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Chlorine in wadsleyite and ringwoodite: An experimental study

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ABSTRACT

We report concentrations of Chlorine (Cl) in synthetic wadsleyite (Wd) and ringwoodite (Rw) in the system NaCl–$(Mg,Fe)_2SiO_4$ under hydrous and anhydrous conditions. Multi-anvil press experiments were performed under pressures (14–22 GPa) and temperatures (1100–1400 °C) relevant to the transition zone (TZ: 410–670 km depth). Cl and H contents were measured using Particle Induced X-ray Emission (PIXE) and Elastic Recoil Detection Analysis (ERDA) respectively. Results show that Cl content in Rw and Wd is significantly higher than in other nominally anhydrous minerals from the upper mantle (olivine, pyroxene, garnet), with up to 490 ppm Cl in anhydrous Rw, and from 174 to 200 ppm Cl in hydrous Wd and up to 113 ppm Cl in hydrous Rw.

These results put constrains on the Cl budget of the deep Earth. Based on these results, we propose that the TZ may be a major repository for major halogen elements in the mantle, where Cl may be concentrated together with H_2O and F (see Roberge et al., 2015). Assuming a continuous supply by subduction and a water-rich TZ, we use the concentrations measured in Wd (174 ppm Cl) and in Rw (106 ppm Cl) and we obtain a maximum value for the Cl budget for the bulk silicate Earth (BSE) of 15.1×10^{22} g Cl, equivalent to 37 ppm Cl. This value is larger than the 17 ppm Cl proposed previously by McDonough and Sun (1995) and evidences that the Cl content of the mantle may be higher than previously thought. Comparison of the present results with the budget calculated for F (Roberge et al., 2015) shows that while both elements abundances are probably underestimated for the bulk silicate Earth, their relative abundances are preserved. The BSE is too rich in F with respect to heavy halogen elements to be compatible with a primordial origin from chondrites CI-like (carbonaceous chondrites CC) material only. We thus propose a combination of two processes to explain these relative abundances: a primordial contribution of different chondritic-like materials, including EC-like (enstatite chondrites), possibly followed by a distinct fractionation of F during the Earth differentiation due to its lithophile behavior compared to Cl, Br and I.

1. Introduction

Halogen elements (fluorine F, chlorine Cl, bromine Br, iodine I) are minor volatiles compared to hydrogen and carbon. Major halogens F and Cl have been mostly studied for their role in the shallowest Earth's reservoirs: lithosphere, crust, atmosphere, and hydrosphere, mostly because they are the most abundant halogens and because they have been shown to be strongly involved in volcanic and igneous processes. Indeed, Cl is an important constituent of volcanic fumaroles and plumes, and form individualized fluids such as brines and molten salts. These brines are strongly involved in hydrothermal systems and in ore forming processes (see the reviews after Pyle and Mather, 2009; Aiuppa et al., 2009). Cl is particularly used to trace igneous processes and ore-forming processes, and to track magmas from their genesis to their eruption Cl is known to affect magma properties (see Pyle and Mather, 2009), it is significantly degassed from subaerial volcanic activity (e.g. Aiuppa et al., 2009), and it can impact the stratosphere chemistry. Cl is enriched in sea water, it has been shown that oceanic subduction delivers fluids to the mantle

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through serpentinites related processes (serpentinization and deserpentinization), that are significantly Cl-rich (e.g. Ito et al., 1983; John et al., 2011; Kendrick et al., 2011), making this last one an important constituent in mantle metasomatism processes, that enriches the sources for arc magmatism (e.g. Tatsumi, 1989; Philippot et al., 1998; Scambelluri et al., 2004). Indeed magmas from subduction zones are among the most enriched in Cl (Ito et al., 1983; Straub and Layne, 2003; Kendrick et al., 2012).

During subduction, the interaction between seawater and rocks produces secondary minerals containing significant amounts of Cl (Ito et al., 1983; Pagé et al., 2016). It has thus been proposed that the subduction of oceanic lithospheric material at convergent plate boundaries would drive an annual global flux of 2.9–22 × 10^{12} g Cl to the Earth's interior (John et al., 2011). It has also been proposed that a part of the subducted Cl would reach high depths in the mantle (>200 km) and would possibly enrich the sources for Ocean Island Basalts (Kendrick et al., 2015; Joachim et al., 2015). Cl is significantly present in ultrahigh pressure metamorphic rocks (Scambelluri et al., 2004; Ottolini and Fèvre, 2008; Pagé et al., 2016), in inclusions of saline brines in diamonds (Weiss et al., 2014). Recent studies show that Cl is present in olivine, pyroxene, and garnet: the highest contents of Cl are measured in minerals formed by metamorphic dehydration of serpentine, olivines and pyroxenes (up to 400 ppm Cl, Scambelluri et al., 2004; Ottolini and Fèvre, 2008). In natural upper mantle nominally anhydrous minerals, the Cl contents are very low: up to 6.3 ppm in olivine (Beyer et al., 2012). Partitioning experiments performed for natural compositions however demonstrate the capability of upper mantle minerals to be the Cl carriers: up to 148 ppm Cl in orthopyroxene, 17 ppm Cl in clinopyroxene, 13 ppm in garnet, 5 ppm in plagioclase, up to 170 ppm in olivine (Dalou et al., 2012). To our knowledge, there is currently no evidence about the presence of Cl in the transition zone and in the lower mantle. Recently we have suggested that a strong link connects the water global cycle and that of fluorine at depth (Crépisson et al., 2014; Roberge et al., 2015). We have proposed that the transition zone can be a major reservoir for fluorine (Roberge et al., 2015). It could be similar for Cl.

This study aims at constraining the possible deep storage and cycling of Cl through the determination of Cl potential contents in wadsleyite (Wd) and ringwoodite (Rw), the major minerals of the transition zone (TZ). We use these data to discuss the Cl content of the bulk silicate Earth.

2. Materials and methods

2.1. Starting materials an experimental strategy

The starting bulk composition was olivine Fo_{90} with a slight excess of silica ((Mg+Fe)/Si atomic ratio = 1.75), obtained with a mixture of (1) oxide powders of MgO, SiO_2, FeO, or (2) natural Fo_{90} olivine with SiO_2 powder. 5 wt% of Cl was added to the mixture as crushed NaCl powder. NaCl was chosen as the source of Cl because it is enriched in sea water and in subducted oceanic floor. For experiments under hydrous conditions, 2 wt% of water was added as brucite $Mg(OH)_2$, an amount close to the expected water solubility in wadsleyite and ringwoodite in the transition zone. Samples were synthesized in multi-anvil presses at LMV Clermont-Ferrand (France) and at the Bayerisches Geoinstitut of Bayreuth (Germany) following the procedure described in Frost et al. (2001) and Demouchy et al. (2005). Experiments were performed from 14 to 22 GPa and from 1100 °C to 1400 °C during 0.5 to 9 h, (Table 1). The samples were enclosed in Re, Pt or Au–Pd capsules. Temperatures were monitored with W3Re/W25Re thermocouples located at the top of the capsules. After the run, the experiments were quenched by switching off the electric power before decompression.

2.2. Sample characterization

The mineral assemblages were recovered, embedded in epoxy and mirror polished on one side. They were analyzed with Raman spectroscopy and scanning electron microscopy at first. The textures were investigated with a Zeiss Ultra 55 field emission scanning electron microscope (SEM) equipped with an Energy Dispersive X-ray spectroscopy (EDX) system. Major elements compositions of wadsleyites and ringwoodites were subsequently measured by Electron Probe Micro Analysis (EPMA) on CAMECA-SX100 at CAMPARIS facility (UPMC, France). For these quantitative analyses, we used an acceleration voltage of 15 kV and a beam current of 10 nA with an 15 μm defocused beam.

A thin section of ringwoodite sample was prepared with a Focus Ion Beam (FIB), using a gallium beam with a FEI Strata DB 235 at IEMN (Lille, France). A transmission Electron Microscopy (TEM) study was performed on this FIB section at UMET, Lille (France) with a FEI Tecnai G2-20 twin operating at 200 kV.

Chlorine and hydrogen contents were measured using ion beam analysis, Particle Induced X-Ray Emission (PIXE) for Cl and Elastic Recoil Detection Analysis (ERDA) for H at the nuclear microprobe of the Laboratoire d'Etude des Eléments Légers (LEEL), CEA Saclay. Cl concentrations of the mineral phases Wd and Rw were obtained using incident beams of $3 * 3\ \mu m^2$ mapped on large areas ($50 * 50$ to $200 * 20\ \mu m^2$). The procedure is detailed in Bureau et al. (2009, 2016). We used different incident beams (H^+ and $^4He^+$ from 1.7 to 3 MeV) in order to control the depth of investigation in the samples. With mineral phases a few tens of μm in size embedded in a quenched Cl–Si-rich glass (present at grain boundaries), compromise had to be found between energy and detection in order to avoid any chlorine contribution from glassy phase. Indeed the depths investigated by the ion beams depend both on the nature of the incident ion (H^+, $^4He^+$) and on the energy of the beam, (i.e. the highest the energy is the deepest is the investigation). For a San Carlos olivine, the depth of analysis for a proton beam is 50 μm at 3 MeV and 25 μm at 1.7 MeV. For one given energy, this depth is reduced when the incident ion is heavier than H^+, at 2 MeV the investigated depth of $^4He^+$ is 6 μm.

Hydrogen (i.e. water) contents of Rw and Wd were measured using ERDA. We used a 3 MeV $^4He^+$ beam, following the protocol described in Bureau et al. (2009) and Withers et al. (2012). Simultaneous Cl analysis were also performed by PIXE during ERDA.

We scanned the beam on selected areas of the sample (from 30 × 30 to 150 × 100 μm^2). Durations of analysis were chosen from 1800 to 7200 s. ERDA and PIXE were associated to simultaneous Rutherford Backscattering Spectrometry (RBS) measurements used to monitor the cumulated charge delivered to the sample during the acquisition (see Bureau et al., 2009). They also provided information on the matrix chemical composition of the samples. For all ion beam analysis, the software RISMIN (Daudin et al., 2003) was used to process the data by selecting the areas of interest in the chemical maps (see Fig. 1). It was particularly useful for the detection of NaCl-rich glasses (grain boundaries, cracks or surface contamination), which would affect H and Cl contents. Once the areas were selected, ERDA spectra were processed by using SIMNRA (Mayer, 1997) and PIXE spectra were processed by using the GUPIXWIN software (Campbell et al., 2000). Analysis were cross-checked against: NIST SRM610 glass (Rocholl et al., 1997), KE12 (pantellerite lava from Kenya, Metrich and Rutherford, 1992), EtC3 (Cl–Br–I-bearing $NaAlSi_3O_8$ glass, Bureau et al., 2000). The sensitivity (i.e. detection limit) with respect to Cl was of a few tens of ppm (30–40 at maximum) depending on the conditions (beam energy, grain size, size of the selected areas).