V4p) samples. This can be related to F and water substitution mechanism, suggested by Valley et al. (1983), where F is incorporated with OH:

$$Si_{Si}^{\times} + 4NaF_{melt} + 4O_{O}^{\times} = V_{Si}^{''''} + 4F_{O}^{\bullet} + SiO_{2melt} + Na_2O_{melt};$$

$$2Al_{Al}^{\times} + 2O_{O}^{\times} + 2NaF_{melt} + 2MeO_{melt} = 2Me'_{Al} + 2F_{O}^{\bullet} + Al_2O_{3melt} + Na_2O_{melt}$$

wherein $Me = Mg^{2+}$, Fe^{2+} . Assuming that Cl can be incorporated the same way, F and Cl partition coefficients are correlated to water content of the samples. This is observed for the two studied samples.

4.4 Conclusion

I reported F and Cl partition coefficients between minerals (orthopyroxene, clinopyroxene, olivine, garnet, amphibole) and hydrous basaltic melt, and between phlogopite and hydrous shoshonitic melt. This study illustrates the complexity of the variations in both trace element and F and Cl partitioning, where both temperature, bulk water content and mineral compositions are variables. Main conclusions are:

- 1. Both temperature and water content strongly influences crystal chemistry of studied minerals.
- 2. The lattice strain models fit to trace element partitioning data.

3. Both changes in melt structure and in mineral composition could influence F and Cl partitioning, as well as partition coefficient for cation trace elements.

Note that for some minerals: olivine, amphibole and especially orthopyroxene, the F and Cl partition coefficients varies more than other trace elements, due to water content and crystal chemistry changes. This could be explained by the fact that, unlike trace elements which are substituted into cation sites, F and Cl are substituted into the oxygen site which highly depends on mineral structure (for instance, M - O distances).

4.5 The role of water molecule on F and Cl behavior in magmas. (paper in preparation)

4.5.1 Introduction

Trace element study of subduction-related volcanic rocks and, more recently, of arc melt inclusions provides fundamental information about melt generation in the sub-arc mantle. Their trace element abundance pattern, enriched in large ion lithophile elements (LILE; e.g. Sr, K, Ba, U, Th, Tatsumi, 1989; Brenan et al., 1995b; Schmidt and Poli, 1998) and depleted in high field strength elements (HFSE, e.g. Ti, Zr, Nb, Hf compared to LILE, light elements B, Be, Li and light rare earth elements), is most likely the results of a metasomatism of sub-arc peridotite, by an H₂O-rich component derived from the subducting oceanic lithosphere (e.g. Elliott et al., 1997; Rapp et al., 1999; Kelemen et al., 2003a; Plank, 2005). A recent study of Mt Shasta melt inclusions shows that fractionation of F and Cl may fingerprint the signature of two different slab-derived components (Le Voyer et al., 2010), which are indistinguishable by commonly used trace elements (Sr, Ba, K₂O). They also show that these signature may reflect the presence of hydrous minerals, amphibole and phlogopite, which are formed by infiltration of fluids from the subducted slab.

The development of element fractionation models to describe the behavior of F and Cl in the mantle wedge requires experimental determinations of F and Cl partition coefficients between lherzolite minerals (olivine, orthopyroxene, clinopyroxene and garnet), and also hydrous minerals (mantle high pressure mica and amphibole, phlogopite and pargasite, respectively) and hydrous silicate melt, at temperature and pressure comparable to those in the sub-arc mantle. In this contribution, we present new experimental determinations of Cl and F partition coefficients between hydrous basaltic or hydrous shoshonitic melt and mantle minerals: such as olivine, orthopyroxene, clinopyroxene, garnet and also pargasite and phlogopite. The values were compiled from more than 150 measurements in 9 hydrous melting experiments, conducted at 12 and 25 kbars and between 1180 and 1430°C. Hydrous experiments were run with 0.2, 2.6, 4.3, 4.9 and 5.9 wt% of H₂O dissolved in the melt. The abundance F, Cl measurements in run products were done by Cameca IMS 1280 at WHOI using negative secondary ion mode. For volatile-rich minerals as phlogopite and pargasite, measurements were done by both electron microprobe and ion probe.

4.5.2 Materials and Methods

Starting materials

As starting materials, we prepared five synthetic powders: two basaltic, one peridotitic and two shoshonitic gel mixtures, following the procedure of Hamilton and Henderson (1968). Basalts and peridotites were made to be as close as possible to the Gaetani and Grove (1998) basalt-peridotite pair and the shoshonite to be close to the sample B883 of Holbig and Grove (2008) composition (Table 1). Compositions were chosen in order to obtain liquidus saturation of mantle wedge phases, including hydrous phases: Olivine (Ol) + orthopyroxene (Opx) \pm clinopyroxene (Cpx) \pm amphibole (Amp) \pm spinel (Sp) \pm garnet (Grt) concerning the basalt-peridotite pair and Phlogopite (Phlo) \pm Ol \pm Amp, concerning the shoshonite, while maintaining large melt fraction (Table 2). A basalt and a shoshonite mixtures were created without Al₂O₃ in order to introduce water into the systems by gypsite (Al(OH)₃) addition. We conditioned gels for 12 hours at 800°C in a 1 atm gas-mixing furnace, with fO2 about 1 log units above the Quartz-Fayalite-Magnetite buffer, chosen to be close to the oxidation state of sub-arc upper mantle according to Parkinson and Arculus (1999).

Before weighing, every powder was dried in a oven (110°C) for several hours. The basalt-peridotite pair was weighed out the desired proportions: 70:30 wt% respectively. Water content of starting materials was controlled by mixing H₂O-bearing powders to H₂O-free powders. A drop of liquid water (1-3 μ L) was also added in samples H4V4p, H5V4p, H6V04, Grt3V4p, SHO1 and SHO4, to recoup potential gypsite destabilization occuring during arc welding. MgCl₂ and MgF₂ powders were added into the mixtures to achieved about 400 ppm in samples H4V4p, H5V4p, C4p#25kb, Grt3V4p, 1000 ppm in samples SHO1 and SHO4, 4000 ppm in sample H3V04 and H6V04 of Cl₂- or F₂ concentration level and 4wt% of Cl₂- in sample CC4#7b (corrected from Mg content, see Dalou et al., 2011). The MgO increase that corresponds to 4000 ppm of volatile doping is less than 0.26 wt%. Powders were doped to the 100 ppm concentration level with a suite of trace elements that were added to powders as a multi-element solution (1000 ppm, 0.5 M (HNO₃)⁻ dilution). Element concentration in the final mixture was approximately 100 ppm (Li, B, Be, As, Sr, Sc, La, Eu, Gd, Ho, Lu, V, Hf, Zr, U, Th), except 1000 ppm for Pb. Trace elements have been chosen to minimize molecular and isotope interferences during SIMS analyses. Each mixture was then grinded in an agate mortar with ethanol for 45 min. In order to promote cpx growth, cpx seeds (Table 1) were added to the basalt-peridotite mixture in experiments CC4#7b and H3V04.

	Basalt	Peridotite	Hydrous	Hydrous	Cpx seeds	Shoshonite
			basalt	peridotite		
SiO_2	47.70(47)	45.97(47)	46.10(45)	38.83(38)	53.20(60)	46.20(45)
TiO_2	0.62(2)	0.18(1)	2.27(7)	0.29(1)	0.57(6)	1.06(3)
Al_2O_3	19.05(21)	14.76(16)	$\sim 7.4^*$	$\sim 12.1^a$	5.62(30)	12.01(13)
$\mathrm{Cr}_2\mathrm{O}_3$	0.12(0.3)	0.47(1)	0.10(0.2)	0.31(0.7)	1.07(20)	ND
FeO^*	7.82(8)	7.54(7)	7.38(7)	6.24(6)	3.12(11)	9.89(10)
MnO	0.15(0.3)	0.13(0.3)	0.14(0.3)	0.11(0.2)	0.07(6)	0.16(0.2)
MgO	10.49(3)	37.79(11)	$7.32(2)^{b}$	32.24(9)	15.60(30)	10.00(3)
CaO	11.75(35)	3.21(10)	13.09(39)	3.04(9)	19.20(40)	11.50(26)
Na_2O	2.35(5)	0.33(1)	0.43(1)	0.19(4)	ND	3.10(7)
K_2O	0.08(0.2)	0.03(0.1)	0.60(2)	0.16(5)	2.11(13)	4.14(12)
P_2O_5	0.01(0.02)	0.03(0.1)	ND		ND	1.22(3)
${\rm H}_2{\rm O}$			$\sim 7.8^*$	$\sim 6.4^a$		
Total	100.13	99.99	100	100	100.56	99.28

Table 4.5.1: Composition of starting materials.

Al-free powder compositions are not presented. $Al(OH)_3$ were added so as to complete Al_2O_3 contents of compositions presented here as Hydrous basalt and Hydrous peridotite. Those two compositions were calculated after the weighting and the addition of $Al(OH)_3$ in Al-free basalt and peridotite. ^{*a*} Because $Al(OH)_3$ was added by weight, these concentrations are not precise.

 b MgO of basalt is low to allow the addition of $\rm MgF_2$ and $\rm MgCl_2.$

Other presented composition were analyzed by ICP-AES on basalt and peridotite powder and by electron microprobe for cpx seeds. Units in parentheses represent one standard deviation. Standard deviations were determined from analytical error compared to the standard BHVO-1. (FeO* total Fe as FeO). ND: not determined.

Experimental procedure

Experiments were conducted at conditions ranging from 12 to 25 kbars and from 1180 to 1370°C using $\frac{3}{4}$ and $\frac{1}{2}$ inch piston-cylinder apparatus, for duration of 4 to 6 days (Table 2). Experimental procedure and used assemblies are described in details in Dalou et al. (2011). In this study, MgO crushable pieces were replaced by hexagonal boron nitride (hBN) pieces and we used a double capsule Au₈₀Pd₂₀, instead of the graphite slice. A thin saphire slice was put between the AuPd capsule and the thermocouple point to avoid reactions. In order to prevent the Fe loss, AuPd capsules were saturated in Fe before experiments. Conditioning Au₈₀Pd₂₀ inner an outer capsules for experiments was done by packing capsules with the basalt used in high-pressure experiment mixtures. Capsules were placed into a pyrophyllite support, prepared for each size of capsules, and hanged in the hotspot of a vertical gas mixing furnace (LMV), using loops of Pt wire passing thought four holes in the middle of the part. The whole is hold at 1250°C, with fO_2 controlled at 1 log unit below the FMQ

buffer, for 72 hours. To not to damage capsules, we decided not to break the silicate glass. We put it directly in a HF bath during 48 hours on a heating plate at 90°C and then in a distilled water bath under ultrasounds. Finally, capsules were cleaned in a HNO_3^- bath at 60°C to dissolved SiF precipitate and rinse with distilled water. Then capsules were dried in an oven at 110°C and inspected under a binocular. This procedure allows the perfect dissolution of basaltic melt, but revealed that F polluted the metallic capsules (up to several percents). Conditioning of AuPd capsule minimized Fe loss from the sample but like presented in Table 2, it sometimes produced Fe gain from the capsule to the sample.

The outer capsule was filled up with dried and grinded olivine (San Carlos, $\sim 10 \ \mu m$) and the inner capsule contains the starting material. We measured 238 ± 1 ppm of water content in the outer olivine in sample H3V04 by SIMS. This water content is negligible compared to percents we put in the sample powder. Sample H5V4p was double-polished and analyzed by the FTIR of the 'Laboratoire Magmas et Volcans'. Less than 100 ppm of CO₂ was measured.

Analytical procedure

Analytical procedure for major element analyzes on electron microprobe of the LMV is described in Dalou et al. (2011), for Ol, Opx, Cpx, Sp, Grt and quenched hydrous melt. Phlogopites and amphiboles were analyzed with a beam current of 15 nA with a defocused beam of 10 μ m. Fluorine, chlorine and water abundances were determined at Woods Hole Oceanographic Institution with a Cameca IMF 1280 ion probe following the procedure described in Rose-Koga et al. (2008) and Shimizu et al. (2009), using a Cs⁺ primary beam, with the same settings and standards used in Dalou et al. (2011). During analyses, initial primary beam intensity of ~1.43 nA was decreased to 520 nA for volatile-rich phases as phlogopite, amphibole and melts.

For trace elements, LA-ICPMS analyses analyses were carried out on an Agilent 7500 cs ICP-MS coupled to a 193nm Resonetics M-50E laser ablation system at the Laboratoire Magmas et Volcans. The laser wavelength was 193 nm with maximum output energy of 8 mJ. We used a laser pulse frequency of 2 Hz with a 5 ns pulse. The beam diameter was between 15 and 20 μ m. Seventeen masses were collected with an integration time of 30 ms per mass: ⁷Li, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁸⁸Sr, ⁹⁰Zr, ¹³⁹La, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶⁵Ho, ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb, ²³²Th, ²³⁸U, except 10 ms for ²⁸Si and ⁴⁴Ca. Silica abundance measured on electron microprobe was used as internal standard. Detailed procedure can be found in Hammouda et al. (2010); Gannoun et al. (2011); Dalou et al. (2011).

Run	Ь	H	Duration	H ₂ O ^a bulk	H_2O^b melt	Run proc	lucts (%						r^2	Fe
	(kbars)	(0°C)	(days)	(wt%)	(wt%)	Olivine	Opx	Cpx	Garnet	Amp	Mica	Melt	(%)	$\operatorname{exchange}^{c}$
CC4#7b	12	1310	6		0.2			37.1	32.3			30.6	11.0	-1.23
H3V04	12	1240	5	3	2.6	13.3	20.0	51.2				15.5	28.6	+ 0.32
H4V4p	12	1180	2	5.4^{*}	4.3		21.5			33.5		45.0	1.9	- 0.01
H5V4p	12	1190	5.5	5.4^{*}	4.9		21.4	14.2				64.4	2.4	- 0.02
H6V04	12	1200	4	6.1^{*}	5.9		11.0			79.2		9.8	24.5	- 2.06
C4p#25kb	25	1430	2		0.8			2.0	43.7	32.8		13.4	0.01	0.9
Grt3V4p	25	1370	4.5	*	1.6		14.5	55.5	22.2			7.8	<i>p</i> -	ı
SH01	12	1300	4.5	*	4.3	5.2					3.2	91.6	5.52	+ 2.0
SHO4	12	1230	9	*	4.8					4.3	26.1	69.69	6.5	+ 1.64

Table 4.5.2: Experimental conditions and phase assemblages.

Abbreviations used: Opx, orthopyroxene; Cpx, clinopyroxene Amp, amphibole; Melt, quenched basaltic melt.

 r^2 is the sum of weighted squared residuals from phase proportions calculations, modified from Albarède and Provost (1977). The calculation had to take account of F, Cl and H₂O addition to the starting materials (that diluted the initial element concentrations). The uncertainties linked to doping processes increase the r^2 .

^a Water in the starting materials put under the form of gypsite. *Add of one drop of liquid water $(1-3 \ \mu L = \sim 12 \text{wt}\%)$, main part of this water evaporates during welding. ^b Concentration of H₂O dissolved in the melt, measured by the SIMS 1280 of WHOI. ^c Fe exchange is the difference between the FeO content of the bulk composition used in the starting material and the FeO in the sample bulk composition as determined by the mass balance calculation, in relative weight percent. Positive value indicates apparent Fe gain, while negative value indicates apparent Fe loss ^d Mass balance of sample Grt3V4p failed to converge, apparently because of clinopyroxene composition. We assume that the measured clinopyroxenes compositions were far from the equilibrium. Clinopyroxenes of this sample are too small to be analyzed with SIMS or LA-ICPMS.

4.5.3 Results

Textural description of experimental samples

The Figure 4.5.1 shows the back-scattered electron images (BSE) of representative samples. Generally crystals accumulate in one side of the capsule, while quenched melt segregates from grains and forms a separate volume. In all runs melt forms a homogeneous quenched pool. The degree of crystallization in runs varies from 26.9 to 92.2%, and the size of grains varies from a run to another. All runs produce quenched melt. The basaltic system runs always produce orthopyroxene, while the shoshonitic system runs produce mica. All crystals forms polyhedral grains, except some clinopyroxene (cpx) are grown around orthopyroxene crystals showing reaction overgrowth. Often cpx dendrites are observed at the boundary between crystallized part and quenched melt part.Lastly, the grain sizes are large enough (> 50 μ m, except for H5V4p and Grt3V4p, > 30 μ m; see Figure 4.5.1 a) and b) for analyses by SIMS and LA-ICPMS.

The mineral assemblage varies from one run to another because of P-T condition and volatile element $(H_2O, F, and Cl)$ abundance of the experiments. Olivine is found only in 12 kbars experiments, as previous hydrous experiments from a primitive nepheline basanite composition show lack of olivine saturation in the experiments above 25kbars (Adam and Green, 2006). Specifically, olivine is present in H₂O-poor samples, and is big (> 50 μ m) euhedral crystals. Clinopyroxene is found in samples without amphibole, because experimental temperature was too high to stabilized amphibole. Garnet $(< 30 \ \mu m)$ forms above 25 kbars, and is evenly distributed in a capsule. Amphibole have crystallized at unexpected conditions (at 1180 and 1200 °C in the basaltic system and 1230°C in the shoshonitic system), in the temperature condition higher than a typical stability of amphibole. In previous experiments, F in magma stabilized alkali amphibole to higher temperatures (Ferguson, 1978), and possibly to higher pressure. It forms huge euhedral crystals (two spliced crystals of > 100 μ m, Figure (4.5.1 b) in the crystallized part of the capsule; sometimes, it forms dendritic crystals of $20 - 30 \ \mu\text{m}$, in the middle of the melt, likely formed during the quench. Phlogopite stability is enhanced to higher pressure than in the experiments by Holbig and Grove (2008), in which no phlogopite was found at pressure > 10 kbars. As in the case for amphibole, F increases photopite stability to higher P-Tconditions (Harlow, 2002). In my samples, phlogopite crystals form euhedral sheet-form crystals, and sometimes contain lamellar structure, as shown in Figure 4.5.1 c). In many experiments, mineral grains are concentrated at the opposite side from quenched melt.

Equilibrium considerations

From several lines of observations, we conclude that close equilibrium conditions were attained in the experiments with 4 to 5 days of run durations. Mineral texture shows 1) polygonal shapes of crystals



Figure 4.5.1: Back-scattered electron images of hydrous samples in the basaltic (a and b) and shoshonitic systems. Experimental temperature conditions (P = 12 kbars) and water content dissolved in the melt are indicated above each image. Samples are a) H3V04 and an enlarged section of the charge is shown on the right panel, b) H6V04 and, c) SHO4. Abbreviations used: Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Amp, amphibole; Phlo, phlogopite mica and Melt, quenched melt. White part is the metal capsule noted as Fe-AuPd, *i.e.* AuPd with some iron. In the outer capsule, recrystallized olivine is visible. Mineral grains have > 30 μ m diameter, which is appropriated for SIMS and LA-ICPMS measurements.

suggesting equilibrium growth (Fig. 4.5.1), 2) the lack of detectable compositional zoning in crystals, 3) the compositional homogeneity of melt judging from small standard deviations of replicate analyses (Table 4.5.3). In addition, a large melt fraction in the charge promotes equilibration and crystal growth. Major element chemical compositions of minerals and melt are close to an earlier work (samples B333, B305, B304, B330 and B329) in which the attainment of equilibrium was demonstrated via reversal experiments (Gaetani and Grove, 1998). However, there are some compositional deviations in our experiments (samples H3V04, H4V4p, H6V04 and particularly H5V4p). In such cases, the differences are caused by variable water content, temperature and temperature gradient within the sample charges.

The attainment of chemical equilibrium is also inferred by comparing a Fe-Mg exchange coefficient between olivine and melt, $Ol/Melt Kd_{Fe-Mg} = (Ol Fe^{2+}.Melt Mg) / (Melt Fe^{2+}.Ol Mg)$, with that of a experimentally calibrated value (Roeder and Emslie, 1970; Toplis, 2005). The $Ol/Melt Kd_{Fe-Mg}$ value of a dry sample (CC01#8kb4, Dalou et al., 2011) is 0.31, while the predicted value is 0.33 (± 0.03). For a wet sample, the value is 0.30, for H3V04, and the predicted value is 0.29 (± 0.03). The Fe-Mg exchange coefficients of orthopyroxene and clinopyroxene against melt are compared to those obtained by Gaetani and Grove (1998). The Kd values for the volatile-poor experiments (H3V04 and Grt3V4p, (0.25) and (0.32) are similar to those of (Gaetani and Grove, 1998, (0.30) to (0.34) for orthopyroxene, and they vary from 0.29 to 0.39 for clinopyroxene ((Gaetani and Grove, 1998, 0.32 to 0.35)). Nevertheless, among volatile-rich samples (containing ¿ 6 wt% of total volatile), Kds values are highly variable (between 0.18 and 0.52 for orthopyroxene and 0.59 for H5V4p clinopyroxene, no olivine crystallized). Filiberto et al. (2010) observed that Kd increase with increasing F content of the melt. They suggested that F complexes with Mg in the melt and thus increases the silica activity of the melt, depresses the liquidus, and changes the composition of the crystallizing minerals. The ^{Opx/Melt}Kd of the sample H5V4p (0.18) is lower than the expected value. This suggests that a significant portion of Fe in melt is ferric, most likely due to the loss of H during the anneal.

Fluorine and chlorine are relatively homogeneous in minerals and melt for all the experiments, with standard deviations less than 5% relative for F and less than 12% for Cl in olivine, opx, cpx, and garnet. High volatile concentration phases show larger standard deviation values (< 12% relative and <17% relative for F and Cl respectively). While these variations are larger than the internal precision of a typical analysis, they are close to external reproducibility (5% for F and 10% for Cl, Le Voyer et al., 2010). In addition, the lithophile trace element partition coefficients are in agreement with previous data at the similar experimental conditions. We conclude that the experiments achieved near equilibrium conditions including F, Cl and trace element partitioning.

Chemical compositions

Analyses of major and minor elements in crystals and quenched melts from experiments are presented in Table 3. Fluorine and chlorine mineral/melt partition coefficients derived from SIMS 1280 measurements and trace elements mineral/melt partition coefficients derived from LA-ICPMS measurements are given in Tables 4 for pyroxenes and 5 for olivine, garnet, pargasite and phlogopite. To achieve reliable on F and Cl concentration measurements, 1) 3 to 10 spots were measured per phase, and 2) data with stable signals (less than 20% signal variation) were selected and used to determine the element abundance. For trace elements, the precision and the accuracy of analyses varied depending upon absolute concentration, crystal size and the presence or absence of other included phases. The quality of measurements was assessed by accordance with mass-balances calculations (calculated total concentration must be within ± 100 ppm of the initial concentrations). Furthermore, the disparity from Onuma diagram identifies minor analytical contamination. The data showing significant deviation from the parabolic trends are excluded.
Sample	Phase	SiO_2	TiO ₂	Al ₂ O ₃	Cr_2O_3	FeO*	MnO	MgO	CaO	Na_2O	K ₂ O	Ĺъ	G	$Total^a$	H ₂ O
H3V04	Melt [4]	45.88(42)	0.71(7)	15.56(20)	0.04(5)	10.13(12)	0.14(3)	10.28(12)	10.94(4)	2.69(10)	0.13(2)			96.5	2.59(1)
	Opx [7]	53.74(11)	0.11(3)	5.25(27)	0.86(5)	7.50(19)	0.16(4)	30.78(22)	1.74(10)	0.07(1)	0.01(1)	I	ı	100.3	0.203(7)
	Cpx [5]	51.04(16)	0.22(3)	6.36(36)	0.94(2)	5.07(27)	0.14(3)	17.30(6)	18.57(24)	0.62(3)	0.001(2)	I	ı	100.3	0.211(2)
	OI [5]	40.36(16)	0.00(0)	0.09(2)	0.04(3)	13.58(9)	0.16(1)	45.78(42)	0.24(2)	0.003(6)	0.003(5)	I	ı	100.5	0.1(2)
H4V4p	Melt [6]	44.95(23)	0.58(7)	13.35(10)	0.04(2)	7.87(16)	0.18(4)	12.75(13)	13.35(25)	1.46(8)	0.09(3)	8.06(9)	0.0190(4)	99.3	4.3(4)
	Opx [6]	53.52(83)	0.08(5)	3.70(66)	0.49(5)	12.16(36)	0.24(3)	27.65(20)	1.87(19)	0.11(2)	0.01(1)	0.18(5)	0.003(5)	100.0	0.95(5)
	Amp [5]	46.78(22)	0.20(7)	10.38(47)	0.63(11)	6.84(11)	0.15(3)	21.10(14)	8.52(33)	2.79(8)	0.10(2)	4.2(1)	0.002(6)	100.0	1.27(2)
H5V4p	Melt [5]	50.92(16)	0.60(4)	14.63(22)	0.04(4)	6.73(17)	0.14(7)	9.30(12)	9.56(11)	2.79(10)	0.17(3)	1.21(4)	0.22(1)	95.8	4.89(2)
	Opx [7]	54.39(34)	0.06(2)	4.93(34)	0.23(8)	4.53(11)	0.18(4)	34.41(19)	1.29(23)	0.08(2)	0.005(9)	0.04(2)	0.003(3)	100.2	0.49(1)
	Cpx [8]	49.43(34)	0.20(4)	6.01(32)	0.30(6)	6.80(36)	0.14(3)	15.72(17)	20.16(19)	0.88(4)	0.01(2)	0.07(1)	0.003(3)	99.7	0.54(1)
H6V04	Melt $[7]$	43.69(19)	0.59(6)	12.44(12)	0.11(3)	7.71(14)	0.13(4)	14.84(13)	12.65(16)	1.81(9)	0.09(3)	6.8(1)	0.036(6)	98.1	5.9(3)
	Opx [10]	54.58(61)	0.05(3)	3.83(62)	0.89(17)	8.42(11)	0.21(2)	31.03(45)	1.25(8)	0.05(1)	0.007(6)	0.10(4)	0.01(1)	100.3	1.2(2)
	Amp [8]	45.79(20)	0.21(4)	11.12(22)	0.98(12)	5.04(13)	0.10(3)	21.61(23)	9.40(18)	3.09(6)	0.12(2)	3.84(6)	0.005(5)	99.7	4.4(1)
Grt3V4p	Melt $[5]$	53.04(44)	1.28(6)	15.01(24)	0.04(3)	6.51(11)	0.11(5)	6.77(4)	7.46(34)	3.51(15)	0.51(5)	0.77(2)	0.44(2)	95.0	1.582(8)
	Grt [12]	41.24(35)	0.39(18)	23.04(70)	0.37(9)	9.92(25)	0.23(3)	19.45(48)	4.80(57)	ND	ND	ı	ı	99.5	0.166(2)
	Opx [4]	53.87(45)	0.10(5)	6.32(42)	0.36(6)	8.64(19)	0.14(3)	28.25(11)	1.71(7)	0.40(1)	0.01(1)	0.008(7)	0.001(1)	99.8	0.45(1)
	Cpx [4]	52.91(26)	0.24(2)	9.23(52)	0.31(8)	7.31(4)	0.15(5)	19.35(40)	8.90(22)	1.66(6)	0.002(4)	0.045(4)	0.003(3)	100.1	0.070(6)
SHO1	Melt [4]	38.78(33)	0.05(6)	10.03(8)	ND	6.56(15)	0.98(2)	19.37(23)	10.30(23)	2.30(9)	2.35(17)	6.97(8)	2.88(31)	97.4	4.31(3)
	Phlo [8]	42.36(51)	0.48(4)	12.75(19)	ND	1.54(5)	0.00(0)	26.96(28)	0.05(4)	0.59(2)	10.36(10)	8.20(8)	0.24(1)	100.0	1.2(1)
	Ol [6]	41.37(22)	0.03(3)	0.07(2)	0.02(1)	8.72(9)	0.20(4)	49.84(28)	0.14(3)	0.01(1)	0.04(4)	I	I	100.4	0.016(1)
SHO4	Melt $[5]$	40.93(10)	1.12(5)	10.02(14)	0.03(4)	9.30(15)	0.15(5)	15.55(12)	12.71(14)	2.61(10)	0.86(6)	6.15(5)	0.98(2)	97.6	4.8(2)
	Phlo [2]	41.60(9)	0.48(3)	12.48(10)	0.06(2)	2.69(11)	0.02(2)	25.60(18)	0.17(3)	1.53(6)	9.09(23)	8.10(6)	0.072(5)	98.4	4.2(2)
	Amp [3]	44.25(20)	1.24(5)	10.22(8)	0.02(1)	8.12(14)	0.16(4)	18.47(57)	9.89(19)	2.92(24)	0.77(13)	4.35(10)	0.017(1)	99.0	-
Numbers in	brackets in	dicate numb	er of individ	lual electron	microprobe	analyses inc	luded in a	verage. (FeO	ı* total, assu	ming all Fe	as FeO). Nı	umbers in p	arentheses re	presents o	ne standard
deviation in	terms of le	ast units cite	ed. ND : not	t determined.											

Table 4.5.3: Electron microprobe analyses of experimental run products.

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^a [New total] = [total of oxides, F, and Cl] – [F*0.42+C]*0.23, where F and Cl are concentrations measured by SIMS].

	Orthopyroxene						Clinopyrox	ene	
Run	CC4#7b	H3V04	H5V4p	H6V04	C4p#25kb	Grt3V4p	CC4#7b	H3V04	H5V4p
D_F	0.123(4)	0.0563(3)	0.042(4)	0.021(31)	0.0158(11)	0.0462(9)	0.153(4)	0.114(2)	0.083(4)
D_{Cl}	0.0021(4)	0.0203(6)	0.037(2)	0.07(1)	0.0022(2)	0.0064(5)	0.0086(5)	0.0113(9)	0.0145(8)
D_{traces}									
\mathbf{Li}	0.27(3)	0.136(16)	0.17(1)	0.25(1)	0.32(3)	0.25(3)	0.271(3)	0.145(13)	0.265(3)
\mathbf{Sc}	0.87(4)	0.83(14)	0.624(3)	0.64(2)	0.44(3)	0.33(2)	1.16(4)	1.27(26)	1.24(2)
\mathbf{V}	1.93(9)	0.16(4)	0.0218(1)	0.50(4)	1.11(1)	0.39(3)	3.31(6)	0.71(16)	0.084(9)
\mathbf{Cr}	4.6(2)	12(3)	4.8(6)	11.11(4)	4.4(5)	4.3(5)	6.54(2)	13(2)	3.45(35)
Со	1.10(4)	1.34(7)	1.7(1)	1.94(3)	1.14(8)	0.89(6)	0.84(2)	0.55(6)	0.76(4)
\mathbf{Sr}	0.0028(8)	0.015(7)	0.006(2)	0.02(4)	0.0023(1)	0.00134(8)	0.083(37)	0.14(4)	0.116(4)
\mathbf{Zr}	0.025(5)	0.04(1)	0.021(6)	0.019(5)	0.015(0.3)	0.0063(6)	0.095(23)	0.15(3)	0.157(8)
La	0.0012(2)	0.004(9)	0.002(1)	0.0044(9)	0.0102(2)	0.0008(3)	0.054(18)	0.049(2)	0.094(8)
$\mathbf{E}\mathbf{u}$	0.026(1)	0.05(2)	0.021(6)	0.022(7)	0.015(2)	0.0054(2)	0.273(6)	0.31(4)	0.411(7)
\mathbf{Gd}	0.047(1)	0.06(1)	0.029(7)	0.036(7)	0.021(3)	0.0127(7)	0.322(27)	0.36(5)	0.443(8)
Но	0.102(2)	0.10(2)	0.058(8)	0.047(9)	0.045(5)	0.018(1)	0.467(6)	0.46(6)	0.49(1)
$\mathbf{L}\mathbf{u}$	0.186(4)	0.15(4)	0.107(8)	0.083(3)	0.079(9)	0.043(3)	0.461(9)	0.40(4)	0.41(1)
$\mathbf{H}\mathbf{f}$	0.039(2)	0.07(3)	0.036(7)	0.04(1)	0.0075(1)	0.009(1)	0.15(5)	0.18(2)	0.25(2)
\mathbf{Pb}	0.002(0.04)	0.12(2)	0.0018(7)	0.083(5)	0.007(3)	0.0067(3)	0.002(1)	0.36(2)	0.048(8)
\mathbf{Th}	0.0012(1)	0.007(9)	0.0030(4)	0.0058(9)	0.007(3)	0.0011(2)	0.03(6)	0.014(2)	0.068(7)
U	0.001(0.0004)	0.007(9)	0.0030(3)	0.0061(8)	0.008(3)	0.0015(6)	0.03(6)	0.0113(6)	0.06(1)

Table 4.5.4: Pyroxene-melt partition coefficients $D_i^{pyroxene-melt} = c_i^{pyroxene}/c_i^{melt}$ in run products. Fluorine and chlorine were measured in run products by SIMS 1280, and other trace elements were measured by LA-ICPMS.

Numbers in parentheses represents one standard deviation in terms of least units cited.

	Olivine		Garnet		Pargasite		Phlogopite	
Run	CC01#8kb4	H3V04	C4p#25kb	Grt3V4p	H4V4p	H6V04	SHO1	SHO4
D_F	0.1164(63)	0.0045(1)	0.0123(4)	0.166(2)	0.36(7)	0.63(9)	1.2(1)	1.3(2)
D_{Cl}	0.0012(1)	0.0043(4)	0.0029(1)	0.087(4)	0.12(4)	0.38(8)	0.10(1)	0.08(2)
D_{traces}								
\mathbf{Li}	0.215(16)	0.307(6)	0.015(8)	0.033(7)	0.41(3)	0.29(4)	0.18(3)	0.19(3)
\mathbf{Sc}	0.196(13)	0.33(3)	6.81(16)	1.59(8)	0.5(1)	0.75(5)	0.16(1)	0.097(6)
\mathbf{V}	0.415(36)	0.06(3)	2.13(18)	0.30(5)	1.1(2)	0.74(5)	0.55(3)	0.11(1)
\mathbf{Cr}	1.1(2)	1.3(5)	10.6(11)	3.2(3)	10(3)	9.96(3)	1.85(5)	1.71(7)
Со	3.00(4)	4.58(1)	1.24(9)	0.72(12)	2.0(6)	0.81(6)	0.34(1)	0.51(6)
\mathbf{Sr}	0.0007(3)	0.001(1)	0.0009(3)	0.007(5)	0.028(2)	0.036(6)	0.34(2)	0.25(1)
\mathbf{Zr}	0.0017(3)	0.005(2)	0.033(3)	0.064(14)	0.05(5)	0.017(52)	0.020(6)	0.0061(2)
La	$0.0006(4)^a$	$0.002(1)^{a}$	0.0007(3)	$0.005(3)^{a}$	0.012(63)	0.017(52)	0.0027(7)	0.0013(4)
\mathbf{Eu}	0.003(1)	0.005(4)	0.029(2)	0.098(13)	0.12(3)	0.16(4)	$0.072(9)^{b}$	$0.0121(5)^{b}$
\mathbf{Gd}	0.006(3)	0.012(8)	0.57(5)	0.18(2)	0.13(2)	0.18(5)	$0.010(1)^{b}$	$0.0055(7)^{b}$
Ho	0.013(4)	0.018(8)	2.37(20)	0.64(2)	0.17(1)	0.22(4)	0.0018(5)	0.0.0018(5)
$\mathbf{L}\mathbf{u}$	0.033(4)	0.05(2)	5.9(5)	1.5(2)	0.17(1)	0.20(4)	0.0024(6)	0.0021(6)
$\mathbf{H}\mathbf{f}$	0.004(2)	0.008(4)	0.031(3)	0.06(1)	0.010(4)	0.010(4)	0.028(9)	0.0082(4)
Pb	0.0004(2)	0.04(4)	0.0001(1)	0.014(7)	0.3(3)	0.13(4)	0.21(3)	0.1(1)
$\mathbf{T}\mathbf{h}$	0.0004(3)	0.003(1)	0.0006(4)	0.008(5)	0.004(66)	0.005(17)	0.0031(1)	0.0039(9)
\mathbf{U}	0.0009(9)	0.0035(6)	0.008(1)	0.011(7)	0.005(71)	0.007(17)	0.0047(3)	0.003(1)

Table 4.5.5: Mineral-melt partition coefficients $D_i^{mineral-melt} = c_i^{mineral} / c_i^{melt}$ in run products. Fluorine and chlorine were measured in run products by SIMS 1280, and other trace elements were measured by LA-ICPMS.

Numbers in parentheses represents one standard deviation in terms of least units cited.

 a We suspect a contamination of melt during olivine analysis. This appears on the olivine Onuma diagram.

 b We assess that these values are affected by variations of oxygen fugacity, as explained in the text.

Olivine

Olivine synthesized in the dry experiment is Fo_{88} (CC01#8kb4, Dalou et al., 2011) and Fo_{85} in the wet system (this study). We compared our results with those of Gaetani and Grove (1998) for runs at similar P - T conditions and close major element starting composition. The difference of the olivine compositions may reflect the influence of the high F content in cation activities in melt (1.8 wt%, Filiberto et al., 2010). All olivine compositions are stoichiometrically balanced (Table 4.5.6). On Figure 4.5.2, we compare our data with recent literature data from McDade et al. (2003b) and Zanetti et al. (2004). While general patterns of trace elements partition coefficients are similar, our data agree with those of literature only for Li, Co, Sr, Zr, Ho, and Lu. Other elements, such as V, Cr, La, Eu, Pb, Th, and U, differ significantly from the previous studies. It is shown that a range of the partition coefficients between olivine and melt (e.g. $D_{Cr}^{Ol/melt}$ ranges from 0.23 to 0.46, from 3 to 14 GPa respectively), correlates strongly with pressure (Taura et al., 1998). Here in the figure 4.5.2 the reported partition coefficients were obtained at similar P conditions (15 kbars, (McDade et al., 2003b) and 14 kbars, (Zanetti et al., 2004)). The disparity therefore must be due to different temperature and bulk compositions used in these experiments. For example, CC01#8kb4 data is comparable to those of (McDade et al., 2003b), whose bulk composition is peridotitic. The hydrous sample (H3V04) is comparable to that of (Zanetti et al., 2004), whose experiment was conducted at 1050°C, instead of 1240°C in our case. Lastly, it should be noted that there are significant changes of $D^{Ol/melt}$, specifically F, V, Pb, for dry and wet experiments. The and U are significantly more compatible in this study compared to those from McDade et al. (2003b). These elements are very difficult to measure, and the large error bars are due to the poor ion counts for both SIMS and LA-ICPMS on these elements. While we did not find analytical problems, such as misplaced beam spot, compositional zoning, and inclusions, we consider the partition coefficients of these elements (and Pb) reported here as consultative values. In literature, these partition coefficients show a broad range of variation (approximately factor of 20 or more in opx and cpx, Figures 4.5.3 and 3.7.3). For olivine, McDade et al. (2003b) provides U and Th partition coefficients from one olivine measurement in one experiment, and overall, two sets of U, Th partition coefficients are available.



Figure 4.5.2: Olivine/melt partition coefficient obtained in this study, Dalou et al. (2011) (solid curves), and previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the standard deviations of measurements. Data of U and Th are only from McDade et al. (2003b); the large field is due to reported error bars in respective studies. The elements are ordered in their atomic numbers.

Orthopyroxene

The experiments produced aluminous orthopyroxenes with variable fractions of enstatite (from 0.85 to 0.91), ferrosilite (from 0.03 to 0.08), and jadeite (from 0.002 to 0.02) components. Their compositions vary with changes of temperature, pressure and water content of experiments, and the values are closed to those of Gaetani and Grove (1998). Their Mg numbers (Mg# = 100 Mg/(Mg + total Fe)), varying from 87.6 to 91.6, are presented in the Table 4.5.6. The some values are lower than those of Gaetani and Grove (1998), such as more ferreous orthopyroxenes found in H4V4p. While majority of orthopyroxenes have a good stoichiometry (Table 4.5.6), the orthopyroxenes of H4V4p and Grt3V4p have the deviation of stoichiometric sum of the cations > 0.5%. These data will be excluded from the rest of the discussion.

Our trace element data are in an agreement with literature data (Figure 4.5.3; McDade et al., 2003b,a; Adam and Green, 2006; Frei et al., 2009; van Kan Parker et al., 2010). In general, many of trace element partition coefficients decrease with the increasing pressure and temperature. Some elements show more variation than others. Notably, V and Cl vary 88 and 35 fold respectively. Other elements show moderate variation (7 to 10 fold changes for F and Sr, and less than 4 times variations for the rest of elements). As it was the case for olivine, partition coefficients for Pb, Th, U are poorly measured with large uncertainties and variations.



Figure 4.5.3: Orthopyroxene/melt partition coefficients obtained in this study and Dalou et al. (2011) (solid curves) and reported in previous work (grey field, references in the legend). Hatched part of the grey field is an extrapolation. Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Clinopyroxene

Clinopyroxenes formed in the experiments are ferreous and aluminous clinopyroxene with variable fraction of diopside (from 0.33 to 0.56), enstatite (from 0.17 to 0.49), ferrosilite (from 0.05 to 0.10). Variable Al₂O₃ abundance is reflect on a range of Ca-tschermaks (from 0.04 to 0.10), jadeite (from 0.01 to 0.06) and eskola (0.001 to 0.06) components. In general, their compositions are close to those of Gaetani and Grove (1998). However, clinopyroxene in H5V4p sample is more ferreous, thus lower Mg# (Table 4.5.3), than the clinopyroxenes of Gaetani and Grove (1998). Majority of clinopyroxene oxide compositions are consistent with pyroxene stoichiometry (Table 4.5.6). As in the case for orthopyroxene, clinopyroxenes of Grt3V4p has questionable stoichiometry (the sum of cations < 4, maybe due to Ca-Eskola component that lowers sum of cations due to its stoichiometry $Ca_{0.5}\square_{0.5}AlSi_2O_6$) and the mass balance of this sample failed to converge. Clinopyroxene data of Grt3V4p are excluded from the rest of the discussions.

Compared to recent literature data, such as Gaetani et al. (2003); McDade et al. (2003b,a); Adam and Green (2006), our clinopyroxene/melt trace element partition coefficients are in a good agreement. Pb partition coefficients have to be considered as auxiliary, because trace element concentrations did no add up to recover the initial Pb abundance by mass balance. Except for sample H5V4p, for which about 1000 ppm were recover after mass balance, the recovery is only about 10% of the starting Pb composition. Therefore, Pb partition coefficients for some samples are in disagreement with previous work. As shown by Figures 4.5.3 and 4.5.4, Pb partition coefficients between pyroxenes and melt vary between samples. It is not clear if D_{Pb} variation is caused by water content or temperature, or just due to an analytical issue.



Figure 4.5.4: Clinopyroxene/melt partition coefficients obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the standard deviation of several measurements.

Water abundance measurements in pyroxenes found high concentrations in pyroxenes, especially in orthopyroxenes: from thousands of ppm to 1.2 wt% in the orthopyroxene of sample H6V04. This unusually high concentration cannot be attributed to an analytical issue since the 3 carried out measurements were reproducible within less than 2000 ppm variation. As far as we know, there is no published work studied water solubility in orthopyroxene in a natural system, such as ours. Nevertheless, the review by Mierdel et al. (2007) shows that water content in orthopyroxene at pressure of 10 to 35 kbars commonly reach thousands of ppm, even more than 8000 ppm (Bell et al., 1995). Furthermore, they suggested that water solubility increases with Al content of orthopyroxene. In the same time, the thermodynamic models suggest that water solubility increases with the decreasing temperature (Mierdel and Keppler, 2004; Mierdel, 2006; Keppler and Bolfan Casanova, 2006). Those models even reach water solubility of about 2 wt% in 'Al-saturated enstatite' that refers to enstatite in equilibrium with forsterite and the stable aluminous phase, *i.e.* MgAl₂O₄ spinel or pyrope, at temperature of 700°C, and at pressure between 10 and 20 kbars. Those models can be applied to our pyroxenes since the decreasing relation between Al₂O₃ and temperature is observed between studied pyroxenes.

With regards to those studies, 1000 to 6000 ppm of water content we found in orthopyroxene and clinopyroxene is commonly found in pyroxenes. Concerning the measured 1.2 wt% of water in orthopyroxene, this value can be plausible. Nevertheless, the high water abundance is equally possibly due to amphibole lamellae and/or inclusions in these pyroxenes. However, the mineral stoichiometry shows that there can not be significant amphibole component; CaO and Al_2O_3 are too low, while SiO₂, MgO and FeO are too high to accommodate amphibole stoichiometry.

Garnet

The synthesized garnet is a mixture of three dominant component: pyrope, grossular and almandine ($Py_{67}Gr_{11}Alm_{20}Uv_{01}$). These garnets are less calcic and more ferrous and magnesian than garnets obtained by Gaetani et al. (2003) and Green et al. (2000), but these are formed at lower temperature (between 1200 and 1230 °C than the one in our experiments (1370 and 1430 °C). The stoichiometry of the synthesized garnets are balanced (Table 4.5.7).

A comparison of garnet/melt trace element partition coefficients from this study with those from the literature (Figure 4.5.5; Hauri et al., 1994; Johnson, 1998; Gaetani et al., 2003; Pertermann et al., 2004; Adam and Green, 2006) show that in the dry system, our data are in very good agreement with the literature data, while under hydrous conditions, partition coefficients for the REEs are systematically, although not significantly, lower in our experiments. The variation in the Cpx/melt partition coefficient for REE, corresponding to those of Green et al. (2000), is likely attributable to experiment-

formulae.
structural
clinopyroxene
and
orthopyroxene
Olivine,
Table $4.5.6$:

	OIIVIII	e				Orthop	yroxene				Clinop	yroxene	
run —	CC01#8kb4	H3V04		CC4#7b	H3V04	H4V4p	H5V4p	H6V04	Grt3V4p	CC4#7b	H3V04	H5V4p	Grt3V4p
Si	1.000	1.000	Si	1.867	1.869	1.906	1.867	1.901	1.884	1.872	1.849	1.829	1.874
Al^{IV}	0.002	0.002	Al^{IV}	0.133	0.131	0.094	0.133	0.099	0.116	0.128	0.151	0.171	0.126
sum T	1.002	1.002	sum T	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Ë	0.000	0.000	Ë	0.002	0.003	0.002	0.002	0.001	0.003	0.005	0.006	0.006	0.006
Al^{VI}	0.000	0.001	Al^{VI}	0.108	0.085	0.061	0.067	0.058	0.145	0.123	0.121	0.091	0.259
Cr	0.003	0.001	Cr	0.026	0.024	0.014	0.006	0.025	0.010	0.026	0.027	0.009	0.009
Fe^{3+}	0.024	0.028	Fe^{3+}	0.019	0.022	0.036	0.013	0.025	0.025	0.014	0.015	0.021	0.022
Fe^{2+}	0.217	0.253	Fe^{2+}	0.175	0.196	0.326	0.117	0.221	0.227	0.129	0.138	0.189	0.195
Mg	1.727	1.690	Mg	1.571	1.596	1.468	1.761	1.611	1.473	1.085	0.934	0.867	1.022
sum M	1.971	1.972	sum M1	1.901	1.925	1.907	1.966	1.967	1.883	1.389	1.241	1.184	1.513
			\mathbf{Mn}	0.004	0.005	0.007	0.005	0.006	0.004	0.004	0.004	0.004	0.005
			Ca	0.079	0.065	0.071	0.047	0.047	0.064	0.567	0.721	0.799	0.338
			Na	0.005	0.005	0.008	0.005	0.003	0.027	0.029	0.044	0.063	0.114
			sum M2	0.089	0.074	0.086	0.058	0.056	0.095	0.600	0.769	0.867	0.456
Total cations	2.985	2.985		3.991	4.000	3.993	4.024	3.997	3.979	3.989	4.010	4.051	3.969
Mg#	87.7	85.7		89.0	88.0	80.2	93.1	86.8	85.4	88.3	85.9	80.5	82.5

 $Mg\# = Mg/(Mg + \sum Fe)$

The Fe³⁺ was calculated assuming Fe³⁺/ \sum Fe = 0.11

Olivine stoichiometry was calculated assuming 3 cations per 4 oxygens. Orthopyroxene and clinopyroxene stoichiometries were calculated assuming 4 cations per 6 oxygens. tal conditions that are at lower temperature and higher pressure (between 3 and 7.5 GPa) than our experiments and consequently to garnet composition variations. Indeed, Green et al.'s X-site garnet (2000) are richer in MgO and poorer in CaO than our garnets. Thus X-site of our garnets are smaller and accommodate less REE than Green et al.'s garnet (2000).



Figure 4.5.5: Garnet/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Amphiboles

The amphiboles are fluor-pargasitic hornblende, following the nomenclature of calcic amphibole of (Leake, 1978, F > 2wt%). In the basaltic system, they show relatively little compositional variation, while the amphibole crystallized in the shoshonitic system has higher Ti, Fe^{2+} , Na, K and lower Cr, Mg than this of basalt (see Table 4.5.7). Amphibole is a trace-element accommodating mineral, including REE, HSFE, LILE (*e.g.* Adam and Green, 2006) and volatile elements. Partition coefficients of these elements are higher than those of other commonly occurring igneous minerals, except for F, which is more compatible in micas than in amphiboles. Most of measured partition coefficients between amphibole and basaltic melt are in agreement with literature data (Figure 4.5.6, comparing with Brenan et al., 1995a; Adam and Green, 2003, 2006). Some disparity can be noticed for Li, Sc, V,

HSFE as Zr, Hf and REE, for which our values are lower. These discrepancies is likely attributable to the amount of Mg in the M4-site (considered to house REE) of amphibole, which is absent from the amphibole of earlier study (Brenan et al., 1995a; Adam and Green, 2003, 2006). Furthermore, our amphiboles are poorer in Ca in the M4-site, and poorer in Ti in the M1–3 sites (assumed to house Hf and Zr) compared to those of previous work (Brenan et al., 1995a; Adam and Green, 2003, 2006). Such compositional differences contribute to a distortion of the amphibole structure, and the M4 and M1–3 sites are smaller than those in previous studies (Mg ionic radius < Ca ionic radius). In consequence, the M4 and M1–3 sites accommodates less REE, and Zr, Hf, in this study than the others. Alternatively, some differences of partition coefficient values could be attributed to changes in activity coefficients of these elements in association with the changes in the degree of melt polymerization. On Figure 4.5.6, we compare our partition coefficients in basaltic system with data obtained from more polymerized melts: andesitic system (Brenan et al., 1995a) and basanitic system (Adam and Green, 2003, 2006).



Figure 4.5.6: Amphibole/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, references in the legend). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

Micas

The micas from experiments are all tri-octahedral phlogopites, with only limited substitutions of di-octahedral components, indeed the sum of cations in octahedral sites is closed to 6 (5.9, see Table

	Gari	net			Amphibole	;		М	ica
run	C4p#25kb	Grt3V4p	-	H4V4p	H6V04	SHO4	-	SHO1	SHO4
Si (Z-site)	2.966	2.962	Si	6.623	6.478	6.475	Si	5.945	5.940
			Al^{IV}	1.377	1.522	1.525	Al^{IV}	2.055	2.060
Al	1.988	1.946	sum T	8.000	8.000	8.000	sum T	8.000	8.000
Fe^{3+}	0.049	0.059							
Cr	0.027	0.021	Ti	0.021	0.022	0.137	Mg	5.640	5.449
Ti	0.015	0.021	Al^{VI}	0.356	0.332	0.238	Al^{VI}	0.054	0.041
sum Y	2.079	2.047	Cr	0.071	0.110	0.002	Fe^{2+}	0.163	0.289
			Fe^{3+}	0.081	0.060	0.099	Fe^{3+}	0.018	0.032
Ca	0.344	0.369	Fe^{2+}	0.729	0.537	0.894	Ti	0.051	0.052
Mn	0.011	0.014	Mg	3.743	3.940	3.630	\mathbf{Cr}	0.000	0.007
Fe^{2+}	0.442	0.535	sum M1–3	5.000	5.000	5.000	Mn	0.000	0.002
Mg	2.145	2.077					sum M	5.926	5.872
sum X	2.943	2.995	Mn	0.018	0.012	0.020			
			Ca	1.293	1.425	1.551	Κ	1.855	1.656
			Na	0.000	0.284	0.429	Na	0.161	0.424
			Mg	0.711	0.617	0.399	Ca	0.008	0.026
			$\mathrm{sum}~\mathrm{M4}$	2.021	2.000	2.000	sum I	2.023	2.106
			Na	0.766	0.563	0.429			
			Κ	0.018	0.022	0.144			
			sum A	0.784	0.585	0.573			
Total cations	7.987	8.004		15.805	15.923	15.942		15.949	15.978
Mg#	81.4	77.8		84.6	88.4	80.2		96.9	94.4

Table 4.5.7: Garnet, amphibole and phlogopite structural formulae.

 $Mg\# = Mg/ (Mg + \sum Fe)$

The ${\rm Fe^{3+}}$ was calculated assuming ${\rm Fe^{3+}}/$ ${\rm \Sigma Fe}$ = 0.11

Garnet stoichiometry was calculated assuming 8 cations per 12 oxygens. Pargasite and phlogopite stoichiometry were determined excluding (OH)-site, assuming that 2 $OH^- = 1 O^{2-}$. Pargasite pfu were calculated with 22 O and phlogopite with 23 O, both assuming 16 cations.

Z is for the tetrahedral site, Y, the octahedral site and X, the dodecahedral site in garnet. T is for tetrahedral site, and M (1 or 2) is for octahedral site in amphibole and micas. I is for the interlayer in micas.

4.5.7). The phlogopites synthesized in my two experiments have similar composition.

Phlogopite easily accommodates Sr, Pb (assumed to be substituted in the interlayer), with partition coefficients of the same order of magnitude as for amphiboles, while other elements, especially REE (assumed to be substituted in the octahedral site), are highly incompatible in phlogopite. Note that Eu and even Gd partition coefficient is abnormally high compared to other REE, by a factor 2 to 30 above La partition coefficient values. This cannot be attributed to an analytical odd effect, since Eu measurements are well reproducible within 8% of maximum variation. Most of measured partition coefficients between phlogopite and basaltic melt are globally in agreement with literature data (Figure 4.5.7, with Green et al., 2000; Adam and Green, 2006). Here, contrary to amphibole case, our data are higher that Adam and Green (2006) data. As it is the case for amphibole, the discrepancy among pholopite partitioning data can be the result of the higher amount of Mg (bigger cation) and the lower amount of small cations as Al, Ti, Cr and Mn in the octahedral site of our phlogopites compared to those of Adam and Green (2006). Thus, in our experiments, phlogopite better accommodates trace elements, such as REE. However, there are no potential model explaining why Sc, V, Cr and Co partition coefficients of our phlogopites are lower than those of Adam and Green (2006). Hypotheses based neither on crystal structure nor the degree of melt polymerization provides coherent explanations.

Also note that F is compatible and Cl is incompatible in the phlogopite. On the contrary, F was less compatible than Cl in the amphibole.

Water measurements in hydrous minerals are presented in Table 2. The measured water content in the amphibole (sample H4V4p, 1.27 wt%) is in a good agreement with the water measured in the amphibole of La Tourette et al. (1995) (1.63 wt% H₂O). For both studies, water dissolved in the melt is 4.3 wt% H₂O. The water content measured in the phlogopite (sample SHO1 and SHO4, 4.3, 4.2 wt% H₂O, respectively) is also in an agreement with the water content in the phlogopite of La Tourette et al. (1995) (4.6 wt% H₂O), for a comparable amount of water dissolved in the melt (4.3, 4.8 and 3.3 wt% H₂O for SHO1, SHO4, and La Tourette et al., 1995, respectively).

4.5.4 Discussion

Trace element partitioning

Observed variation of trace element partition coefficients between minerals and melt is commonly attributable to the mineral structure, and therefore the composition of crystals (e.g. Beattie, 1994; Blundy and Wood, 1994) which changes with experimental pressure, temperature and starting bulk composition. Isovalent cation partition coefficients are fitted into the lattice strain model, which illustrates the strain energy caused by the misfit of a substituent cation into a lattice site, and compared



Figure 4.5.7: Phlogopite/melt partition coefficient obtained in this study (solid curves) and from previous work (grey field, Adam and Green, 2006). Error bars on the solid curves correspond to 1 σ uncertainties based on the variability of analyses.

on Onuma diagrams (Onuma et al., 1968; Brice, 1975; Blundy and Wood, 1994; Wood and Blundy, 1997). Given that the misfit strain energy is largely controlled by crystals, this comparison tests trace element dependence to crystal-chemistry. We applied the lattice strain model to our data, with the intention of evaluate the equilibrium of our crystals and the consistency of our trace element data with literature data at similar experimental conditions. We successfully fitted the lattice-strain model to trace element partition coefficients for the minerals presented in this study, which demonstrates that a set of isovalent elements, here 3+ ions, are incorporated into minerals according to the expected strain model, suggesting near equilibrium growth of our minerals. Onuma diagrams applied to our trivalent cation data are available in supplementary material and the derived best-fit values are presented in Table 4.5.8.

For olivine, lattice strain model is fitted without using Cr^{3+} and V^{3+} , because olivine/melt partitioning of Cr and V can be susceptible to the crystal field effect as explained in Zanetti et al. (2004). Moreover, variable amount of Cr^{2+} and V^{4+} , which we did not measure, can also contribute to disparities of $D_{Cr}^{Ol/melt}$ and $D_{V}^{Ol/melt}$ to a 3+ homovalent elastic strain model Canil and Fedortchouk (2001). Lattice strain parameters, E, the effective Young's modulus for the lattice site, and r_0 , the optimum radius for the lattice site, for our olivines (CC01#8kb4 and H3V04) are in agreement with that of Zanetti et al. (2004), within 35% for E and 0.4% for r_0 of relative difference. Differences between our r_0 and Zanetti et al. (2004) is within r_0 error bars. These small differences with our data are significant compared to our uncertainty of the fit parameters (lower than 3% for E and r_0), and expected given the differences of experimental parameters between Zanetti et al. (2004) and ours. For example, the temperature conditions differ by about 200 $^{\circ}$ C (1240 and 1265 in ours, 1050 in the other). The pressure condition differs by 2 to 6 kbars. The E parameter for olivine strongly depends on Al and LREE partition coefficients. Zannetti et al's $D_{Al}^{Ol/melt}$ value (0.004±0.001, Zanetti et al., 2004) is closed to our values $(0.004\pm0.001$ for CC01#8kb4 and 0.006 ± 0.001 for H3V04). Differences of E between the two studies are contributed by LREE and MREE partition coefficients (Eu, Gd and Ho), which are one order of magnitude higher than Zanetti et al. (2004). Our LREE and MREE partition coefficients are similar (same order of magnitude) to those of Canil and Fedortchouk (2001), which run experiments at about same temperature (1375 $^{\circ}$ C) as we used in our experiments and at atmospheric pressure. The difference we found between Zanetti et al. (2004) and our LREE-MREE partition coefficients could be therefore attributed to temperature difference between studies (around 200°C lower in Zanetti et al., 2004). Major difference between Zanetti et al. (2004) study and this study is observed for D_0 parameter (120% of difference). The value of the D_0 parameter is mostly controlled by Sc partition coefficients, that are lower in our studies (0.3 ± 0.03) than in Zanetti et al. (2004) study (0.7 ± 0.04) . This difference is likely explained by the melt composition (basalt vs. basanite and water content) and the temperature conditions between the two studies. Consequently, our

values of D_0 are lower by 70% to 120% compared to that of Zannetti et al. Because D_0 can be related with the degree of melt polymerization Gaetani et al. (2003), the differences in water abundance and temperature of the experiments potentially explain the observed disparity between our and Zannetti et al.'s data.

Pyroxene lattice strain parameters are compared to studies taking into account the combined strain effect on M1 and M2 sites on trace element partitioning. In this section, we use as a reference for nearly dry sample, the sample CC4#7b presented in Dalou et al. (2011), because 1) it contains opx and cpx, at the same pressure than 3 samples presented in this study and, 2) this sample is the poorer in H_2O and in total volatile elements (F + Cl + H_2O) of all the 12 kbars samples of Dalou et al. (2011). Orthopyroxene results are compared to sample 1101-12-06 of Frei et al. (2009) (11 kbars and 1230° C). Our lattice strain parameters are in agreement with Frei et al. (2009)(within the 52% of relative difference, except for D_0^{M1} parameter for which our D_0^{M1} are from 54 to 131% higher). The D_0^{M1} differences between the two studies are mainly due to respective Cr partition coefficients. In our samples, the Cr partition coefficients is highly variable (from 4.6 ± 0.6 to 12 ± 3), while in Frei et al. (2009), D_{Cr} is relatively constant despite a range of P-T conditions (from 1.31 ± 0.06 to 2.2 ± 0.02 , corresponding from 27 kbars - 1510°C to 11 kbars - 1230°C, respectively). Variation in our Cr partition coefficients correlate neither with the variations of T nor water content in samples, but roughly negatively correlate with melt fraction as previously pointed out by Johnston and Schwab (2004). The r_0^{M1} change is within the fit uncertainty and its values are perfectly consistent with Frei et al. (2009) $(0.647\pm0.002$ vs 0.66). The M2 site parameters are consistent with Frei et al. (2009). The r_0^{M2} variation we found are mostly within the error bars for our samples but also within the error bar of sample 1101-12-06 of Frei et al. (2009) refitted using our model (0.83 ± 0.006 Å). Our E^{M2} are consistent with Frei et al. (2009), within 8 to 30 % of relative differences. Difference of E^{M2} between our dry sample (CC4#7b) and sample 1101-12-06 of Frei et al. (2009) is within the E^{M2} (414±10 vs. 453±46 GPa). The E^{M2} of hydrous samples is between 20 and 30 % lower than our dry sample or Frei et al. (2009) E^{M2} . We assess that this slight difference of E^{M2} between hydrous and dry samples (CC4#7b and 1101-12-06 of Frei et al., 2009) is related to CaO content of opx. Dry opx contain >2.2 wt% of CaO, while with decreasing temperature (Lindsey, 1980) and increasing water content, opx become less calcic (<1.3 wt% CaO). The increase of E with CaO content in crystal site has already been suggested for garnet (Dalou et al., 2009a; van Westrenen et al., 2001b). Given that garnet has a more accepting structure than opx, this assumption needs to be tested for orthopyroxene by systematic studies with variable Ca content. As expected because E and r_0 are crystallographic parameters, their variation between samples and between this study and Frei et al. (2009) is valueless. The variation of D_0^{M2} between dry samples (CC4#7b and 1101-12-06 of Frei et al., 2009) is within the error bars $(0.190\pm0.006 \text{ vs. } 0.181\pm0.006)$. Note that from dry to more hydrous samples, D_0^{M2}

significantly decrease (by half from dry to more hydrous sample). This decrease can be attributed both to temperature decrease and water content increase, as it was previously discussed for cpx in Gaetani et al. (2003). To decipher water effect from temperature effect, we corrected our D_0^{M2} from temperature (Table 4.5.8) using the equation of Wood and Blundy (1997). Table 4.5.8 shows D_0^{M2} decrease at constant T with increasing water content. Gaetani et al. (2003) discuss that D_0 is related to melt structure, exploring trace element compatibility change (into cpx) on the basis of the changes in melt polymerization with H₂O content dissolved in. An addition of 6.26 wt% H₂O in melt produces ~ 17 mol% hydroxyl groups and decreases viscosity by ~ 98% relative to an anhydrous melt at the same temperature (Gaetani et al., 2003). They demonstrate that dissolved H₂O decrease trace element compatibility in the solid, thereby explaining the decrease of D_0 with the increasing H₂O.

Clinopyroxene lattice parameter data are compared to those of Adam and Green (2003, 2006) and to M2 site parameters of Gaetani et al. (2003) and Green et al. (2000). For the same reasons we didn't use it for olivine lattice strain model, we choose not to use V partition coefficients to fit pyroxene lattice strain model for M1 site. Because Adam and Green (2003, 2006) fit independently M1 and M2 strain model, using for M1 site D_V and not D_{Cr} , our data for M1 parameters and theirs are therefore not directly comparable. We refitted their data in model, using their D_{Cr} instead of D_V , for sample R79 of Adam and Green (2006), which is closed to our conditions (10 kbars – 1075°C and 5.8 wt% H₂O estimated to be dissolved into the melt). We obtained for D_0 , E and r_0 for M1site: 41 ± 10 , 1553 ± 141 GPa and 0.659 ± 0.003 Å, respectively and, for M2 site: 0.565 ± 0.031 , 364 ± 39 GPa and 1.027 ± 0.004 Å, respectively. The relative difference between our r_0^{M1} and their is lower than 2%. This difference is within the error bars comparing their R79 sample and our H5V4p sample with the same H₂O amount. As previously noted for opx, D_{Cr} mostly determines D_0^{M1} and also E^{M1} values. Adam and Green (2006) D_{Cr} is 26±7, which more than twice higher than our D_{Cr} . Although the variation of D_{Cr} between our samples can be explained as for opx by melt fraction variations, their high D_{Cr} cannot. After Johnston and Schwab (2004), D_{Cr} decreases with the increasing melt fraction in experiments. High D_{Cr} could be explained by the presence of Cr^{2+} measured with Cr^{3+} . The E^{M1} obtained for sample R79 of Adam and Green (2006) remains comparable to our samples, since difference between their E^{M1} and sample H3V04 E^{M1} is within the error bars. Concerning M2 site parameters, our r_0^{M2} value difference with Adam and Green (2003, 2006) is within the error bars and our r_0^{M2} values are closed to Green et al. (2000) (sample 1802, their lower pressure sample 20 kbars - 1080°C) and Gaetani et al. (2003) r_0^{M2} . Values differences are within the error bars for samples CC4#7b and H3V04. Variations we observe between the r_0^{M2} of our samples is within their error bars. Nevertheless, we observe that r_0^{M2} increases with CaO of cpx as predicted by the Wood and Blundy (1997) r_0 prediction. The Wood and Blundy (1997) calculation predicts r_0^{M2} in very good agreement

with our results (CC4#7b 1.005 Å, H3V04 1.016 Å, H5V4p 1.022Å), according to the prediction standard deviation of 0.009 Å. Our E^{M2} of samples CC4#7b and H3V04 are consistent with Green et al. (2000) and Adam and Green (2006) and E^{M2} of sample H5V4p is consistent with Gaetani et al. (2003) (differences within the error bars). The Wood and Blundy (1997) E are not consistent with our data (from 268 to 274 GPa), except for sample H5V4p. Their prediction is calculated from Pand to a lesser extent T. As we previously observed for opx, variation of E^{M2} values between our samples negatively correlates with CaO content of cpx, and the sum of big M2 cations (CaO + Na₂O + K₂O). This implies that E parameter is not only controlled by P-T conditions, but also by cpx composition. As it was suggested for garnet (van Westrenen et al., 2001a), cpx E can be related to r_0 . We observed a negative correlation between E^{M2} and r_0^{M2} of our samples, involving that when the M2 expands, the Young modulus of the crystal (E) decreases. Significant differences (between 30 and 70% of relative difference) is observed between our D_0^{M2} and Green et al. (2000); Gaetani et al. (2003) and refitted Adam and Green (2006). As previously discussed D_0^{M2} is a parameter which is difficult to predict and which can depend of T and water content. Note that from hot and anhydrous sample (CC4#7b) to cold and hydrous sample (H5V4p), our D_0^{M2} increase. The increase is predicted by the Wood and Blundy (1997) D_0 calculation, however the predicted values for D_0 are higher by to a factor up to 2 (from 0.417 to 0.997). This discrepancy was previously reported by Gaetani et al. (2003) and Green et al. (2000). Gaetani et al. (2003) related this mismatch between regression results and Wood and Blundy (1997) model prediction to the fact that parameterization does not take into account the variations in melt structure to calculate D_0 . To decipher T from water effects on D_0 , we corrected D_0 from T as for opx (Table 4.5.8). It appears that at constant T, as for opx and as noted by Gaetani et al. (2003) for cpx, D_0^{M2} decrease with the increase of H₂O content. As for opx, we assume that an increase of dissolved H₂O leads to a decrease of D_0^{M2} , implying that D_0^{M2} is controlled by melt structure.

Garnet lattice parameter data are compared to those of Pertermann et al. (2004). Green et al. (2000) lattice strain parameters are derived from Sc-free model. Absence of Sc in lattice strain model prevents the accurate fitting of the left part of the Onuma sub-parabola. Consequently, it limits the accuracy of lattice strain parameters, in particular E. Our results cannot directly be compared their modeled parameters. While Pertermann et al. (2004) experiments were done at slightly higher pressure (29-31kbars), C4p#25kb and Grt3V4p samples lattice strain parameters are in good agreement (within about 30% of relative difference) with their E and r_0 parameters. Pertermann et al. (2004) strain parameters are highly variable (r_0 0.923-0.936 Å, E 548-800 GPa and D_0 8.9-16.8). They explain these variations with variation of Ca and Ti content (pfu) in garnet. Contrary to what it is expected, the fact that our r_0 are lower than Pertermann et al. (2004) cannot be directly related

to Ca content, given that our garnets are Ca-richer than Pertermann et al. (2004), nor to pressure effect since we expect a higher r_0 at lower pressure. We assess that those differences can come from differences in bulk composition (eclogitic in Pertermann et al., 2004). The predicted value of E, using the model of Draper and van Westrenen (2007) and van Westrenen and Draper (2007), for C4p#25kb (595 GPa) is not significantly lower than the E fitted from our data (684 \pm 46 GPa), and the predicted value of E for Grt3#V4p (588 GPa) is not significantly higher than the E modeled from our data (605 ± 64 GPa). Differences between predicted parameters and regression results are within the error bars. Apparent differences between predicted values of r_0 (0.928 Å for C4p#25kb and 0.932 Å for Grt3#V4p) and r_0 derived from our fits, is within the 0.017 Å error bars predicted by van Westrenen and Draper (2007). The D_0 value of nearly dry sample C4p#25kb (10.5 \pm 0.9) is similar to those obtained by Pertermann et al. (2004) for the two higher T samples (MP214: 8.9 \pm 0.2 and A343: 10.1 \pm 0.3). While E and r_0 parameters are easily predicted constrained by crystal chemistry, D_0 parameter is more complex. Neither thermodynamical nor statistical prediction (21) and 7.8, respectively) can model the low D_0 value obtained for hydrous sample Grt3#V4p (2.2 \pm (0.2). Nevertheless, it was pointed out in Draper and van Westrenen (2007) that their model is not reliable to predict partitioning in hydrous systems. We assess therefore that the discrepancy between the low Grt3V4p D_0 value and Pertermann et al. (2004) D_0 values is explained by the presence of water in our sample.

Our amphibole data, E and r_0 for M4 site are consistent with Adam and Green (2003, 2006) lattice strain parameters (within 40% of relative difference for r_0 and E). As previously noted, our amphibole are richer in Mg and poorer in Ca in the M4-site (REE substitution site), which leads to smaller M4 site than that in Adam and Green (2003, 2006). This explains the observed differences i.e. smaller r_0 and higher E than Adam and Green (2003, 2006). It should be noted that our D_0 are as much as 135% lower than Adam and Green (2003, 2006). This D_0 discrepancy can be attributed to a combined differences in 1) melt composition (basaltic vs. basanitic Adam and Green, 2003, 2006), 2) temperature (our experiments are 120 to 175 °C hotter than theirs), and 3) water content (4.3 and 5.6 wt% H₂O dissolved in our melts vs. 6.2 to 12.0 wt% in theirs). Deciphering the individual effect of melt composition, temperature and water abundance on D_0 of amphibole/melt trace element partitioning requires systematic studies with a range of pressures, temperatures and amphibole compositions, that are yet available.

		Orthopy	roxene			(linopyroxene	e
runs	CC4#7b	H3V04	H5V4p	H6V04	-	CC4#7b	H3V04	H5V4p
		M1 s	site				M1 site	
D_0	7.1(2)	17(4)	6.2(8)	14.9(5)	_	10(1)	15(3)	4.7(5)
r_0	0.647(1)	0.646(2)	0.647(2)	0.645(1)		0.651(1)	0.649(3)	0.656(1)
E_0	1255(31)	1620(136)	1140(66)	1665(58)		1283(59)	1492(101)	822(55)
		M2 s	site				M2 site	
D_0	0.190(6)	0.160(28)	0.115(11)	0.091(2)	-	0.402(50)	0.458(30)	0.489(9)
r_0	0.821(1)	0.831(8)	0.819(11)	0.829(9)		1.009(11)	1.014(6)	1.022(3)
E_0	414(10)	352(58)	368(54)	322(6)		363(125)	368(29)	271(15)
D_{1275}	0.224(10)	0.121(23)	0.072(7)	0.060(3)		0.496(58)	0.390(26)	0.328(6)
	Olivi	ne		Gar	net		Amph	ibole
runs	$CC01\#8kb4^*$	H3V04*	-	$C4p#25kb^*$	$Grt3V4p^*$	-	H4V4p	H6V04
	M si	te		X s	ite		M2	site
D_0	0.19(2)	0.324(8)	-	10.5(9)	2.4(3)	-	0.18(1)	0.23(1)
r_0	0.737(1)	0.736(1)		0.921(3)	0.922(5)		1.00(1)	1.01(1)
E_0	434(13)	412(5)		684(46)	605(64)		354(40)	378(45)

Table 4.5.8: Site parameters for lattice strain models for trivalent cations.

 r_0 values are in angstroms, E_0 values are in GPa.

* This sample data were fitted without La data (analysis seems to be contamined by the melt). D_{1275} is the parameter D_0 , corrected from temperature variation and calculated for 1275 °C, using the equation: $D_{1275} = D_0(T^{\circ}C) \times \exp[\Delta H/R (1/(T+273) - 1/(1275+273))]$, where ΔH , the enthalpy of element incorporation (88750 J.mol⁻¹, Wood and Blundy, 1997) and R, the gas constant and T, the experimental temperature in °C.

F and Cl partitioning under hydrous conditions

We observed in the results section that chlorine is more incompatible than fluorine. This systematic does not change for all studied minerals: olivine, opx, cpx, pargasite and phlogopite. Dalou et al. (2011) previously noted this feature for olivine, opx, cpx and plagioclase in anhydrous basaltic system and demonstrated that it manifests an effect of anion size. Fluorine and chlorine, being anions, are substituted into O site of minerals (Dalou et al., 2011). Moreover, they have significantly different ionic radius: $r_F < r_O < r_{Cl}$. Because chlorine is bigger than oxygen, it is more difficult to incorporate in crystal structure than fluorine, smaller than oxygen.

As well as this systematic, Figures 4.5.2 to 4.5.7 show that F and Cl partition coefficients vary depending on samples. According to the standard deviations on the data (Table 4.5.4 and 4.5.5), F and Cl partition coefficients are homogeneous between minerals and melt within the same sample. This implies that D_F and D_{Cl} change with experimental conditions (P, T, and water content).

We observe that this D_F and D_{Cl} variation with conditions is larger than the variation of trace element partition coefficients. The V and Pb partition coefficients also significantly vary between samples. Nevertheless, D_V variation is likely caused by crystal field effect, while we cannot rely on D_{Pb} . It appears therefore that F and Cl fractionation with condition variations is more significant than for trace elements. How to explain this feature of anions? Since anions are not substituted in the same site than cations, this anion property cannot be controlled by the elasticity of M sites. We examine this problem using pyroxenes data since we do not have enough data for olivine, garnet and hydrous minerals. In the following sections, we investigate the substitution mechanisms of F and Cl and, the differences of substitution energies between anions and cations to be incorporated into pyroxenes under hydrous conditions.

Substitution mechanisms of F and Cl: the example for pyroxenes

Chlorine in orthopyroxenes:

Fluorine and chlorine substitution mechanisms into pyroxenes was probed in Dalou et al. (2011) for anhydrous system and at constant T and P conditions. They show that chlorine is incorporated into orthopyroxene via the jadeite substitution: $Mg_{Mg}^{\times} + O_O^{\times} + NaCl_{melt} = Na'_{Mg} + Cl_O^{\bullet} + MgO_{melt}$. This was demonstrated by a negative correlation $D_{Cl}^{opx/melt}$ with enstatite component and a positive correlation with the jadeite component of orthopyroxenes among samples at constant P and T with variable F and Cl doping. In this study, we observe reverse correlations (Figure 4.5.8 a and b). Because of the combined effect of increasing water content and decreasing temperature, opx become more magnesian (e.g. Lindsey, 1980). After MELTS calculator simulation (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995), water content increase and temperature decrease produces the same evolution of pyroxene compositions. Temperature decrease and water content increase produce an increase of the enstatite component of 6%, a decrease of the CaTs component of 47% and of the jadeite component of 58% of our orthopyroxene from dry to more hydrous samples.

After Rossi et al. (1983), a decrease of the jadeite component increases the M2 – O3 distance. The observed decrease of jadeite component, from dry to more hydrous opx, leads to the lengthening of M2 – O3 with increasing water content and decreasing temperature. Given that Cl is substituted into O3 of opx and bonded to M2 site (Dalou et al., 2011), the lengthening of M2 – O3 lets more space to Cl to be incorporated and thus promotes the Cl incorporation into opx with increasing water content and decreasing temperature.

This does not imply another substitution mechanism than for anhydrous conditions. We assume that with such condition variations among our samples, the important changes in crystal structure prevents the observation of substitution mechanisms as shown in Dalou et al. (2011).



Figure 4.5.8: Variation of Cl partition coefficient in different samples with a) and b) orthopyroxene composition variation and, c) and d) clinopyroxene composition variation in %. We observed a variation of pyroxene composition with water and temperature variation. Those variations are correlated with Cl partition coefficients.

Chlorine in clinopyroxenes:

From the positive correlation between $D_{Cl}^{cpx/melt}$ and cpx CaTs component (Ca Tschermak) among 5 samples of variable P and T conditions and F and Cl doping, it is inferred in Dalou et al. (2011) that chlorine is incorporated into clinopyroxene via the CaTs substitution: $\text{Si}_{Si}^{\times} + \text{O}_{O}^{\times} + \text{AlOCl}_{melt} =$ $\text{Al}'_{Si} + \text{Cl}_{O}^{\bullet} + \text{SiO}_{2melt}$. We do not observe this $D_{Cl}^{cpx/melt} - \text{cpx}$ CaTs relationship among our samples' data.

After Lindsey (1980) and MELTS calculator simulation, with decreasing temperature and increasing water content, cpx become more calcic and aluminous. In this study, from dry to more hydrous sample, we observe that cpx become 52% more diopsidic and nearly 100% less enstatitic.

After Cameron and Papike (1981); Rossi et al. (1983), the O1 – M1 distance in cpx increases with the increase of calcic component, *i.e.* the diopside component. The observed decrease of diopside component, from dry to more hydrous opx, leads to the lengthening of O1 – M1 with increasing water content and decreasing temperature. Since Cl is likely incorporated into the O1 or O2 sites in clinopyroxenes (Dalou et al., 2011), we can assume that the lengthening of O1 – M1 lets more space to Cl to be incorporated and thus promotes the Cl incorporation into cpx with increasing water content and decreasing temperature as shown in Figure 4.5.8 c and d.

As we suggest for opx, to explain the $D_{Cl}^{cpx/melt}$ variations among our samples does not likely require another substitution mechanisms than the one proposed under anhydrous conditions. As for opx, we suppose that the important changes in crystal structure (caused by condition variations among our samples) prevents the observation of substitution mechanisms as shown in Dalou et al. (2011).

Fluorine in orthopyroxene:

Dalou et al. (2011) argued that F is sensitive to melt polymerization since it is smaller than its incorporation site. At constant P-T but variable volatiles doping, they observe that F partition coefficient for pyroxene increase with basalt viscosity (Dalou et al., 2011). On Figure 4.5.9, we reported $D_F^{opx/melt}$ measured in hydrous samples of this study and in anhydrous samples of Dalou et al. (2011), in function of structural change of melt of each samples, represented by melt viscosity. Melt viscosity was obtained using Giordano et al. (2008) calculation, and corrected from temperature which was fixed at 1275°C. It allows to examine $D_F^{opx/melt}$ variation with melt viscosity changes free from Tvariation influence. That way melt viscosity variations result from water content variation among samples. The functional relationship between $D_F^{opx/melt}$ and melt viscosity observed on Figure 4.5.9 demonstrates melt structure influence on F partitioning. Indirectly, $D_F^{opx/melt}$ decrease with increasing water content in samples.



Figure 4.5.9: Fluorine partition coefficient between orthopyroxene and basaltic melt variation with viscosity of melt, calculated following Giordano et al. (2008), where temperature differences were corrected and fixed at 1275°C. Grey circles are data from Dalou et al. (2011) and black circles are hydrous data from this study.

Fluorine in clinopyroxene:

The same relationship between $D_F^{cpx/melt}$ and melt viscosity is observed. It should be noted that recent study of O'Leary et al. (2010) observe a clear positive correlation between $D_F^{cpx/melt}$ and $^{IV}Al^{3+}$ in cpx, implying that F is incorporated into clinopyroxene via CaTs substitution. This relation was not found in our study, we observe a negative correlation between $D_F^{cpx/melt}$ and $^{IV}Al^{3+}$ in our cpx. Compared to O'Leary et al. (2010) study, our bulk composition is poorer in Al₂O₃, our cpx are $^{IV}Al^{3+}$ -poorer, and our melt composition are more variable in H₂O. These differences cannot justify a different mechanism of F substitution in cpx. Reducing their melt data and comparing with our data, we obtained the diagram Figure 4.5.10, where both our and O'Leary et al. (2010) $D_F^{Cpx/melt}$ positively correlate with melt composition. We can therefore assess of the influence of melt composition and structure on F partition coefficients between cpx and melt as we showed $D_F^{opx/melt}$, in opposition to a crystal chemistry influence as suggested by O'Leary et al. (2010). Note that the aim in O'Leary et al. (2010) study was to visualize the effect of ${}^{IV}Al^{3+}$ on H₂O partitioning, therefore their melt composition variation is limited and their *P-T* conditions are fixed, while their ${}^{IV}Al^{3+}$ in cpx is extremely variable. Thereby, their correlation between $D_F^{cpx/melt}$ and ${}^{IV}Al^{3+}$ of cpx is clear and their data are important but their interpretation of crystal chemistry influence on $D_F^{cpx/melt}$ is prematured.



Figure 4.5.10: Fluorine partition coefficient between cpx and basaltic melt variation with melt composition $(CaO/Al_2O_3/(H_2O+F+Cl))$ of basaltic melt in wt%, an ad hoc proxy of melt composition). Grey diamonds are O'Leary et al. (2010) data and black diamonds are data from this study. Note that O'Leary et al. (2010) data shows a correlation between $D_F^{Cpx/melt}$ and melt composition.

Influence of water on F and Cl, and trace element fractionation

In order to represent our data in terms of substitution energy (ΔG , the standard-state Gibbs free energy change for a substitution reaction), we use the familiar thermodynamic expression: ΔG_r^0 = $-RT\ln K_{eq}$, where K_{eq} represents the equilibrium constant for a substitution reaction, R is the gas constant, T is temperature (in Kelvin). Effective use of this equation requires the knowledge of substitution mechanisms. The K_{eq} was calculated from substitution reaction presented in Dalou et al. (2011) for chlorine incorporation in opx (Equation 1) and cpx (Equation 2) and in Gaetani and Grove (1995) for REE incorporation in cpx.

$$K_{eq} = \frac{X_{Na}^{opx} \cdot X_{Cl}^{opx} \cdot X_{MgO}^{melt}}{X_{Mq}^{opx} \cdot X_{NaCl}^{melt}}$$
(4.5.1)

$$K_{eq} = \frac{X_{Al}^{cpx} \cdot X_{Cl}^{cpx} \cdot X_{SiO_2}^{melt}}{X_{Si}^{cpx} \cdot X_{AlOCl}^{melt}}$$
(4.5.2)

, where X_i^j is mole fraction of component *i* in phase *j*. X_{Na}^{opx} is the jadeite fraction in opx and X_{Al}^{opx} is the Tschermakite fraction is cpx. We have obtained values for ΔG presented versus *T* in Figure 4.5.11. While the difference of variation between ΔG of chlorine substitution into opx and cpx is about 80 kJ.mol⁻¹ and within the fit errors, the variation of ΔG of REE substitution into cpx is clearly different. As expected the energy involved during the incorporation of chlorine in pyroxene is signicantly different from that involved during REE incorporation. Using the expression $\Delta G_r^0 = \Delta H +$ $\Delta S.T$ (Wood and Blundy, 2002), we deduce ΔH the enthalpy and ΔS the entropy of the substitution mechanisms during melting. The deduced enthalpy for REE is more than twice higher than the enthalpy for chlorine. This means that REE incorporation into pyroxenes requires more energy than chlorine during melting. One explanation of this behavior is that REE or cations incorporation in crystals is controlled by M site elasticity, while chlorine or anion incorporation depends mostly of M– O distances. The M–O distance appears to be more sensitive to conditions as composition changes than M site size (Cameron and Papike, 1981).

Blundy and Wood (2003) suggest that the smaller the enthalpy of fusion, the less the effect of temperature and the more crystal-melt partition coefficients are changed by water effect. This argument agrees with the observations of partition coefficient changes of Figure 4.5.3 and 4.5.4. For instance, on Figure 4.5.3, Cl partition coefficients increases with the decreasing T and the increasing water content, although sample H6V04 (5.9 wt% H₂O) was run at higher temperature than sample H5V4p (4.9 wt% H₂O) and D_{Cl} of H6V04 > D_{Cl} of H5V4p. We assume that this shows that water effect is greater than temperature effect on chlorine partition coefficients. On the contrary, unlike D_{Cl}, D_{REE} changes with T and water content is not linear. This likely highlights that REE or cations



Figure 4.5.11: Variation in free energy of fusion ($\Delta G=RT \ln K_i$) with temperature. ΔG calculation is explained in the text. Slope of trends give the entropy of fusion, the intercept is the enthalpy of fusion. Each line represents one melting reaction for one component between one phase and the melt. The grey field is REE data from La to Lu, width of the field represents the error bars on data. Data represented by diamonds and circles are Cl data for opx and cpx, respectively. The entropy and the enthalpy of substitution during melting of REE and Cl are different.

incorporation and behavior is more complicated given that they will mostly depend on mineral site elasticity changes with composition and T. Consistently with Blundy and Wood (2003) remark, the enthalpy of Cl substitution during melting being smaller than REE enthalpy, water effect is greater on Cl partition coefficients than those of REE.

Although this argument could be relevant for F partition coefficients, we are not able to demonstrate it since we did not identify substitution mechanisms of F in pyroxenes. Figure 4.5.9 show a relatively straightforward correlation between $D_F^{opx/melt}$ and melt viscosity, aside temperature effect. On the other hand, at fixed P and T, the D_0^{M2} (representing REE) of opx or cpx does not show a clear correlation with melt viscosity (Figure 4.5.12). This means that D_F is more sensitive to melt viscosity changes than REE. Given that water content is the predominant effect that changes melt viscosity (at fixed P and T), we can state that indirectly D_F is more sensitive to water content than D_{REE} . As we previously suggested, REE behavior is mostly controlled by M2 site elasticity, which leads REE to be less sensitive to melt composition and content in water than anions.



Figure 4.5.12: Variation of D_0^{M2} with viscosity of melt, calculated following Giordano et al. (2008). Temperature differences for D_0^{M2} and viscosity were corrected and fixed at 1275°C. Diamonds are opx data and circles are cpx data. White symbols are data from Dalou et al. (2011) and grey circles are data from this study. Note the poor correlations between melt viscosity and D_0^{M2} of opx or cpx, unlike the more straightforward correlation between $D_F^{opx/melt}$ and melt viscosity.

At last, although F and Cl partition coefficients variations are controlled by different processes, it results that both are more sensitive to water content involved during melting than REE. As observed on Figure 4.5.2 to 4.5.7, all cations vary less than F and Cl with water content. Since all cations are substituted into M sites of minerals, the conclusion we made for REE in pyroxene can likely be extended to all cations in minerals.

4.5.5 Conclusion

We reported F and Cl partition coefficients between minerals (orthopyroxene, clinopyroxene, olivine, garnet, amphibole) and hydrous basaltic melt, and between phlogopite and hydrous shoshonitic melt. This study illustrates the complexity of the variations in both trace element and F and Cl partitioning, where both temperature, bulk water content and mineral compositions are variables. Main conclusions are: 1) both temperature and water content strongly influences crystal chemistry of studied minerals, 2) the lattice strain models fit to trace element partitioning data, implying that our partitioning data are near equilibrium conditions and, 3) both changes in melt structure and in mineral composition could influence F and Cl partitioning, as well as partition coefficient for cation trace elements.

Note F and Cl partition coefficients vary more than other trace elements, due to water content and crystal chemistry changes. We also demonstrated that ΔH of Cl during hydrous melting is lower than REE cations, meaning that REE incorporation requires more energy than anions. This can explain why Cl is more sensitive to water content change than REE cations. Moreover F partition coefficient is more dependent on melt viscosity changes with water content than REE. This could be explained by the fact that, unlike trace elements which are substituted into cation sites, F and Cl are substituted into the oxygen site, which distort itself likely more easily than cation sites.

This anion feature makes F and Cl good tracers of mantle processes, especially arc magma genesis. Combining trace elements and F and Cl signature of magmas, water content of the source can likely be estimated.

4.5.6 Supplementary material

Lattice strain models

The choice of fitted trivalent cations and their corrdinance in minerals is explained in the text.



Figure 4.5.13: Relation between the experimentally determined D_i and trivalent substituting cations and their effective ionic radii (Shannon,1976) in orthopyroxene, with the increasing water content dissolved in the melt of samples (from white to black symbols). Solid hyperbola represents fits of the lattice strain model to $D_i^{opx/melt}$ accounting for M1 and M2 site intracrystalline fractionation. Stippled and dashed parabola are resulting fits for $D_i^{M1/melt}$ and $D_i^{M2/melt}$, respectively. Symbols are experimentally determined $D_i^{opx/melt}$.



Figure 4.5.14: Relation between the experimentally determined D_i and trivalent substituting cations and their effective ionic radii (Shannon,1976) in clinopyroxene, with the increasing water content dissolved in the melt of samples (from white to black symbols). Solid hyperbola represents fits of the lattice strain model to $D_i^{cpx/melt}$ accounting for M1 and M2 site intracrystalline fractionation. Stippled and dashed parabola are resulting fits for $D_i^{M1/melt}$ and $D_i^{M2/melt}$, respectively. Symbols are experimentally determined $D_i^{cpx/melt}$.



Figure 4.5.15: Relation between the experimentally determined D_i and trivalent substituting cations and their effective ionic radii (Shannon,1976) in olivine, with the increasing water content dissolved in the melt of samples (from white to black symbols). Symbols are experimentally determined $D_i^{olivine/melt}$.



Figure 4.5.16: Relation between the experimentally determined D_i and trivalent substituting cations and their effective ionic radii (Shannon,1976) in garnet, with the increasing water content dissolved in the melt of samples (from white to black symbols). Symbols are experimentally determined $D_i^{garnet/melt}$.



Figure 4.5.17: Relation between the experimentally determined D_i and trivalent substituting cations and their effective ionic radii (Shannon,1976) in amphibole, with the increasing water content dissolved in the melt of samples (from white to black symbols). Symbols are experimentally determined $D_i^{amphibolet/melt}$.
Chapter 5

F and Cl behavior in the sub-arc mantle

This chapter links the previous two chapters, which deduced F and Cl incorporation mechanism in minerals, and geochemistry of F and Cl abundance in melt inclusions. In the previous chapters, I demonstrated that F and Cl are more sensitive to changes of mineral compositions caused by water abundance. Furthermore, I showed that F and Cl partition coefficients are significantly different for amphibole and phlogopite than other anhydrous minerals during melting under hydrous conditions.

In this chapter, I use these new F and Cl partition coefficients, along with other determined trace element partition coefficients, to build a preliminary model of different melting types that could occur in the sub-arc mantle:

- melting of a lherzolite induced by water-rich slab component of variable quantities,
- melting of an amphibole-bearing lherzolite,
- melting of a phlogopite-bearing lherzolite.

The first model results show that while some arc melt inclusion compositions can be explained by the fluid-induced melting, some can be explained only by melting of an amphibole- or a phlogopitebearing lherzolite.

This chapter presents the results of a preliminary work on a melting model in the sub-arc mantle, which was simplified. This work, particularly the melting model, needs to be improve for further publication.

5.1 Introduction

Element fractionation processes operating in subduction zones are probably the least constrained geochemical processes in the element cycles of the Earth's mantle. Numerous studies on trace element partition coefficients between mantle minerals and basaltic melts (Nicholls and Harris, 1980; Hart and Dunn, 1994; Skulski et al., 1994; Wood and Blundy, 1997; Blundy et al., 1998; Johnson, 1998; Green et al., 2000; van Westrenen et al., 2001a; Gaetani et al., 2003) or andesitic melts (Green and Pearson, 1985; Brenan et al., 1995b) allowed an advance in the understanding of melting processes in subduction zones. Current consensus is that arc magmatism is triggered by a flux, of either volatile-rich fluid or silicate melt, derived from the subducting slab (Gill, 1981; Tatsumi and Eggins, 1995). Over years, geochemists distinguished subduction zone flux (see e.g. McCulloch and Gamble (1991); Maury et al. (1996); Martin (1999); Martin et al. (2005); Hoffer et al. (2008)) by the large fractionation between fluid mobile elements (B, Cs, Rb, U) and fluid immobile, so-called, high-field strength elements (Ti, Zr, Nb, Hf, Ta). The HFSE depletion compared to fluid-mobile element was generally attributed to the precipitation of rutile in the dehydrating subducting crust (Green and Pearson, 1987; Ryerson and Watson, 1987; Foley et al., 2000; Ayers and Watson, 1993).

It was considered that rutile remains as a residual phase at the dehydration condition of the slab, given that rutile is saturated above 30 ppm TiO₂ abundance in hydrous fluid (Ayers and Watson, 1993). In contrast, TiO₂ saturation in basalt was estimated to be 7 to 9 wt% at 1 GPa (Ryerson and Watson, 1987), which induced that rutile is consumed during slab partial melting. Nevertheless, recently it has been demonstrated that TiO₂ saturation in hydrous dacite is from 750 to 720 ppm at pressure from 2 to 4 GPa, lower than the abundance of MORB (Gaetani et al., 2008). Considering that dacite is the likely silicate melt derived from the partial melting of an oceanic crust, the result infer that rutile can be retained in the subducted oceanic lithosphere during both dehydration and/or partial melting. Thus the depletion of HFSE by rutile saturation is possible for either flux coming from slab dehydration and slab melts. This demonstrates that such trace elements cannot be used alone to discriminated flux and melting processes in subduction zone.

With recent advances in microanalytical techniques and melt inclusion studies, there is a growing body of concentration measurements of volatiles, relatively light-atomic mass elements (H, B, C, S, Cl, F) in primitive melts of subduction zone magmas (Sisson and Layne, 1993; Métrich et al., 1999; Wade et al., 2006; Métrich and Wallace, 2008; Le Voyer et al., 2010). While C and H suffer degassing (Dixon et al., 1995), Cl and F do not experience a degassing event (Aiuppa, 2009) and likely retain information of magma genesis along with other lithophile trace elements (such as REE). Furthermore, the Cl affinity to volatile-rich fluid and the F affinity to silicate melts (Schilling et al., 1980) leads to believe that they are promising candidates to distinguish the nature of the slab flux. This was emphasized by the recent study of Le Voyer et al. (2010), which reports Cl/F ratio can distinguish two different origins of primary melt inclusions from Mount Shasta, where commonly used trace elements can only identify one source.

Partition coefficients for Cl and F among solid mantle, silicate melt, and volatile-rich fluid at high pressure conditions are scarcely documented (Webster and Holloway, 1988; Métrich and Rutherford, 1992: Icenhower and London, 1997; Mathez and Webster, 2005 and some preliminary measurements have been reported on natural mantle minerals; Hervig and Bell, 2005; Bromiley and Kohn, 2007). The study of Dalou et al. (submitted to CMP) provides the first F and Cl partition coefficients for mantle minerals olivine, orthopyroxene, clinopyroxene, plagioclase, garnet and anhydrous basaltic melt. Initial work on F and Cl partition coefficients between dry peridotite minerals and basaltic melts led us to show that melting of simple sources, like lherzolite, harzburgite or clinopyroxenite, cannot explain the range of melt inclusion F and Cl variations (Dalou, AGU Fall meeting 2009; Dalou et al., submitted). In this paper, F and Cl partition coefficient database is completed by data for mantle wedge minerals such as olivine, orthopyroxene, clinopyroxene, garnet and volatile-rich minerals amphibole and phlogopite and hydrous silicate melt. The values were compiled from more than 150 measurements in 9 hydrous melting experiments, conducted between 8 and 25 kbars and between 1180 and 1430°C. Hydrous experiments were run with 0.2, 2.6, 4.3, 4.9 and 5.9 wt% of H₂O dissolved in the melt. Using F and Cl partition coefficients in hydrous system, we modeled H_2O -induced melting in mantle wedge, and melting of amphibole- or phlogopite-bearing mantle lithologies. In the following study, we show that the combination of F and Cl with some trace elements as (Zr, Sr, Y) provide new keys to distinguish hydrous mineral-induced melting of hydrous minerals-bearing lherzolite.

5.2 Methods: Construction of melting model

5.2.1 Geodynamic setting and melting model

Volatile elements are more abundant in primitive magmas from subduction zone settings, than those of MORB (Sisson and Layne, 1993; Métrich et al., 1999; Wade et al., 2006; Métrich and Wallace, 2008; Le Voyer et al., 2010). This enrichment is commonly attributed to the addition of a volatile-rich component released from the subducted oceanic lithosphere, into the mantle wedge lherzolite, which triggers melting (Sisson and Grove, 1993a,b; Gaetani et al., 1993), so called fluid-induced melting. Nevertheless, K content of some melt inclusions (MI), e.g. from South Italy volcanoes, requires the melting of phlogopite or K-rich amphibole in the mantle wedge (Schiano et al., 2004). The interaction of the released volatile-rich fluid with the mantle wedge can led to the stabilization of hydrous phases, amphibole or phlogopite, in the lherzolite (e.g. Tatsumi, 1989). The forward melting models that are presented here illustrate the difference of MI volatile element enrichment produced by fluid-induced melting or by the melting hydrous phase-bearing lithology.

In order to model the complexity of melting in subduction zone settings, we chose to use, as a preliminary model, the non-modal fractional melting equation of Shaw (1970):

$$C_L = \frac{C_0}{F} \left[1 - \left(1 - \left(\frac{P * F}{D_0} \right)^{\frac{1}{P}} \right) \right],$$

where $C_0 = \sum_i C_i X_i$ or the concentration of the element in the mineral *i* in the bulk rock, C_L , the concentration of the element in the melt, D_0 , the whole rock partition coefficient: $D_0 = \sum_i D^{i/melt} X_i$, where $D^{i/melt}$ were determined in this study, *F*, the melting rate, $P = \sum_i p_i D^{i/melt}$ (with p_i , the mass fraction of mineral *i* in the melt. Each fraction of liquid generated by aggregate melting is extracted continuously from the preceding liquid and each melt fractions are then aggregated. Using this melting model, we suggest that in the mantle wedge, a parcel of melt start rising towards the surface after its genesis and can be diluted at shallow magma pockets. The contribution of hydrous phases during melting is expected to be significant, particularly for the volatile element budget of the melt. Given that hydrous phases are the first to melt (e.g. Médard and Grove, 2008), it is necessary to take into account the different phase proportions involved during each melting stage (melting mode), therefore, we use is non-modal melting.

In order to evaluate the impact of element fractionation during melting on melt composition, we melt a source previously mixed with a volatile-rich component, instead of simply mix MORB composition with a volatile-rich component.

5.2.2 Partition coefficients

The building of our melting model requires partition coefficients of F, Cl and trace elements in hydrous conditions between mantle minerals (olivine, orthopyroxene, clinopyroxene, garnet) including hydrous minerals (amphibole and phlogopite) and hydrous silicate melt, basaltic or shoshonitic. We performed hydrous experiments using piston-cylinder apparatus, which experimental conditions are described in the Chapter 2.

The maximum amount of fluid-induced melting occurs in the hot core of the mantle wedge that range from 13 to 20 kbars, which corresponds to a temperature range between 1000°C to 1400°C (Grove et al., 2006). The partition coefficient data we present result from experiments ran globally at the mantle wedge hot core P - T conditions (8 – 25 kbars and 1180 – 1370°C).

Basaltic melts produced in the high H₂O experiments are characterized by low SiO₂ (43.69 ± 0.19 to $50.92 \pm 0.16 \text{ wt\%}$), FeO* (6.73 ± 0.17 to $10.13 \pm 0.12 \text{ wt\%}$) and MgO (9.30 ± 0.12 to $14.84 \pm 0.13 \text{ wt\%}$), similar to those obtained by Gaetani et al. (2003). This contrast is illustrated by a comparison of these hydrous melt with others from low H₂O experiments (dry basalts in Chapter 3), as illustrated on Figure 5.2.1. For higher pressure sample Grt3V4p, produced melt composition is more andesitic (53.04 ± 0.44 wt% SiO₂). In shoshonite experiments, produced melt have ultra-basic composition

tending to shoshonitic. As for hydrous basalt, produced melts in shoshonitic system have lower SiO₂ (38.78 ± 0.33 and 40.93 ± 0.10 wt%) but higher MgO (15.55 ± 0.12 and 19.47 ± 0.23 wt%) than shoshonitic melts obtained by Holbig and Grove (2008) in dry system.



Figure 5.2.1: Plot of weight concentrations of SiO₂ versus FeO + MgO, comparing the compositions of experimentally produced high H₂O silicate melts of our study (closed diamonds) and of Gaetani and Grove (1998) (closed circles) and the compositions of experimentally produced low H₂O silicate melts of Dalou et al, 2010 (open diamonds) and of Gaetani and Grove (1998) (open circles), saturated with lherzolite mineral assemblage between 8 and 25 kbars. The grey field represents melt inclusion data from Le Voyer (2009); Le Voyer et al. (2010), Sorbadere et al. (2011) and Sorbadere et al. (in preparation).

The Figure 5.2.1 shows that our experimental hydrous silicate melt compositions are in agreement with primitive melts from arc melt inclusions (Le Voyer, 2009; Le Voyer et al., 2010; Sorbadere et al. (2011) and, Sorbadere et al., in preparation).

Olivine, Opx and Cpx compositions are close to those expected in fertile mantle peridotite and presented in Gaetani et al. (2003): olivine has Mg# between 0.85 and 0.90 (Gaetani et al. (2003) from 0.87 to 0.89), Opx between 0.78 and 0.95 (Gaetani et al. (2003) from 0.88 to 0.90), Cpx between 0.82 and 0.83 (Gaetani et al. (2003) from 0.88 to 0.90) and Garnet 0.77 (Gaetani and Grove (1998) 0.73 at higher water content). The average Fe/Mg exchange coefficient ($K_D^{Fe/Mg} = D_{Fe}^{Mineral/Melt}/D_{Mg}^{Mineral/Melt}$) values for olivine (0.30 ± 0.01 versus 0.34 ± 0.01), Opx (0.42 ± 0.05 versus 0.32 ± 0.02), Cpx (0.43 ± 0.06 versus 0.33 ± 0.02) are in a global agreement with those of Gaetani et al. (2003) at the same pressure. Observed difference can be explained by different temperature and water content between this study and Gaetani et al. (2003) study, but also by F and Cl concentrations in our samples that can change $K_D^{Fe/Mg}$ (Filiberto et al., 2010). The average $K_D^{Fe/Mg}$ for our amphibole synthesized in the basaltic system, are higher (0.52 ± 0.03 in H4V4p and 0.43 ± 0.03 in H6V04, versus 0.32 to 0.39) than values from La Tourette et al. (1995) and Sisson and Grove (1993a), obtained in amphibole in equilibrium with basanite melt and high alumina basalt, respectively and in different P–T conditions. The average $K_D^{Fe/Mg}$ for phlogopite (in average 0.17 versus 0.16 to 0.24) is in a good agreement with those of Holbig and Grove (2008) at similar experimental P - T conditions.

Table 5.2.1 presents also the first F and Cl partition coefficients between studied phases and hydrous basaltic melt, or shoshonitic melt for samples SHO1 and SHO3. Errors on those values are less than 20% for F and less than 25% for Cl. Note that F is more incompatible in opx than in cpx, contrary to Cl. As expected, F and Cl are less incompatible in pargasite and phlogopite than in Ol, Opx and Cpx. Fluorine is even compatible in phlogopite. Fluorine is less incompatible in phlogopite, while chlorine is less incompatible in pargasite than in phlogopite.

Table 5.2.1: Stoichiometry of phases and fluorine and chlorine partition coefficients. $D_i^{mineral-melt} = c_i^{mineral}/c_i^{melt}$ in run products. c_i is the element concentration measured by the SIMS 1280.

Sample	Phase	Κ	Na	Ca	Al	$\mathrm{Fe}(\mathrm{II})$	Fe(III)	Mg	Si	\sum cations	O no.	D_F	D_{Cl}
H3V04	Cpx		0.04	0.72	0.27	0.14	0.02	0.93	1.85	4.01	6	0.114(2)	0.0113(89)
	Opx			0.06	0.22	0.20	0.02	1.60	1.87	4.00	6	0.563(3)	0.0203(6)
	Ol					0.25	0.03	1.69	1	2.98	4	0.0045(1)	0.0043(4)
H4V4p	Amp	0.02	0.77	1.29	1.73	0.73	0.08	4.45	6.62	15.81	23	0.36(7)	0.12(4)
	Opx			0.07	0.16	0.33	0.04	1.47	1.91	3.99	6	0.028(6)	0.055(13)
H5V4p	Cpx		0.06	0.80	0.26	0.19	0.02	0.87	1.83	4.05	6	0.083(4)	0.0145(8)
	Opx			0.05	0.20	0.12	0.01	1.76	1.87	4.02	6	0.028(6)	0.055(13)
H6V04	Amp	0.02	0.85	1.42	1.85	0.54	0.06	4.56	6.48	15.92	23	0.63(9)	0.38(8)
	Opx				0.16	0.22	0.02	1.61	1.90	4.00	6	0.021(2)	0.07(1)
Grt3V4p	Grt			0.37	1.95	0.53	0.06	2.08	2.96	8.00	12	0.166(2)	0.087(4)
	Cpx		0.11	0.34	0.39	0.19	0.02	1.02	1.87	3.97	6	0.070(6)	0.003(4)
	Opx		0.03	0.06	0.26	0.23	0.03	1.47	1.88	3.98	6	0.0462(9)	0.0064(5)
SHO1	Phlo	1.86	0.16		2.11	0.16	0.02	5.64	5.94	15.95	22	1.21(13)	0.10(1)
	Ol					0.16	0.02	1.80	1.00	2.99	4	0.016(12)	0.007(1)
SHO4	Phlo	1.66	0.42	0.03	2.10	0.29	0.03	5.45	5.94	15.98	22	1.3(2)	0.08(2)
	Amp	0.14	0.83	1.55	1.76	0.89	0.10	4.03	6.48	15.94	23	ND	ND

Abbreviations are the same used in Table 2. O no is for oxygen number.

ND, not determined.

We present atoms per formula unit (pfu) when they are $> 10^{-2}$. Pargasite and phlogopite stoichiometry were determined assuming that 2 OH²⁻ = 1 O²⁻. Pargasite pfu were calculated with 22 O and phlogopite with 23 O.

Trace elements partition coefficients were determined between obtained minerals and melt and were presented in the previous chapter (Chapter 4). As illustrated on the Figure 5.2.2 and discussed in the previous chapter (Chapter 4, section 4.2.2), our REE partition coefficients between mantle minerals and silicate melts are in agreement with literature data.

Among the samples shown in the Figure 5.2.2b), c), d) e) and f), there is no pressure difference, while main variable conditions are temperature and water content. It shows that trace elements including F and Cl are sensitive to temperature and water abundance in the system. The conclusion of Gaetani et al. (2003), which H_2O abundance during melting has a significant effect on trace element partitioning, appears to extend to other minerals studied here. Figure 5.2.2 highlights also that F and Cl partition coefficient variations among the samples are higher than partition coefficient variations of other trace elements, which are mostly within the error bars. It implies that F and Cl fractionation are more variable during melting than other REE following the present minerals or the abundance of water.



Figure 5.2.2: Plot of measured REE, F and Cl partition coefficients (classified following the incompatibility order of Workman and Hart, 2005) between olivine a), orthopyroxene b), clinopyroxene c), garnet d), amphibole e) and hydrous basaltic melt, and between phlogopite f) and hydrous shoshonitic melt. Colored field represents literature data, detailed in the previous chapter, section 4.2.2. Note that, in the basaltic system, F and Cl partition coefficients show larger variations than REE partition coefficients with temperature and water content dissolved in the melt, as discussed in the previous chapter (Chapter 4).

5.2.3 C_0 and D_0 of sub-arc lherzolites

Source composition: C_0

All initial compositions are presented in Table 5.2.2. The variable initial compositions of sources, C_0 , were melted, and for each source, a range of initial compositions were melts, producing range of melts for each source. For dry lherzolite, we used DMM composition of Workman and Hart (2005) and the F concentration in DMM of Salters and Stracke (2004). Range of initial composition for dry lherzolite was calculated from error bars on DMM composition values. The C_0 used for the models of the hydrous melting was calculated by mixing DMM with 1.4 or 3.3 % of a slab component. The composition of the slab component was either (a) C1max component composition for the most enriched end member or (b) C2min component composition for the less enriched end member, taken from Le Voyer et al. (2010) slab component compositions. Consequently, range of variation of hydrous lherzolite compositions was created from the difference between DMM + (1.4 or 3.3%) C1max and, DMM + (1.4 or 3.3%) C2min. Note that in the all models, Zr content of the fluid component had to be decreased by 45% and K_2O to be increased of 45% to fit the melt inclusion data. Those C_0 of hydrous lherzolites were also used to calculated the C_0 of amphibole and phlogopite-bearing lherzolites, assuming that the aqueous component that interacts with the lherzolite creates amphibole or phlogopite. Thus the C_0 of amphibole- and phlogopite-bearing lherzolites were calculated by mixing the desired proportion of amphibole or phlogopite with the C_0 of hydrous lherzolites (1.4 or 3.3 %of slab component). The composition in F and Cl of amphibole were determined from Ionov et al. (1987) (one measurement of F 0.4 wt% and Cl 0.02 wt%) and from 3 measurements in an amphibole megacrysts from Kakanui, New Zealand (measured on electron probe at the Laboratoire Magmas et Volcans by N. Shimizu, personal communication, F range: 0.14 - 0.17 wt% and Cl range: 0.02 - 0.02 wt%0.023 wt%); thus F range in amphibole was defined to be between 0.14 and 0.4 wt% and Cl range in amphibole was enlarged between 0.01 and 0.03 wt%. Similarly, the composition in F and Cl in phlogopite were taken from Ionov et al. (1987) (F concentration in phlogopite ranges from 0.03 to 1.03 wt% and Cl ranges from 0.02 to 0.17 wt%) and from 23 measurements in phlogopites from peridotite xenoliths from South African kimberlites (measured on electron probe at the Laboratoire Magmas et Volcans by N. Shimizu, personal communication, F range: 0.14 - 0.94 wt% and Cl range: 0.02 - 0.15wt%). F range in phlogopite was defined to be between 0.03 and 1.03 wt% and Cl range in phlogopite between 0.02 and 0.17 wt%. The chosen F and Cl compositions of phlogopite are in agreement with measurements done by Sobolev et al. (2009) in high pressure phlogopite found in inclusion in kimberlite-hosted diamonds. Trace element concentrations in amphibole and in phlogopite were found in Ionov and Hofmann (1995) and in Marocchi et al. (2010).

	DMM		Fluid		Dry Lherz		1.4% fluid		3.3% fluid		Amp lherz		Phlo lherz	
	min	max	Cmin	Cmax	\min	max	min	\max	min	\max	min	\max	min	max
F	6e-4	1.6e-3	0.13	1.37	8e-3	1.5e-2	2.4e-3	2.1e-2	8.4e-3	8.4e-2	1.4e-1	4e-1	3e-2	1.29
Cl	3e-5	6.3e-5	0.50	1.48	2e-4	4e-4	7e-3	2.1e-2	8.9e-2	3e-2	1e-2	3e-2	2e-2	4.9e-1
La	1.6e-5	2.2e-5	0.004	0.025	1e-3	5e-3	7.6e-5	3.7e-4	2.7e-4	1.5e-3	2.4e-6	3.3e-6	1e-8	4e-6
\mathbf{Sr}	6.5e-4	8.7e-4	0.27	1.10	2e-3	2e-2	4.4e-3	1.6e-2	1.7e-2	6.7e-2	1.9e-2	6e-2	7.7e-5	6.5e-4
K_2O	6.0e-3	6.0e-3	3.18	14.02	4e-1	1	8.7e-2	3.6e-1	2e-1	8.5e-1	5.2e-1	1.56	5.75	11.25
\mathbf{Zr}	4.5e-4	5.6e-4	0.035	0.127	2e-3	2e-2	7.1e-4	1.5e-3	2.5e-3	8.1e-3	2.7e-4	2.9e-4	6e-6	5.9e-5
Υ	3.2e-4	3.5e-4	0.006	0.012	5e-4	5e-3	4e-4	5.1e-4	6.8e-4	1e-2	1.1e-4	3.6e-3	9e-6	2.9e-5

Table 5.2.2: Summary of C₀ compositions for every melting scenarios.

Lherz is for lherzolite. 1.4% and 3.3% are for lherzolite metasomatized by 1.4% and 3.3% of fluid, respectively. Amp lherz is for amphibole-bearing lherzolite. Phlo lherz is for phlogopite-bearing lherzolite.

The bulk partition coefficient: D_0

Bulk partition coefficients D_0 of anhydrous lherzolite was calculated from partition coefficients presented in Dalou et al. (accepted, Chapter 3), with data of opx and cpx of sample CC4#7b for spinel lherzolite, with data of opx, cpx and garnet of sample C4p#25kb for garnet lherzolite. Partition coefficient of olivine was taken from sample CC01#8kb4. The D_0 of the lherzolite with 1.4% of aqueous component provision was calculated from measured $D_i^{olivine/hydrousmelt}$, $D_i^{opx/hydrousmelt}$ and $D_i^{cpx/hydrousmelt}$ of the sample H3V04. The D_0 of the lherzolite with 3.3% of aqueous component provision was calculated from measured $D_i^{olivine/hydrousmelt}$ of the sample H3V04, $D_i^{opx/hydrousmelt}$ of the sample H6V04 and $D_i^{cpx/hydrousmelt}$ of the sample H5V4p. For amphibole-bearing lherzolite, we used the same $D_i^{olivine/hydrousmelt}$, $D_i^{opx/hydrousmelt}$ and $D_i^{cpx/hydrousmelt}$ of hydrous lherzolite with 3.3% of water addition and $D_i^{amphibole/hydrousmelt}$ of sample H6V04. For phlogopite-bearing lherzolite, we used the same $D_i^{olivine/hydrousmelt}$, $D_i^{opx/hydrousmelt}$ and $D_i^{cpx/hydrousmelt}$ of hydrous lherzolite with 3.3% of water addition and $D_i^{amphibole/hydrousmelt}$ of sample H6V04. For phlogopite-bearing lherzolite, we used the same $D_i^{olivine/hydrousmelt}$, $D_i^{opx/hydrousmelt}$ and $D_i^{cpx/hydrousmelt}$ of hydrous lherzolite with 3.3% of water addition and $D_i^{phlogopite/hydrousmelt}$ of sample SHO4. The obtained D_0 of bulk lithologies are presented in the Figure 5.2.3. As discussed in Chapter 4, it highlights that F and Cl partition coefficients calculated for variable lithologies and with different fluid quantity still more variable than REE partition coefficient variations, which are mostly within the error bars.

5.2.4 Melting scenarios

Several scenarios of melting in the sub-arc mantle were tested and are presented in the little sketchs of the Figure 5.3.1. The sketch ① to ④ illustrates the different presented lithologies melted in this model. In melting scenarios ① and ②, I melted a lherzolite lithology: 57% olivine, 28% orthopyroxene and 13% clinopyroxene. The sketch ① shows the melting of the sub-arc mantle without fluid interaction. The sketch ② illustrates the melting of the sub-arc mantle with 1.4 or 3.3 % of fluid addition. This fluid does not change the mineralogy, since such fluid carries insignificant quantity



Figure 5.2.3: Plot of measured REE, F and Cl partition coefficients (classified following the incompatibility order of Workman and Hart, 2005) between spinel lherzolite and basalt, calculated from mineral modal abundance in DMM (Workman and Hart, 2005), 57% olivine, 28% orthopyroxene and 13% clinopyroxene for dry and hydrous lherzolite without bearing hydrous minerals and calculated from 60% olivine, 20% orthopyroxene, 5% clinopyroxene and 10% of pargasite for amphibole-bearing lherzolite, and from 60% olivine, 20% orthopyroxene, 15% clinopyroxene and 5% of phlogopite for phlogopite-bearing lherzolite. For dry lherzolite, D^{bulk} were calculated from sample CC4#7b (Dalou et al. 2011, submitted). Fluid content of hydrous lherzolite was calculated assuming $D_{H_2O} = 0$ with 35% of melting and considering that this fluid was composed in average of 60% of H_2O (Le Voyer et al., 2010). The hydrous lherzolite containing 1.4 wt% of water corresponds to 2.6 wt% of water dissolved in the melt (sample H3V04) and the hydrous lherzolite containing 3.3 wt% of water corresponds to 5.9 wt% of water dissolved in the melt (sample H6V04). To calculated D^{bulk} of the hydrous lherzolite containing 1.4 wt% of water, I used $D^{olivine/melt}$, $D^{opx/melt}$ and $D^{cpx/melt}$ of the sample H3V0. To calculated D^{bulk} of the hydrous lherzolite containing 3.3 wt% of water, I used $D^{olivine/melt}$ of the sample H3V04 and $D^{cpx/melt}$ of the sample H5V4p and $D^{opx/melt}$ of the sample H6V04. For hydrous lherzolite with hydrous phases (5% of pargasite or 10% of phlogopite) data of sample SHO4 were used for phlogopite and data from sample H4V4p were used for pargasite. Modes of hydrous mineral-bearing lherzolite were chosen using Ionov and Hofmann (1995). Because of significant uncertainties on D_{Pb} , we choose not to used those data.

of major element cations. It only induces and participates in melting. In these scenarios, I used p_i for the melting dry and hydrous spinel lherzolite from Gaetani and Grove (1998) and Walter (1998) for garnet lherzolite. The fluid composition is ranged from C1max component composition for the most enriched endmember and C2min component composition for the less enriched end member, from Le Voyer et al. (2010). This range is consistent with previous studies that determined slab fluid composition (Cervantes and Wallace, 2003; Portnyagin et al., 2007; Johnson et al., 2009). Consequence of this fluid provision is that it will change the fractionation of trace element, particularly F and Cl fractionation during melting, but also the fluid will bring significant quantities of trace and volatile elements. The range of the mixing between trace element from the fluid with the mantle is illustrated by big arrows on the figure 5.3.1. In scenario (2), I fixed just two quantities of fluid, but the width of melting field is created by the variation range of C_0 compositions depending on fluid composition, C1max or C2min.

In sketchs (3) and (4), I assume that the released fluid has interacted with the sub-arc mantle prior to the partial melting and created hydrous minerals: amphibole or phlogopite. Consequence of this step is that it will change the fractionation of trace element during melting, particularly F and Cl fractionation, but also the fluid add trace and volatile elements to the source. To model this melting, I used p_i determined for amphibole-lherzolite by Médard and Grove (2008), both for amphibole and phlogopitebearing lherzolite, since to our knowledge no melting reaction was determined for phlogopite-bearing lherzolite. After the melting mode of amphibole-bearing lherzolite, 2.27% amphibole in the source disappears after 1% of melting (Médard and Grove, 2008). Since there is no study describing the melting mode of phlogopite-bearing lherzolite, I assumed the melting mode is closely approximated by the same reaction as the amphibole-bearing lherzolite melting. In the melting scenario (3), the amphibole-bearing lithology is bearing 60% olivine, 20% orthopyroxene, 5% clinopyroxene and 10% amphibole. In the melting scenario (4), the phlogopite-bearing lithology is bearing 60% olivine, 20% orthopyroxene, 15% clinopyroxene and 5% phlogopite. Those two modal composition were chosen after Ionov et al. (1987). In our melting model, I stopped the melting of amphibole-bearing lithologies at 4.4 % of melting, and phlogopite-bearing lithologies (5% initial phlogopite) at 2.2 % of melting. Then, the melting process is restarted using the new dry lherzolite parameters $(D_i \text{ and } p_i)$, and the residual solid composition is taken as the new initial composition of the source. The residue of the melting was calculated from the equation of Shaw (1970):

$$C^{S} = \frac{C_{0}}{(1-F)} \left(1 - \left(\frac{P * F}{D_{0}}\right)^{\frac{1}{P}} \right).$$

The melts produced from this stage was essentially devoid of trace elements, they diluted trace element-rich, early melts from amphibole-bearing and phlogopite-bearing lithologies. The all four models were melted from 1 to 35 % of melting. I am aware that model is very simple, since after

melting of each C_0 , fluid component will go into melt immediately, but this is just a preliminary model, proposed to illustrate the usefulness of F and Cl.

5.2.5 Result of modelling

5.3 Model Results

Melting trends are represented by thin arrows on the Figure 5.3.1, where the arrowhead is 1 % of melting (when the melt field is limited by the figure boundaries, it means that melting path starts outside of the figure) and the tail of arrow indicate 35 % of melting. Modeled melts were also compared to primitive melts from arc melt inclusions provided by Le Voyer (2009); Le Voyer et al. (2010); Sorbadere et al. (2011), Sorbadere et al. (in preparation) and Bouvier et al. (2010b,a, 2008). Number of plotted melt inclusion compositions is different following diagrams given that some study did not report the elements of interest.

Since the partition coefficient of Y was not measured in this study, I substituted with Ho to create the diagrams of Figure 5.3.1. On Figure 5.3.1a, melt compositions are normalized to Y and K_2O . Such normalization can reduce compositional variations due to crystal fractionation prior to melt entrapment in the host olivine, since Y and K_2O are both incompatible elements. This permits the direct comparison of natural melting inclusion data with the melt compositions modeled by the three scenarios.

Those diagrams show that modeled melt fields reproduce the composition variations of melt inclusions. Variation in these diagrams reflects mixing between mantle and fluids and/or melting processes, since calculated melting fields have different shape in all plots.

The diagram F/Y versus Zr/K₂O (Figure 5.3.1a) was chosen among other diagrams since it shows really different melting trend between H₂O-rich fluid induced-melting and the melting of a hydrousmineral bearing source. This comes from the fact that the D_{Zr}/D_{K2O} ratio is much smaller for hydrous minerals (0.04 for amphibole and 0.0006 for phlogopite) than for common lherzolite minerals (olivine 2-0.01, opx 0.075-0.47, cpx 1.42-12.71). In the diagram F/Y versus Zr/K₂O (Figure 5.3.1a), the majority of melt inclusions are distributed along the mixing line between DMM and fluid compositions. From this diagram, melt inclusion distribution could be interpreted as resulting melts of the source mixed with various proportion of fluid. The fluid-induced melting field (grey) is narrow in this diagram since the Zr/K₂O cannot be varied by fluids addition, and melting does not change the Zr/K₂O ratio in melts because of $D_{Zr}/D_{K2O} \sim 1$ during hydrous melting. Nevertheless, some melt inclusions are out this mixing line, and they seem to be explained by melts from hydrous minerals lithologies. Given K₂O being compatible in amphibole and phlogopite, the D_{Zr}/D_{K2O} ratio is ≤ 0.1



Figure 5.3.1: Diagrams resulting from melting modeling, showing different fields of melt produced by various lithologies, detailed on the sketches of the left side. Details of the modeling are in the text. It shows that fields are variable in extension and in shape, following fluid amount or lithologies.

and Zr/K_2O ratio increase in the melts during melting of amphibole- and phlogopite-bearing lithologies.

On the diagram F/Y versus Sr/K₂O (inset Figure 5.3.1a), I can distinguish a melting of a herzolite mixed with 3.3 % of fluid, from a melting of a phlogopite-bearing herzolite, from a melting of an amphibole-bearing herzolite, and from a melting induced by small fluid contribution (1.4 %). Melt composition from the melting of hydrous minerals-bearing herzolite strongly depends on the initial concentration of trace elements in amphibole and phlogopite, likely coming from the fluid. For hydrous induced melting, melting process depends only on fluid composition and its mixing with the source mantle, and on partition coefficients. The D_{Sr}/D_{K2O} ratio is higher for melting with 1.4 % of fluid contribution (0.65) than for melting with 3.3 % of fluid contribution (0.49). This explains the difference of melting trend slope, but the extent of the field is explained by difference of fluid contribution. Since more fluid decreases the Sr/K₂O ratio, the melts with small fluid contribution have high Sr/K₂O ratios. In this diagram, the distribution of melt inclusions is no longer along mixing trend between mantle and fluids. Melt inclusions data are rather scatter into the fields defined by various degree of melting, most of them can be interpreted with multiple melting models. The diagram better suited to decipher the degree of melting than the source of melt inclusions.

Using the diagram Cl/Y versus F/Y (Figure 5.3.1b, I can clearly distinguish melting with 1.4 and 3.3% of fluid, because, as previously noted, F and Cl partition coefficients are very sensitive to the quantity of water in melt. It clearly appears in this diagram that melting trend with 1.4 % of fluid does not mainly depend on fluid composition (light gray). Concerning hydrous minerals bearing lherzoltite melts, shape of fields is similar since the signature of hydrous minerals is diluted by melting of olivine, opx and cpx. Nevertheless, I can distinguish the field since enrichment in F and Cl will be higher in melts of phlogopite-bearing source than in amphibole-bearing source than in hydrous mineral free source. This is mainly caused by the fact that initial fixed range of phlogopite volatile content (F: 0.03 - 1.03 wt% and Cl: 0.02 - 0.17 wt%) is larger than amphibole's range (F: 0.14 - 0.17wt% and Cl: 0.02 - 0.023 wt%). The different F and Cl enrichment in modeled melts may be used to explain F and Cl enrichment in melt inclusions, which show in this diagram very distinct trends. The last diagram Cl versus Cl/F is a diagram showing highly incompatible element versus highly incompatible element / moderately incompatible, which allow to easily distinguish mixing process from melting process (e. g. Schiano et al., 2010). On this diagram, if the variation in melt inclusion compositions is produced by various mixing degree between a mantle end-member and a fluid, melt inclusions would be distributed along mixing lines. On the contrary, when the variation in melt inclusion compositions is produced by various melting degree, melt inclusions would be distributed along melting trends. As it was the case for the previous diagram (Figure 5.3.1b), melts with various degree of fluid contribution generate very different fields due to the variation of halogen partition coefficients.

Melts of amphibole- or phlogopite-bearing lithology and hydrated by 1.4 % of fluid lherzolite create the melt fields that cover large part of the diagram, with the same shape but different in size.

Some inconsistencies appear on diagrams 5.4.1 b) and c): melting rate of some melt inclusions differ from one figure to the other. This likely comes from the fact that this melting model is very simplified. Increasing degrees of melting correspond to increase in temperature as melt moves upward in the inverted temperature gradient with depth. The alignment of La Sommata melt inclusions can reflect that point.

The various fractionation among elements depending on fluid contribution or on lithology is summarized in Figure 5.3.2. Compositional differences among melts derived from various lithologies are subtle. Major variations appear to follow the quantity of fluid involved in the melting (Figure 5.3.2). In such diagram, melt inclusion compositions seem to be the result of mixings between the mantle (here DMM , 1 on the Figure 5.3.2) and fluids. This confirms that, for the studied elements, chosen fluid composition is suitable for our modeling.

On Figure 5.3.2, I observe a crossing between two melt compositions produced by amphiboleand phlogopite-bearing lherzolite. This crossing is especially well illustrated for highly incompatible elements as Cl and K and moderately incompatible elements such as F and Y. Nevertheless, this difference in fractionation is very small for the high degree of melting of these melts ($\pm 24\%$). Fractionation difference between lithologies appears clearer either for low degree of melting or for melting paths indicated in Figure 5.3.1.

5.4 Discussion: implications for the source of arc melt inclusions.

Combined with trace elements, F and Cl signature in melts are helpful to decipher the source of arc magmas. Assuming that melt inclusions are representative primitive magmas, they are used to determine the source of arc magmas. On figure 5.4.1, I distinguish melt inclusions from different arcs: Shasta, Italy, Vanuatu, Ecuador and Antilles from Le Voyer (2009); Le Voyer et al. (2010); Sorbadere et al. (2011); Bouvier et al. (2010b,a, 2008), in diagrams previously detailed where I kept fields of different modeled melts. Using those fields, it can be possible to determine the source processes of arc magmas.

As described in Le Voyer (2009), 'the Cascades volcanic arc is characterized by subduction of young (12-14 Ma beneath Mt. Shasta; Green and Harry, 1999) oceanic lithosphere from the Juan de Fuca and Gorda plates beneath the North American plate, and has one of the lowest subduction



Figure 5.3.2: Spiderdiagram comparing modeled produced melts of various lithologies, and fluid composition determined by Le Voyer et al. (2010) and primitive melts from arc melt inclusions (Le Voyer, 2009; Le Voyer et al., 2010); Sorbadere et al. (2011); Sorbadere et al. (in preparation), normalized to DMM composition (Workman and Hart, 2005; Salters and Stracke, 2004). Determined melts result from one degree of melting: 24% for dry lherzolite, lherzolite with 1.4% of fluid and hydrous minerals-bearing lherzolite melting and 27% for lherzolite with 3.3% of fluid melting. Note that Lu melt concentration was modeled without fluid addition, since data of Lu in fluid is not available.

rates observed (40 mm/year; Wilson, 1988). Consequently, the slab undergoes extensive dehydration before reaching sub-arc depths, where the slab-derived flux is expected to be smaller than at typical cool subduction arcs such as Marianna arc (e.g. Leeman et al., 2005). Both nearly anhydrous and hydrous mafic lavas erupted in the vicinity of Mt. Shasta and belong to three groups: high aluminium olivine tholeites (HAOT, also referred to as highalumina basalts, HAB), basaltic and esites (BA) and primitive magnesium and esites (PMA; Baker et al., 1994; Grove et al., 2002). According to previous studies (Bartels et al., 1991; Sisson and Grove, 1993a; Baker et al., 1994; Grove et al., 2002), the HAOT are derived from decompression melting of a mantle source only insignificantly affected by slab-derived fluids. The BA and the PMA, however, display more variable compositions with a stronger fluid imprint compared to the HAOT. They represent flux melting of a depleted mantle with a variable and high water content (3-5 wt% H_2O for the BA and up to 6 wt% for the PMA; Baker et al., 1994; Gaetani and Grove, 1998; Grove et al., 2002). However, the origin of the PMA, a nearly primary magma (Grove et al., 2002; Barr et al., 2007, 2008) versus a product of mixing between basic and dacitic terms (Streck et al., 2007), is still under debate.' In Le Voyer et al. (2010) study, they focused only on the source of the HAOT and the BA and found four different signatures of arc melt inclusions for Shasta arc magmas (see figure 5.4.1). The inclusions 85-38 are depleted in volatile elements, and regarding to figures 5.4.1 b) and c), they are likely produced by the melting of a dry lherzolite, in other words, a non-metasomatized mantle. Their signature thus corresponds to decompression melting of a non-metasomatized mantle source. Other Shasta melt inclusions (85-47, 85-1a and 95-15) are more enriched in F and Cl. Most of them fits into melt field of fluid-induced melting: difference between families of melt inclusions can be explained by the quantity of fluid involved in the melting and by various melting degrees. Melt inclusions 95-15 are likely produce by melting involving more fluid (dark grey field 5.4.1) than melt inclusions 85-47 and 85-1a (light grey field 5.4.1).

Described in Sorbadere et al. (2011), 'the Vanuatu arc is generated by the northeastward subduction of the Australian plate beneath the Pacific plate (Pascal et al., 1978; Daniel et al., 1989). The central block of the Vanuatu arc is a complex zone of intra-arc shortening at rate, between Aoba island and the eastern back-arc thrust belt, of ± 20 mm year⁻¹ (Bergeot et al., 2009)'. Melt inclusions from three volcanoes from the Vanuatu arc were studied in Sorbadere et al.(in prep). Melt inclusions show various enrichment in volatile elements in figure 5.4.1 b) and c). Data from Santa Maria (Gaua) melt inclusions belong clearly to the field of amphibole-bearing lherzolite melt field on figure 5.4.1 b), while Ambrym melt inclusions belong to fields of melting of common lherzolite with fluid contribution. On figure 5.4.1 c), it appears that Ambrym melt inclusions are scatter into the two fields of fluid induced melting with 1.4 and 3.3 wt% of fluid contribution. Nevertheless, using figure 5.4.1 c), I cannot determine if variability of those melt inclusions comes from various degree of fluid mixing or various degree of melting. Regarding at the figure 5.3.1, Ambrym melt inclusions do not to be aligned along mixing trend, but rather than melting trends. As well as Ambrym melt inclusions, Aoba melt inclusions seems also to be produced by various melting degrees of a source metasomatized by 1.4 % of fluid. Those melt inclusions also appear to belong to other fields as field of phlogopite-bearing lherzolite melts. With major element measurements in those Vanuatu melt inclusions compared to experimental work, Sorbadere et al.(in preparation) also infer that Ambrym and Aoba melt inclusions signature results from the melting of a hydrated lherzolite, while Santa Maria melt inclusions results from the melting of an amphibole-bearing clinopyroxenite.

The islands of Vulcano and Alicudi belong to the Quaternary Aeolian island arc, where a sinking slab dips $50-60^{\circ}$ in a northwest direction beneath the Tyrrhenian Sea. Their volcanic products range in composition from basalt to rhyolite of the high-K calc-alkaline to show show the potassic series (e.g. Schiano et al., 2004). Work of Le Voyer (2009) and Sorbadere et al. (in preparation) provides F and Cl in melt inclusions from two volcanoes of the Aeolian arc. Alicudi melt inclusions can belong to several melting fields of the figure 5.4.1, although using the combination of several diagrams. They belong both to the amphibole-bearing lherzolite melts and phlogopite-bearing lherzolite melts field in the F/Y versus Zr/K₂O diagram and both to the amphibole-bearing lherzolite melts and fluid induced melting with 1.4% of fluid field in the F/Y versus Sr/K₂O diagram (Figure 5.4.1 a). It seems, therefore, that those inclusions are the result of an amphibole-bearing source. On figure 5.4.1 b, it is clear that Cl enrichment found in La Sommata melt inclusions (Le Voyer, 2009) can only be explained by the melting of a phlogopite-bearing source. On this figure, some inclusions are outside of the phlogopite-bearing lherzolite melt field, likely because chosen phlogopite initial composition was not rich enough in volatile elements. I noted that volatile element abundance data are poorly documented and were fixed by data from two studies. While such initial assumption is critical to the construction of the figure, it seems to suggest that phlogopite-bearing lherzolite is the most likely source of La Sommata primary magmas. The model of a phlogopite-bearing source was previously suggested by Schiano et al. (2004) to explain trace element characteristics of the Vesuvius and Phlegrean Fields melt inclusions, which belong to the Campanian arc system. The Vesuvius and Phlegrean Fields are close but are not a part of the Aeolian arc system. Following Schiano et al. (2004), Vulcano melt inclusions are generated from a K-poor fluid while the Vesuvius and Phlegrean Fields melt inclusions are the results of the melting of phlogopite- or K-rich amphibole- bearing mantle produced by the metasomatism of K-rich fluids or melts at higher pressure. Concerning our model, it can be ignored that La Sommata cone represents a singular explosive event, whose magma cannot be considered as representative of the Vulcano lava series. Consequently, I can assume that my model is not in disagreement, with Schiano et al. (2004) conclusions that Vulcano magma source does not bear

phlogopite. I just can assume that the source that produced La Sommata primitive magma bears phlogopite.

Data from two Ecuadorian volcanoes (Pichincha and Pan de Azucar, Le Voyer, 2009) were also studied. Pichincha and Pan de Azucar volcanoes are located in the front arc and rear arc of the Ecuadorian Andes, respectively. Ecuador is located in the northern part of the Andean cordillera, an orogenic belt formed by the eastward subduction of the Nazca plate beneath the South American margin. At the latitudes of Ecuador, the Carnegie Ridge, i.e., the Galapagos hot spot track on the Nazca plate, collides with the South American plate. It was suggested that the shallow dip of the downgoing plate (25-30°) (Guillier et al., 2001) is caused by the subduction of the Carnegie Ridge and controls the surface expression of volcanism. Indeed, chemical characteristics of Ecuadorian lavas indicate that slab melts participate in their formation (e.g. Monzier et al., 1997; Bourdon et al., 2003; Samaniego et al., 2005). Nevertheless, because I do not have Y data from those inclusions, their data were plotted in only one diagram. This prevents to decipher their source using my model. Le Voyer et al. (2008) attribute the origin of the Pichincha and Pan de Azucar melt inclusions to 'a mixing between partial melts of amphibole-bearing olivine clinopyroxenite lithologies (similar to those found in lower crustal or shallow upper mantle cumulates in arc environments) and of peridotitic lithologies. They also note variation in trace element and boron isotopic composition between the Pichincha and Pan de Azucar melt inclusions that result from the change of the slab input with increasing slab depth, and from the variation of the sediment-derived component.

I also looked at volatile compositions of melt inclusions from Saint Vincent and Grenada (Lesser Antilles). Described in Bouvier et al. (2010a), 'St. Vincent and Grenada are located in the southern part of the Lesser Antilles island arc, generated by the 2 cm/a westward subduction of the Atlantic Plate beneath the Caribbean Plate. These two islands are characterized by the presence of basalts with MgO contents higher than 10 wt%, thought to be representative of the primary magmas. These basalts are designated 'M-series basalts' at Grenada (Thirlwall et al., 1994, 1996; Devine, 1995) and 'high-Mg basalts' at St. Vincent (Heath et al., 1998; Macdonald et al., 2000; Pichavant et al., 2002; Pichavant and MacDonald, 2007).' Bouvier et al. (2010b,a, 2008) demonstrated that mobile/immobile element ratios (e.g. K/La, Sr/Y) track the involvement of early aqueous fluids and increase Cl/F, B and Cl recorded by the melt inclusions. This is what my diagrams 5.4.1 shows: most of the Antilles melt inclusions can be explained by the melting of a lherzolite metasomatized by 1.4% of an aqueous fluid. On figure 5.4.1, some inclusions are out of this melting field. Bouvier et al. (2010b,a) also found Grenada melt inclusions display unusual Zr enrichment (up to 1274 ppm), a rare feature in basaltic melts that possibly involves the localized dissolution of zircon. Disparities of those melt inclusions

could be explained by this zircon dissolution, present in the subducted sediment lithologies. On Figure 5.4.1 c), Saint Vincent melt inclusion compositions belong to the field of fluid induced melting with 1.4% of fluid. On Figure 5.4.1 b) and c), some Grenada melt inclusion compositions belong to the field of melting of an amphibole and a phlogopite-bearing source and the other belong to the field of fluid induced melting with 1.4% of fluid. Bouvier et al. (2010b) using trace elements suggest that Saint Vincent and Grenada melt inclusions have similar influences of aqueous fluids on the mantle sources. They also discuss a magma interaction with the surrounding mantle after melt inclusion entrapment, diluting and fractionating trace element abundances by mineral reaction and/or creation (e.g. amphibole). My model predicts the involvement of amphibole and phlogopite minerals in the source of some Grenada melt inclusions, while high Nb concentrations measured in some Grenada melt inclusions suggest an amphibole contribution after melt inclusion entrapment. Nevertheless, in this work, I consider that no modifications occured after melt inclusion entrapment.

More arc melt inclusions are needed to make extended interpretation of the nature of arc magma sources. Range of data including different subduction setting, such as oceanic or continental subductions, variable dip of the subducting slabs should provide variable data vectors. Nevertheless, at this point, I can suggest an hypothesis that the variability of F and Cl signature is best explained by the presence of hydrous mineral-bearing lherzolite melting beneath arc, along with the fluid-induced melting.

In Italian arcs (Aeolian and Campanian), I observed a clear signature of hydrous minerals bearing lherzolite melts. Those hydrous minerals could be the result of either the mantle interaction with aqueous fluids and metasomatism, or by interaction with hydrous siliceous melts and hybridization (Wyllie and Sekine, 1982) during early stage of subduction. Our modeling does not retain information on the nature of the component that creates hydrous phases.

As proposed by Tatsumi (1986), the melting reactions can occur in the dragged hydrated peridotites that overlie the down going slab. He suggested that the down going slab draggs the hydrated mantle wedge, and goes through several hydrous reactions forming chlorite, amphibole and phlogopite, respectively with the increasing pressure. Furthermore, following his model, partial melting occurs at two different depth beneath the volcanic arc coinciding with chlorite and amphibole, and phlogopite decompositions, that corresponds on the surface to the volcanic front and the back-arc volcanic chains. Nevertheless, in this model, it is the water released by those hydrous phases at their decompositions, which initiates the partial melting in the sub-arc mantle, when the migrating water reaches the region of the hydrous peridotite solidus.

In this study, our model involving hydrous phases-bearing sources does not require two steps of water



Figure 5.4.1: Same diagram as figure 5.3.1, with differing melt inclusion symbols. Origin and references are on the figure.

migration. In our model, only one step is needed, during which the released fluid or component from the slab creates amphibole and phlogopite. While Tatsumi (1986) model stressed that solidus temperature of hydrated peridotite cannot be attained in normal subduction zone, current thermal structure models of subduction zones (Kelemen et al., 2003b) is hot enough that amphibole- and phlogopitebearing peridotite could melt. This implies that amphibole-bearing lithology melts at shallower depths than phlogopite-bearing lithology. Consequently, I infer, from the Tatsumi (1986) model, that volcanic front primitive melt signatures is more likely produced by melting of amphibole-bearing sources, while back-arc primitive melt signatures is more likely produced by melting of phlogopite-bearing sources, as illustrated on Figure 5.4.2.

This assumption could be a part of the explanation of the presence of an amphibole signature observed in Alicudi melt inclusions and the phlogopite signature observed in La Sommata (Vulcano) melt inclusions and in Vesuvius and Phlegrean Fields melt inclusions (Schiano et al., 2004; Foley, 1992; Peccerillo, 1985), if their sources melted at different depths.

On the other hand, phlogopite signature were not find in Vanuatu melt inclusions, and neither phlogopite nor amphibole signature were found in Shasta melt inclusions. In Shasta case, melts result from the partial melting initiated by an influx of a hydrous rich fluid into the peridotite. I observed that various amount of fluid and various melting degrees can explained the compositional variations of that type of melt inclusions. Nevertheless, among Vanuatu melt inclusions, Santa Maria melt inclusions show amphibole signatures.

I assume that differences between arc melts having a hydrous mineral signature or having a fluid signature could be related to stability fields of hydrous minerals in the dragged hydrous peridotite and to dip of slabs. As illustrated on Figure 5.4.2, more the slab is sloping, more its surface is hot (e. g. Grove et al., 2009) thus reducing the stabilization of hydrous phases in the dragged hydrous peridotite (e. g. Fumagalli et al., 2009). Figures 5.4.2a and b simplify the idea that the presence or absence of amphibole- and phlogopite-bearing source signature is related to slab dips. In dipped subduction zones, isotherms are closer than in flatter subductions, and thus, destabilization temperature of hydrous minerals and solidus of hydrated lithologies or hydrous-bearing lithologies is reached more easily. Consequently, in flatter subduction zones, primitive melts have an hydrous minerals signature, while in steeper subduction zones, fluid induced melting signature hide the more or less negligible contribution of hydrous mineral bearing lherzolite melting.

Applying such idea to studied subduction zones, we observed fluid-induced melting for melt inclusions from Shasta volcano, which slab steeply dips (55 – 60 °, Cruciani et al., 2005), and from Vanuatu, even Ambrym melt inclusions have also a amphibole-bearing lithology melting signature, which slab is also very dip (70°, Pascal et al., 1978), while Aeolian and Antilles subduction, for which I found phlogopite and amphibole-bearing lithologies melt signature, is flatter (45 – 60°, Barberi et al.,



Figure 5.4.2: Sketchs explaining the relation between dip of slabs, thermal structure of subduction zones (dashed lines, drawned from Grove et al., 2009) and stability fields of hydrous minerals, determined from Fumagalli et al., 2009).

1974a,b for Aeolian subduction and see Bouvier et al., 2008 and Wadge and Sheperd, 1984).

5.5 Summary

The F and Cl partition coefficients I provided among with some trace element partition coefficients have shown a significant variations with the amount of aqueous fluid involved in melting at sub-arc P - T conditions (D_F between bulk rock and the silicate melt decreases and D_{Cl} increases of one order of magnitude between the melting of a dry lherzolite and the melting of a lherzolite with 3.3 % of water-rich fluid). Furthermore, I measured that F was compatible in phlogopite while it is not in amphibole and that Cl was more incompatible in phlogopite than in amphibole, that leads to a different fraction of F and Cl during melting of amphibole- or phlogopite- bearing lithologies. Consequently, these elements seemed to be a suitable candidate as tracers of the metasomatized arc magmas sources.

I presented several types of melting models that potentially occurs in the sub-arc mantle: dry melting, fluid induced melting with several percents of aqueous fluid, and melting of amphibole-bearing source or phlogopite-bearing source. Using our determined partition coefficients, the models allowed me to generate F, Cl and some trace element concentrations in the primitive melts. It appeared that our model could reproduce melt inclusion compositions, and that the melts from different lithologies. Having involved various amount of fluids could change F and Cl enrichments, which could be used to distinguish the source characters of different melt inclusion compositions.

I demonstrated that sources of some primitive melts, for instance from Italy, bear amphibole and phlogopite, while some primitive melts seem to be resulting from fluid induced melts. In that case, hydrous minerals are in the source and completely melt, they are not in the residu. I assume that difference between the two types of melting could be explained by variable slab dips. This model is not able to define the amphibole-bearing source depth. To test if the hydrous minerals signature come from the mantle source or from a crust root cumulate, other lithologies like amphibole-bearing clinopyroxenite has to be tested. Nevertheless, those lithologies bear around 30% of amphibole and their signature must be really different of what I calculated...

Conclusions and outlooks

The aim of the PhD work was to provide the first F and Cl partition coefficients between mantle minerals and melts. It represented an analytical challenge since no low abundance F and Cl measurement was so far achieved in anhydrous minerals. Thanks to mean collaborations, I succeeded to measure F and Cl partition coefficients between olivine, orthopyroxene, clinopyroxene, plagioclase, garnet, pargasite, phlogopite and silicate melts, in doped high-pressure experimental samples. Those new data allow me to study 1) F and Cl incorporation mechanisms in anhydrous minerals, 2) water influence on F and Cl fractionation and, 3) F and Cl potential as source tracers during arc magma genesis. As anions substituted in particular oxygen sites in crystals, F and Cl partitioning during melting could not be processed as commonly studied trace elements, but gave the opportunity to have access to new information on arc melting processes or sub-arc lithologies, given that they are more sensitive than trace elements to crystal chemistry and water amount variations thus melting conditions. In the following sections, I summarize the main results of this study that led me to this conclusion and I suggest new outlooks to pursue or improve this project.

Summary and outlook of the study on F and Cl incorporation in mantle minerals.

This study provided the first F and Cl partition coefficients for anhydrous conditions ranging 8 to 25 kbars and 1280 to 1430°C, between orthopyroxene, clinopyroxene, olivine, garnet, plagioclase and basaltic melt. It indicated that Cl incorporation into minerals in strongly dependant of crystal chemistry which is directly relevant to its big ionic radius (30% higher than O), while F substitution process depends mostly on melt viscosity, given its small ionic radius (5% smaller than O). It has been observed that Cl incorporation was eased by jadeite component in orthopyroxene and by CaTs component in clinopyroxene. Although no crystal structural and chemical variation with F content in crystals was found in this study, a recent study of O'Leary et al. (2010) have showed that F substitution was eased in clinopyroxene by CaTs component during hydrous experiments. This discrepancies can be explained that by the fact that, in my study, CaTs variation among clinopyroxene is not sufficient to change F incorporation. Nevertheless, this must be verified carrying out similar experiments as made here, but with variable amount of Al at the same pressure and temperature conditions.

This study highlighted also that Cl enters into the bigger O site and F into the smaller O site, in orthopyroxene, and Cl mainly coordinates with M1 site and F with the M2 site, in clinopyroxene.

This was inferred from Raman spectra and compositional correlations, but it could be confirmed by a electromagnetic propagation resistivity (EPR) (or electron spin resonance, RSE) study of F and Cl doped crystals. It is used to describe the local environment around a paramagnetic element. A project on F measurements is in process with the LMI ('Laboratoire des matériaux inorganiques') of Clermont-Ferrand, requiring new kind of experiments to grow highly doped single-phase samples. New developments on pyroxene lattice strain models indicated that trace elements partitioning changed with the F and Cl incorporation in the pyroxene structure. Finally, it pointed out that melt structure can also change F, Cl and trace elements partition coefficients in pyroxenes. With more F and Cl paralleled with trace element measurements in olivines, garnets and plagioclases, last points could be also extent to other minerals.

Summary and outlook of the study on the role of water on F and Cl behavior.

This study presented F and Cl partition coefficients between orthopyroxene, clinopyroxene, olivine, garnet, and hydrous basaltic melt and between phlogopite and hydrous shoshonitic melt for the conditions ranging 12 to 25 kbars and 1180 to 1370° C. It highlighted the complexity of understanding partitioning among hydrous experiments, where temperature, bulk water content and mineral compositions are variables. That is why a systematic study is required at fixed parameters as water amount with temperature variations and fixed temperature with water variations. Nevertheless, hydrous experiments are quite difficult, and furthermore peridotite basalt mix proportions have to be adapted following the amount of water and the temperature in order to avoid too high melting degrees. At this point, the study revealed that for some minerals: olivine, amphibole and especially orthopyroxene, F and Cl partition coefficients are more sensitive to water content and crystal-chemistry changes than other studied trace elements. I explained it by the fact that, unlike trace elements which are substituted into cation sites, F and Cl are substituted into the oxygen site which substitution depends on mineral structure (for instance, M – O distances).

Summary and outlook of the study on F and Cl behavior in the sub-arc mantle.

In this study, noted F and Cl variation with water amount and F and Cl partition coefficients measured between amphibole and phlogopite, were exploited to build melting models of sub-arc potential lithologies with variable water amount. A lot of assumptions were made to build this modeling, which requires further investigations, as for examples:

• Phlogopite-bearing lherzolite melting reactions had to be investigated. This is actually an ongoing M2 project put forward by Etienne Médard ('Laboratoire Magmas et Volcans'). Afterwards, those data will be used in my modeling to better constrain phlogopite-bearing lherzolite.

- Data on F and Cl concentrations in natural phlogopites and amphiboles from sub-arc lherzolite xenoliths have to be determined, in order to adjust initial compositions used in the model. This was so far not done, since the interest of F and Cl was not demonstrated. However, in phlogopite and amphibole, electron microprobe is often sufficient to achieve right measurements. Data of F and Cl abundances in others natural sub-arc mantle minerals (as olivines, pyroxenes or garnets) have also to be measured in order to better constrain the model, but it would require ion probe measurements. Those measurements have to be done in fresh, non-altered minerals from sub-arc xenoliths, which are rare samples.
- In order to better constrain fluid compositions, the amount of F and Cl released by slab minerals during subduction process, solubility of F and Cl in fluids and partitioning experiments between fluids and slab minerals are needed. This work is being carried out by Wu Jia, currently in PhD at the 'Laboratoire Magmas et Volcans'.

Despite limitations, my modeling plotted in F/Y versus Zr/K_2O or Sr/K_2O , Cl/Y versus F/Y or Cl versus Cl/F diagrams unable to distinguish: 1) amount of water involved in melting, 2) melting induced by fluid or melting of an hydrous mineral-bearing source and 3) melting of amphibole-bearing lithology from melting of phlogopite-bearing lithology.

Furthermore, this model was used to decipher some melt inclusion sources. It demonstrated that sources of some primitive melts, for instance from Italy, bear amphibole and phlogopite, while some primitive melts seem to be resulting of fluid-induced melts. I assumed that difference between the two types of melting could be explained by variable slab dips. Nevertheless, to verify this assumption, more F and Cl concentration measurements are required in arc melt inclusions, from various type of subduction zones.

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Appendices

Appendix A

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Trace element partitioning between carbonatitic melts and mantle transition zone minerals: Implications for the source of carbonatites

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Abstract

The occurrence of CO₂-rich lavas (carbonatites, kimberlites) and carbonate-rich xenoliths provide evidence for the existence of carbonatitic melts in the mantle. To model the chemical composition of such melts in the deep mantle, we experimentally determined partition coefficients for 23 trace elements (including REE, U-Th, HFSE, LILE) between deep mantle minerals and carbonatite liquids at 20 and 25 GPa and 1600 °C. Under these conditions, majoritic garnet and CaSiO₃ perovskite are the main reservoirs for trace elements. This study used both femtosecond LA-ICP-MS and SIMS techniques to measure reliable trace element concentrations. Comparison of the two techniques shows a general agreement, except for Sc and Ba. Our experimentally determined partition coefficients are consistent with the lattice strain model. The data suggest an effect of melt structure on partition coefficients in this pressure range. For instance, strain-free partition coefficient (D_0) for majorite–carbonatite melts do not follow the order of cation valence, $D_0^{2+} > D_0^{3+} > D_0^{4+}$, observed for majoritic garnets found as inclusions in diamond to model trace element patterns of deep-seated carbonatites. The result compares favorably with natural carbonatites. This suggests that carbonatites can originate from the mantle transition zone. © 2008 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Degassing of CO₂ from mid-ocean ridge basalts (Javoy and Pineau, 1991; Sarda and Guillot, 2005), CO₂-rich lavas like kimberlites (Price et al., 2000) and carbonatites (Krafft and Keller, 1989; Keller and Krafft, 1990) attest to the presence of CO₂ in the Earth's mantle. As CO₂ mass-balance demonstrates, only 20–40% of the subducted CO₂ is degassed by volcanoes (Zhang and Zindler, 1993; Coltice et al., 2004). These observations require the existence of a deep carbon reservoir in the mantle. Furthermore, experimental studies indicate that CO₂ forms stable phases at var-

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ious depths (including great depths) during subduction

Carbonatitic melts are considered as effective metasomatic agents because of their excellent wetting properties (Hunter and McKenzies, 1989; Watson et al., 1990), high migration rates (Hammouda and Laporte, 2000) and characteristic chemical signature (Green and Wallace, 1988; Jones, 1989; Meens et al., 1989). For example, rare earth element (REE) enrichment and high field strength element (HFSE) depletion in oceanic and continental xenoliths are often attributed to carbonatitic metasomatism (e.g. Menzies and Wass, 1983; O'Reilly and Griffin, 1988; Yaxley et al., 1991; Dupuis et al., 1992; Hauri et al., 1993; Ionov

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processes (Molina and Poli, 2000; Hammouda, 2003; Dasgupta et al., 2004) and that CO_2 in the deep mantle likely induces the formation of carbonatitic melts (Wyllie and Huang, 1975; Eggler, 1976; Green and Wallace, 1988).
et al., 1993; Rudnick et al., 1993; Ionov, 2001). Furthermore, the inferred presence of high-pressure mineral inclusions in diamond (Harte et al., 1999; Hutchison et al., 2001; Kunz et al., 2002) suggests the existence of carbon-bearing fluids at pressures corresponding to depths of 600 km or more. Chemical interactions between carbonatitic melts and upper mantle minerals have previously been modeled using trace element partition coefficients collected between 2 and 6 GPa (Sweeney et al., 1992; Klemme et al., 1995; Blundy and Dalton, 2000; Adam and Green, 2001; Keshav et al., 2005). However, element partitioning at higher pressures for example at the conditions of the transition zone, is still unknown. Here we present new major and trace element partitioning data between majoritic garnet, CaSiO₃ perovskite and carbonatitic melts at conditions of the lowermost transition zone and uppermost lower mantle. To emphasize the specific nature of carbonatitic and silicate metasomatism, we compare our new partitioning data with previous studies obtained in CO2-free compositions (Corgne and Wood, 2004; Walter et al., 2004; Corgne et al., 2005).

2. MATERIALS AND METHODS

2.1. Experimental procedure

The starting material was prepared by mixing 79.8 wt% of a pyrolite composition (Green and Ringwood, 1963; Table 1) with 20.2 wt% of a natural dolomite. This composition was chosen to achieve liquidus saturation of mantle phases with sufficiently large quantity of liquid. The pyrolite powder was prepared from a synthetic gel that was annealed for 40 min at 1400 °C in a 1 atm gas-mixing furnace,

at about 2 log units above the iron-wüstite oxygen buffer (Table 1). The natural dolomite (from Ben Gasseur, Tunisia) was chosen because its major element composition is close to that calculated for a dolomite in equilibrium with the deep mantle. This dolomite was crushed and sieved. and from the 400 µm fraction clean dolomite grains were handpicked under a binocular microscope. After grinding to µm-size grains, the dolomite and pyrolite powders were homogenized under ethanol in an agate mortar. The mixture was doped at the 100-200 ppm concentration level with a suite of trace elements that were added to the powder as a multi-element solution (Table 2). Element concentration in the final mixture was approximately 100 ppm (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu and Sc, Nb, Ta and U) except for Zr, Hf, Ba, Rb and Th, for which doping was 200 ppm. The doped mixture was stored in a drying oven at 150 °C. Although the starting powder was kept dry, the final mixture retained approximately 1500 ppm H₂O by weight, determined by the infrared absorption of a compacted powder pellet.

The experiments were performed at conditions ranging from 1500 to 1700 °C and from 10 to 25 GPa using a multi-anvil apparatus (Kawai and Endo, 1970) fitted with a Walker-type module (Walker et al., 1990) at the "Laboratoire Magmas et Volcans" (LMV) in Clermont-Ferrand, France. The starting powder was packed in an Au capsule (1mm outer diameter), which was welded shut by electric arc welding. We have employed a standard sample assembly, which consists of a ceramic octahedron (MgO with 5% Cr₂O₃), a ZrO₂ sleeve used as thermal insulator (except for 7/2.5 assembly), a LaCrO₃ stepped or straight furnace (stepped for 14/8 assembly and straight for 10/4 and 7/2.5 assemblies), and a MgO sleeve that isolates the capsule

Table 1

Major and minor element concentrations of starting materials and run products

				-		-						
Oxides (wt%)	SiO ₂	TiO ₂	Al ₂ O	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	CO ₂ ^c	Total
Starting compo	sitions											
Pyrolite ^a	42.70	0.18	3.14	0.453	7.49	0.14	37.70	2.91	0.41	0.001		95.27
Dolomite [20] ^b					14.30(88)	0.38(14)	12.02(58)	28.45(58)	0.03(6)	0.008(20)	44.80(102)	99.99
Mixture	34.10	0.14	2.51	0.36	8.86	0.19	32.53	8.06	0.33	0.002	9.03	96.22
#743 (20 GPa-	1600 °C)											
Maj [13]	49.38(145)	0.11(10)	8.56(62)	1.00(12)	6.14(38)	0.18(8)	27.11(135)	6.60(106)	0.05(4)	0.001(10)	0,138	98.30
CaPv ^d [8]	37.29(126)	4.54(24)	2.54(21)	0.35(12)	1.44(52)	0.03(6)	0.74(20)	40.13(89)	0.03(4)	0.006(28)		87.12
P [7]	40.03(94)	0.24(90)	0.45(20)	0.15(6)	7.46(80)	0.10(4)	49.73(252)	0.04(4)	0.04(2)	0.003(3)		98.24
Per [3]	0.16(8)	0.02(4)	0.18(4)	0.39(8)	23.86(100)	0.29(8)	72.22(272)	0.07(2)	0.14(2)	0.000 (0)		97.34
Melt [5]	11.50(20)	0.32(32)	0.10 4)	0.04(8)	4.90(22)	0.25(4)	20.85(118)	27.62(46)	1.43(4)	0.257 (4)	32.72	100.00
#787 (25 GPa-	1600 °C)											
Maj [6]	46.73(100)	0.019(29)	14.09(58)	1.48(19)	7.32(27)	0.47(3)	25.05(19)	4.98(30)	0.18(4)	0.007(26)		100.32
CaPv [9]	48.57(99)	0.69(7)	.08(25)	0.07(5)	0.35(39)	0.06(8)	0.10(2)	46.32(95)	0.02(1)	0.003(6)		97.26
MgPv [5]	53.03(187)	0.23(7)	4.37(70)	0.43(11)	9.15(173)	0.12(6)	33.39(134)	0.11(4)	0.008(22)	0.007(11)		100.84
γ [4]	40.34(58)	0.012(48)	0.08(4)	0.15(5)	13.94(15)	0.07(2)	43.91(114)	0.05(5)	0.008(19)	0.009(17)		98.57
Mst [3]	0.18(52)	0.02(3)	0.03(10)	0.04(8)	2.65(65)	0.08(10)	43.16(940)	0.24(27)	0.00(0)	0.01(2)	53.46	100.00
Melt [3]	7.46(114)	0.15(5)	0.63(11)	0.14(1)	8.57(73)	0.45(3)	22.13(25)	16.21(402)	0.71(9)	0.13(1)	43.42	100.00

Number in parentheses represents two standard deviations (2σ) in terms of least significant digits. Maj, majorite garnet; β , wadsleyite; γ , ringwoodite; CaPv, CaSiO₃ perovskite; MgPv, MgSiO₃ perovskite; Per, periclase; Mst, magnesite; Melt, quenched carbonate melt.

^a Analysed by ICP-AES.

^b Numbers of electron microprobe analyses given in square brackets.

^c CO₂ was calculated by difference.

Table 2	
Trace element concentrations (in ppm) of starting material and run product #743 (20 GPa, 1600	°C)

Starting of	loped powder	Majorite		Melt		$D_{\rm Maj/Melt}$			CaPv	PvCaPv/Melt
		LA-ICP-MS [3] ^a	SIMS [4]	LA-ICP-MS [2]	SIMS [3]	LA-ICP-MS	SIMS	Preferred ^c	SIMS [I]	
Sc	97	33(5)	54(6)	5.78(6)	19.3(6)	5.71(90)	2.8(7)	_	27.0(5)	1.40(7)
Rb	103	n.m.	6.4(6)	n.m.	1151(64)	_ `	0.0055(14)	0.0055(14)	15.11(9)	0.013(1)
Sr	102	1.9(2)	2.8(4)	637(14)	636(20)	0.0030(4)	0.0044(12)	0.0031(12)	279(5)	0.44(2)
Y	104	242(7)	279(29)	123(2)	109(10)	1.97(9)	2.57(78)	1.98(78)	3320(15)	30(3)
Zr	194	557(46)	733(173)	747(18)	546(42)	0.75(8)	1.34(74)	0.75(74)	2098(25)	3.8(3)
Nb	74	3.4(10)	4.6(14)	558(10)	412(49)	0.006(2)	0.01(1)	0.007(10)	361(7)	0.88(12)
Ba	187	0.43(4)	0.16(10)	1154(23)	1221(137)	0.00038(4)	0.0001(2)	$0.0001(2)^*$	5.5(7)	0.005(1)
Lc^{b}	82	12.2(88)	12.0(55)	3981(55)	4050(81)	0.0031(23)	0.0003(1)	0.003(2)	24900(89)	6.2(1)
Ce	102	4.4(13)	5.6(19)	288(7)	308(33)	0.015(5)	0.018(8)	0.016(8)	5505(30)	18(2)
Nd	94	n.m.	16(5)	n.m.	258(29)	_	0.061(25)	0.061(25)	6925(79)	27(3)
Sm	94	32(4)	45(16)	142(2)	196(36)	0.22(3)	0.23(12)	0.22(3)	7230(48)	37(7)
Eu	93	45(5)	68(14)	124(0.09)	207(66)	0.37(4)	0.33(17)	0.36(17)	7240(40)	35(11)
Gd	93	66(5)	n.m.	122(0.05)	149(5)	0.54(4)	_ `	0.54(4)	5235(33)	35(1)
Tb	94	n.m.	142(25)	n.m.	120(17)	_	1.2(4)	0.46(13)	5960(53)	50(7)
Dy	95	n.m.	194(27)	n.m.	126(13)	_	1.5(4)	0.64(13)	4825(59)	38(4)
Ho	91	150(5)	225(30)	82(0.6)	94(8)	1.83(8)	2.4(5)	1.84(2)	3538(27)	38(3)
Er	96	185(5)	260(25)	77(0.04)	88(16)	2.40(6)	2.9(8)	2.4(9)	2877(38)	33(6)
Yb	95	204(2)	315(20)	58(0.6)	74(9)	3.55(7)	4.3(8)	3.6(8)	1900(33)	26(4)
Lu	96	243(13)	353(16)	58(0.3)	64(6)	4.2(3)	5.5(8)	4.3(8)	1535(13)	24(2)
Hf	192	324(38)	n.m.	358(0.07)	236(8)	0.91(11)	_	0.91(11)	1128(24)	4.8(3)
Та	41	2.7(7)	n.m.	428(0.05)	n.m.	0.006(2)	_	0.006(2)	n.m.	
Th	189	1.9(13)	3.7(11)	58(0.5)	49(8)	0.034(2)	0.08(6)	0.04(6)	_	d
U	121	2.09(12)	3.5(27)	92(1)	69(17)	0.023(13)	0.05(9)	0.023(90)	6580(60)	95(24)

Number in parentheses represents two standards deviations in terms of least units cited. n.m., not measured. Doped powder was analysed by ICP-MS. ^a Numbers in square brackets are numbers of LA-ICP-MS and SIMS analyses. ^b La concentration in melt and mass-balance are suspect (see text). La data are presented because they are consistent with lattice strain models (see below). ^c Preferred *D* are weighted mean calculated from *D* determined by LA-ICP-MS and SIMS, except for * notation, *D* are chosen for reasons justified in the text. ^d The concentration analysis is suspect and is not presented.

from the furnace (Hammouda, 2003). All assembly parts except the capsule were fired for 2 h at 1000 °C in a 1 atm furnace immediately before the experiments. During the experiment, temperature was monitored by a W₉₅Re₅-W₇₄Re₂₆ thermocouple axially placed above the capsule and was controlled by a constant power setting (the uncertainty due to this procedure is estimated to +5/-15 °C), using a Eurotherm 900 controller. The 10 GPa experiments were performed with a 14/8 assembly calibrated against the coesite-stishovite transition (Akaogi et al., 1995) and the Mg₂SiO₄ α - β transition (Morishima et al., 1994). The 15 and 20 GPa experiments were performed with a 10/4 assembly calibrated against the forsterite β - γ transition (Katsura and Ito, 1989; Irifune et al., 1996; Katsura et al., 2003). The 25 GPa experiments were performed with a 7/2.5 assembly calibrated against the ZnS transition (Pan et al., 2002), GaAs transition (Mc Mahon et al., 1998) and GaP transition (Itie et al., 1989). Our high temperature calibration of this assembly is incomplete and we have reported the pressure on the basis of the room temperature calibration. The previous Mg-perovskite forming experiments by LMV group suggest a -5% relative correction to the room temperature calibration curve. After pressurization, the sample was annealed at high temperature for more than 23 h. Before decompression, the power applied to the furnace was shut and the experiments were quenched rapidly (500 °C in the first second of the quench). The recovered capsule was mounted in epoxy resin and polished for microanalyses by electron microprobe, femtosecond laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry SIMS.

2.2. Analytical procedure

Major element abundances in the samples were analyzed with a CAMECA SX100 electron microprobe at the LMV. For silicate phases, analytical conditions were 15 kV accelerating voltage and 15 nA beam current and a focused beam was used. For melt and carbonate phases, a 8 nA beam current was selected and a 5 μ m defocused beam or a 20 \times 20- μ m scanning area were employed depending on phase morphology. The calibration standards used in our laboratory, the detail of counting time, choices of spectrometers were described elsewhere (Hammouda, 2003).

Trace element concentrations were determined at the LMTG, Toulouse with an Agilent 7500 quadrupole ICP-MS coupled to a Ti: sapphire femtosecond laser ablation (Pulsar-10, Amplitude Technologies). The laser wavelength was 800 nm with maximum output energy of 12 mJ. Analyses were made with a laser pulse frequency of 5 Hz when each pulse lasts 50–60 fs. Additional details on the LA-ICP-MS techniques used can be found in Freydier et al. (2008). Twenty-two masses were collected with an integration time per mass of 25 ms. The beam diameter was 26 µm. The following masses were analyzed: ²⁹Si, ⁴³Ca, ⁴⁴Ca, ⁴⁵Sc, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ²³²Th and ²³⁸U. Calcium abundance measured on electron microprobe was used as internal standard. A typical signal acquisition started by collecting a background

signal for 30 s, and then, depending of crystal size, laser firing lasted from 30 to 80 s. The NIST 610 glass was used as an external standard (Reed, 1992; Pearce et al., 1997). Previous work has shown that matrix-matching calibration is not required for accurate femtosecond LA-ICP-MS analyzes of variety of sample matrix (Poitrasson et al., 2003). The glass BCR-2G (Wilson, 1997) was analyzed also to check analyses accuracy and precision. The maximum detection limit was about 2 ppm for Sc, and it was typically lower by two orders of magnitude for the other elements.

Secondary ionic mass spectrometry analyses were carried out on a Cameca IMS3f (Woods Hole Oceanographic Institution, WHOI, USA) and on a Cameca IMS4f (Laboratoire Géosciences Montpellier, GM, France). A primary O⁻ ion beam of 6 nA was accelerated to 10 kV before hitting the sample. To reduce mass interference by molecular ion species, the energy filtering method was used where secondary ions were subjected a 4500 V accelerating voltage with a -90 V offset with ± 25 eV energy window for WHOI SIMS, and with an -80 V offset with ± 30 eV energy window for GM SIMS (Shimizu and Hart, 1982). The primary beam size was set to approximately 20 µm on WHOI SIMS and to 50 µm (Kohler illumination) on GM SIMS. Counting time for each mass was chosen to attain a minimum of 1000 counts per cycle for 500 ppm concentration, and varied from 10 to 30 s. Five to ten cycles of acquisitions were done for each mass. The following masses were analyzed: done for each mass. The following masses were analyzed: ²⁴Mg, ²⁸Si (WHOI), ³⁰Si (GM), ⁴⁰Ca, ⁴⁵Sc, ⁴⁷Ti, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba (GM), ¹³⁸Ba (WHOI), ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁹Gd (WHOI), ¹⁶⁰Gd (GM), ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁷²Yb (GM), ¹⁷⁴Yb (WHOI), ¹⁷⁵Lu, ¹⁷⁸Hf, ²⁰⁸Pb (WHOI), ²³²Th and ²³⁸U. The trace element concentrations were determined by taking ratios of each mass over ²⁸Si (WHOI) and ³⁰Si (GM), and the ratio was multiplied by a calibration factor after correcting for isotopic abundances. Concentrations recalculated using ⁴⁰Ca as the reference mass showed no systematic offset induced by the choice of the reference element. The calibration factor was determined from the measurement of NIST 610 (Reed, 1992; Pearce et al., 1997) at the beginning and the end of each analytical session. Geostandard KL2-G (Jochum and Stoll, 2006) was used as a secondary standard to estimate accuracy and precision. After trace element analyses, scanning electron microscopy (SEM) imaging was used to check for signal contamination (Fig. 1a and b). Signal stability was also carefully monitored for every analysis.

3. RESULTS AND DISCUSSION

3.1. Comparison between femtosecond LA-ICP-MS and SIMS

Our measurements on basalt standards BCR-2G and KL2-G (Fig. 2) provide a first order comparison of uncertainty and accuracy between the femtosecond LA-ICP-MS measurement takes less than 3 min, we have managed to analyze several basalt standards throughout the course of the analytical session. On the contrary, the total analytical duration for a SIMS measurement over 17 elements takes



Fig. 1. Back-scattered electron images of run products. *Abbreviations used*: Maj, majoritic garnet; β , wadsleyite; γ , ringwoodite; CaPv, CaSiO₃ perovskite; MgPv, MgSiO₃ perovskite; Per, periclase; Mst, magnesite; Melt, quenched carbonate melt. (a) Overview of the experimental charges (#743; d, #787). (b) SIMS craters in a well-crystallized majorite garnet are visible, while laser pit may slightly overlap with β . (c) The melt forms homogeneous quench (#743) and poikilitic CaPv is observed next to melt and gas bubbles (#743 on a) probably formed during the quench. The melt has dendritic quench texture, and CaPv is around 50 µm across. (d) Sample #787, majorite garnet, MgPv and ringwoodite can only be recognized by microprobe analysis, see (e) and (f). These pictures were taken after repolishing, which explains the irregular form of the laser ablation craters and the occurrence of particles inside the craters (both SIMS and LA-ICP-MS).

nearly one hour; therefore fewer basalt standards were measured during these sessions. Therefore, the uncertainty of BCR-2G measurements (LA-ICP-MS) is given by the 2 standard deviation of the distribution of 4 measurements. The uncertainty of KL2-G measurement by SIMS is approximately 20% relative for most of the elements. These conservative estimates are based on the counting statistics of a typical counting rate. The analyses obtained by fs LA-ICP-MS measurements are accurate to within 10% (except to within 17% for U) when compared with recommended concentrations of BCR-2G (Fig. 2). The concentrations obtained agree with the recommended values of BCR-2G (Fig. 2). The two standard deviations are approximately less than 8% relative for heavy REE, Hf, U and Th, while less than 5% for the other elements.



Fig. 2. Measurements of trace element compositions of known samples divided by the certified values. White circles are LA-ICP-MS data using BCR-2G, and black diamonds are SIMS data using KL2-G. Error bars are two standard deviations. The grey field represents $\pm 20\%$ relative deviation of standard values. Overall, LA-ICP-MS measurement show systematic variation within 20% of the standard value, while SIMS measurements could vary significantly more than ICP-MS measurements, suggesting severe matrix effects (e.g. oxide mass interferences). Especially, Sm shows an irreconcilable offset from the true value for SIMS analysis.

The accuracy of the SIMS results is less than previously reported values with the same instruments (5% relative for diopside PHN2661, Shimizu and Le Roex, 1986; with the IMS 3f at WHOI). Because of low counts, the offsets of Th and U are within the uncertainty based on the counting statistics (Fig. 2). This is most likely explained by the mass interferences since measurements of Sc, and mid to heavy REE (especially Sm, Eu) are notoriously prone to mass interferences. For example, there exists an interference with 29 Si¹⁶O⁺ molecule at mass of 45 Sc⁺ (Steele et al., 1981; Weinbruch et al., 1993). We suspect that the offset of Sm is due to an interference with ¹³⁵Ba¹²C, and ¹³⁴Ba¹³C, since the samples had carbon coating prior to SIMS analyses, and is a carbonate-bearing experiment. Therefore, as we used the same isotopes for most of the element analyzed by LA-ICP-MS and SIMS, the offset of accuracy between LA-ICP-MS and SIMS is due to instrumental characteristics rather than the choice of mass peaks. This instrumental difference is, as a first order, the total count achieved by each technique, thus precision. The femtosecond LA-ICP-MS provides equivalent to more precise measurements than those of SIMS, due to its higher counting statistics. For instance, because of the higher counts, the femtosecond LA-ICP-MS is more suitable to measure U and Th in natural glasses than the SIMS. For SIMS, Th and U in KL2-G (1.0 and 0.55 ppm, respectively) give about 55 and 50 counts total, respectively. In contrast, for femtosecond LA-ICP-MS, these counts on BCR-2G (Th = 5.9 and U = 1.7 ppm) give about 1000 and 2300 counts total, respectively (total duration of analysis, approximately 2 min).

Despite these limitations, we presented all the SIMS measurements in this study since the partition coefficients by SIMS and LA-ICP-MS show a good agreement. The cal-

culation of the partition coefficient appears to cancel out SIMS the molecular interferences that appear to be similar are identical for minerals and liquid.

3.2. Experimental products

We have conducted more than 10 experiments between 10 and 25 GPa, only two experiments (#743 obtained at 20 GPa 1600 °C during 23 h 30 min and #787 obtained at 25 GPa 1600 °C during 23 h) resulted in grain sizes and textures, that are suitable for trace element analyses. For sample #743, the experimental products consists of approximately 30% of majoritic garnet, 40% of wadsleyite, 25% of quenched carbonatitic melt and few percents of CaSiO₃ perovskite (CaPv) and periclase (Fig. 1a). Sample #787, consists of approximately 5% of majoritic garnet, 10% of Ca-Pv, 15% of MgSiO₃ perovskite (MgPv), 50% of ringwoodite, 10% of magnesite and 10% of quenched carbonate melt (Fig. 1b). Phase proportions reported here are calculated by mass-balance. Mineral assemblages of our samples are consistent with those obtained in peridotite compositions between 15 and 30 GPa (e.g. Zhang and Herzberg, 1994; Litasov and Ohtani, 2002). The nature of garnet (majoritic content: 51% for 743 sample and 31% for 787 sample) and the olivine polymorphs (wadsleyite and ringwoodite) were confirmed by Raman spectroscopy. Sample texture is appropriate for trace element analysis since grains are generally close to 50 µm in size (Fig. 1a and d). The liquid phase forms a separated volume situated at the edge of the capsule. In sample #743, periclase and CaPv are formed in proximity of melt. In sample #787, magnesite crystals are located opposite in the charge relative to the pooled melt. These textural observations suggest that a temperature gradient promoted phase segregation.

Major element compositions of each phase are presented in Table 1. The liquidus saturation of mantle phases was attained in both experiments. While the Mg-numbers (Mg/ (Fe+Mg) molar) of the phases in sample #743 are consistent with those expected for mantle (e.g. wadsleyite = 0.92), the Mg-numbers of MgPv and ringwoodite in sample #778 are richer in Fe (0.87 and 0.85, respectively) due to the precipitation of magnesite. The lack of compositional zoning in crystals, indicates that a run duration of 23 h is sufficient to reach local chemical equilibrium. However, the mass-balance calculations using major elements failed to converge. Systematic excess or lack of oxides (CaO, MgO or Al₂O₃) from 20% to 30% was determined depending on the combination of oxides and phases. As inferred from the observed sample texture, the temperature gradient (<100 °C) is likely to have caused some disequilibrium at the scale of the entire sample. Nevertheless, CO₂ mass-balance succeeds with an excess of less than 2%. This suggests that CO₂ was equilibrated in the sample.

Trace element contents and corresponding partition coefficients $(D_i^{\min/\text{melt}}, \text{ wherein } D_i^{\min/\text{melt}} \text{ is the concentration of element } i$ in the mineral divided by concentration of the element i in the melt) for the phases in samples #743 (20 GPa, 1600 °C) and #787 (25 GPa, 1600 °C) are presented in Tables 2 and 3, respectively.

We have compared the sum of initial trace element masses with calculated sum based on the phase proportion of the charges. Nearly all elements converge within 40% deviation from the initial total. We admit that the recoveries of the calculated total trace element masses are poor, but this should be considered as reasonable results considering analytical uncertainty and poorly constrained mass-balance. The calculated total of all trace elements are in the same order of excess from the initial value, except for La in sample #743. Excess La could result from cell assembly contamination, although we did not identify excess of Cr or Zr.

Concentration differences between SIMS and LA-ICP-MS have little influence on calculated partition coefficients, in particular for rare earth element (REE) (Tables 2 and 3). However for Sc, Ba, Th and U, derived partition coefficients are significantly different. Because of significant difference in SiO₂ concentrations between carbonatitic melt and silicate minerals, it is possible that $^{29}\mathrm{Si}^{16}\mathrm{O}^+$ molecule causes the disparity in D_{Sc} . Nevertheless, even if this interference is corrected, the difference between ICP-MS values and SIMS values remains. Although we are unable to conclude which Sc partition coefficient is correct, we have used LA-ICP-MS Sc partition coefficients in the following discussion since they fit the elastic strain model better than those obtained by SIMS. Due the high incompatibility of Ba, the analyses in majoritic garnet were close to the detec-

Table 3

Trace element concentrations (in ppm) of run product #787 (25 GPa, 1600 °C) D^{Ca-Pv/Melt} Ca-Pv Melt LA-ICP-MS [2] SIMS [1] LA-ICP-MS [3] SIMS [1] LA-ICP-MS SIMS Preferred Sc 97(3) 156(3) 64(2) 101(4) 1.53(10) 1.54(9)1.54(10) Rb n.m. 211(15) n.m. 864(84) 0.24(4)0.24(4)427(2)269(7) 726(15) 902(10) 0.588(14)0.30(1)0.40(1)Sr Y 817(23) 1099(27) 12.8(3)19(1) 64(6) 58(4) 60(6) 831(30) 1010(30) 199(11) 246(17) 4.18(37)4.11(41) 4.15(41)Zr Nb 254(11) 121(6) 561(38) 1092(26) 0.45(5) 0.111(8)0.12(5) 658(24) 2545(33) 0.032(3)Ba 1854(30) 0.35(2)0.032(3)81(6) Lc^{t} 677(10) 830(14) 132(2) 6.4(3) 104(3)6.5(3)6.3(2) 896(7) 1018(15)21.5(6) 42.5(9) 47.4(20)43.4(20) Ce 21.1(3)Nd n.m. 1191(21) n.m. 22.1(7) 54(3) 54(3) Sm 788(9) 1075(40) 11.2(2) 14.9(7) 70.4(18) 72(6) 71(6) Eu 800(9) 1254(23) 10.9(2) 19.7(4) 73.5(18) 64(3) 70(18) Gd 759(20) 1076(33) 10.3(3) 12.7(5) 73.6(41) 85(6) 77(6) 1030(13)10.7(2)96(4) 96(4) Tb n.m. n.m. Dy 1143(29) 12.5(5)91(6) 91(6) n.m. n.m. 69.9(41) 89(3) 11.6(2)81(3) Ho 750(21) 1024(16)10.7(3)761(25) 12.7(3) 13.5(4)59.8(33) 75(5) 67(6) Er 1013(22) Yb 734(17)986(36) 18.8(5) 19.2(8) 39.1(19) 51(4)41(4)750(25) 22.3(3) 39(2) Lu 945(16) 24.1(9) 31.1(21) 42(1)Hf 373(10) 501(28) 226(4)154(2)1.65(7)3.3(2) 1.8(2)Та 223(8) 467(4) n.m. 0.48(2)0.48(2)n.m. 1209(40) Th 1460(43)11.4(4) 8.2(10) 106(8) 178(26) 112(26) U 1036(48) 917(29) 7.3(4) 261(26) 168(26) 3.5(2) 141(14)

Number in parentheses represents two standards deviations in terms of least units cited. n.m.: not measured.

^a Numbers in square brackets are numbers of LA-ICP-MS and SIMS analyse.

^b La concentration in melt and mass-balance are suspect (see text). La contents are presented because they are consistent with other data (see below).

² Preferred D are weighted mean calculated from D determined by LA-ICP-MS and SIMS, except for * notation, D are chosen for reasons justified in the text.

tion limits of the LA-ICP-MS. The lower D_{Ba} obtained with the SIMS was chosen as the most representative. Because of better counting statistics, we prefer Th and U data from the LA-ICP-MS rather than SIMS. Our preferred partition coefficient values are noted D preferred in Tables 2 and 3 and are used in the following discussion.

3.3. Majoritic garnet-melt partitioning

Light rare earth elements (LREE), middle rare earth elements (MREE) and Sr, Zr, Hf, Ta, U and Th are incompatible in majoritic garnet whereas heavy rare earth elements (HREE), Sc and Y are compatible. The only previous studies on trace element partitioning between garnet and carbonatite melt are those from Sweeney et al. (1992) and Adam and Green (2001) which present partitioning data at pressures lower than 3 GPa, and that of Hammouda et al. (2008) at 7 GPa for Gd and Yb. There is a qualitative agreement on the compatible and incompatible nature of trace elements when we compare our data with data for low-pressure garnet (Sweeney et al., 1992; Adam and Green, 2001). A notable difference is that trace element partition coefficients are globally higher at 20 GPa, except for Zr, and HREE (Eu, Yb and Lu), which are less compatible than at lower pressure. These differences are likely related to variations of pressure and temperature conditions, and garnet major element composition (Adam and Green, 2001; van Westrenen et al., 2001a; e.g. Draper et al., 2003; Draper and van Westrenen, 2007; van Westrenen and Draper, 2007).

Fig. 3a compares our *D*-values with those for majoritic garnet–silicate melt, from this study with *D*s obtained at 23–25 GPa, 2300 °C in CO_2 -free mantle compositions (Corgne and Wood, 2004; Walter et al., 2004). Even though par-

titioning patterns look globally alike, differences in partitioning values between the two systems are significant. Sc and Y are more compatible in the carbonate system, while HREE, which are moderately incompatible in the CO_2 -free silicate systems, are compatible in the carbonate system. Tetravalent HFSE (Zr, Hf) and MREE are less incompatible in the carbonate system with D_{Hf} is approach-



Fig. 3. Crystal-melt partitioning values for (a) Majorite garnet in comparison with Walter et al. (2004) and Corgne and Wood (2004) experimental data on majorite garnet–silicate melt partitioning at 23 and 25 GPa, respectively; (b) $CaSiO_3$ perovskite at 20 and 25 GPa. (c) Comparison of CaPv partitioning obtained in this study with Corgne et al. (2005) experimental data on $CaSiO_3$ perovskite at 25 GPa. Note that for REE D^{Mineral/Carbonatitic melt} are 5 to 10 times higher than D^{Mineral/Silicate melt}. Temperature and melt composition appear to be the major factor controlling trace element partitioning. Elements are ordered with increasing atomic number.

ing 1.0. On the other hand, highly incompatible elements such as Sr, Nb, and La are more incompatible in the carbonate system. As shown in Fig. 3a, trace element patterns are more fractionated between majoritic garnet and carbonatitic melt than between majoritic garnet and silicate melt.

3.4. CaSiO₃ perovskite-melt partitioning

In agreement with the literature data, we found that REE, Y, Zr, Th and U are clearly compatible and Rb, Sr, Nb and Ba are incompatible, in CaPv at 20 and 25 GPa. Fig. 3b shows that the two patterns are similar, except for the most incompatible elements Rb, Nb and Ba. Rb and Ba are more incompatible at lower pressure while Nb is more compatible. Globally, Fig. 3b shows that between 20 and 25 GPa pressure has a minor effect on CaPv-melt partitioning of trace element. This result is consistent with the results from Corgne et al. (2005) who found that the combined effects of P and T between 20 GPa-2100 °C and 25 GPa-2300 °C are insignificant (their Fig. 2b).

Fig. 3c compares D-values from this study at 25 GPa with D-values obtained in a CO₂-free peridotite composition (25 GPa, 2300 °C; Corgne et al., 2005). Both CaPv were synthesized at the same pressure (25 GPa), therefore we can isolate the effects of temperature and composition on trace element partitioning. Although patterns are alike, notable differences are observed between the CO₂-bearing and CO₂-free systems. First Zr, Y, REE and Th and U are more compatible in CaPv in our 25 GPa experiment, and Sr and Ba are more incompatible. As previously noted for majoritic garnet, trace elements are more fractionated in carbonate systems than in CO₂-free silicate systems. The difference in D-values between both studies can be attributed to different temperature conditions (700 °C of difference between Corgne et al. (2005), and our study) and to differences in major element compositions: either crystal or melt major element composition. We note that there exist differences of major element compositions of majoritic garnet and of CaPv between our study and studies conducted in CO₂-free silicate systems (Corgne and Wood, 2004; Walter et al., 2004; Corgne et al., 2005). The majorite in the present study is less magnesian and three times more calcic than the majorite in CO₂-free silicate systems (Corgne and Wood, 2004; Walter et al., 2004). Similarly for CaPv at the same pressure of 25 GPa: CaPv in the CO₂-bearing system has less than 0.1% of MgO while in the CO₂-free silicate system CaPv is less calcic and contains more than 3% MgO.

3.5. Lattice strain models and their relations to crystal chemistry

3.5.1. Regression of **D** to the lattice strain model

Elemental partitioning between solid and liquid is partly controlled by crystal chemistry (e.g. Blundy and Wood, 1994, see also review by Blundy and Wood, 2003). Elements are incorporated in different crystal sites according to their ionic radius and charge. Each site is characterized by the parameters of the lattice strain model (Brice, 1975; Blundy and Wood, 1994). According to this model, for an isovalent-ion series of valence n+ and of radius r_i , which enters into a given crystal lattice site M, the partition coefficient (D_i) is described by three parameters: $r_{0(M)}^{n+}$, the ideal crystal site radius; E_M^{n+} , the elastic response of the site to the elastic strain caused by larger or smaller r_i than $r_{0(M)}^{n+}$; and $D_{0(M)}^{n+}$, the fictive strainless partition coefficient for a cation of radius $r_{0(M)}^{n+}$.

$$D_{i} = D_{0(M)}^{n+} \times \exp\left\{\frac{-4\pi N_{A}E_{M}^{n+}\left[\frac{1}{2}r_{0(M)}^{n+}(r_{i} - r_{0(M)}^{n+})^{2} + \frac{1}{3}(r_{i} - r_{0(M)}^{n+})^{3}\right]}{RT}\right\}$$

where N_A is the Avogadro number, R is the gas constant and T is the temperature in K. Earlier studies focussed on low-pressure equilibria (see review by Blundy and Wood, 2003). However, this model is also applicable to high-pressure minerals like majoritic garnet and silicate perovskite (Corgne and Wood, 2002, 2004; Corgne et al., 2005).

Most majoritic garnets have a cubic symmetry (some have a tetragonal symmetry, Nakatsuka et al., 1999) with the general structural formula $X_3Y_2Z_3O_{12}$, where X-, Yand Z-positions are dodecahedral, octahedral and tetrahedral cation sites, respectively (Heinemann et al., 1997). The presence of Si in both Y- and Z-sites is characteristic of a majorite component in the garnet. Accordingly, the increasing majorite component in garnet is characterized by: (1) increased Si (the Si excess, compared to pyrope garnet, is located in the Y-site), (2) presence of Fe and Mg in the Y-site, and lower Al. These variations are expressed by the substitution $^{VI}Si^{4+} + ^{VI}[Ca + Mg + Fe] = 2^{VI}Al^{3+}$ (Draper et al., 2003). Here, we utilized a model wherein only Mg substitutes in the Y-site. Calcium and trivalent trace elements are assigned to the garnet X-site. CaSiO₃ perovskites has a cubic structure at lower mantle conditions (Kurashina et al., 2004; Ono et al., 2004) and contains two cation sites, an octahedral Si-site (6-fold coordination) and a dodecahedral Ca-site (12-fold coordination).

Because all trace elements investigated in this study have cation radii greater than r_{Mg} , they were allocated to the Xsite of majoritic garnet and to the dodecahedral site of silicate perovskite. In principle, Sc³⁺, Zr⁴⁺ and Hf⁴⁺ could enter in the X-site or Y-site of majoritic garnet and the dodecahedral or octahedral site of CaSiO₃ perovskites (Corgne and Wood, 2004; Corgne et al., 2005). As we succeed to fit these cation partition coefficients with partition coefficients of other isovalent cations on single lattice strain parabolas, we conclude that Sc³⁺, Zr⁴⁺ and Hf⁴⁺ are predominantly substituted in the X-site in majoritic garnet and in the dodecahedral site in CaSiO₃ perovskites.

Fig. 4 shows that our data are accurately modeled using the lattice strain theory for most elements. This observation underlines the crystal structure contribution to majoritic garnet–carbonatitic melt partitioning and to CaSiO₃ perovskite–carbonatitic melt partitioning. Best-fit parameters of the lattice strain model r_0 , D_0 and E are presented in Table 4, for divalent, trivalent and tetravalent cations, in 8-fold coordination for majorite and 12-fold coordination for Ca-SiO₃ perovskites.



Fig. 4. Lattice strain models (Brice, 1975; Blundy and Wood, 1994) applied to crystal–carbonatite melt partition coefficients for (a) Majorite from run #743 and (b) CaSiO₃ perovskite from run #787. Note that, *E* increases with the increasing charge (width of parabolae). The position of the parabolae indicates that r_0 decreases with the increasing charge. Fit parameters obtained are listed in Table 4. Ionic radii are from taken Shannon (1976) and ionic radii for elements in 12-fold coordination have been linearly extrapolated with respect to coordination number. Despite the fact that Ca and Mg are not expected to behave like trace elements following Henri's law, 2+ cations lattice strain models are determined with Ca and Mg partition coefficient following Blundy and Wood (1994).

Measured D_{Ba} values, for both majorite and calcium silicate perovskites, are orders of magnitude too high to fit the divalent parabola. Consequently, D_{Ba} was excluded from the calculation for 2+ cations. Walter et al. (2004) previously noted that D_{Ba} is too large relative to lattice strain models in several minerals. Given that Ba^{2+} has the same ionic radius as O^{2-} , a substitution, $\text{Ba}^{2+} \leftrightarrow O^{2-} + \text{Si}^{4+}$, may occur in silicate minerals (e.g. Walter et al., 2004). This substitution would increase the compatibility of Ba in majoritic garnet and in CaSiO₃ perovskite.

3.5.2. Comparisons with predictive models of van Westrenen and Draper (2007) and Draper and van Westrenen (2007)

We compared our experimental data and measured parameters r_0 , D_0 and for 3+ cations in the X-site of garnet



Fig. 5. The results of lattice strain modelling of partitioning of trivalent cations between the X-site of majorite garnet and carbonatite melt the experimental data of this study compared to the predictive garnet models from van Westrenen and Draper (2007) and Draper and van Westrenen (2007). The upper boundary is calculated using the thermodynamical prediction (van Westrenen and Draper, 2007) and the lower one is calculated employing the statistical prediction (Draper and van Westrenen, 2007). The parameters determined from the prediction models are presented in Table 4.

with those calculated by the predictive model of Draper and van Westrenen (2007) and van Westrenen and Draper (2007), in Fig. 5 and Table 4. The value of E was successfully predicted using the model of van Westrenen and Draper (2007). The predicted r_0 is significantly lower than the r_0 modeled from our data, but within the reported uncertainty of 0.017 A (1o, van Westrenen and Draper, 2007). The difference can be explained by the fact that van Westrenen and Draper (2007) did not use majoritic components in their equation for r_0 . We suggest that excess of Si entering in the garnet Y-site exerts an effect on r_0 of the X-site. We modeled D_0 with the statistical and the thermodynamic expression (Draper and van Westrenen, 2007; van Westrenen and Draper, 2007, respectively). Statistical prediction of D_0 appears to be closer to experimental value. The thermodynamic D_0 is especially affected by the Fe partition coefficient because it varies with melt composition and structure. Therefore, the thermodynamic D_0 is less likely to be applicable to carbonatitic melt system than the statistical D_0 . Furthermore, activity model for REE species in van Westrenen and Draper's (2007) model assumes that dissolved species of REE in the melt conform with garnet stoichiometry. This assumption is highly unlikely in the case of carbonatitic melts, where the structure is dominated by carbonate anions (Treinman, 1989; Genge et al., 1994).

3.5.3. Majoritic garnet: comparison of carbonate and CO₂free silicate systems

Comparison between lattice strain model fits for 2+, 3+and 4+ cations for majoritic garnet in CO₂-free silicate systems (Corgne and Wood, 2004; noted with "silic" superscript hereafter) and in carbonate systems (noted with "carb" superscript hereafter) are presented in Fig. 6a. We

Best-fit parameters for lattice strain model				
Run	Charge	E (GPa)	r_0 (Å)	D_0
#743	Majorite garnet			
	2+	215(2)	0.940(1)	1.46(3)
	3+	522(3)	0.910(6)	6.9(13)
	4+	416(120)	0.80(26)	0.924(1)
#743	$CaSiO_3$ perovskite			
	2+	529(1)	1.355(4)	1.5(4)
	3+	585(0.7)	1.260(1)	41(4)
	4+	994(448)	1.18(50)	105(2)
#787	2+	900(5)	1.360(8)	3.6(61)
	3+	729(3)	1.260(5)	82(30)
	4+	1510(72)	1.175(5)	156(8)
	Majorite parameters from C	Corgne and Wood (2004)		
	2+	261	0.987	1.62
	3+	521(24)	0.908(3)	1.14(4)
	4+	522(327)	0.856(35)	0.15(3)
	Recalculated CaPv parameter (2005)	ers (25 GPa) with 12-fold co	oordination fron	<i>i</i> Corgne et al.
	2+	258	1.35	5(1)
	3+	373(2)	1.270(7)	21(1)
	4+	459(42)	1.18(10)	11(1)
	Predicted parameters for me	ajorite garnet from #743		
Model (20 GPa and 1600 °C)	3+	524	0.869	135.296 ^a 4.405 ^b

Number in parentheses represents one standard deviation in terms of least units cited.

Fitting was made for 2+ cations: Mg, Ca, Sr; for 3+ cations: Sc and REE; for 4+ cations: Hf, Zr and U (and Th for CaPv of #787).

^a Thermodynamical prediction, van Westrenen and Draper (2007).

^b Statistical prediction, Draper and van Westrenen (2007).

Table 4

found that E^{4+} and r_0 for 4+ cations in the carbonate system are significantly lower than in the CO₂-free silicate systems while D_0 is higher (Table 4, Corgne and Wood, 2004). The r_0^{3+} does not vary significantly between the two systems, but E^{3+} and D_0^{3+} are higher in the carbonated system (Fig. 6a). Concerning 2+ cations, r_0 is higher in the carbonated system while *E* and notably, D_0 for divalent cations are essentially the same in the two systems. We find: ${}^{carb}r_0^{4+} < {}^{sili}r_0^{3+} < {}^{sili}r_0^{3+}$ and ${}^{carb}r_0^{2+} < {}^{sili}r_0^{2+}$; ${}^{carb}E^{4+} < {}^{sili}e^{3+} < {}^{sili}e^{3+} < {}^{aili}e^{3+} < {}^{sili}e^{2+} < {}^{sili}e^{2+}$; ${}^{carb}D_0^{2+} < {}^{sili}e^{2+}$; and ${}^{carb}D_0^{3+} > {}^{sili}D_0^{3+}$ and ${}^{carb}D_0^{2+} < {}^{sili}e^{2+} < {}^{sili}e^{2+}$

According to van Westrenen and Draper (2007), r_0 , E and D_0 depend on pressure, temperature and composition. The r_0 decreases with pressure and increases with temperature, while E and D_0 increase with pressure and decrease with temperature. Our majorite experiment is conducted at 5 GPa lower and 700 °C lower temperature than that of Corgne and Wood (2004). If the pressure is the dominant factor, the resulting relationship should be $^{\text{carb}}r_0 > ^{\text{silic}}r_0$, $^{\text{carb}}E < ^{\text{silic}}E$ and $^{\text{carb}}D_0 < ^{\text{silic}}D_0$. On the contrary, if the temperature is the dominant factor, it should be ${}^{\mathrm{carb}}r_0 < {}^{\mathrm{silic}}r_0$, ${}^{\mathrm{carb}}E > {}^{\mathrm{silic}}E$ and ${}^{\mathrm{carb}}D_0 > {}^{\mathrm{silic}}D_0$. Table 4 shows that 2+ and 4+ data are consistent with temperature influence, whereas 3+ are ${}^{\mathrm{carb}}r_0 \sim {}^{\mathrm{silic}}r_0$ and ${}^{\mathrm{carb}}E \sim {}^{\mathrm{silic}}E$. Furthermore, Blundy and Dalton (2000) show for clinopyroxene-melt partitioning at 3 GPa and between 1375 and 1640 °C that r_0 and E values for the silicate system, at the same pressure and temperature conditions, are significantly different from those of carbonate system.

CaO content of majoritic garnet should have an influence on r_0 and E. Since Ca²⁺ is the major cation in the X-site, r_0 is expected to increase with Ca content (van Westrenen et al., 2001b). Comparing the major element composition of majoritic garnets, we note that our garnet has a Ca content 3 times higher than majoritic garnet in silicate system. Nevertheless, our current data cannot independently quantify the influence of CaO content on element partitioning excluding the pressure and temperature effect. Furthermore, van Westrenen and Draper (2007) predict that an increase in Ca garnet content should lower D_0 , while all of our D_0 values are higher than those of Corgne and Wood (2004). We consider that our lower run temperature, which causes the increase of D_0 (van Westrenen and Draper, 2007), compensates the increase of Ca influence in garnet. To conclude, temperature has a major influence on the differences in lattice strain parameters between Corgne and Wood's (2004) study and our study, but is not sufficient to explain the r_0^{3+} and E^{3+} data. We suggest that high Ca content of our garnet might also have an effect on r_0 and E.



Fig. 6. Lattice strain model fits obtained for this study (solid black lines), compared with those obtained for the same minerals in silicate systems (solid gray lines, Corgne and Wood (2004) and Corgne et al. (2005) experimental data fits). Note that for all *D*-values of majorite garnet (3+, 4+) and CaPv (3+, 4+), carbonatitic system reveal higher *D*-values than silicate system, except for the larger ionic radii.

Lastly, we note that on top of these interpretations, the structure of the liquid can play a significant role in determining the value of D_0 . According to Wood and Blundy (2001), the electrostatic work involved in the substitution $(\Delta G_{\text{elec}} = W_{\text{elec}}^{\text{crystal}} - W_{\text{elec}}$ where ΔG_{elec} is the free energy of substitution, W_{elec} refers to the electrostatic work done by either the crystal or the liquid in placing an ion in the crystal and in the liquid) varies according to the square of the charge difference between the tracer and the main site atom $(W = \frac{N_A(Z_c - Z_0)^2 e_0}{2\epsilon r}$ where N_A is the Avogadro's number, $Z_{\rm c} - Z_0$ is the effective radius of the defect of charge, e_0 is the charge of the electron, ε is the dielectric constant, r is the substituted ion radius). Furthermore, it concludes that the melt contribution to the electrostatic work is small compared to that of the crystal, because of the high disorder state of the melt and the presence of charge balancing cations. Because larger charge difference requires more electrostatic work for the substitution, the following relationship is generally inferred: $D_0^{2+} > D_0^{3+} > D_0^{4+}$. We, however, found that $D_0^{3+} > D_0^{2+} > D_0^{4+}$, while the majorite-CO₂- free silicate melt system resulted in $D_0^{2+} > D_0^{3+} > D_0^{4+}$. This suggests that there are non negligible electrostatic effects in the melt. Carbonatitic melts are based on $(CO_3)^{2-}$ anions with no tendency for polymerization (Treinman, 1989) and highly charged cation are not favored within such environment. Consequently, D_0^{3+} is greater than of D_0^{2+} while D_0^{4+} approaches D_0^{2+} (Fig. 6a). As another example, some clinopyroxene–carbonatite partitioning experiments (Blundy and Dalton, 2000) show $D_0^{3+} > D_0^{2+}$, while the clinopyroxene–silicate melt experiments result in $D_0^{2+} > D_0^{3+}$ (Wood and Blundy, 2001). However, at lower pressure, the order of D_0 always follows $D_0^{3+} > D_0^{2+}$ for the garnet–silicate melt system (see Draper and van Westrenen, 2007, for the data source). We propose here that the anomalous order of D_0 on partitioning in the majorite–carbonatite system is best explained by the influence of the melt structure above 20 GPa; however we cannot offer an explanation for the ubiquitous $D_0^{3+} > D_0^{2+}$ relationship for the low-pressure garnet–silicate melt system.

3.5.4. $CaSiO_3$ perovskite: comparison of carbonate and CO_2 -free silicate systems

We found that r_0 decreases and D_0 increases with increasing charge. Comparing our data at 20 and 25 GPa, we found that there is no variation of r_0 with pressure, in contrast to *E*, which increases with increasing pressure. D_0^{2+} and D_0^{3+} are increased by a factor of 2 and D_0^{4+} is increased by ~30% when pressure is raised from 20 to 25 GPa. Theses variations could be due to a pressure effect or a variation of composition of the CaPv between 20 and 25 GPa. Available data do not allow discriminating between the two possibilities. Furthermore, we noted that CaPv at 20 GPa contains 10.5 wt% of trace elements, implying that Henry's law is surely violated. Corgne and Wood (2005) for example show that $D_{T_h}^{\text{CaPv/CO}_2-\text{freemelt}}$ reduces for high Th abundance in CaPv.

Fig. 6b shows a comparison between the CaPv data in the carbonated system (this study) and those of Corgne et al. (2005) in CO₂-free silicate systems. Note that Corgne et al. (2005) used r_i for an 8-fold coordinated site, and here we recalculated their model fits with r_i values for 12-fold coordinated site by using to a linear extrapolation of relation between coordination and ionic radii values tabulated by Shannon (1976). We note that values of r_0 are similar in the two systems. E values are higher in the carbonate system than in CO₂-free silicate systems, which is most likely due to higher temperature in the study of Corgne et al. (2005). We infer that the temperature affects similarly on CaPv E parameter as in the case of majoritic garnet. As temperature increases, the X-site expands, thus E (or the Young modulus of the crystal) decreases. In both cases, r_o decreases with ionic charge increase whereas E increases, in agreement with lattice strain modeling (e.g. Wood and Blundy, 1997). A major feature of Fig. 6b is that values of D_0 are markedly higher in a carbonate system than in CO2-free silicate systems. In a manner similar to the majorite case, the difference in D_o values can be addressed in terms of temperature and melt structure. We previously concluded that temperature increases D_0 values, but some melt influence is noteworthy. We note that $^{\operatorname{carb}}D_0^{2+} \sim ^{\operatorname{silic}}D_0^{2+}$, whereas $^{\operatorname{carb}}D_0^{3+} > ^{\operatorname{silic}}D_0^{3+}$ and $^{\operatorname{carb}}D_0^{4+} > ^{\operatorname{silic}}D_0^{4+}$. We found also that $D_0^{4+} > D_0^{3+} > D_0^{2+}$. Both studies conform that D_0 -values for 3+ and 4+ are higher than D_0^{2+} . Although substitution mechanisms in perovskite appear to be rather complex and might involve Ca vacancies (Corgne and Wood, 2005) we cannot exclude that the change in the relative order of the parabolas in Fig. 6b can be attributed to an effect of the melt structure. On the basis of the electrostatic argument discussed above for majoritic garnet, we also suggest that, for perovskite–carbonate liquid partitioning, the melt structure has a measurable influence.

3.6. Implications for high-pressure carbonatitic melt metasomatism

Our liquidus saturation experiment suggests that a dolomite-bearing pyrolite composition can achieve an equilibrium between carbonatitic melt and transition zone mantle along the geotherm (our run condition 20 GPa, $1600 \,^{\circ}$ C; also extrapolation from Dalton and Presnall, 1998). Furthermore, an experimental study showed that Na-rich pyroxene–enstatite inclusions in diamonds (Wang and Sueno, 1996) originate from lower mantle and/or transition zone conditions, and that the result from mantle metasomatism by a Na-rich carbonate melts (Gasparik and Hutchison, 2000). Carbonatitic melt cannot only be generated at transition zone conditions but also at conditions of the uppermost lower mantle (1600 °C, Gasparik and Litvin, 2002). A recent experimental and geochemical study on silicate mineral inclusions in diamond suggests the presence of carbonatitic melt at transition zone depths (Walter et al., 2008). Note however, that extrapolation of the melting phase diagram of carbonate-bearing peridotite from Dasgupta and Hirschmann (2006) suggests that carbonated peridotite melting never occurs along the geotherm at transition zone depths. This offset of carbonated peridotite melting between Dasgupta and Hirschmann (2006) and the present study can potentially be explained by the presence of 1500 ppm of H₂O in our samples. That could have lowered the carbonated peridotite solidus. We admit that there is considerable uncertainty whether cabonatitic melt can coexist with transition zone mantle. In following discussion, based on the reasons listed above, we consider the case where carbonatitic melt exists at transition zone depths.

It was previously suggested that magnesiocarbonatites, the most primary carbonatites are generated at pressures higher than 3 GPa (Bailey, 1989; Dalton and Presnall, 1998). However, carbonatite maximum source depth is still undetermined and our experimental data can provide additional constrains. While carbon-bearing, occasionally diamond-forming, fluid likely exists at transition zone depths, the investigations of carbonatite generation using major element composition are often hindered



Fig. 7. Chondrite-normalised trace elements concentrations in natural magnesio- and calciocarbonatite compositions (data from von Maravic and Morteani, 1980; Gerlach et al., 1988; Nelson et al., 1988; Hornig-Kjarsgaard, 1998; Schultz et al., 2004) are shown as a grey area. Filled diamonds represent Kankan majorite inclusions in diamonds (Stachel et al., 2000). (a) REE patterns (b) patterns including other trace elements. Concentrations are normalized to Cl chondrite (McDonough and Sun, 1995). The bold lines represent the hypothetical melt compositions in equilibrium at 20 GPa with majoritic garnet composition (Stachel et al., 2000; majoritic garnets equilibrated at 13 GPa) with partition coefficients determined experimentally in this study. D_{Nd} , D_{Tb} and D_{Dy} have been calculated from our lattice strain modeling to limit the influence of analytical uncertainty on these data ($D_{Nd} = 0.04$, $D_{Tb}=1.05$ and $D_{Dy} = 1.08$). Note that the REE concentration of the carbonatitic melt in equilibrium at 20 GPa is in agreement with the high HREE concentration of the carbonatites. We stress that this deep carbonatitic melt also has the same relative element depletion and enrichment as carbonatites, except for Ba.

by crystallization and decarbonation reactions (e.g. Dalton and Presnall, 1998).

In contrast, trace element compositions are less prone to such limitation. Combining our partition coefficients for majorite-carbonatitic melt (run #743) with trace element compositions from majoritic garnets in inclusions in Kankan diamonds (Guinea, Stachel et al., 2000), we can estimate the trace element compositions of the carbonatitic melt that was potentially in equilibrium at 20 GPa and 1600 °C. Comparison with a range of REE patterns from natural carbonatites (von Maravic and Morteani, 1980; Gerlach et al., 1988; Nelson et al., 1988; Hornig-Kjarsgaard, 1998; Schultz et al., 2004) reveals that the transition zone carbonatitic melt REE pattern falls within the natural carbonatite field (Fig. 7a). Furthermore, the geochemical signature of deep carbonatitic melt is consistent with the flat HREE pattern of carbonatites. The geochemical signature of carbonatites is usually characterized by a depletion in Rb, Zr and Hf, and high Zr/Hf ratio (Hauri et al., 1993; Hoernle et al., 2002), and the Zr/Hf ratio of the deep carbonatitic melt is consistent with the carbonatites. However the model deep carbonatitic melt fails to reproduce the similar extent of the observed Ba enrichment relative to Rb (Fig. 7b). Perhaps, the appropriate value for D^{Ba} is much smaller than the one we have determined here. Alternatively, assuming that carbonatites are derived from deep carbonatitic metasomatism, some disparity of carbonatite geochemical signature (including for Ba) may be due to lower pressure reactions during the ascent of carbonatitic melt.

We have compared the trace element abundance of observed carbonatites at the surface and a carbonatitic melt equilibrated at 20 GPa. According to this model, carbonatitic melts must ascent to the surface, and preserve their trace element signature acquired at depth. Carbonatitic melts should interact with the surrounding mantle during ascent, but due to the highly enriched trace element abundance in carbonatitic melt, it is possible that the trace element signature is little affected by the interaction with olivine dominated mantle. The physical properties of carbonatitic melts may also reduce the potential interaction between melt and mantle. They have a low viscosity and density (Treinman, 1989; Genge et al., 1995; Dobson et al., 1996). They also form an interconnected network due to low wetting angle (Hunter and McKenzies, 1989; Watson, 1991), if there is no mixing with silicate melt (Minarik and Watson, 1995). They can quickly impregnate mantle rocks on a large scale by interfacial-driven infiltration (Hammouda and Laporte, 2000). Consequently, the residence time of carbonatitic melt in the mantle may be too short to result in a significant chemical exchange.

4. CONCLUSION

Here we report trace element partition coefficients measured between majoritic garnet and carbonatitic melt and between CaSiO₃ perovskite and carbonatitic melt. Trace element partition coefficients are more fractionated in carbonate system than in CO₂-free silicate systems, although similar patterns are obtained. Ba, Sr and LREE are more incompatible in carbonate systems while Sc, Y, HFSE, Zr and Hf, MREE and HREE are more compatible. Lattice strain models indicate that the difference of trace element partitioning between CO₂-free silicate melt and carbonatitic systems can mostly be attributed to different temperature conditions of respective experiments. Additionally, there are some potential influences by mineral and melt compositions.

Using partition coefficients determined in this study, we found that a carbonatitic melt potentially in equilibrium with majoritic garnet inclusions in diamonds has a geochemical signature similar to that of some natural carbonatite lavas. This suggests that carbonatitic metasomatism can exist in the transition zone.

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Appendix B

List of experiments

of powder compositions : quenchs and restarts quenchs and restarts temperature variation cooling system purge cooling system purge electrode oxydation electric cut (storm) electric cut (storm) electric cut (storm) see Lambart (2009) see Lambart (2009) need reajustement basalt-peridotite test proportion assemblage assemblage water leak TC loose TC loose Remarks **TC** loose melt Opx, QuCpx, Sp, few melt N. E. Opx, Cpx, Ol, melt Opx, Ol, Cpx, Plag, melt Opx, Ol, Cpx, Plag, melt + 10 & 15% F salt, melt Opx, Ol, Cpx, Plag, mel Zoned opx, big Ol, melt reaction with graphite Opx, Ol, QuCpx, melt Opx, QuCpx, Sp, few Zoned opx, melt Zoned opx, melt Opx, Cpx, melt Opx, Cpx, melt Ol , melt Opx, Ol, melt Opx, melt all melted all melted Opx, melt Phases Opx, 400 ppm Cl_2 , 1% Cl_2 , 400 ppm F_2 and 1000 ppm F_2 + c.s. 2000 ppm Cl_2 , 1000 ppm F_2 little hole (0.8 mm diameter) 5000 ppm Cl_2 , 400 ppm Cl_2 , 1% F_2 , 400 ppm F_2 + c.s. 5000 ppm Cl_2 , 400 ppm Cl_2 , 1% F_2 , 400 ppm F_2 + c.s. 5000 ppm Cl_2 , 400 ppm Cl_2 , 1% F_2 , 400 ppm F_2 + c.s. 5000 ppm Cl_2 , 400 ppm Cl_2 , 1% F_2 , 400 ppm F_2 + c.s. 5000 ppm Cl_2 , 400 ppm Cl_2 , 1% F_2 , 400 ppm F_2 + c.s. 400 ppm Cl_2 , 800 ppm Cl_2 , 100 ppm F_2 , 200 ppm F_2 400 ppm Cl_2 , 800 ppm Cl_2 , 100 ppm F_2 , 200 ppm F_2 400 ppm Cl_2 , 800 ppm Cl_2 , 100 ppm F_2 , 200 ppm F_2 400 ppm $Cl_2,$ 800 ppm $Cl_2,$ 100 ppm $F_2,$ 200 ppm F_2 400 ppm $Cl_2,$ 800 ppm $Cl_2,$ 800 ppm $Cl_2,$ 100 ppm F_2 200 ppm F_2 400 ppm Cl_2 , 2% Cl_2 , 400 ppm F_2 and 2% F_2 + c.s. 400 ppm Cl_2 , 1000 ppm Cl_2 and 400 ppm F_2 + c.s. 400 ppm Cl_2 , 1000 ppm Cl_2 and 400 ppm F_2 + c.s. $2\% Cl_2$, 200 ppm Cl_2 , $5\% F_2$, 1000 ppm F_2 + c.s. π w/ MgO, π w/o MgO, β w/ MgO, β w/o MgO β w/ MgO, β w/o MgO, oxydized β 2000 ppm Cl_2 , 2% Cl_2 , 1% F_2 and 5% F_2 + c.s. 5000 ppm Cl_2 , 2% Cl_2 , 1% F_2 , 5% F_2 + c.s. and 1000 ppm F_2 (1.5 mm diameter) + c.s. mix $\beta - \pi$ in proportion 80:20-70:30-60:40 mix $\beta - \pi$ in proportion 80:20-70:30-60:40 1000 ppm Cl_2 and 1000 ppm F_2 + c.s. $100 \text{ ppm } Cl_2 \text{ and } 400 \text{ ppm } F_2 + \text{ c.s.}$ $400 \text{ ppm } Cl_2 \text{ and } 400 \text{ ppm } F_2 + \text{c.s.}$ 4000 ppm Cl_2 , 1000 ppm F_2 + c.s. 400 ppm Cl_2 , 400 ppm F_2 + c.s. $1\% \ F_2^{-}, \ 5\% \ F_2, \ 10\% \ F_2, \ 15\% \ F_2$ 2000 ppm Cl_2 , 1000 ppm F_2 $4000 \text{ ppm } Cl_2, 400 \text{ ppm } F_2$ $\begin{array}{c} 1\% \ Cl_2, \ 2\% \ Cl_2, \ 5\% \ F_2 \\ 1\% \ Cl_2, \ 2\% \ Cl_2, \ 5\% \ F_2 \\ 1\% \ Cl_2, \ 2\% \ Cl_2, \ 5\% \ F_2 \end{array}$ 5000 ppm Cl_2 , 4% Cl_2 $100 \text{ ppm } Cl_2 + \text{c.s.}$ $400 \text{ ppm } F_2 + \text{c.s.}$ Starting materials seeds (c.s.) and variation of temperature) : Duration 2008 samples : same P-T conditions and variation of F and Cl doping 5d 5d 6.5d 5d 7d 6d 5d 3h 23h 39h 39h36h 55d 77h 77h 55d 15h 55d 55d 55d 5d 3d 7d 7d 5d 5d 5d 7d 5d 5d 5d~1300 (man) $1280 - 1265^a$ 13151360 (man) $280 - 1265^a$ 1360 (man) 1360 (man) $1350 - 1330^{a}$ $280 - 1265^a$ (0°) T 1450 1413 1360 13601360 1360 1360 1360 1360 1360 1360 13101305 13551360 1360 1360 1360 1360 1295 1305 .280 12801350 355 1360P (kbars) 2008-2009: Looking for Cpx (addition of cpx \rightarrow decision to use the mix $\beta - \pi$ (70:30) in most of the following experiments 8 110 8 8 1212128 8 11 12 12 16 8 8 8 12 12 12 $C4p^{**}, 8p^{**}F1p^{*}, 2p^{**}$ [4] $\begin{array}{c} F1, 4p, \ C05, 4p \ [4] \\ F1, 4p, \ C05, 4p \ [4] \end{array}$ F1**,5**,10,15 [4] C4p,8pF1p,2p [4] C4p,8pF1p,2p [4] C4p,8pF1p,2p [4] C4p,8pF1p,2p [4] gels test 1 [4] basalt compo [3] C4pF4p 8b* [2] C04**F4p** [2] C05*C4** [2] Melt test [3] Melt test [3] C1,2F5 [3] C1,2F5 [3] F4p Pt [1] C4p Pt [1] 10b* [2] 8c* [3] 11b** [3] 8bisc [3] 12b** [4] 9c [2] C02F01[2] 7b* [4] 8b* [4] 7c** [4] 6c** [4] Samples 9b [3] 5c [4] 6b [2] 07/29/0808/01/0806/26/0906/29/0907/02/0807/12/0807/12/0807/18/0808/15/0805/07/0908/01/0808/06/0808/08/0880/60/80 08/10/0808/10/0808/11/0808/16/0811/04/0811/21/0801/08/0901/14/0901/15/0901/30/0902/14/0903/19/0905/02/0905/13/0905/19/0905/19/0906/01/0906/10/0906/21/0906/22/0907/01/09Date PC1-2009-23 PC2-2009-27 PC1-2008-18 PC2-2008-10PC1-2008-21 PC1-2008-23 PC1-2008-24 PC1-2009-14 PC1-2009-15 PC1-2009-16 PC1-2009-18 PC2-2009-25 PC1-2009-22 PC1-2008-25 PC1-2008-26 PC1-2008-28 PC1-2008-29 PC3-2008-10 PC1-2008-30 PC1-2008-34 PC1-2008-35 PC2-2009-23 PC1-2009-17 PC2-2009-26 PC1-2008-27 PC1-2009-13 PC1-2008-9 PC3-2008-8 PC3-2008-9 PC1-2009-1 PC1-2009-5 PC2-2009-9 PC1-2009-2 PC2-2009-2 PC2-2009-3 °

Opx, melt

000 ppm Cl_2 and 1000 ppm F_2 + c.s.

 $.330 - 1310^{a}$

13b [3]

07/05/09

PC1-2009-24

Table B.0.1: List of experiments run during its project. First table: samples presented in Chapter 3.

° z	Date	Sample name(s)	P (kbars)	T (°C)	Duration	Starting materials	Phases	Remarks
	2009–201	0: Hydrous experi	iments and	other compos	itions:			
PC1-2009-25	07/10/09	14b [2]	12	$1210 - 1195^a$	3d	$+ 5.4\%$ H ₂ O $+ 4000$ ppm Cl_2 and 4000 ppm F_{2} + c.s.	dendrites Opx, Cpx, melt	no Al: powder issue
PC2-2009-28	07/10/09	10c [2]	12	1315	3d	$+5.4\%$ H ₂ O + 4000 ppm Cl_2 and 4000 ppm F_2 + c.s.	dendrites Opx, Cpx, melt	no Al: powder issue
PC1-2009-26	07/16/09	15b [2]	12	$1240 - 1230^a$	6d	$4\% Cl_2$ and $5\% F_2 + c.s.$	Opx, melt	•
PC2-2009-29	07/17/09	11c [2]	12	1270	3d	$+ 3\%H_2O + 4000 \text{ ppm } Cl_2 \text{ and } 4000 \text{ ppm } F_2 + \text{c.s.}$	dendrites Opx, Cpx, melt	no Al: powder issue
PC1-2009-27	07/23/09	16b [2]	12	$1205 - 1195^a$	5d	+ 5.4%H ₂ O + 4000 ppm Cl ₂ and 4000 ppm F ₂ + c.s.	Opx, Cpx, <i>i</i> melt	water loose
PC2-2009-30	07/23/09	$12c^{**}$ [2]	12	1230	5d	$+ 3\%H_2O + 4000 \text{ ppm } Cl_2 \text{ and } 4000 \text{ ppm } F_2 + c.s.$	Opx, Ol, Cpx, melt	
PC3-2009-9	07/23/09	4a [2]	12	1185	5d	+ 6.1%H ₂ O $+ 4000$ ppm Cl ₂ and 4000 ppm F ₂ + c.s.	Opx, Cpx, <i>i</i> melt	water loose
PC1-2009-30	09/29/09	17b [1]	12	1185	5d	$+ 6.1\% H_2 O + 4000 ppm F_2 + 4000 ppm Cl_2 + c.s.$	all melted	water loose
PC2-2009-33	09/29/09	13c [1]	12	1195	5d	$+ 5.4\%H_2O + 4000 \text{ ppm } F_2 + 4000 \text{ ppm } Cl_2 + \text{c.s.}$	Opx, Cpx, <i>i</i> melt	water loose
PC1-2009-31	10/13/09	$18b^{**}$ [1]	12	1200	4d	$+ 6.1\% H_2 O + 4000 ppm F_2 + 4000 ppm Cl_2$	Amp, Ol, Opx, melt	
PC2-2009-34	10/13/09	13c [1]	12	1215	4d	$+ 5.4\% H_2 O + 4000 ppm F_2 + 4000 ppm Cl_2 + c.s.$	Opx, Cpx, <i>i</i> melt	water loose
PC1-2009-32	10/21/09	SHO1** [1]	12	1300	4.5 d	showshonite + 1000 ppm F_2 + 1000 ppm Cl_2))	Phlo, Ol, melt	
PC1-2009-33	10/26/09	18b [1]	12	1045	5d	mix B715 (andesite) $-\pi$ (50:50) + 4000 ppm F_2 + 4000 ppm Cl_2	carbonated minerals	old powder (CO ₂)
PC2-2009-35	10/27/09	14c [1]	12	1205	5d	$+ 5.4\% H_2 O + 4000 ppm F_2 + 4000 ppm Cl_2 + c.s.$	Opx, Cpx, <i>i</i> melt	water loose
PC1-2009-36	11/05/09	SHO2 [1]	10	1270	4d	shoshonite + 1000 ppm F_2 + 1000 ppm Cl_2	Phlo, Ol, melt	water leak
PC2-2009-37	11/06/09	15c [1]	10	1040	5d	mix B715 (and esite) – π (70:30) + 1000 ppm F_2 + 1000 ppm Cl_2	carbonated minerals	old powder (CO ₂)
PC1-2009-37	11/11/09	SHO3 [1]	10	1270	5d	shoshonite + 1000 ppm F_2 + 1000 ppm Cl_2	Phlo, Ol, melt	
PC2-2009-38	11/12/09	16c [1]	12	1210	5d	+ $5.4\%H_22O$ + $5\% \pi$ + $4000 \text{ ppm } F_2$ + $4000 \text{ ppm } Cl_2$)	Opx, Cpx, <i>i</i> melt	add π to change
								eutectic T
	2009–201	0: Hydrous experi	iments, garı	let growth an	d trying to	grow big amphiboles :		
PC3-2010-1	01/14/10	Grt1V4p [1]	25	1400	6d	$+ 400 \text{ ppm } F_2 + 400 \text{ ppm } Cl_2$	Grt, Opx, Cpx, <i>i</i> melt	
PC3-2010-3	01/29/10	$C4p#25kb^{**}$ [1]	25	1430	5.5d	$+ 400 \text{ ppm } F_2 + 400 \text{ ppm } Cl_2$	Grt, Opx, Cpx, melt	
PC1-2010-1	02/13/10	19b [1]	10	1040	5d	mix B715 (and esite) – π (50:50) + 6% H2O + 400 ppm F_2 + 400 ppm Cl_2		new B715 powder
PC2-2010-2	02/13/10	17c [1]	12	1210	5d	+ 6.1%H ₂ O + liquid water drop + 4000 ppm F_2 + 4000 ppm Cl_2	Opx, Cpx, <i>i</i> melt	water loose
PC2-2010-3	02/19/10	SHO4** [1]	10	1270	5d	showshonite + liquid water drop + 1000 ppm F_2 + 1000 ppm Cl_2	Phlo, Ol, melt	
PC2-2010-4	03/01/10	H4V4p [1]	12	1180	5d	+ 5.4% water + liquid water drop + 400 ppm F_2 + 400 ppm Cl_2	Opx, Amp melt	
PC1-2010-3	03/04/10	20b [1]	10	1090	5.5d	mix B715 (and esite) – π (50:50) + 6%H ₂ O + liquid water drop		
						$+$ 400 ppm F_2 + 400 ppm Cl_2	tiny amp, Qz	water loose during welding
PC2-2010-5	03/10/10	H5V4p [1]	12	1190	5.5d	+ 5.4% water + liquid water drop + 400 ppm F_2 + 400 ppm Cl_2	Opx, Cpx, melt	0
PC1-2010-4	03/11/10	21b [1]	10	1060	5.5d	mix B715 (and esite) – π (50:50) + 6%H ₂ O + liquid water drop		
						$+$ 400 ppm F_2 + 400 ppm Cl_2	tiny amp, Qz, melt	water loose
PC3-2010-5	03/11/10	$Grt3V4p^{**}$ [1]	25	1370	4.5d	+ liquid water drop + 400 ppm F_2 + 400 ppm Cl_2	Grt, Opx, Cpx, melt	Suinew Suime

Abbreviations for phases are the same than used in chapters, Qz, quartz . h : hours, d : days, β : basalt, π : peridotite, N. E. : non equilibrated, *i* : interstiticial. F_2 , add with MgF₂, see Chapter 2. Cl_2 , add with MgCl₂ see Chapter 2. Cl_2 , add with MgCl₂ see Chapter 2. r_{120} , add with MgCl₃ see Chapter 2. r_{20} using "celia-cool" program, slow temperature decrease, see Chapter 2. *prepared for ion probe analyses, but not analyzed. * samples used in the studies

Table B.0.2: continued. Second table: samples presented in Chapters 4 and 5.

Appendix C

Standards LA-ICPMS and SIMS

Standards	NIST610	NIST612	KL2-G	BCR-2G
SiO_2	69.63	71.9	50.30	54.97
TiO_2			2.56	2.32
Al_2O_3	2.039	2.11	13.30	13.10
FeO^*			10.70	13.86^{a}
MnO			0.17	0.21
MgO			7.34	3.57
CaO	11.45	11.93	10.90	7.10
Na_2O	12.87	13.98	2.35	3.14
K_2O			0.48	1.77
Total	95.99	99.92	98.1	100.04
Li	484.6	41.54	5.1	9.9
\mathbf{Sc}	441.1	41.05	31.8	32
V	441.7	39.22	309	425
\mathbf{Cr}	405.2	36	294	17
Co	405	35.26	41.2	38
\mathbf{Sr}	515.5	78.4	356	321
\mathbf{Zr}	439.9	38	152	167
La	457.4	35.8	13.1	25
Eu	461.1	35	1.92	1.91
Gd	444	36.7	5.92	6.5
Но	449.4	37.87	0.961	1.20
Lu	434.7	36.9	0.285	0.47
Hf	432	34.77	3.93	4.5
$^{\rm Pb}$	426	38.57	2.07	10.9
Th	457.2	37.23	1.02	5.5
U	461.5	38	0.548	1.70

Table C.0.1: Compositions in major elements (wt%) and trace elements (ppm) of standards used during SIMS and LA-ICPMS analyses.

a Fe₂O₃

Appendix D

Concentrations in samples of Chapter 3

				F4p#3a		F1#3b		F5#3b		C4p#2b		C8p#2b	•	
	Melt [3]	OI [4]	Opx [3]	Melt [2]	Opx [7]	Melt [4]	Opx [5]	Melt [5]	Opx [5]	Melt [2]	Opx [3]	Melt [2]	OI [3]	Opx [4]
Li	47(2)	14.3(9)	8.0(2)	20.5(6)	4.7(1)	25.8(8)	5.4(5)	24.5(4)	3.8(5)	46.6(7)	8.2(1)	47(2)	13.8(8)	7.7(1)
$\mathbf{S}^{\mathbf{C}}$	81(1)	17(1)	79(1)	78(1)	82(2)	78(2)	(2)	86.3(9)	83(3)	71.9(5)	82(4)	79.6(8)	17.4(9)	75(1)
>	70(1)	21(1)	177(4)	57.0(5)	147(5)	57(1)	107(17)	63.4(2)	173(8)	66(1)	173(9)	73(3)	24(1)	170(2)
$\mathbf{C}^{\mathbf{r}}$	1075(15)	855(38)	3222(42)	506(4)	3622(88)	854(14)	4765(534)	777(7)	4723(178)	896(2)	5270(150)	991(96)	882(93)	5084(84)
Co	60(1)	167(12)	87(1)	58.6(5)	94(4)	58(1)	87(3)	59(1)	104(9)	62.4(5)	91(1)	61(3)	162(8)	84(1)
\mathbf{Sr}	85.6(1)	0.003(1)	0.2(1)	96.0(6)	0.8(2)	91.2(8)	1.9(9)	116(1)	0.136(3)	75(1)	0.18(2)	89(4)	0.05(2)	0.4(3)
\mathbf{Zr}	97(1)	0.06(3)	3.1(1)	114(2)	5.1(6)	91.5(7)	3.6(4)	107.2(5)	3(1)	94.8(6)	2.8(5)	96(4)	0.12(4)	2.8(3)
\mathbf{La}	96(1)	0.006(1)	0.2(4)	118(2)	1.4(2)	94.6(9)	0.3(2)	111.0(7)	0.9(10)	87.6(4)	0.1(2)	97(4)	0.04(2)	0.3(2)
Eu	109(1)	0.03(2)	1.9(6)	133(1)	8.1(3)	108(1)	6(2)	125(1)	4(1)	100.035(7)	2.1(2)	112(5)	0.13(3)	4.6(2)
Gd	89.1(8)	0.10(7)	3.1(3)	108(2)	11.4(5)	83(3)	7(2)	101(2)	5(1)	81(2)	3.7(4)	88(3)	0.25(9)	7.06(2)
Но	92.9(6)	0.56(5)	8.2(7)	110(2)	13.7(3)	88(2)	11(1)	100(9)	11(1)	85(1)	9.3(7)	95(4)	0.65(5)	13.97(3)
Lu	90.1(8)	2.6(2)	17.0(7)	104(2)	24(5)	85(2)	15.6(8)	96(2)	20(1)	83(1)	19(1)	88(4)	2.8(2)	15.96(2)
Ηf	87(1)	0.08(4)	5.3(5)	104(1)	7.76(4)	84(1)	0.88(7)	99(5)	5.0(8)	80.9(7)	5.0(5)	86(4)	0.15(5)	4.60(1)
\mathbf{Pb}	114(4)	0.21(4)	1.4(2)	145(1)	0.9(5)	115(1)	0.1(1)	129(2)	0.015(2)	111.4(5)	0.7(4)	111(5)	0.10(6)	0.47(56)
$\mathbf{T}\mathbf{h}$	96(1)	0.005(18)	0.25(19)	115(2)	0.8(3)	91(1)	0.2(1)	105.9(6)	0.06(1)	89(1)	0.4(2)	92(5)	0.02(3)	0.2(2)
D	102(2)	0.006(19)	0.4(3)	126(3)	0.9(4)	95(1)	0.6(4)	118(1)	0.14(3)	98.5(6)	0.1(3)	101(5)	0.03(2)	0.3(3)

Table D.0.1: Trace element concentrations (in ppm) of run products measured by LA-ICPMS (Laboratorire Magmas et Volcans).

	C04#3a			C4#4a		CC01#8	3kb4			CF1#8k	$\mathbf{b5}$		
	Melt [2]	O1 [4]	Opx [3]	Melt [2]	Opx [3]	Melt [3]	O1 [3]	Opx [2]	Cpx [2]	Melt [2]	OI [1]	Opx [2]	Cpx [2]
·	16.5(3)	4.8(3)	2.5(2)	14(5)	3.5(1)	58(2)	12.5(6)	7.6(7)	10.3(5)	78.6(8)	17(1)	10.4(3)	16.3(1)
с С	79(1)	16(1)	81(2)	80(2)	93(3)	55(1)	10.7(5)	53(6)	83(2)	83.1(4)	12.7(9)	63(6)	130(3)
~	60.9(4)	13.9(9)	134(5)	57.5(9)	171(6)	48.5(9)	20(1)	181(13)	233(10)	71(1)	43(3)	234.2(3)	438(3)
'n	611(8)	500(85)	3791(214)	735(76)	4470(76)	917(9)	1017(211)	5376(570)	6484(420)	1570(3)	1259(73)	5868(394)	7211(317)
ò	41.7(6)	129(9)	80(5)	63.9(8)	128(9)	34.80(7)	105(1)	55(5)	33(1)	43(1)	131(10)	81(7)	64(18)
ч	97(1)	0.06(1)	0.4(1)	99(4)	0.1(1)	86(1)	0.06(2)	0.10(2)	4(1)	110.5(3)	0.02(3)	0.22(3)	4.9(5)
ų	131(3)	0.10(2)	4.2(4)	108(2)	4(1)	76.8(6)	0.13(3)	2.3(3)	8(1)	136.2(9)	0.07(5)	1.9(3)	9(2)
ğ	107(2)	0.05(2)	1.5(5)	114(2)	0.2(10)	84(2)	0.054	0.075(3)	2.7(8)	116(1)	d.l.	0.05(6)	3.2(6)
'n	118(2)	0.10(2)	4.6(7)	127(3)	2.6(20)	72(3)	0.18(8)	1.3(1)	14.2(9)	119(1)	0.003(46)	1.3(4)	14(1)
p	98(2)	0.12(6)	5.5(5)	105(1)	3.6(13)	67(2)	0.2(2)	2.8(5)	28(3)	95(2)	0.04(14)	2.6(1)	29(6)
ю	100(2)	0.52(4)	12.4(6)	106(3)	12(1)	69(2)	0.7(2)	7.3(9)	37(2)	95.0(1)	0.32(5)	5.9(6)	39(5)
'n	95(2)	2.4(2)	21.7(7)	102(2)	23(1)	66(2)	2.2(1)	13(2)	34.6(2)	89.7(1)	1.9(2)	12(1)	38(2)
Η	96(2)	0.05(4)	6.5(7)	99.5(5)	6.4(5)	71(2)	0.3(1)	4.5(6)	12(3)	97(2)	0.04(9)	3.1(2)	12(4)
\mathbf{p}	136.195(7)	0.109(1)	0.4(3)	134(4)	0.2(1)	765(41)	0.3(1)	0.15(6)	3(2)	140(3)	0.19(9)	0.2(2)	0.7(8)
q	109(2)	0.04(2)	0.1(7)	115.2(9)	0.21(9)	73(3)	0.03(2)	0.031(5)	0.7(1)	99(2)	d.l.	0.06(5)	0.4(3)
Б	121(1)	0.04(2)	0.3(7)	131.0(9)	0.25(7)	78(4)	0.074	0.09(2)	0.9(2)	100(2)	0.04(4)	0.20(6)	0.75(31)

Table D.0.2: Continued.

Numbers in parentheses represents one standard deviations in terms of least units cited.

Numbers in square brackets are numbers of LA-ICPMS analyses.

Abbreviations used: Melt, quenched basaltic melt; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene.

	CC01#8	kb4		CF1#8k	b 5		CC4#7b	-		CF5#7c			CF01#10	3kb1
	Melt [2]	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx	Cpx	Melt	Opx
Ŀ	30.8(2)	12.98(6)	9.72(7)	43.0(3)	20.1(1)	9.89(7)	19.91(6)	4.98(9)	7.0(1)	22.85(8)	3.97(8)	10.67(7)	36.7(1)	13.32(3)
\mathbf{Be}	63.8(2)	6.04(6)	6.00(2)	102.0(4)	9.4(1)	6.10(1)	107.1(2)	9.32(6)	15.9(1)	103.3(2)	2.48(3)	28.2(1)	94.9(1)	14.75(6)
В	586(2)	21.0(3)	10.9(1)	268(2)	32.5(4)	11.1(1)	330.2(5)	31.0(1)	51.5(4)	196.0(4)	3.24(9)	56.4(4)	156(5)	24.2(2)
$\mathbf{S}_{\mathbf{C}}$	59.1(3)	61.8(3)	119.9(9)	85.2(3)	33.4(3)	122.1(9)	89.9(6)	79.0(4)	110(1)	90.1(6)	82.4(7)	110.3(6)	72.0(4)	66.5(4)
>	53.2(4)	93.3(7)	284(2)	76.2(4)	58.8(5)	289(2)	87.1(6)	181.9(6)	242(2)	87.3(6)	190(1)	220(1)	75.3(5)	149.9(9)
$\mathbf{C}^{\mathbf{r}}$	887(7)	1296(3)	6165(52)	1492(19)	2009(5)	6275(53)	1035(1)	5811(37)	6773(12)	976(1)	6371(41)	6536(8)	603(9)	3784(3)
Co	53(1)	158(1)	79(1)	94(1)	246(2)	80(1)	126(2)	155(2)	114(1)	130.1(1)	161(2)	126(1)	77.5(5)	98.9(5)
\mathbf{Sr}	66.5(5)	3.1(2)	7.0(2)	85.8(7)	8.0(2)	7.1(2)	89.0(8)	6.1(1)	14.4(4)	104(1)	0.43(2)	27.6(7)	84.0(6)	13.3(4)
\mathbf{Zr}	72.9(8)	5.5(1)	12.6(2)	126(1)	11.9(3)	12.8(2)	111(1)	10.8(2)	18.2(4)	109.4(8)	3.02(6)	31.1(7)	84.5(6)	15.1(3)
La	77.2(4)	3.13(9)	6.6(2)	106.2(7)	9.2(3)	6.7(2)	109.3(6)	7.4(1)	14.4(3)	110.4(7)	0.16(1)	25.2(4)	91(1)	14.2(2)
Eu	68.0(5)	3.98(6)	15.6(2)	108.1(6)	8.9(1)	15.9(2)	117(1)	9.0(1)	31.2(4)	116(1)	2.28(8)	43.9(7)	86.5(9)	15.3(2)
Gd	50.9(5)	3.87(7)	23.9(3)	72(1)	5.9(2)	24.3(3)	78.3(7)	7.8(2)	29.4(3)	82(1)	3.10(9)	37.5(3)	65(1)	12.6(2)
Но	68.6(5)	9.2(1)	39.4(4)	93.0(7)	8.1(1)	40.1(4)	103.3(7)	15.5(2)	48.2(4)	103.8(8)	9.4(2)	58.4(3)	85(7)	19.5(1)
$\mathbf{L}\mathbf{u}$	61.6(6)	14.0(2)	33.8(1)	82.7(6)	9.1(1)	34.4(1)	91.4(8)	20.0(3)	42.3(4)	92.1(6)	16.5(3)	51.5(3)	76(6)	22.4(3)
Ηf	62.5(7)	6.4(2)	13.8(1)	83(1)	7.5(2)	14.1(1)	91.5(8)	10.3(2)	18.9(4)	90(1)	4.3(1)	30.7(7)	90(1)	17.9(4)
\mathbf{Pb}	1851(22)	76(2)	11.2(9)	296(6)	23(2)	11(1)	339(3)	19.8(8)	40(2)	310(3)	0.5(1)	68(2)	2219(24)	305(9)
$\mathbf{T}\mathbf{h}$	66.2(4)	2.63(5)	3.7(2)	88.8(4)	7.8(1)	3.8(2)	100.5(4)	6.9(1)	10.8(4)	100.8(8)	0.074(6)	21.6(6)	83.8(6)	13.3(1)

Table D.0.3: Trace element concentrations (in ppm) of run products measured by IMS 5f SIMS (Géosciences Montpellier).

Numbers in parentheses represents one standard deviations in terms of least units cited.

Numbers in square brackets are numbers of SIMS analyses. Most of the analyses represent on spot analysis.

Abbreviations used: Melt, quenched basaltic melt; Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene.

Appendix E

Lattice strain models applied to pyroxenes of the Chapter 4



Figure E.0.1: Lattice strain models applied to orthopyroxene – hydrous basaltic melt (a, b, c) and clinopyroxene – hydrous basaltic melt (d and e). Solid hyperbola represent fits of the lattice strain model to $D_i^{opx/melt}$ or $D_i^{cpx/melt}$, this represents the sum of the resulting fits for $D_i^{M1/melt}$ (stippled parabola) and for $D_i^{M2/melt}$ (dashed parabola). Lattice strain parameters are given on figure, E_0 is GPa and r_0 is in Å. Criteria Nash and RMSE were used to select best fits.

Appendix F

Detection limits of the LA-ICPMS

Table F.0.1: Range of LA – ICPMS detection limits.

Elements	Range (ppm)
Li	0.13 - 0.39
\mathbf{Sc}	0.23 - 0.53
V	0.24 - 0.59
Cr	8.12 - 14.83
Co	0.04 - 0.12
\mathbf{Sr}	0.02 - 0.06
Zr	0.03 - 0.07
La	0.015 - 0.08
Eu	0.04 - 0.10
Gd	0.13 - 0.33
Но	0.02 - 0.08
Lu	0.02 - 0.11
Hf	0.08 - 0.22
Pb	0.08 - 0.50
Th	0.02 - 0.09
U	0.02 - 0.09