Highly oxidising fluids generated during serpentine breakdown in subduction zones

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Subduction zones facilitate chemical exchanges between Earth’s deep interior and volcanism that affects habitability of the surface environment. Lavas erupted at subduction zones are oxidized and release volatile species. These features may reflect a modification of the oxidation state of the sub-arc mantle by hydrous, oxidizing sulfate and/or carbonate-bearing fluids derived from subducting slabs. But the reason that the fluids are oxidizing has been unclear. Here we use theoretical chemical mass transfer calculations to predict the redox state of fluids generated during serpentine dehydration. Specifically, the breakdown of antigorite to olivine, enstatite, and chlorite generates fluids with high oxygen fugacities, close to the hematite-magnetite buffer, that can contain significant amounts of sulfate. The migration of these fluids from the slab to the mantle wedge could therefore provide the oxidized source for the genesis of primary arc magmas that release gases to the atmosphere during volcanism. Our results also show that the evolution of oxygen fugacity in serpentine during subduction is sensitive to the amount of sulfides and potentially metal alloys in bulk rock, possibly producing redox heterogeneities in subducting slabs.

During subduction, the increase of pressure and temperature conditions in the subducting plate results in hydrous mineral breakdown and the release of volatile-rich fluids. The oxidized or reduced nature of the released fluids is controlled by mineral local equilibrium changes and can be monitored through the oxygen fugacity ($f_{O2}$). Although large variabilities of $f_{O2}$ were shown to occur in subduction zones, especially in melange zones constituting the plate/mantle interface1, previous petrological and geochemical studies have shown that the redox state of the subducted mafic crust does not change during prograde metamorphism and that its redox budget remains relatively constant2. Therefore, other sources of fluids must be considered to explain the oxidized nature of arc magmas3–5.

Serpentinized mantle peridotites can constitute a major source of water at depth in subduction zones6. Those rocks comprise a significant part of subducting oceanic lithosphere hydrated near the seafloor at slow or ultra-slow spreading ridges7,8 or slab-bending related faults9, and are also present as part of the slab-wedge interface or mantle wedge that is percolated by aqueous fluids emanating from the slab during subduction10,11. Serpentinites are thus ubiquitous in subduction zones. Furthermore, several studies have suggested that the breakdown of these rocks is the most likely source of fluid-mobile elements (e.g. B), volatiles and halogens enriched in arc magmas (e.g. 12–17). The dehydration of serpentinized mantle results in a net decrease in bulk rock volatile concentrations6,16,17 and Fe$^{3+}/\sum$e18,19. In addition, observations of hematite-magnetite assemblages in dehydrated serpentinites10,21 suggest a high $f_{O2}$, from one to five log units above the Quartz-Fayalite-Magnetite (QFM) oxygen buffer, during antigorite breakdown in subduction zones which could be compatible with the release of oxidized S and C in slab-derived fluids. If correct, this model would have major implications for the cycling of volatiles between the Earth’s surface and interior, volcanic degassing (e.g. SOX, COX species emitted from volcanoes), and the occurrence of metal sulfide ore deposits22,23. Although several studies have indicated some evidence of variations of $f_{O2}$ in antigorite-bearing serpentinites that can be related to the extent of initial serpentinization24,25, there is at this time no consensus on the evolution of $f_{O2}$ or the redox state of serpentine-derived fluids during antigorite breakdown in subduction zones.

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Recent advances in theoretical and experimental aqueous geochemistry resulting in the Deep Earth Water (DEW) model now enable the calculation of equilibrium constants involving minerals and aqueous ions, metal complexes, and organics to 6.0 GPa and 1,200 °C. In the present study, we model the dehydration of antigorite-bearing serpentinite to investigate its potential to liberate highly oxidizing fluids in subduction zones. The model uses a conceptual scenario in which an initial fluid chemistry was set by reaction of water with an antigorite-bearing serpentinite at 630 °C before undergoing an increase of temperature to 660 °C at constant pressure. The initial model assemblage is composed of antigorite, olivine \(\text{XMg} = 0.885\), clinochlore, magnetite, and tremolite in agreement with field observations from Padron-Navarta et al. This assemblage sets the initial \(f_{\text{O}_2}\) which ranges from near QFM at 500 °C and 2.0 GPa to QFM +4.2 at 650 °C and 2.0 GPa (Supp. Fig. S1). At the lowest temperature in this range the \(f_{\text{O}_2}\) is in agreement with recent work on natural samples. However, at 630 °C the \(f_{\text{O}_2}\) is several units above QFM just before the breakdown of antigorite. In this study, we explore the further dramatic \(f_{\text{O}_2}\) changes on heating through the breakdown of antigorite.

Modelling serpentinite dehydration during subduction

Figure 1 displays the evolution of \(f_{\text{O}_2}\), mineral reactants, aqueous phase composition, and mineral products during antigorite breakdown at 2 GPa in a sulfur-free model. (a) Evolution of temperature and \(f_{\text{O}_2}\) in the system. QFM and magnetite-hematite buffers are reported in dashed lines. (b) Abundances of key minerals involved. Hematite appears at the beginning of the reaction and remains stable until the disappearance of antigorite and magnetite. (c) Concentrations of major species in the aqueous fluid. (d) Minerals produced during antigorite breakdown. The x axis represents the logarithm of the reaction progress variable \(\xi\), which is equal to the number of moles of each reactant mineral destroyed during the reaction progress.

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Figure 1 displays the evolution of \(f_{\text{O}_2}\), mineral assemblages, and fluid composition during antigorite breakdown at 2 GPa (modelling carried out at 4 GPa displays a similar evolution as presented in Supp. Info Fig. S2). In agreement with natural observations, the reaction progress leads to the successive growth of olivine, clinochlore, and orthopyroxene and the progressive decrease of the amount of magnetite. During the first part of the reaction path (log \(\xi\) < −4), the crystallization of olivine and chlorite is accompanied by a progressive increase of \(f_{\text{O}_2}\) up to four log units above QFM oxygen buffer (Fig. 1a). At these conditions, hematite becomes in equilibrium with magnetite and buffers the \(f_{\text{O}_2}\). The reaction progress is then accompanied with a progressive decrease of the amount of magnetite and the appearance of orthopyroxene (tremolite) in the rock (Fig. 1d). A second increase of \(f_{\text{O}_2}\) appears later (log \(\xi\) > −1.4) and corresponds to the disappearance of magnetite (Fig. 1a,b).

Few variations in pH and the composition of the released fluids (Fig. 1c) are observed during the reaction progress. The pH is alkaline and varies slightly around 5 (neutral pH is about 3.4 at these conditions; Supp. Info Fig. S3), while the aqueous species are dominated by \(\text{Na}^{+}\), \(\text{Cl}^{-}\), and \(\text{Si(OH)}_4\) with minor amounts of \(\text{NaHCO}_3\), \(\text{Al(OH)}_3\), \(\text{Ca(OH)}_2\), \(\text{Mg(OH)}_2\), and \(\text{FeCl}_2\). The presence of equilibrated hematite-magnetite assemblages in our models is compatible with recent observations in meta-peridotites from the Cerro Del Almirez massif or partly dehydrated serpentinites from Western Alps meta-ophiolites. It therefore suggests that the dehydration of serpentinites in subduction zones can take place at high \(f_{\text{O}_2}\), close to
the hematite-magnetite buffer. At such P-T-fO₂-pH conditions, volatile and redox-sensitive elements, such as sulfur or carbon, are expected to be mobilized under in their oxidized form (e.g. CO₃<sup>2-</sup> or SO₄<sup>2-</sup>) rather than reduced species (e.g. CH₄ or HS⁻). Fig. 1a).

### The importance of sulfides

Although the progressive increase in fO₂ during prograde metamorphism is suggestive of oxidized fluids release during antigorite breakdown, previous studies have shown that the presence of Ni-Fe alloys and/or sulfides can buffer the fO₂ down to four or five log units below the QFM buffer in serpentinites. In addition, several studies have shown that sulfides can persist or even be formed during serpentinite devolatilization. In order to test the impact of sulfur-bearing phases during the progressive devolatilization of serpentinites in subduction zones, we ran a suite of models containing various amounts of pyrrhotite (0.001, 0.01 and 0.1 moles), which is commonly observed in abyssal and orogenic serpentinites. The most pronounced difference between sulfide-free and sulfide-bearing models is the evolution of fO₂ during the reaction progress (Fig. 2a). The presence of a relatively small amount of pyrrhotite (0.001 to 0.01 moles of pyrrhotite) is accompanied with a decrease of fO₂ from three to two log units above QFM buffer (log fO₂ = −3 or −2, Fig. 2a). This stage is associated with the total destruction of the pyrrhotite and an increase of sulfur concentration in the serpentinite-derived fluids. Interestingly, even if hematite is absent from the system at this stage, sulfate-bearing species (HSO₄<sup>−</sup>, SO₄<sup>2-</sup>, CaSO₄<sub>(aq)</sub>, MgSO₄<sub>(aq)</sub>) are dominating the fluid composition relative to sulfide-bearing species (H₂S and HS⁻, Fig. 2b). This suggests that even at modestly oxidizing fO₂ values, sulfates are continuously released in serpentinite-derived fluids. As the reaction progresses (from log fO₂ < −3 to −1.4), the destruction of sulfide and then magnetite is accompanied by an increase of fO₂ and the appearance of hematite (Fig. 2b). In these conditions, sulfide species are at negligible concentrations in the fluid phase which is mainly composed of HSO₄<sup>−</sup>, SO₄<sup>2-</sup>, CaSO₄<sub>(aq)</sub> and MgSO₄<sub>(aq)</sub>. For high sulfide concentrations (0.1 mole of pyrrhotite), aqueous sulphide species remain at significant concentrations in the fluid during the whole reaction progress and become more abundant than sulphate species above log fO₂ < −1.5 (Fig. 2c). These species buffer the fO₂ at three units above QFM buffer but below the Hematite-Magnetite buffer, therefore preventing hematite crystallization (Fig. 2a). However, it should be noted that, even if the presence of these high amounts of pyrrhotite buffer the fO₂ at relatively low values, the amount of sulfur and sulfate dissolved in the fluid is significantly higher in those models (Fig. 2b and c).

### Evolution of oxygen fugacity and implications for the nature of slab derived fluids

Iron, carbon and sulfur are the main redox sensitive elements that can be transferred by fluids from the slab to the mantle wedge, having thus the potential to modify the redox state of the source region of arc magmas above subduction zones. In a previous Fe isotope study on subducted meta-ophiolites, it was shown that Fe can be mobile in slab-derived fluids in the form of Fe(II)-Cl, and/or Fe(II)-SO₄. In good agreement with these observations, thermodynamic calculations predict that during serpentinite dehydration, the magnetite modal amount significantly decreases (Fig. 1a,b) while the amount of Fe release in the fluid remains very low (Fig. 1c) and is dominated by the FeCl₂ species. We note that the complexation of Fe(II) to sulfate is not considered in the DEW model and even though Fe(III)-complexes are included, they are completely unimportant at the relatively high temperatures and low chloride concentrations of the present study. In other words, with our present state of knowledge of aqueous Fe-complexes, there are none known that could contribute significantly to the transport of Fe(III). It should also be noted that chlorine concentrations in fluid inclusions hosted by metamorphic olivines range up to 2 wt% NaCl. Such chlorine concentrations could potentially lead to a higher mobility of Fe(II) in subduction zones. Iron, carbon and sulfur are the main redox sensitive elements that can be transferred by fluids from the slab to the mantle wedge, having thus the potential to modify the redox state of the source region of arc magmas above subduction zones. In a previous Fe isotope study on subducted meta-ophiolites, it was shown that Fe can be mobile in slab-derived fluids in the form of Fe(II)-Cl, and/or Fe(II)-SO₄. In good agreement with these observations, thermodynamic calculations predict that during serpentinite dehydration, the magnetite modal amount significantly decreases (Fig. 1a,b) while the amount of Fe release in the fluid remains very low (Fig. 1c) and is dominated by the FeCl₂ species. We note that the complexation of Fe(II) to sulfate is not considered in the DEW model and even though Fe(III)-complexes are included, they are completely unimportant at the relatively high temperatures and low chloride concentrations of the present study. In other words, with our present state of knowledge of aqueous Fe-complexes, there are none known that could contribute significantly to the transport of Fe(III). It should also be noted that chlorine concentrations in fluid inclusions hosted by metamorphic olivines range up to 2 wt% NaCl. Such chlorine concentrations could potentially lead to a higher mobility of Fe(II) in subduction zones.
assemblages equilibrated at high $f_{O_2}$. As a consequence, the $f_{O_2}$ of the slab is likely to be heterogeneous, reflecting different pre-subduction mineralogy. However, in highly serpentinized peridotites, regardless of the considered models, sulfur seems to be highly mobile in fluids during antigorite breakdown (Fig. 2b,c). Interestingly, although sulfide can buffer the $f_{O_2}$ to relatively modest elevations above QFM, sulfate-bearing species ($\text{HSO}_4^{-}$, $\text{SO}_4^{2-}$, $\text{CaSO}_4^{(aq)}$, $\text{MgSO}_4^{(aq)}$) always represent a significant proportion of the sulfur-bearing phases carried by the fluid. The migration of these fluids from the slab to the slab-mantle interface or mantle wedge can therefore enhance the oxidation of the mantle wedge Fe$^{2+}$ to Fe$^{3+}$ in response to the reduction of slab fluid $\text{SO}_4^{2-}$ to $\text{S}^{2-}$. Such processes may provide an oxidized mantle source region for primary arc magmas. In this way, the origin of the oxidized signature carried by fluids from the slab may be an inevitable consequence of the breakdown of antigorite during subduction.

Figure 2. Predicted evolution of $f_{O_2}$ and aqueous phase composition in the presence of pyrrhotite during antigorite breakdown at 2 GPa. (a) Evolution of $f_{O_2}$ for different amounts of pyrrhotite (No pyrrhotite, 0.001, 0.01 and 0.1 moles). (b,c) Number of moles of sulfur dissolved into the fluid per kg of water with the evolution of major aqueous sulfur species. In b and c, the amount of sulfur present in the initial assemblage varies from 0.001 to 0.1 moles of pyrrhotite.
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**Acknowledgements**

This research was supported by grants from the Sloan Foundation through the Deep Carbon Observatory (Extreme Physics and Chemistry program), and a community-building Officer Grant from the Sloan Foundation, as well as support from NSF grants EAR-1624325 and ACI-1550346, and a grant from the W.M. Keck Foundation (The Co-Evolution of the Geo- and Biosphere) Grant #10583–02 to Sverjensky. BD acknowledges his F.R.S.-FN.R.S. research fellowship (Chargé de recherché) and support from an ERC starting grant ("HabitablePlanet", 306655) to H. Williams (University of Cambridge, UK). The beginning of this work was catalysed by discussions with Isabelle Daniel and Muriel Andreani (Laboratoire de Géologie de Lyon). The authors are grateful for the help and support of the Johns Hopkins University and the University of Cambridge. We also wish to acknowledge helpful discussions with Daniel Viete, Fang Huang, and Jingyi Huang (Johns Hopkins University), Alberto Vitale Brovarone (IMPMC Paris), Jose-Alberto Padrón-Navarta (Géosciences Montpellier) and Pierre Bouilhol (LMV, Clermont-Ferrand).

**Author Contributions**

B.D. and D.S. conceived the article, wrote the main manuscript and prepared the figures. D.S. performed the chemical modeling.

**Additional Information**

Supplementary information accompanies this paper at doi:10.1038/s41598-017-09626-y

**Competing Interests:** The authors declare that they have no competing interests.

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