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# Isotopic evidence for iron mobility during subduction

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## ABSTRACT

**Subduction zones are one of the most important sites of chemical interchange between the Earth's surface and interior. One means of explaining the high Fe<sup>3+</sup>/ΣFe ratios and oxidized nature of primary arc magmas is the transfer of sulfate (SO<sub>4</sub><sup>2-</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>), and/or iron (Fe<sup>3+</sup>) bearing fluids from the slab to the overlying mantle. Iron mobility and Fe stable isotope fractionation in fluids are influenced by Fe redox state and the presence of chlorine and/or sulfur anions. Here we use Fe stable isotopes (δ<sup>56</sup>Fe) as a tracer of iron mobility in serpentinites from Western Alps metaophiolites, which represent remnants of oceanic lithosphere that have undergone subduction-related metamorphism and devolatilization. A negative correlation (R<sup>2</sup> = 0.72) is observed between serpentinite bulk δ<sup>56</sup>Fe and Fe<sup>3+</sup>/ΣFe that provides the first direct evidence for the release of Fe-bearing fluids during serpentinite devolatilization in subduction zones. The progressive loss of isotopically light Fe from the slab with increasing degree of prograde metamorphism is consistent with the release of sulfate-rich and/or hypersaline fluids, which preferentially complex isotopically light Fe in the form of Fe(II)-SO<sub>x</sub> or Fe(II)-Cl<sub>2</sub> species. Fe isotopes can therefore be used as a tracer of the nature of slab-derived fluids.**

## INTRODUCTION

Magmas erupted at subduction zones display high ratios of oxidized to total iron (Fe<sup>3+</sup>/ΣFe) and are enriched in volatiles relative to other mantle-derived magmas (e.g., Kelley and Cottrell, 2009). It has therefore been suggested that the source region of arc magmas has been modified by oxidized and volatile-rich fluids released from the subducting slab. Possible oxidizing agents include sulfate- and/or carbonate-bearing fluids derived from subducted sediments or serpentinites (Kelley and Cottrell, 2009; Frezzotti et al., 2011; Evans, 2012; Debret et al., 2014a, 2015), as well as Fe<sup>3+</sup> transferred directly via supercritical fluids and brines (Mungall, 2002; Kelley and Cottrell, 2009), which have been shown to mobilize other trivalent, normally fluid-immobile elements (Kessel et al., 2005). Evidence in support of direct Fe<sup>3+</sup> and/or SO<sub>4</sub><sup>2-</sup> transfer includes positive correlations between Fe<sup>3+</sup>/ΣFe and trace element ratios indicative of slab-derived fluids (e.g., Ba/La) in arc magma melt inclusions (Kelley and Cottrell, 2009).

The devolatilization of serpentinite within the subducting slab and the fluids released play a fundamental role in mantle wedge redox evolution (Evans, 2012) and arc magma genesis (Spandler and Pirard, 2013). At mid-oceanic ridges or oceanic-continent transition zones, serpentinites are formed by the hydration and oxidation of the oceanic lithosphere, which leads to the replacement of olivine (Ol) and orthopyroxene by Fe<sup>3+</sup>-rich lizardite, which contains as much as 13% water, and magnetite, increasing bulk-rock Fe<sup>3+</sup>/ΣFe (e.g., Andreani et al., 2013; Klein et al., 2014). During subduction, the lizardite (Liz, low-temperature form of serpentine) to antigorite (Atg, high-temperature form of

serpentine) transition is accompanied by magnetite dissolution and a decrease in serpentinite mineral Fe<sup>3+</sup>/ΣFe (Schwartz et al., 2013; Debret et al., 2014a). At higher pressures and temperatures, antigorite breakdown to secondary olivine results in the loss of H<sub>2</sub>O (e.g., Ulmer and Trommsdorff, 1995) and the growth of other Fe<sup>2+</sup>-rich minerals (Debret et al., 2015). The major consequence of serpentinite prograde metamorphism during subduction is thus a net decrease in bulk-rock Fe<sup>3+</sup>/ΣFe. It is, however, unknown whether this reflects (1) the direct loss of Fe<sup>3+</sup> during prograde metamorphism and/or (2) the oxidation and loss of other redox-sensitive species (e.g., SO<sub>4</sub><sup>2-</sup>) to the mantle wedge.

To date there has been no direct means of tracing the loss of oxidizing components or Fe from the subducting slab and their transfer to the mantle wedge (Evans, 2012). New tools that can be used to trace and quantify the mobility of Fe during subduction-related devolatilization and metamorphism are thus required. Iron stable isotopes can serve as such a tracer, as significant isotopic variations can only be achieved by either the addition or loss of Fe-bearing components. Theory predicts that stable isotope variations will be driven by changes in oxidation state, coordination, and bonding environment (Polyakov and Mineev, 2000; Fujii et al., 2011), in particular for Fe the presence of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions (Hill et al., 2010). Here we explore the mobility of Fe during slab devolatilization with a Fe stable isotope study of subducted serpentinites from Western Alps metaophiolites. We show a striking negative correlation between the Fe isotope compositions (δ<sup>56</sup>Fe) of serpentinites and bulk-rock Fe<sup>3+</sup>/ΣFe, providing the first direct evidence for the open-system behavior of iron in serpentinites during subduction-related prograde metamorphism.

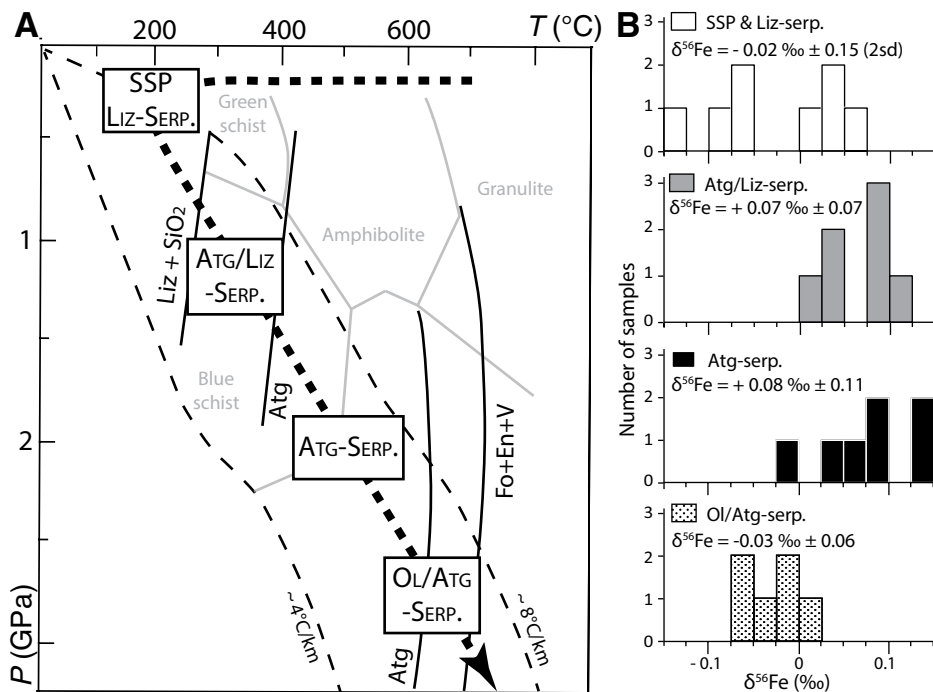
## SELECTED SAMPLES AND RESULTS

Alpine metaophiolites are interpreted as remnants of oceanic lithosphere formed and serpentinized in magma-poor settings before being metamorphosed and devolatilized at various pressure-temperature (*P-T*) conditions during subduction (Fig. 1A; e.g., Hattori and Guillot, 2007; Debret et al., 2013). We selected a set of 29 representative serpentinite samples encompassing the full range of prograde metamorphic grades for this study (Table DR1 and Fig. DR1 in the GSA Data Repository<sup>1</sup>). These samples have been characterized in previous petrological and geochemical studies (Schwartz et al., 2013; Debret et al., 2013; Lafay et al., 2013). They display the progressive replacement of lizardite by antigorite (Atg/Liz- to Atg-serpentinites; Fig. 1A), and the first stages of serpentinite dehydration at eclogite facies (Ol/Atg-serpentinites). The Atg-serpentinites are characterized by low amounts of magnetite relative to Atg/Liz-serpentinites (Debret et al., 2014a) and can display equilibrated hematite-magnetite assemblages (Fig. DR2). The Ol/Atg-serpentinites are generally present as metamorphic veins and shear zones composed of olivine and antigorite, and are interpreted as high-permeability reaction zones where the fluids released during serpentinite devolatilization have been localized (Debret et al., 2013). For reference we also analyzed a suite of Alpine slightly serpentinized peridotites (SSP), unmetamorphosed lizardite (Liz-) serpentinites, and abyssal serpentinites, which are considered to be representative of the presubduction lithospheric hydrated mantle. No retrograde phases (e.g., talc, chrysotile, amphibole) are observed in the studied sample suite, suggesting that the samples are poorly affected by retrograde metamorphism.

Bulk-rock Fe isotope (δ<sup>56</sup>Fe), Fe<sup>3+</sup>/ΣFe, and trace element concentration data for the studied serpentinites are reported in Tables DR1 and DR2. There is a progressive increase in serpentinite δ<sup>56</sup>Fe value with metamorphic grade (Fig. 1; Fig. DR3): the mean δ<sup>56</sup>Fe value of the Atg-serpentinites (+0.08‰ ± 0.11‰, 2 standard deviations, sd) and Atg/Liz-serpentinites (+0.07‰ ± 0.07‰) is greater than that of the Liz-serpentinites (δ<sup>56</sup>Fe = -0.02‰ ± 0.14‰), SSP (δ<sup>56</sup>Fe = -0.03‰ ± 0.15‰), and abyssal serpentinites (δ<sup>56</sup>Fe = -0.05‰ ± 0.07‰, this

<sup>1</sup>GSA Data Repository item 2016064, geological settings, methods, seven supplemental figures, and iron isotope and trace element data, is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.-

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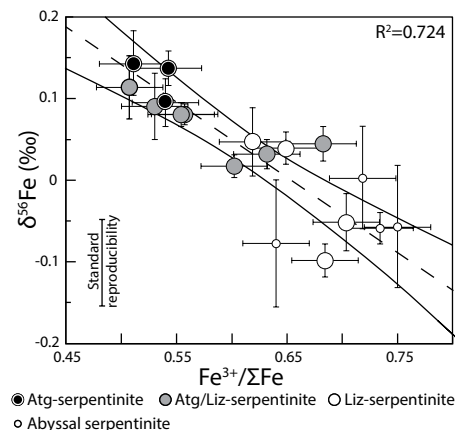
**Figure 1. Distribution of  $\delta^{56}\text{Fe}$  values in serpentinites during subduction. A: Schematic pressure-temperature ( $P$ - $T$ ) path of the Ligurian oceanic lithosphere showing the transitions from lizardite (Liz) to antigorite (Atg) and olivine (Ol) + antigorite assemblages. SSP—slightly serpentinized peridotite. The maximum temperatures recorded by eclogitic ophiolites are 580–620 °C (Schwartz et al., 2013), much lower than expected solidus for these rocks. Hot (~8 °C/km) and cold (~4 °C/km) geotherms are from Peacock and Wang (1999). Serp.—serpentine; Fo—forsterite; En—enstatite; V—vapor. B: Iron isotope compositions of bulk peridotites and serpentinites from Western Alps ophiolites (sd—standard deviation).**

study;  $\delta^{56}\text{Fe} = +0.01\text{‰} \pm 0.08\text{‰}$ , Craddock et al., 2013). Furthermore, Fe isotopes are negatively correlated with serpentinite  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (Fig. 2), suggesting that prograde metamorphism in serpentinite and the associated decrease in  $\text{Fe}^{3+}/\Sigma\text{Fe}$  is accompanied with the release of a low- $\delta^{56}\text{Fe}$  fluid. In contrast, the eclogite facies Ol/Atg-serpentinites are characterized by lower  $\delta^{56}\text{Fe}$  values ( $\delta^{56}\text{Fe} = -0.03\text{‰} \pm 0.06\text{‰}$ ).

## DISCUSSION

Although the progressive increase in  $\delta^{56}\text{Fe}$  during prograde metamorphism is suggestive of open-system behavior of iron during slab

devolatilization, several processes must be first taken into account. These are (1) the mobility of Fe and associated isotopic fractionation during the initial ocean-floor serpentinization of lithosphere, and (2) preexisting protolith Fe isotope heterogeneity. The Liz-serpentinites display a broad range in  $\delta^{56}\text{Fe}$  values, which range from  $-0.098\text{‰}$  to  $+0.047\text{‰}$  and are similar to those of SSP, which range from  $-0.069\text{‰}$  to  $+0.063\text{‰}$ . Both sets of values overlap with the  $\delta^{56}\text{Fe}$  values of abyssal serpentinites ( $-0.094\text{‰}$  to  $+0.108\text{‰}$ ; Craddock et al., 2013), and may be considered representative of presubduction oceanic lithosphere. It is important that, while

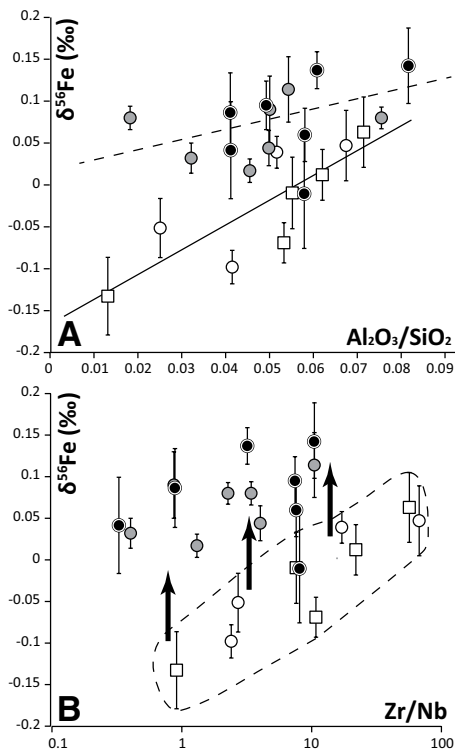


**Figure 2. Increase in  $\delta^{56}\text{Fe}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in serpentinites during subduction. Bulk sample iron isotope composition versus  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in subducted Alpine Liz-, Atg/Liz-, and Atg-serpentinites are compared to the one of abyssal serpentinites (small white circles). The error crosses are 2 standard deviations; the long-term reproducibility is shown for reference as an error bar in the lower left corner of this plot. The slope of the correlation is  $-0.92 \pm 0.28$  and the 95% confidence interval is represented by two lines (mean square of weighted deviates = 3.6).**

ridge-axis serpentinization processes are known to increase  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (Evans, 2008), the  $\delta^{56}\text{Fe}$  values of oxidized and hydrous Liz-serpentinites are similar to those of the comparatively reduced and anhydrous SSP and are uncorrelated with  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (Fig. DR4). This suggests that Fe behaves conservatively during ocean-floor serpentinization and that no appreciable Fe stable isotope fractionation takes place during this process. Previous studies have demonstrated that a relationship between bulk  $\delta^{56}\text{Fe}$  values and rock fertility exists, with pyroxene-rich and less depleted peridotites displaying isotopically heavier compositions (Williams et al., 2005). In Alpine ophiolites, serpentinite protolith fertility can be assessed using fluid-immobile elements poorly affected by serpentinization (e.g.,  $\text{Al}_2\text{O}_3/\text{SiO}_2$ , Zr/Nb; Bodinier and Godard, 2013). As illustrated in Figure 3, the  $\delta^{56}\text{Fe}$  values of Alpine Liz-serpentinites and SSP form broad positive arrays with  $\text{Al}_2\text{O}_3/\text{SiO}_2$  and Zr/Nb, which provide evidence for some level of source fertility control on protolith  $\delta^{56}\text{Fe}$ . Similar correlations between the  $\delta^{56}\text{Fe}$  values of Atg/Liz- or Atg-serpentinites and indices of peridotite fertility are present, but are demonstrably offset to overall heavier  $\delta^{56}\text{Fe}$  values (Fig. 3).

The comparatively heavy  $\delta^{56}\text{Fe}$  values of the Atg/Liz- and Atg-serpentinites relative to the SSP and Liz-serpentinites and the correlation between bulk serpentinite  $\delta^{56}\text{Fe}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  (Fig. 2) must therefore relate to the loss or addition of Fe-bearing fluids during prograde metamorphism. Sediment dehydration releases a significant amount of fluids and volatiles that can potentially interact with serpentinites and modify their isotopic signatures during subduction (Deschamps et al., 2010). However, no correlations between  $\delta^{56}\text{Fe}$  and elemental tracers of sediment-serpentinite interaction (e.g., As, Sb, Cs) are present (Fig. DR5), suggesting that interactions between sediment-derived melts or fluids and serpentinites cannot explain the heavy  $\delta^{56}\text{Fe}$  values of the Atg/Liz- and Atg-serpentinites. Furthermore, sediment melting requires an elevated subduction geotherm (e.g., Bouilhol et al., 2015), which is inconsistent with the inferred  $P$ - $T$  conditions of Alpine ophiolites (Fig. 1). The most straightforward means of interpreting the  $\delta^{56}\text{Fe}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  correlation is thus the release of isotopically light Fe-bearing fluid during prograde serpentinite devolatilization. In agreement with this interpretation, the Ol/Atg-serpentinites, which are interpreted as high-permeability reaction zones where fluids released during prograde metamorphism have been concentrated, display isotopically light  $\delta^{56}\text{Fe}$  values relative to the Atg-serpentinites (Fig. 1) and high concentrations of fluid-mobile elements (Debret et al., 2013).

Iron stable isotope fractionation is usually attributed to redox effects and experimental and theoretical studies that predict that, at



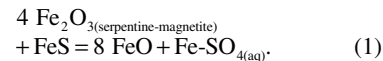
**Figure 3. Evolution of  $\delta^{56}\text{Fe}$  as a function of peridotite fertility. Iron isotope compositions of Alpine slightly serpentinized peridotite (SSP, white squares), Liz-serpentinites (white circles) and subducted Atg/Liz-serpentinites (pale gray circles), and Atg-serpentinites (gray circles). A: Plotted against  $\text{Al}_2\text{O}_3/\text{SiO}_2$ . B: Plotted against  $\text{Zr}/\text{Nb}$ . Subducted serpentinites are comparatively enriched in heavy iron relative to SSP and Liz-serpentinites (black arrows). Major and trace element data are from Debret et al. (2013), Lafay et al. (2013), and this study.**

equilibrium,  $\text{Fe}^{2+}$ -bearing phases should be isotopically lighter than  $\text{Fe}^{3+}$ -bearing phases (Polyakov and Mineev, 2000; Hill et al., 2010). This is in apparent contradiction with the inferred loss of a low- $\delta^{56}\text{Fe}$  fluid and the inverse correlation between bulk serpentinite  $\delta^{56}\text{Fe}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . One possible explanation is that the isotopically light composition of the fluids reflects kinetic (disequilibrium) isotope fractionation and the preferential mobility of the lighter isotope. In this case, the inverse correlation between  $\delta^{56}\text{Fe}$  and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  could reflect the direct loss of  $\text{Fe}^{3+}$  during serpentinite prograde metamorphism. However, the mobility of  $\text{Fe}^{3+}$  relative to  $\text{Fe}^{2+}$  in aqueous fluids and brines is known to be low (e.g., Ding and Seyfried, 1992) and unrealistic amounts of  $\text{Fe}^{3+}$  (~3 wt%  $\text{Fe}_2\text{O}_3$ ) would need to be lost to explain the observed decrease in  $\text{Fe}^{3+}/\Sigma\text{Fe}$  from 0.7 to 0.5 (Fig. DR6). An alternative explanation is that isotopically light Fe is lost in the form of  $\text{Fe}(\text{II})\text{-S}$  or  $\text{Fe}(\text{II})\text{-Cl}$  complexes, as theory predicts that these complexes should show a preference for isotopically light Fe (Hill et al., 2010). In agreement with

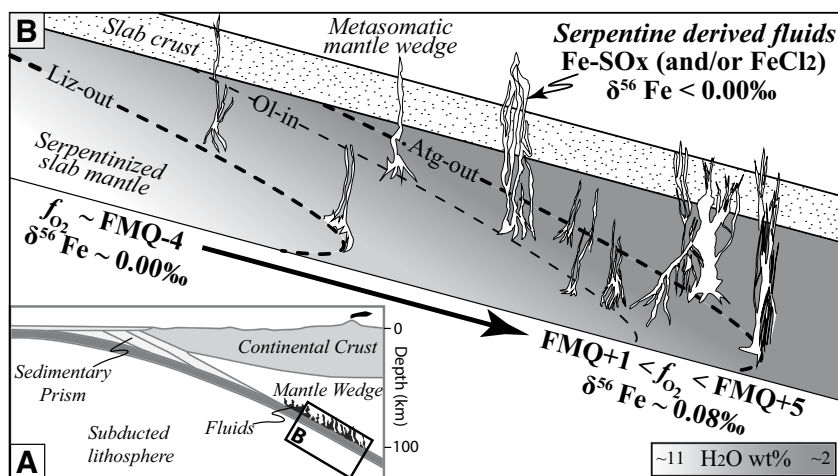
this scenario, subducted Alpine serpentinites have low S and Cl contents relative to abyssal serpentinites, providing evidence in support of the mobility of these elements in serpentinite-derived fluids (e.g., Alt et al., 2012; Debret et al., 2014b). This is confirmed by the presence of Cl- and S-rich polyphase fluid inclusions preserved within metamorphic olivine and garnet from Alpine metaophiolites (e.g., Scambelluri et al., 2015). The release of such fluids during serpentinite devolatilization can have a large impact on element mobility, since many nominally immobile elements are mobile in Cl-rich fluids (e.g., Rapp et al., 2010).

Perhaps most important, the proposed loss of isotopically light Fe associated with  $\text{SO}_x$  species during serpentinite devolatilization may also have a large effect on mantle wedge redox evolution (e.g., in the case of  $\text{SO}_4^{2-}$ , 1 mol of  $\text{S}^{6+}$  can oxidize 8 mol of  $\text{Fe}^{2+}$  as  $\text{SO}_4^{2-}$  is reduced to  $\text{S}^{2-}$  in the mantle wedge). The S budget of abyssal serpentinites is dominantly controlled by sulfides (e.g., Alt and Shanks, 2003). The decrease in serpentinite S concentration with prograde metamorphism therefore suggests that serpentinite dehydration is associated with sulfide breakdown and the release of sulfur (Hattori and Guillot, 2007). The presence of equilibrated hematite-magnetite assemblages (Fig. DR2) in the most depleted, low  $\text{Fe}^{3+}/\Sigma\text{Fe}$  and heavy  $\delta^{56}\text{Fe}$  serpentinites shows that S transport in serpentinite-derived fluids must have taken place at high oxygen fugacity ( $f_{\text{O}_2}$ ), close to the hematite-magnetite buffer (Debret et al., 2015; Tumiati et al., 2015). At such  $P$ - $T$ - $f_{\text{O}_2}$  conditions, sulfur will be mobilized as  $\text{SO}_4^{2-}(\text{aq})$  (aq—aqueous) rather than reduced species such as  $\text{HS}^-(\text{aq})$  (Fig. DR7). This is consistent with recent observations of  $\text{SO}_4^{2-}$  in

diamond-bearing fluid inclusions from Western Alps metaophiolites (Frezza et al., 2011). In this scenario, the oxidation of slab sulfides ( $\text{FeS}$  in Equation 1 for simplicity) to sulfates can also explain the concurrent decrease in serpentinite bulk  $\text{Fe}^{3+}/\Sigma\text{Fe}$ , e.g.,



Given that typical ocean-floor serpentinites and eclogite facies Atg serpentinites have  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of ~0.7 and ~0.5, respectively, and both contain ~8 wt% of  $\text{Fe}_2\text{O}_3(\text{total})$  (Fig. DR6), Equation 1 predicts that as much as ~800 ppm sulfur and a minor quantity of Fe (~0.1 wt%) will be released in serpentinite-derived fluids. This value, although speculative, is broadly consistent with the observed decrease in sulfur content (Hattori and Guillot, 2007; Alt et al., 2012; Debret et al., 2014b) and the relatively constant  $\text{Fe}_2\text{O}_3(\text{total})$  (Fig. DR6) of serpentinites during subduction. This is, however, a minimum estimate. For example, if S was originally present as  $\text{S}^-$  and released as  $\text{SO}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , or  $\text{SO}_3^{2-}$ , then the amount of S released would be significantly larger for the same amount of Fe loss. Our results therefore suggest that slab serpentinite devolatilization is associated with Fe reduction and the oxidation and mobilization of sulfides, and potentially other reduced species. The migration of these fluids from the slab to the slab-mantle interface or mantle wedge and the reduction of slab fluid  $\text{SO}_x$  to  $(\text{Fe})\text{S}^{2-}$  and concomitant oxidation of mantle wedge  $\text{Fe}(\text{II})$  to  $\text{Fe}(\text{III})$  may therefore provide an oxidized mantle source region for primary arc magmas (e.g., Kelley and Cottrell, 2009; Fig. 4).



**Figure 4. Schematic diagrams (not to scale) illustrating the redox and isotopic evolution of slab serpentinites and released fluids during subduction. A: Subduction zone. B: Subducting lithosphere. Prograde metamorphism enhanced the formation of antigorite (Atg) and then olivine (Ol). Liz—lizardite. These metamorphic reactions occur at high oxygen fugacity ( $f_{\text{O}_2}$ ) and result in the release of isotopically light Fe from the serpentinites in the form of  $\text{Fe}(\text{II})\text{-SO}_x$  and/or  $\text{Fe}(\text{II})\text{-Cl}$  complexes, with the Fe isotopically heavy residue returning to the deep mantle. FMQ—fayalite-magnetite-quartz. \*See Evans, 2008, and references therein.**

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## REFERENCES CITED

- Alt, J.C., and Shanks, W.C., III, 2003, Serpentinization of abyssal peridotites from the MARK area, Mid-Atlantic Ridge: Sulfur geochemistry and reaction modeling: *Geochimica et Cosmochimica Acta*, v. 67, p. 641–653, doi:10.1016/S0016-7037(02)01142-0.
- Alt, J.C., Garrido, C.J., Shanks, W.C., III, Turchyn, A., Padrón-Navarta, J.A., López-Sánchez-Vizcaíno, V., Gómez-Pugnaire, M.T., and Marchesi, C., 2012, Recycling of water, carbon, and sulfur during subduction of serpentinites: A stable isotope study of Cerro del Almirez, Spain: *Earth and Planetary Science Letters*, v. 327–328, p. 50–60, doi:10.1016/j.epsl.2012.01.029.
- Andreani, M., Muñoz, M., Marcaillou, C., and Delacour, A., 2013,  $\mu$ XANES study of iron redox state in serpentine during oceanic serpentinization: *Lithos*, v. 178, p. 70–83, doi:10.1016/j.lithos.2013.04.008.
- Bodinier, J.L., and Godard, M., 2013, Orogenic, ophiolitic, and abyssal peridotites, in Carlson, R.W., ed., *Treatise on geochemistry: Volume 2. The mantle and core* (second edition): The Netherlands, Elsevier, p. 103–151, doi:10.1016/B978-0-08-095975-7.00204-7.
- Bouilhol, P., Magni, V., van Hunen, J., and Kaislaniemi, L., 2015, A numerical approach to melting in warm subduction zones: *Earth and Planetary Science Letters*, v. 411, p. 37–44, doi:10.1016/j.epsl.2014.11.043.
- Craddock, P., Warren, J.M., and Dauphas, N., 2013, Abyssal peridotites reveal the near-chondritic Fe isotopic composition of the Earth: *Earth and Planetary Science Letters*, v. 365, p. 63–76, doi:10.1016/j.epsl.2013.01.011.
- Debret, B., Andreani, M., Godard, M., Nicollet, C., Schwartz, S., and Lafay, R., 2013, Trace element behavior during serpentinization/deserpentinization of an eclogitized oceanic lithosphere: A LA-ICPMS study of the Lanzo ultramafic massif (Western Alps): *Chemical Geology*, v. 357, p. 117–133, doi:10.1016/j.chemgeo.2013.08.025.
- Debret, B., Andreani, M., Muñoz, M., Bolfan-Casanova, N., Carlot, J., Nicollet, C., Schwartz, S., and Trcera, N., 2014a, Evolution of Fe redox state in serpentine during subduction: *Earth and Planetary Science Letters*, v. 400, p. 206–218, doi:10.1016/j.epsl.2014.05.038.
- Debret, B., Koga, K., Nicollet, C., Andreani, M., and Schwartz, S., 2014b, F, Cl and S input via serpentinization in subduction zones: Implications for the nature of the fluid released at depth: *Terra Nova*, v. 26, p. 96–101, doi:10.1111/ter.12074.
- Debret, B., Bolfan-Casanova, N., Padrón-Navarta, J.A., Martín-Hernández, F., Andreani, M., Garrido, C., López Sánchez-Vizcaíno, V., Gómez-Pugnaire, M.T., Muñoz, M., and Trcera, N., 2015, Redox state of iron during high-pressure serpentinization dehydration: Contributions to Mineralogy and Petrology, v. 169, 36, 18 p., doi:10.1007/s00410-015-1130-y.
- Deschamps, F., Guillot, S., Godard, M., Chauvel, C., Andreani, M., and Hattori, K., 2010, In situ characterization of serpentinites from forearc mantle wedges: Timing of serpentinization and behavior of fluid-mobile elements in subduction zones: *Chemical Geology*, v. 269, p. 262–277, doi:10.1016/j.chemgeo.2009.10.002.
- Ding, K., and Seyfried, W.E., 1992, Determination of Fe-Cl complexing in the low pressure supercritical region (NaCl fluid): Iron solubility constrains on pH of seafloor hydrothermal fluids: *Geochimica et Cosmochimica Acta*, v. 56, p. 3681–3692, doi:10.1016/0016-7037(92)90161-B.
- Evans, B., 2008, Control of the products of serpentinization by the  $\text{Fe}^{2+}/\text{Mg}$ , exchange potential of olivine and orthopyroxene: *Journal of Petrology*, v. 49, p. 1873–1887, doi:10.1093/ptrology/egn050.
- Evans, K.A., 2012, The redox budget of subduction zones: *Earth-Science Reviews*, v. 113, p. 11–32, doi:10.1016/j.earscirev.2012.03.003.
- Frezzotti, M.L., Selverstone, J., Sharp, Z.D., and Compagnoni, R., 2011, Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps: *Nature Geoscience*, v. 4, p. 703–706, doi:10.1038/ngeo1246.
- Fujii, T., Moynier, F., Pons, M.L., and Albarède, F., 2011, The origin of Zn isotope fractionation in sulfides: *Geochimica et Cosmochimica Acta*, v. 75, p. 7632–7643, doi:10.1016/j.gca.2011.09.036.
- Hattori, K., and Guillot, S., 2007, Geochemical character of serpentinites associated with high- to ultrahigh-pressure metamorphic rocks in the Alps, Cuba, and the Himalayas: Recycling of elements in subduction zones: *Geochemistry, Geophysics, Geosystems*, v. 8, Q09010, doi:10.1029/2007GC001594.
- Hill, P.S., Schauble, E.A., and Young, E.D., 2010, Effects of changing solution chemistry on  $\text{Fe}^{3+}/\text{Fe}^{2+}$  isotope fractionation in aqueous Fe-Cl solutions: *Geochimica et Cosmochimica Acta*, v. 74, p. 6669–6689, doi:10.1016/j.gca.2010.08.038.
- Kelley, K., and Cottrell, E., 2009, Water and the oxidation state of subduction zone magmas: *Science*, v. 325, p. 605–607, doi:10.1126/science.1174156.
- Kessel, R., Schmidt, M., Ulmer, P., and Pettke, T., 2005, Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth: *Nature*, v. 437, p. 724–727, doi:10.1038/nature03971.
- Klein, F., Bach, W., Humphris, S.E., Kahl, W.-A., Jons, N., Moskowitz, B., and Berquó, T.S., 2014, Magnetite in seafloor serpentinite—Some like it hot: *Geology*, v. 42, p. 135–138, doi:10.1130/G35068.1.
- Lafay, R., Deschamps, F., Schwartz, S., Guillot, S., Godard, M., Debret, B., and Nicollet, C., 2013, High-pressure serpentinites, a trap-and-release system controlled by metamorphic conditions: Example from the Piedmont zone of the western Alps: *Chemical Geology*, v. 343, p. 38–54, doi:10.1016/j.chemgeo.2013.02.008.
- Mungall, J.E., 2002, Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits: *Geology*, v. 30, p. 915–918, doi:10.1130/0091-7613(2002)030<0915:RTMSMA>2.0.CO;2.
- Peacock, S.M., and Wang, K., 1999, Seismic consequences of warm versus cool subduction zone metamorphism: Examples from northeast and southwest Japan: *Science*, v. 286, p. 937–939, doi:10.1126/science.286.5441.937.
- Polyakov, V.B., and Mineev, S.D., 2000, The use of Mössbauer spectroscopy in stable isotope geochemistry: *Geochimica et Cosmochimica Acta*, v. 64, p. 849–865, doi:10.1016/S0016-7037(99)00329-4.
- Rapp, J.F., Klemme, S., Butler, I.B., and Harley, S.L., 2010, Extremely high solubility of rutile in chloride and fluoride-bearing metamorphic fluids: An experimental investigation: *Geology*, v. 38, p. 323–326, doi:10.1130/G30753.1.
- Scambelluri, M., Pettke, T., and Cannao, E., 2015, Fluid-related inclusions in Alpine high-pressure peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps): *Earth and Planetary Science Letters*, v. 429, p. 45–59, doi:10.1016/j.epsl.2015.07.060.
- Schwartz, S., Guillot, S., Reynard, B., Lafay, R., Debret, B., Nicollet, C., Lanari, P., and Auzende, A.L., 2013, Pressure-temperature estimates of the lizardite/antigorite transition in high pressure serpentinites: *Lithos*, v. 178, p. 197–210, doi:10.1016/j.lithos.2012.11.023.
- Spandler, C., and Pirard, C., 2013, Element recycling from subducting slabs to arc crust: A review: *Lithos*, v. 170–171, p. 208–223, doi:10.1016/j.lithos.2013.02.016.
- Tumati, S., Godard, G., Martin, S., Malaspina, N., and Poli, S., 2015, Ultra-oxidized rocks in subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a Mn-rich metasomatic environment: *Lithos*, v. 226, p. 116–130, doi:10.1016/j.lithos.2014.12.008.
- Ulmer, P., and Trommsdorff, V., 1995, Serpentine stability to mantle depths and subduction-related magmatism: *Science*, v. 268, p. 858–861, doi:10.1126/science.268.5212.858.
- Williams, H.M., Peslier, A.H., McCammon, C., Halliday, A.N., Levasseur, S., Teutsch, N., and Burg, J.P., 2005, Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity: *Earth and Planetary Science Letters*, v. 235, p. 435–452, doi:10.1016/j.epsl.2005.04.020.

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