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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 Fe3+/ΣFe ratios and oxidized nature of primary arc magmas is the transfer of sulfate (SO4), carbonate (CO3), and/or iron (Fe3+) 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 (δ56Fe) 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 (r2 = 0.72) is observed between serpentinite bulk δ56Fe and Fe3+/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)-SOX or Fe(II)-Cl species. Fe isotopes can therefore be used as a tracer of the nature of slab-derived fluids.

INTRODUCTION

Mmagmas erupted at subduction zones display high ratios of oxidized to total iron (Fe3+/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 Fe3+ 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 Fe3+ and/or SO42- transfer includes positive correlations between Fe3+/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 (OI) and orthopyroxene by Fe-rich lizardite, which contains as much as 13% water, and magnetite, increasing bulk-rock Fe3+/ΣFe (e.g., Andreani et al., 2013; Klein et al., 2014). During subduction, the lizardite (Liz, low-temperature form of serpentine) transition is accompanied by magnetite precipitation and a decrease in serpentine mineral Fe3+/ΣFe (Schwartz et al., 2013; Debret et al., 2014a). At higher pressures and temperatures, antigorite breakdown to secondary olivine results in the loss of H2O (e.g., Ulmer and Trömsdorff, 1995) and the growth of other Fe2+-rich minerals (Debret et al., 2015). The major consequence of serpentinite prograde metamorphism during subduction is thus a net decrease in bulk-rock Fe3+/ΣFe. It is, however, unknown whether this reflects (1) the direct loss of Fe3+ during prograde metamorphism and/or (2) the oxidation and loss of other redox-sensitive species (e.g., SO42-) 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 track 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 and SO42- (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 (δ56Fe) of serpentinites and bulk-rock Fe3+/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 serpentinitized 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 Repository1). 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 (OIl/AIg-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 OIl/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 serpentinitized 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 (δ56Fe), Fe3+/ΣFe, and trace element concentration data for the studied serpentinites are reported in Tables DR1 and DR2. There is a progressive increase in serpentinite δ56Fe value with metamorphic grade (Fig. 1; Fig. DR3): the mean δ56Fe 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 (δ56Fe = −0.02‰ ± 0.14‰), SSP (δ56Fe = −0.03‰ ± 0.15‰), and abyssal serpentinites (δ56Fe = −0.05‰ ± 0.07‰), this

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1GSA 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, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
Atg/Liz-serpentinite
Liz-serpentinite

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of open-system behavior of iron during slab

Figure 1. Distribution of δ56Fe 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.—serpentinite.

Figure 2. Increase in δ56Fe and Fe3+/ΣFe ratio in serpentinites during subduction. Bulk sample iron isotope composition versus Fe3+/ΣFe 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).

Atg/Liz-serpentinite
Atg-serpentinite
Liz-serpentinite
Abyssal serpentinite


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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 metamorphic assemblages (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 SO_x species during serpentinite devolatilization may also have a large effect on mantle wedge redox evolution (e.g., in the case of SO_2, 1 mol of S^{2-} can oxidize 8 mol of Fe^{2+} as SOX is reduced to S^{2-} in the mantle wedge). The S budget of abyssal serpentinites is dominated by sulfides (e.g., Alt and Shanks, 2003). The decrease in serpentinite S concentration 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 Fe^3+/ΣFe and heavy δ^{56}Fe serpentinites shows that S transport in serpentinite-derived fluids must have taken place at high oxygen fugacity (f_{O2}), close to the hematite-magnetite buffer (Debret et al., 2015; Tumiati et al., 2015). At such P-T-f_{O2} conditions, sulfur will be mobilized as SO_x^{2-} (aq) rather than reduced species such as HS^- (aq) (Fig. DR7). This is consistent with recent observations of SO_2– in diamond-bearing fluid inclusions from Western Alps metaophiolites (Frezzotti et al., 2011). In this scenario, the oxidation of slab sulfides (FeS in Equation 1 for simplicity) to sulfates can also explain the concurrent decrease in serpentinite bulk Fe^{3+}/ΣFe, e.g.,

\[ 4 \text{Fe}_2\text{O}_3_{(serpentinite-mag)} + \text{FeS} = 8 \text{FeO} + \text{Fe}_2\text{SO}_4_{(aq)} \]  

Given that typical ocean-floor serpentinites and eclogite facies Atg serpentinites have Fe^{3+}/ΣFe ratios of ~0.7 and ~0.5, respectively, and both contain ~8 wt% of Fe_2O_3_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 Fe_2O_3_total (Fig. DR6) of serpentinites during subduction. This is, however, a minimum estimate. For example, if S was originally present as S_2O_3^2– and Fe^3+ and SO_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 mantle-mantle interface or mantle wedge and the reduction of slab fluid SO_x (and Fe^3+/SO_x) and concomitant oxidation of mantle wedge Fe(II) to Fe(III) may therefore provide an oxidized mantle source region for primary arc magmas (e.g., Kelley and Cottrell, 2009; Fig. 4).

![Figure 3. Evolution of δ^{56}Fe as a function of peridotite fertility. Iron isotope compositions of Alpine slightly serpentinized peridotite (SS, white squares), Liz-serpentinites (white circles) and subducted Atg/Liz-serpentinites (gray circles), and Atg-serpentinites (black arrows). Major and trace element data are from Debret et al. (2013), Lafay et al. (2013), and this study.](image)

![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_{O2}) and result in the release of isotopically light Fe from the serpentinites in the form of Fe(II)-SO_x and/or Fe(II)-Cl complexes, with the Fe isotopically heavy residue returning to the deep mantle. FMQ—fayalite-magnetite-quartz. *See Evans, 2008, and references therein.](image)
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