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Fractionation of oxygen and iron isotopes by partial melting processes: Implications for the interpretation of stable isotope signatures in mafic rocks

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ABSTRACT

Recycling of oceanic crust into the deep mantle via subduction is a widely accepted mechanism for creating compositional heterogeneity in the upper mantle and for explaining the distinct geochemistry of mantle plumes. The oxygen isotope ratios ($\delta^{18}O$) of some ocean island basalts (OIB) span values both above and below that of unmetasomatised upper mantle (5.5 ± 0.4‰) and provide support for this hypothesis, as it is widely assumed that most variations in $\delta^{18}O$ are produced by near-surface low-temperature processes. Here we show a significant linear relationship between $\delta^{18}O$ and stable iron isotope ratios ($\delta^{57}Fe$) in a suite of pristine eclogite xenoliths. The $\delta^{18}O$ values of both bulk samples and garnets range from values within error of normal mantle to significantly lighter values. The observed range and correlation between $\delta^{18}O$ and $\delta^{57}Fe$ is unlikely to be inherited from oceanic crust, as $\delta^{57}Fe$ values determined for samples of hydrothermally altered oceanic crust do not differ significantly from the mantle value and show no correlation with $\delta^{18}O$. It is proposed that the correlated $\delta^{57}Fe$ and $\delta^{18}O$ variations in this particular eclogite suite are predominantly related to isotopic fractionation by disequilibrium partial melting although modification by melt percolation processes cannot be ruled out. Fractionation of Fe and O isotopes by removal of partial melt enriched in isotopically heavy Fe and O is supported by negative correlations between bulk sample $\delta^{57}Fe$ and Cr content and bulk sample and garnet $\delta^{18}O$ and Sc contents, as Cr and Sc are elements that become enriched in garnet- and pyroxene-bearing melt residues. Melt extraction could take place either during subduction, where the eclogites represent the residues of melted oceanic lithosphere, or could take place during long-term residence within the lithospheric mantle, in which case the protoliths of the eclogites could be of either crustal or mantle origin. This modification of both $\delta^{57}Fe$ and $\delta^{18}O$ by melting processes and specifically the production of low-$\delta^{18}O$ signatures in mafic rocks implies that some of the isotopically light $\delta^{18}O$ values observed in OIB and eclogite xenoliths may not necessarily reflect near-surface processes or components.

1. Introduction

The Earth's mantle is rendered compositionally heterogeneous by melting and recycling of surface fractionated components via subduction (White and Hofmann, 1982). It has also been proposed that at least some of this heterogeneity may also arise from the recycling of mantle components such as continental (Gibson et al., 2005) or oceanic mantle lithosphere (Widom, 2002). These processes of admixing and partial homogenization of recycled material are sampled and identified primarily using the radiogenic isotopic compositions of trace elements in basalts at mid ocean ridges and hotspots, the latter often thought to be derived from the re-melting of buoyant mantle plumes. Oxygen stable isotopes have been used to fingerprint crustal components in mantle source regions (e.g. Eiler, 2001) as they are strongly fractionated within the basaltic and gabbroic oceanic crust as a result of fluid alteration (Muehlenbachs and Clayton, 1972; Alt et al., 1986; Staudigel et al., 1995; Alt et al., 1996) at high and low-temperatures leading to $\delta^{18}O$ values that are distinct from that of pristine (anhydrous) mantle (5.5 ± 0.4‰) (Mattey et al., 1994). Mixing significant quantities of such material into a mantle source can generate isotopically distinct reservoirs, reflected in the compositions of OIB, which are the melting products

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of mantle plumes. As oxygen is a major element with approximately the same concentration in all likely silicate reservoirs, isotopic variations can in principle be converted simply into mass proportions. However, application of this approach has in some instances led to apparently irreconcilable paradoxes (Niu and O'Hara, 2003). For example mixing calculations show that large proportions of oceanic crust (>60%) are required to explain the δ^{18}O values of some OIB, but this is inconsistent with aspects of their major and trace element chemistry (Thirlwall et al., 2006). It has also been proposed that some of the geochemical characteristics of OIB can be explained by recycling of sub-continental lithospheric mantle (SCLM) (Gibson et al., 2005). More recently, stable isotope variations in lithium (Li) (Elliott et al., 2006) and thallium (Tl) (Nielsen et al., 2006) have been employed as tracers of recycled material in mantle source regions because these systems are all dominantly fractionated by low temperature processes that operate at or near the Earth's surface. Iron isotopes may also be used to constrain mantle processes. Whereas there is little variation in the δ^{57}Fe of oceanic basalts (Beard and Johnson, 2004; Weyer and Ionov, 2007), significant isotopic variations are preserved in mantle peridotites and pyroxenites, which have been explained in terms of melt extraction, melt percolation and metasomatism (Williams et al., 2004, 2005; Weyer and Ionov, 2007).

Orogenic massifs and mantle xenoliths provide samples of oceanic crust and mantle lithosphere and can be used to evaluate the nature and composition of recycled material. In this paper we present the first combined Fe and O isotope study of eclogite xenoliths, which have also been characterised for their major and trace element abundances and $Fe^{3+}/\Sigma Fe$ ratios. Many such eclogite xenolith suites have a much wider range of δ^{18}O values than that of pristine mantle and these variations are widely interpreted as being produced by near-surface processes, specifically hydrothermal alteration of oceanic crust from which the eclogites are assumed to be derived (e.g. Jacob, 2004 and references therein). In many cases, there are clear independent lines of evidence which support this reasoning. For example, mass independent sulphur isotope variations in sulphide inclusions in eclogitic diamonds (Farquhar et al., 2002), require the sulphur to have an atmospheric, rather than a mantle, origin. However, the interpretation of the δ^{18}O data is not always straightforward, as oxygen isotopes are known to be susceptible to metasomatism and fluid infiltration (Chacko et al., 1996; Zhang et al., 2000). It has also been proposed that some eclogite xenolith suites may represent cumulates derived from asthenospheric melts that crystallized at the base of cratonic SCLM (O'Hara, 1969; Caporuscio and Smyth, 1990; Griffin and O'Reilly, 2007), in which case another explanation needs to be sought for their variable δ^{18}O values.

The eclogite xenoliths chosen for this study are from the Kaalvallei and Bellsbank kimberlite pipes, South Africa, and consist of garnet and omphacitic pyroxene without additional accessory phases (e.g. plagioclase, kyanite, coesite, quartz). Whereas the presence of accessory phases such as coesite can be used to infer a silica-saturated protolith and hence an ocean crust origin (Schulze et al., 2000), the origin of purely bimineralic eclogites such as these is more equivocal. The aim of this study is to use Fe isotopes, which can be modified by melting and metasomatism processes, in conjunction with O isotopes to determine whether or not the O isotope signatures of eclogite xenoliths are directly inherited from the eclogite protolith(s) or whether they are a consequence of isotopic fractionation by open-system processes operating during either slab dewatering/melting (if the eclogite xenoliths are derived from crustal protoliths) or during eclogite residence in the SCLM. To complement the Fe and O-isotope data set for these eclogite xenoliths, we also present Fe isotope data for high-temperature altered oceanic crust samples from ODP Hole 504B, which have previously been characterized for their O-isotope and major element compositions.

2. Materials and methods

2.1. Samples

The eclogite xenoliths analysed here were collected from concentrates at the Kaalvallei (or Bellsbank) kimberlite pipes, and typically range in size from 2 cm to 5 cm. The samples for this study were selected based on the degree of alteration and foreign material visible in hand specimens. All samples consist of coarse-grained garnet and omphacitic pyroxene and are texturally similar to Group I (coarse rocks with rounded garnets) and Group II (finer-grained rocks with straight grain boundaries) eclogite xenoliths recognised at this mine and elsewhere (Viljoen et al., 2005). Group I eclogite xenoliths at Kaalvallei are characterized by large (3–8 mm), rounded, dark red-brown garnet set in enclosing dark green clinopyroxenes, which range from 1 to 2 mm in size (samples 375, Kaalvallei-A). Garnet grain boundaries are curved, but triple junctions are visible between garnet and clinopyroxene and between clinopyroxenes. Garnet: clinopyroxene ranges from 35:65 to 60:40 (Table 1). The Group II eclogites (samples 382, 402, 423) are characterised by smaller crystals of bright green clinopyroxene and pale pink garnet which range from 0.5 to 1.5 mm. Grain boundaries are straight, and triple junctions common. Garnet:clinopyroxene ranges from 20:80 to 65:35 (Table 1). The xenolith from the Bellsbank kimberlite (referred to as Bellsbank hereafter) is texturally similar to the Kaalvallei Group I xenoliths; it is composed of large (>6 mm) interlocking dark red-brown garnets with interstitial dark green clinopyroxene (0.5–1 mm). Garnet grain boundaries are straight, and triple junctions are observed between garnet and clinopyroxene. In all samples minor oxide (<2 μm) inclusions in both garnet and pyroxene were observed in thin section, but no other accessory mineral phases (e.g. quartz, kyanite, rutile, sulphides) were apparent.

A sub-set of altered basaltic dikes and a glass from ODP Hole 504B were also analysed for their iron isotope compositions (Table 2). Oxygen isotope, major and trace element data are available for these samples (Alt et al., 1985a,b; Alt and Emmermann, 1985; Alt et al., 1989, 1996; Bach et al., 1996). The samples were provided as bulk-rock powders and full sample descriptions are available in the references above.

2.2. Iron isotope analysis

Iron isotope data for the eclogites and 504B samples are presented in Tables 1 and 2, respectively. Sample dissolution and iron extraction procedures followed methods described previously (Williams et al., 2004); additional details applicable to this work are given below. The eclogite xenoliths were hand-crushed and optically pure garnet and pyroxene fractions without visible oxide inclusions were separated by hand-picking under ethanol using a binocular microscope. Separated fractions consisted of 40–60 grains, weighing 2–4 mg. We did not make direct measurements of bulk samples due to the small size of the eclogite xenoliths, which meant that it would not be possible to prepare any kind of bulk rock powder that would be meaningfully representative of the bulk mineralogy of the sample. In the case of the 504B samples, ~50 mg of powder was dissolved from each sample. All samples were treated with ~10:1 concentrated HF: HNO_3 followed by 2 reflux and evaporation cycles of 6 M HCl at 180 °C. Fe was purified using anion exchange chromatography in HCl form. Following a final evaporation and treatment with concentrated H_2O_2 and HNO_3 to decompose any resin particles from the columns, the samples were dissolved in 0.05 M HCl for mass spectrometry. Total procedural blanks were <10 ng. As documented in Williams et al. (2004), Fe yields were quantitative and no measurable Fe isotope fractionation took place on the columns following these procedures.

Iron isotope analyses were carried out at standard resolution ($M/\delta M \sim 400$) on a HR Nu Instruments (Wrexham, UK) multi-