Contents lists available at ScienceDirect

Earth and Planetary Science Letters

Controls on the iron isotopic composition of global arc magmas

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ARTICLE INFO

ABSTRACT

We determined the iron isotope composition of 130 mafic lavas from 15 arcs worldwide with the hypothesis that the results would reflect the relatively high oxidation state of arc magmas. Although this expectation was not realized, this Fe isotope data set reveals important insights into the geodynamic controls and style of the melting regimes in the sub-arc mantle. Samples are from oceanic arcs from the circum-Pacific, the Indonesian Sunda–Banda islands, Scotia and the Lesser Antilles as well as from the eastern Pacific Cascades. Their mean δ^{57}Fe value is $+0.075 \pm 0.05$‰, significantly lighter than MORB ($+0.15 \pm 0.03$‰). Western Pacific arcs extend to very light δ^{57}Fe (Kamchatka $= -0.11 \pm 0.04$‰). This is contrary to expectation, because Fe isotope fractionation factors (Sossi et al., 2016, 2012) and the incompatibility of ferric versus ferrous iron during mantle melting, predict that melts of more oxidized sources will be enriched in heavy Fe isotopes. Subducted oxidation capacity flux may correlate with hydrous fluid release from the slab. If so, a positive correlation between each arc's thermal parameter (ϕ) and δ^{57}Fe is predicted. On the contrary, the sampled arcs mostly contribute to a negative array with the ϕ value. High ϕ arcs, largely in the western Pacific, have primary magmas with lower δ^{57}Fe values than the low ϕ, eastern Pacific arcs.

Arcs with MORB-like Sr-, Nd- and Pb-isotopes, show a large range of δ^{57}Fe from heavy MORB-like values (Scotia or the Cascades) to very light values (Kamchatka, Tonga). Although all basalts with light δ^{57}Fe values have MORB-like Pb-, Nd- and Sr-isotope ratios some, particularly those from eastern Indonesia, have heavier δ^{57}Fe and higher Pb- and Sr- and lower Nd-isotope ratios reflecting sediment contamination of the mantle wedge. Because basalts with MORB-like radiogenic isotopes range all the way from heavy to light δ^{57}Fe values this trend is *process*-, not *source composition*-driven. Neither the slab-derived influx of fluids with light iron or sediment-derived melts with heavier iron can drive the iron isotopic shifts. The trend to light iron isotopes is partly the result of repeated, hydrous flux-driven, fO_2-buffered, melting of initially normal-DMM-like mantle. However the most negative δ^{57}Fe must also reflect re-melting of sources that have experienced prior diffusive (disequilibrium) stripping of heavy Fe isotopes due to rapid melt extraction and metasomatism.

Data from intra-arc to back-arc rifts in the western Pacific show that these arc signatures are rapidly dispersed by influx of DMM or OIB mantle once intra- and back-arc rifting and slab rollback gains momentum. We suggest that the characteristic light arc signatures only form when the source is lodged under arcs where sub-arc mantle undergoes corner flow forming an isolated roll. This process of heavy iron depletion is most efficient in the high ϕ arcs of the western Pacific and least prevalent in the low ϕ arcs of the eastern Pacific where δ^{57}Fe values are MORB-like. This implies that there is a fundamental change in character of sub-arc mantle melting between east and west Pacific, percolative and fluid fluxed in the west and diapiric and decompressional in the east.

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1. Introduction

It is well established that basalts and andesites and their intrusive equivalents emplaced in volcanic arcs at subduction zones are significantly more oxidized than mantle-derived magmas from other settings (Plank et al., 2010). The oxygen fugacity of a magma is quantified by the log unit deviation with respect to a mineral oxygen buffer, such as Quartz–Fayalite–Magnetite, expressed as $\Delta \log$ QFM. The general consensus is that MORB are typically at $\Delta \log$ QFM 0 ± 0.5 (Cottrell and Kelley, 2011), whereas arc basalts and andesites are at $\Delta \log$ QFM $+2.5 \pm 1$ (Evans et al., 2012;

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Kelley and Cottrell, 2009, 2012). The few examples of mantle-derived peridotite from beneath arcs (probably from the upper-plate sub-arc lithospheric mantle) are also relatively oxidized, between $\Delta \log$QFM +0.5 to +2 (Parkinson and Arculus, 1999). This evidence notwithstanding, the origin of the more oxidized state of arc basalts remains controversial. Does it originate from relatively oxidized primary peridotite sources in the mantle wedge (Evans and Tomkins, 2011) or is the mantle wedge no more oxidized than the source of MORB and the oxidized state of arc magmas just a result of processes acting during the ascent of these volatile-rich magmas towards to the surface (e.g. Lee et al., 2005, 2010; Humphreys et al., 2015)?

Delivering about 25% of the total annual global mantle-derived magma flux (Spandler and Pirard, 2013; Scholl and von Huene, 2009), subduction zones are one of the key sites of terrestrial magma generation and continental crustal growth. The subducted oceanic lithosphere is hydrated at several sites including both at the MOR and also during flexure as it descends into the trench (Faccenda et al., 2009). Subduction of the oceanic lithosphere introduces a range of contaminants first to the lithosphere of the hanging wall upper plate and, at increasing depth, to the convective asthenospheric mantle wedge. These subduction components (e.g. Debret et al., 2016; Scott et al., 2017) migrate up from their sources in the downgoing slab and invade the overlying mantle. Where the slab is at subsolidus temperatures, this discharge is dominated by hydrous fluid with a range of dissolved components, possibly including dissolved Fe (Debret et al., 2016), whereas under conditions where the slab surface temperature exceeds 750 °C the escaping fluid will be a partial melt of the sediment veneer (Spandler et al., 2007; Hermann and Spandler, 2008; Schmidt, 2015) or even of the altered mafic oceanic crust (Freymuth et al., 2016).

The addition of the subduction component to mantle wedge peridotite produces the characteristic lithophile element patterns and strongly contributes to the isotopic compositions of subduction-related basalts (McDermott and Hawkesworth, 1991; Turner and Foden, 2001). Although the mantle wedge is commonly assumed to have a depleted-MORB mantle (DMM) composition, there is good evidence it is often more depleted (Woodhead et al., 1993). However the question remains: if and how much this slab-derived component influences the oxidation state of the wedge (Kelley and Cottrell, 2012, 2009; Evan and Tomkins, 2011; Lee et al., 2010, 2005).

Olivine-hosted basaltic melt inclusions from a range of tectonic settings have water contents that progressively increase from mid ocean ridges (MOR) and back arc basins (BAB) to arcs, and this is positively correlated with directly-measured Fe redox state (Kelley and Cottrell, 2009). This is not taken to imply that water is the direct source of oxidation, but that the transport of water to arc sources also transports oxidizing agents, most probably S^{6+}. Evans and Tomkins (2011) and Evans et al. (2012) made a quantitative assessment of the time-dependent delivery of oxidative capacity (redox-budget) to the supra-slab mantle wedge. Given plausible assumptions applicable to Phanerozoic subduction, they concluded that subduction should raise the oxygen fugacity of parts of the mantle wedge by 2 to 3 log units (to $\Delta \log$QFM +2 to +3.5) once subduction was established for 10^4 to 10^6 yr. This was complemented by further work (Evans et al., 2012) that related the transport of redox-budget at a range of specific arcs to their individual physical parameters. These parameters included duration of subduction and velocity of convergence, and a positive correlation was found with each, reflecting the de-stabilisation of sulfate to greater depths, and therefore its increased ability to oxidise the mantle wedge (Newton and Manning, 2005). The ϕ factor (Kirby et al., 1996) also referred to as the thermal parameter (Syracuse et al., 2010; van Keken et al., 2011) is the product of the age of the sub-ducting slab and its vertical descent rate (units kilometres)[1] and is itself expected to positively correlate with redox-budget.

Iron isotopes are potentially a powerful tool for tracking magmatic processes, particularly in developing understanding of redox-controlled equilibria in these high temperature systems (e.g. Dauphas et al., 2009). Variations arise because Fe^{3+} enters smaller tetrahedral sites, while the larger Fe^{2+} ion prefers octahedral coordination. As ^{IV}Fe–O and Fe^{3+}–O bonds are shorter and stiffer than ^{VI}Fe–O and Fe^{2+}–O bonds, they tend to concentrate the heavy isotopes (e.g. Schauble, 2004). Expected iron isotope compositions of mineral phases calculated by Mössbauer spectroscopy and NRIXS (Roskosz et al., 2015; Dauphas et al., 2014, 2012; Polyakov and Mineev, 2000; Polyakov et al., 2007) reveal force constants, K, (a quantitative description of bond stiffness) which increase with $Fe^{3+}/\sum Fe$ in the sequence $K_{Hem} > K_{Mtn} > K_{Ol,Px}$. Iron isotope partitioning in the quartz–fayalite–magnetite system, typical phases found in granitic rocks, confirmed enrichment in $^{57}Fe/^{54}Fe$ in magnetite over fayalite, expressed as: $\Delta^{57}Fe_{Mtn-Fay} = +0.30\text{‰} \pm 0.024\text{‰} \times 10^6/T^2$ (Shahar et al., 2008). In the closed system differentiation of mafic tholeiite to granophyre, Sossi et al. (2012) made precise determinations of melt–pyroxene and melt–magnetite fractionation factors yielding; $\Delta^{57}Fe_{Px-Melt} = -0.25\text{‰} \times 10^6/T^2$ and $\Delta^{57}Fe_{Mtn-Melt} = +0.20\text{‰} \times 10^6/T^2$. As ferric iron is effectively an incompatible element during partial melting (e.g. Canil et al., 1994), the fundamental controls on iron isotopic partitioning between ferrous and ferric sites leads to heavy iron isotope enrichment in mantle melts relative to their sources. The extraction of these heavier melts from the residual source leaves it isotopically lighter (Sossi et al., 2016; Craddock et al., 2013; Weyer and Ionov, 2007; Williams et al., 2005; Dauphas et al., 2009; Nebel et al., 2015b). For a given fraction of melting, more oxidised mantle sources should produce melts with isotopically heavier iron than more reduced sources (Dauphas et al., 2009). This redox control on iron isotope fractionation provides the theoretical basis for this research. If subduction redox-budget is controlled by Fe^{3+}/Fe^{2+} equilibria, then a positive correlation is expected between ϕ (and hence redox-budget) and the iron isotope composition of arc magmas. Furthermore, this working hypothesis states that, all else being equal, the oxidised mantle wedge source to arc magmas should yield basalts with heavy Fe isotopic composition relative to MORB, $\delta^{57}Fe = 0.15 \pm 0.03$ (Teng et al., 2013), sourced from DMM (Fig. 2) with $\delta^{57}Fe \approx 0.05\text{‰}$ (Weyer and Ionov, 2007; Craddock et al., 2013; Sossi et al., 2016).

2. Samples

This study involved the collection of new iron isotope and Fe^{2+} and Fe^{3+} data on 130 predominantly mafic to intermediate lavas from 15 separate, modern, active arc systems from the circum-Pacific, Indonesia and the Lesser Antilles (Table 1, Supplementary Data Table). Many of these samples have been the subject of prior published geochemical projects and have a comprehensive range of analytical results including major and trace elements as well as Nd-, Pb- and Sr-isotopes. Of this prior data, a few selected elements are also included in Table 1 and Supplementary Data Table whose caption includes references to the original published source of the analyses. The definitive physical characteristics of these arcs have been assembled from the compilations of Jarrard (2003), Syracuse et al. (2010) and van Keken et al. (2011).

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[1] The ϕ *factor* as defined by Kirby et al. (1996) was the product of the plate age, the convergence velocity and the sine of the slab dip angle. The product of the sine of the slab angle of dip and the convergence velocity is the vertical descent velocity (Syracuse et al., 2010; van Keken et al., 2011).