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Effect of saline fluids on chlorine incorporation in serpentine

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Abstract

The incorporation of chlorine in serpentine minerals is crucial for the recycling of chlorine in subduction zones. Fluid inclusions of natural serpentinites have up to 50 wt% Cl, but effect of fluid salinity on chlorine distribution in serpentine minerals is poorly constrained. In this study, natural serpentinites (Lichi Melange, Taiwan) with starting grain sizes of 100−177 μm were equilibrated in saline solutions (2.93 wt%, 8.78 wt %, and 19.30 wt% NaCl) at ambient temperature and pressure for experimental duration from 18 to 43 days. The concentrations of chlorine in serpentine minerals were analyzed using electron microprobe with a detection limit of 33 ppm. Serpentine before experiments has very low chlorine, 0.017 ± 0.009 wt%. In contrast, serpentine equilibrated in saline solutions contains chlorine around three times higher, e.g., serpentine equilibrated in 2.93 wt% NaCl has 0.077 ± 0.033 wt% Cl after 18 days. The serpentine was re-equilibrated in pure water for around 24 h in order to testify chlorine is hosted in a weak-bound or structurally-bound position. For serpentine minerals equilibrated in low-salinity solutions (2.93 wt% and 8.78 wt% NaCl), they lost ~40% of Cl after re-equilibrated in pure water. Despite such release, chlorine in serpentine minerals is still higher than that of serpentine before experiment, which indicates that saline solutions increase structurally-bound chlorine of serpentine minerals. This is more efficient for high-salinity solution (19.30 wt% NaCl), and chlorine in serpentine re-equilibrated in pure water is essentially the same as that of serpentine equilibrated in the saline solution. Our experimental results suggest that chlorine in serpentine can be greatly modified by saline fluids. The structurally-bound chlorine may not necessarily reflect the T-P information of natural serpentinites.

Keywords: Chlorine; Serpentinization; Serpentinites; Fluid salinity; Subduction zones

1. Introduction

Serpentinization, a low-temperature (≤500 °C) hydrothermal alteration of ultramafic rocks (mainly peridotite and komatiite), widely occurs in many geological settings, including ocean floor, mid-ocean ridges, and subduction zones (e.g., Charlou et al., 2000; Hyndman and Peacock, 2003; Evans et al., 2013). Serpentine minerals, the main secondary minerals produced after serpentinization, contain abundant H_2O (up to 13.5 wt%), fluid-mobile elements (e.g., Ba, Cs, and Pb) and chlorine (e.g., Rucklidge, 1972; Scambelluri et al., 2004; Bonifacie et al., 2008; Huang et al., 2017a). Experimental and thermodynamic simulations have shown that serpentine minerals can be stable at depths of greater than 150 km (e.g., Ulmer and Trommsdorff, 1995; Schmidt and Poli, 1998). Therefore, serpentinization plays an important role for the recycling of H_2O, fluid-mobile elements, and chlorine in subduction zones (e.g., Scambelluri et al., 1995; Hattori and Guillot, 2003; Deschamps et al., 2012; Guillot and Hattori, 2013).

Fresh peridotite typically has very low Cl, e.g., <30 ppm (e.g., Scambelluri et al., 2004), whereas serpentine minerals

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contain chlorine around 1−2 orders of magnitude higher (e.g., Rucklidge, 1972; Scambelluri et al., 2004; Bonifacie et al., 2008; Huang et al., 2017a). This suggests that chlorine is incorporated in serpentine minerals during the interaction between peridotite and saline solutions. Earlier studies were mainly focused on chlorine distribution in natural serpentinites (e.g., Earley, 1958; Rucklidge, 1972; Rucklidge and Patterson, 1977; Anselmi et al., 2000; Scambelluri et al., 2004), and they showed that serpentine minerals have up to 0.8 wt% Cl (e.g., Rucklidge, 1972). Sharp and Barnes (2004) found that serpentine minerals lost some of Cl when they were equilibrated in pure water at ambient temperature for ~24 h or at 150 °C for 2 h. Based on these observations, they proposed that chlorine is hosted in serpentine minerals in two ways: (1) in a weak bound position that can be readily leached by pure water and (2) substitution for the −OH group in the structure of serpentine. A recent experimental study has shown that the incorporation of structurally-bound chlorine in serpentine minerals greatly depends on temperature (Huang et al., 2017a). It increases with increasing temperature and reaches a maximum at 200 °C, and it decreases at higher temperature, e.g., serpentine formed at 200 °C has up to 1.2 wt% Cl, and serpentine produced at 500 °C and 3.0 kbar contains ~0.1 wt% Cl (Huang et al., 2017a), consistent with analyses of natural serpentinites (Scambelluri et al., 2004; Bonifacie et al., 2008). This suggests that structurally-bound chlorine may reflect T-P information of serpentine formation.

However, the concentrations of chlorine in serpentine minerals vary greatly especially at low temperatures, e.g., chlorine in abyssal serpentinites varies from ~0.001 wt% to 1.2 wt% (e.g., Scambelluri et al., 2004; Huang et al., 2017a). This suggests that chlorine distribution in serpentine may be influenced by other factors, e.g., the salinity of aqueous fluids. Analyses of natural serpentinites have shown that fluid inclusions are salt-saturated and contain up to 50 wt% NaCl (e.g., Scambelluri et al., 1997). The influence of fluid salinity is indicated by a decrease in chlorine of serpentine when serpentine was equilibrated in 5 wt% NaCl at 462 °C and 2.0 kbar (Rucklidge, 1972). However, effect of fluid salinity on the incorporation of chlorine in serpentine minerals has not been systematically investigated. In particular, the influence of fluid salinity on weak-bound and structurally-bound chlorine in serpentine minerals is not clear. In this study, we performed hydrothermal experiments at ambient temperature and pressure by equilibrating natural serpentinites in saline fluids in order to study the effect of saline solutions on chlorine incorporation in serpentine.

2. Materials and methods

The starting material used in experiments of this study is natural serpentinites sampled at Lichi Melange, Taiwan (Huang et al., 2017b). The serpentinite is composed of >95% serpentine, and a small amount of magnetite and chromite (Fig. 1). Electron microprobe analyses show that serpentine has 0.017 ± 0.009 wt% Cl (Table 1). The sample was crushed, ground in an agate mortar, and subsequently sieved into

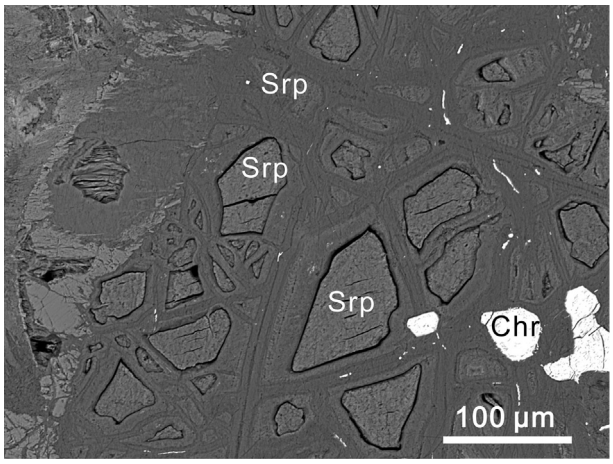

Fig. 1. Backscattered electron imaging of serpentinites from Lichi Melange, Taiwan. Serpentinites were composed of >95% serpentine (Srp), and a small amount of chromite (Chr).

starting grain sizes of 100−177 μm. Saline solutions with 2.93 wt%, 8.78 wt% and 19.30 wt% NaCl were prepared using deionized water and analytical-reagent sodium chloride.

Serpentinite powders (~100 mg) were equilibrated in saline solutions (~10.0 ml) at ambient temperature and pressure for experimental durations ranging from 18 to 45 days. After experiments, ~10 mg solid products were taken by using pipette, and they were dried at 60 °C. This process has a negligible influence on water/rock ratios. After 45 days, the solid experimental products were taken, which were re-equilibrated in pure water (~20.0 ml) at ambient temperature and pressure for around 24 h in order to study the incorporation of weak-bound chlorine in serpentine.

The solid experimental products were mounted in epoxy resin, and they were polished using Al_2O_3/SiC grit papers and diamond paste. Ethanol was used instead of water in order to avoid possible dissolution of Cl-bearing phases. Compositions of the solid experimental products were determined using JEOL JXA 8100 electron microprobe with four wavelength-dispersive spectrometers at Second Institute of Oceanography, State Oceanic Administration. Operating conditions for serpentine analyses include 15 kV and 20 nA with a beam diameter of 15 μm. Calibration standards are jadeite (Si, Na), olivine (Mg), almandine garnet (Fe, Al), diopside (Ca), sandine (K), chromium oxide (Cr), rutile (Ti), nickel silicide (Ni), cobalt metal (Co), rhodonite (Mn), and tugtupite (Cl). The counting times for Ni, Co, Cl and Mn are 30 s for peak and 15 s for background, whereas other elements were analyzed with 10 s for peak and 5 s for background. The detection limit of chlorine is ~33 ppm.

3. Results

Serpentine before experiment has very low chlorine, 0.017 ± 0.009 wt%. For serpentine minerals equilibrated in saline solutions, their chlorine increased by around three times (Fig. 2, Table 2), e.g., serpentine equilibrated in 2.93 wt%

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