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)-SO₄ or Fe(II)-Cl 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 (Fe³⁺/ΣFe) and are enriched in volatile relative to other mantle-derived magmas (e.g., Kelley and Cotrell, 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 Cotrell, 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 Cotrell, 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 SO₄⁻⁻ transfer includes positive correlations between Fe³⁺/ΣFe and trace element ratios indicative of slab-derived fluids (e.g., Ba/La) in arc magmas (Kelley and Cotrell, 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 Fe³⁺-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 dissolution 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 Trommsdorff, 1995) and the growth of other Fe³⁺-rich minerals (Debret et al., 2015). The major consequence of serpentine 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., SO₄⁻⁻) 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⁻ and SO₄⁻⁻ 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 (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 (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 serpentinitized peridotites (SSP), un metamorphosed 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, 2σ) 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

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 on 07 February 2019 by guest

The open-system behavior of iron during slab subduction is characterized by lower Fe values (serpentinites are accompanied with the release of a low-temperature (~8 °C/km) and cold (~4 °C/km) geotherms are from Peacock and Wang (1999). Serp.—serpentinite; Fo—forsterite; En—enstatite; V—vapor. B: Iron isotope compositions of bulk peridotites and serpentinites from Western Alps ophiolites (sd—standard deviation).

Although the progressive increase in δ56Fe 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 serpentinitization of lithosphere, and (2) preexisting protolith Fe isotope heterogeneity. The Liz-serpentinites display a broad range in δ56Fe values, which range from +0.09% to +0.047% and are similar to those of SSP, which range from +0.069% to +0.063%. Both sets of values overlap with the δ56Fe values of abyssal serpentinites (+0.094% to +0.108%; Craddock et al., 2013), and may be considered representative of presubduction oceanic lithosphere. It is important that, while ridge-axis serpentinitization processes are known to increase Fe56/ΣFe (Evans, 2008), the δ56Fe values of oxidized and hydrous Liz-serpentinites are similar to those of the comparatively reduced and anhydrous SSP and are unrelated with Fe56/ΣFe (Evans, 2008). This suggests that Fe behaves conservatively during ocean-floor serpentinitization and that no appreciable Fe stable isotope fractionation takes place during this process. Previous studies have demonstrated that a relationship between bulk δ56Fe 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 serpentinitization (e.g., Al2O3/SiO2, Zr/Nb; Bodinier and Godard, 2013). As illustrated in Figure 3, the δ56Fe values of Alpine Liz-serpentinites and SSP form broad positive arrays with Al2O3/SiO2 and Zr/Nb, which provide evidence for some level of source fertility control on protolith δ56Fe. Similar correlations between the δ56Fe values of Atg/Liz- or Atg-serpentinites and indices of protolitic fertility are present, but are demonstrably offset to overall heavier δ56Fe values (Fig. 3).

The comparatively heavy δ56Fe values of the Atg/Liz- and Atg-serpentinites relative to the SSP and Liz-serpentinites and the correlation between bulk serpentinite δ56Fe and Fe56/ΣFe (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 δ56Fe 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 δ56Fe values of the Atg/Liz- and Atg-serpentinites. Furthermore, sediment melting requires an elevated subduction geotherm (e.g., Boulhol et al., 2015), which is inconsistent with the inferred P-T conditions of Alpine ophiolites (Fig. 1). The most straightforward means of interpreting the δ56Fe and Fe56/ΣFe correlation is thus the release of isotopically light Fe-bearing fluid during prograde serpentinite devolatilization. In agreement with this interpretation, the Oi/Atg-serpentinites, which are interpreted as high-permeability reaction zones where fluids released during prograde metamorphism have been concentrated, display isotopically light δ56Fe 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 Alpin slightly serpentinitized peridotite (SSP, white squares) and subducted Atg/Liz-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 $\text{Zr}$ and $\text{Nb}$ with the Fe isotopically heavy residue returning to the deep mantle. FMQ—fayalite-magnetite-quartz. *See Evans, 2008, and references therein.

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 $\text{Fe(II)}\text{SO}_x$ and/or $\text{Fe(II)}\text{Cl}_x$ complexes, with the Fe isotopically heavy residue returning to the deep mantle. FMQ—fayalite-magnetite-quartz. *See Evans, 2008, and references therein.
ACKNOWLEDGMENTS

We thank G. Nowell (Durham University, UK) for technical support; L. Cottrell, S. Guillot, S. Klimm, and N. Malaspinia for constructive reviews; and J. Brendan Murphy for his careful editorial handling. This work was supported by a Natural Environment Research Council (NERC) Deep Volatiles Consortium Grant (NE/A000101/15) and an European Research Council (ERC) Starting Grant (HabitablePlanet; 306655) to Williams. Williams also acknowledges NERC Advanced Fellowship NE/F014295/1. Bouilhol acknowledges support from an ERC Starting Grant (MASE; 279828).

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Manuscript received 25 November 2015
Manuscript revised 20 January 2016
Manuscript accepted 20 January 2016
Printed in USA