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# Experimental insight into redox transfer by iron- and sulfur-bearing serpentinite dehydration in subduction zones

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ABSTRACT

Dehydration of antigorite in subduction zones releases a large amount of aqueous fluid and volatile elements, which can potentially oxidize the mantle wedge. The redox capacity of three synthetic serpentinites with variable $Fe_{total}$, $Fe^{3+}$ and $S^{-}$ contents is investigated using XANES spectroscopy at both, Fe and S *K*-edges. Experiments are performed between 450 and 900 °C, at 2 GPa and $fO_2 \sim$ QFM-2; conditions similar to those encountered in subduction zones.

Redox reactions in the synthetic serpentinites, which involve Fe and S can be summarized as follows: 1) the reduction of ($S^{-}$)-pyrite into ($S^{2-}$)-pyrrhotite (~450 °C), with ~4.4 mg/g of the sulfur degassed most likely as $H_2S$, 2) the consumption of magnetite that reacts with antigorite to form Fe-rich olivine (<500 °C), 3) the reduction of ($Fe^{3+}$)-antigorite into ($Fe^{2+}$)-antigorite (~580 °C), occurring about 100 °C below the temperature of antigorite breakdown, 4) the main ($Fe^{2+}$)-antigorite breakdown that forms olivine and enstatite (~675 °C), and 5) the decomposition of minor amounts of ($Fe^{2+/3+}$)-clinochlore (~800 °C). The bulk $Fe^{3+}/Fe_{total}$ ratio is found to decrease with run temperature from ~0.82–0.97 depending on the hydrous starting material, down to 0.1–0.2 in the high-temperature anhydrous assemblages.

The evolution of mineral modes and $Fe^{3+}/Fe_{total}$ with temperature in our synthetic samples shows similar trends to what has been reported in serpentinite rocks collected, for example, along a metamorphic transect in the western Alps. We show that a large amount of $O_2$-equivalent – up to 10 mol/kg of rock – can be generated at temperature around 450 °C due to the presence of oxides and sulfides such as magnetite and pyrite. Owing to the poor capacity of aqueous fluid to transfer redox conditions, we surmise that this $O_2$-equivalent is "consumed" at the scale of the lithospheric-mantle top which is partially serpentinized and therefore bear strong redox gradients.



## 1. Introduction

Subduction of sediments, metabasalts and serpentinites of the oceanic lithosphere is accompanied by a release of aqueous fluids to the mantle wedge, which are likely involved in the formation of arc magmas and generation of earthquakes (e.g., Schmidt and Poli, 1998; Kerrick and Connolly, 2001a; Hacker et al., 2003). As a consequence, fore-arc mantle rocks and arc magmas inherit part of their geochemical signature from the subducting oceanic slab (e.g., Plank and Langmuir, 1998; Kerrick and Connoly, 2001b). Dehydration reactions in the slab are likely to occur continuously with increasing depth (Schmidt and Poli, 1998). Each lithological component releases water for a given slab thermal structure to a different extent depending on depths (e.g., Rüpke et al., 2004). Sediments which are located at the top of the slab, start dehydrating at shallow depths, followed by oceanic crust and then abyssal serpentinites (Rüpke et al., 2004). The depth of the slab top below the volcanic arc (sub-arc depth) is around 70–150 km worldwide (Syracuse et al., 2010), corresponding to pressures of 2.5–5 GPa.

Sediments and igneous rocks of the oceanic crust are expected to release most of their water in the sub-arc region

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(Kerrick and Connolly, 2001b; Hacker, 2008) whereas serpentinite-bearing lithosphere can carry water to greater depths (e.g., Rüpke et al., 2004) due to the wide stability field of antigorite (Ulmer and Trommsdorff, 1995) and clinochlore (Bromiley and Pawley, 2003). The contribution of serpentinites to the slab water budget is not firmly established but it is estimated that serpentinization of the uppermost subducting abyssal mantle peridotites can reach 20% corresponding to ca. 2.4 wt.% $H_2O$ (Hacker et al., 2003), whereas metabasalts and sediments host about 3 wt.% and 6 wt.% $H_2O$, respectively (Kerrick and Connolly, 2001a, 2001b). Serpentinite dehydration is expected to mostly contribute to the water release to the sub-arc region in the context of "hot" subduction (Rüpke et al., 2004; Merkulova et al., 2016).

Arc magmas are shown to be more oxidized than MORB and OIB (Evans et al., 2012b). The question remains open whether the sub-arc mantle-wedge source of these magmas is also oxidized (e.g., Evans et al., 2012b). Slab-derived fluids possibly contribute to oxidation of the mantle wedge in two ways, either by the oxidized species dissolved in the aqueous fluid or melt (Frost and Ballhaus, 1998) or directly by the oxygen dissolved in the fluid itself (Brandon and Draper, 1996), the latter being by far a less efficient way than the former (Frost and Ballhaus, 1998). Merkulova et al. (2016) showed that antigorite (Atg) dehydration in Fe-bearing systems relevant to natural serpentinite compositions proceeds over a temperature range of several hundreds of Kelvin with two maxima of fluid release. The aim of the present experimental study is to investigate the redox characteristics of the fluids that are liberated during antigorite breakdown to better understand redox transfer in subduction zones.

The capacity of a rock to reduce or oxidize another medium (fluid, rock or both) is directly linked to the concentration and charge of redox-sensitive elements, such as Fe, C and S (Evans, 2006; Evans et al., 2012b), in the reacting systems. Minerals that host these redox-sensitive elements have the potential to control the oxygen fugacity ($fO_2$) of their host rock through phase relationships. Oxygen fugacity is commonly used to characterize the oxidizing/reducing potential of a rock. However, it is an intensive parameter that does not depend on the quantity of redox sensitive elements in the system. Therefore, oxygen fugacity alone cannot be used to infer the redox capacity of a rock. For that reason, Evans (2006) introduced the concept of redox budget (RB), an extensive parameter, which corresponds to the molar amount of electrons that are transferred from the initial to the final redox state of a rock. The redox state is basically calculated from the charge and molar amount of redox sensitive elements in the rock. We slightly modified the latter concept by replacing the molar amount of electrons by its $O_2$ equivalent ($n_{O_2} = 4n_{e^-}$).

Redox-sensitive elements that are in significant concentration in serpentinites are Fe, S and C. Total Fe content in serpentinites can range from ~4 wt.% to ~11 wt.% (Guillot et al., 2001; Marchesi et al., 2013). $Fe^{3+}/Fe_{total}$ in serpentinites is variable and found to average around 0.7 (Debret et al., 2014, 2015). Sulfur content in serpentinites varies from ~0.03 to ~1 wt.% (Alt et al., 2013), sulfur is present in serpentinites as sulfides ($S^{1-}$ in dianion, and $S^{2-}$) and sulfates ($S^{6+}$) (Alt et al., 2013). Sulfate content over total sulfur in serpentinites varies from 0.19 to 0.96 (Alt et al., 2013). Carbon content varies greatly since carbon is mostly hosted in carbonate veins. Evans (2012) proposed an average C-content of 0.28 wt.% in the form of $C^{4+}$. Since $C^{4+}$ is not expected to change oxidation state in the course of antigorite dehydration, we only examined, in the present work, the redox behavior of Fe and S during the dehydration of serpentinite at the *P–T* conditions of subduction zones and $fO_2 \sim$ QFM-2. Our approach is to combine experimental data, X-ray absorption spectroscopy and thermochemical modeling to evaluate the redox capacity of serpentinites and to investigate possible connection between $O_2$ transfer and release of aqueous fluid from serpentinized slabs.

**Table 1**
Composition of starting materials for three experimental sets. $H_2O$ of the starting material was assumed to be held by antigorite only and $H_2O$ wt.% was calculated from the difference between total wt.% and 100 wt.% of the starting antigorite EPMA analysis.

| Oxide (wt.%) | Set#1 | Set#2 | Set#3 |
|---|---|---|---|
| $SiO_2$ | 44.12 | 39.02 | 38.99 |
| $TiO_2$ | 0.02 | 0.45 | 0.00 |
| $Al_2O_3$ | 1.11 | 1.92 | 1.66 |
| FeO | 1.37 | 6.07 | 3.24 |
| MgO | 41.49 | 38.52 | 40.71 |
| CaO | 0.1 | 2.43 | 0.99 |
| $Cr_2O_3$ | 0.00 | 0.16 | 0.16 |
| NiO | 0.00 | 0.04 | 0.00 |
| $H_2O$ | 12.14 | 11.50 | 12.00 |
| $SO_3$ | 0.00 | 0.00 | 2.20 |
| Total | 100.00 | 100.12 | 100.00 |
| $Fe^{3+}/Fe_{tot}$ | 0.97 | 0.96 | 0.82 |

## 2. Methods

Three starting materials containing antigorite were prepared: (1) 100 wt.% natural $Fe^{3+}$-bearing antigorite; (2) 95 wt.% natural $Fe^{3+}$-bearing antigorite + 5 wt.% magnetite (Magnox powder, 99% purity); (3) 97 wt.% natural $Fe^{3+}$-bearing antigorite + 3 wt.% natural pyrite. Experiments performed with these starting materials will be referred to as set#1, set#2 and set#3, respectively. The antigorite sample used in all three starting mixtures was collected at the Mont-Cenis massif, French Alps (Muñoz et al., 2013). High $Fe^{3+}/Fe_{total}$ ratio of 0.97 for this antigorite sample (Muñoz et al., 2013) is similar to the $Fe^{3+}/Fe_{total}$ ratio encountered for lizardite from serpentinized abyssal peridotite (e.g., Evans et al., 2012a; Debret et al., 2014). Furthermore, this antigorite sample was selected because of its chemical homogeneity and its availability in sufficient quantity for experimental petrology. The pyrite content in set#3 was adjusted to 3 wt.%, corresponding to 3 times more pyrite than in natural serpentinites (Alt et al., 2013), in order to perform X-ray absorption near edge structure (XANES) measurements at the S *K*-edge on the run products with sufficient signal to noise ratio.

The major-element composition of the three starting materials was measured by X-ray fluorescence (XRF) using EDAX Eagle III spectrometer (ISTerre, Grenoble) and mineral abundance was determined using X-ray powder diffraction (XRPD). CaO and $Al_2O_3$ (up to 2.43 wt.% and 1.92 wt.%, respectively) are accounted for by minor andradite (Adr) and clinochlore (Clc) in all starting mixtures. Bulk compositions of the three starting materials are shown in Table 1 together with $Fe^{3+}/Fe_{total}$ ratios obtained from XANES spectroscopy measurements at the Fe *K*-edge.

Experiments were carried out in an end-loaded piston-cylinder apparatus (PC) at pressures from 1.5 to 2 GPa and temperatures from 450 to 900 °C, with experimental durations ranging from 5 to 9 d. The detailed experimental procedure is described in Merkulova et al. (2016). The oxygen fugacity ($fO_2$) was controlled by the cell assembly of the experimental device and no $fO_2$ buffer was added. The $fO_2$ in the $H_2$-permeable sample-capsule (gold) between QFM and QFM-2 (e.g., Truckenbrodt et al., 1997) was imposed, at least transiently, by the $fH_2$ of the graphite furnace – cell moisture system. The capacity of the cell assembly to behave as an "infinite" source of $H_2$ has been tested (Supplementary material: Appendix B in Merkulova et al., 2016). Table 2 summarizes the *P–T* conditions, run duration, starting material and mineral products.