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Osmium isotopes and Fe/Mn ratios in Ti-rich picritic basalts from the Ethiopian flood basalt province: No evidence for core contribution to the Afar plume

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ABSTRACT

Variations in the Fe/Mn ratio and Osmium isotopes in magnesium-rich mafic rocks from plume-related volcanic provinces have been exploited to imply the entrainment of core material in mantle plumes and the involvement of ancient recycled oceanic lithosphere. Here we present new major and trace element, $^{187}Os/^{188}Os$ ratios and precise Fe/Mn ratios on a suite of MgO-rich basalts, picritic basalts and ankaramites from the 30 Ma Ethiopian flood basalt province that shed new light on these arguments. The lavas show a range of compositions with MgO varying from 5 to 20 wt.% although the primary magma is inferred to have an MgO content of 15–16 wt.%. The lavas are also characterised by low Al_2O_3 contents (7–9 wt.% at 15 wt.% MgO), implying an origin from ~150 km depth at a temperature in excess of 1600 °C, consistent with an origin in the early phases of Afar mantle plume activity. Osmium isotopes in samples with >10 wt.% MgO are unradiogenic with $^{187}Os/^{188}Os<0.127$ while those with lower MgO define a positive correlation with Re/Os and appear to have been contaminated by crustal material. Fe/Mn ratios determined by ICP-MS vary from 65.4 to 78.5 in rocks with >10 wt.% MgO and show greater variation to both higher and lower values in less magnesian samples. These values are high compared with MORB and Icelandic basalts, comparable with the Fe/Mn ratios of Hawaiian and other selected ocean island basalts, and are a characteristic of the primary magma. There is no evidence to suggest that Fe/Mn is fractionated during peridotite melting at low pressures less than 5 GPa, implying in agreement with previous studies that high Fe/Mn ratios are a compositional feature of the magma source region. The lack of association of radiogenic $^{187}Os/^{188}Os$ with the high Fe/Mn ratios of the Ethiopian picritic basalts calls into question the link to possible entrainment of core material in the source of the Afar mantle plume. Similarly, the unradiogenic $^{187}Os/^{188}Os$ ratios preclude a significant contribution from ancient recycled oceanic lithosphere. An alternative model is suggested in which melts generated at high pressures (>7 GPa) during the initial turbulent ascent of the Afar plume head form pyroxene rich veins with high Fe/Mn ratios and high incompatible element contents in a peridotite matrix. These highly fertile source regions contribute significantly to melt compositions during the early phases of plume emplacement.

1. Introduction

The source of mantle plumes remains the subject of controversy, in particular whether or not they originate from the core–mantle boundary and, if so, whether or not they entrain components from the core and carry them towards the Earth's surface (Courtillot et al., 2003; Anderson, 2000; Meibom et al., 2003; Brandon et al., 1998; Humayun et al., 2004). Models of the convective flow in the mantle reveal the likelihood of whole-mantle convection (van Keken et al., 2002) while tracer models clearly demonstrate that much of the mantle must have been processed by melting in an environment close to the Earth's surface at least once during the history of the Earth (Huang and Davies, 2007). Mantle plumes, while not universally accepted as a real component of mantle convection (Foulger and Natland, 2003), originate at major thermal or compositional boundaries within the Earth and the most significant occurs at the base of the mantle. Images from seismic tomography reveal velocity anomalies that may be related to temperature variations extending from regions affected by intra-plate volcanic activity, through the upper and lower mantle to the core–mantle boundary (Montelli et al., 2004; Lei and Zhao, 2006). Thus there is the possibility that material once close to the core-mantle boundary is convected into the upper mantle where it may undergo partial melting and contribute to surface volcanism.

Compositional evidence for core material in surface volcanism is much more equivocal. While some have argued that the core may act as a source of unradiogenic He in ocean island and other plume-related basalts (Dale et al., 2009; Porcelli and Halliday, 2001; van

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Keken et al., 2002), the strongest argument for core entrainment is the association of radiogenic $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios with high Fe/Mn ratios in primitive basalts (Brandon et al., 1998; Humayun et al., 2004). The primary case for this association is Hawaii where picritic basalts show correlated Os isotope ratios (Brandon et al., 1998), implying a source with elevated time-integrated Re/Os and Pt/Os ratios. Given that the primitive mantle has close to chondritic values of these two ratios (Brandon et al., 2000; Meisel et al., 2001; Drake and Righter, 2002), the argument has been made for the entrainment of the material from a deep, non-mantle source that is rich in the highly siderophile elements (HSE), arguably the outer core (Brandon et al., 1998). The same suite of Hawaiian picrites has also been shown to possess elevated Fe/Mn ratios that are independent of fractionation and other magmatic processes (Humayun et al., 2004). The mantle has a canonical Fe/Mn ratio of 60 ± 10 and primary magmas with Fe/Mn ratios greater than 60 have been interpreted to imply a magma source with a higher than usual Fe content which could be a result of interaction with the core (Humayun et al., 2004). Subsequently additional analyses have revealed that basalts and picrites from other plume-related ocean islands, notably Tahiti and Reunion, are also characterised by high Fe/Mn ratios (Qin and Humayun, 2008).

Various counter arguments have been made that the time-integrated HSE ratios implied by Os isotope ratios in the Hawaiian picrites are developed in mantle sulphides (Luguet et al., 2008) while iron-rich source regions in the mantle can be produced by pyroxenite veining (Sobolev et al., 2007). Sobolev et al. (2008) have also shown that Os isotopes in Hawaiian and Icelandic picrites are consistent with a recycled pyroxenite contribution. While the recycling of ferromanganese crusts and nodules from the ocean floor has also been suggested as a possible source of radiogenic Os (Baker and Jensen, 2004), this has been contested because of a lack of correlation between Tl and Os isotopes in Hawaiian picrites (Nielsen et al., 2006). Limited variations in W isotopes in a range of plume-related and other mantle-derived rocks appear to preclude a core-derived contribution to surface volcanism via any route (Schersten et al., 2004). Consequently, the unusual compositional characteristics of the Hawaiian picrites may simply be the result of relatively shallow intra-mantle processes of melt migration and sulphide fractionation or plate recycling.

To investigate the possibility of a core contribution to plume-related basalts we present major element and $^{187}Os/^{188}Os$ isotope analyses, together with high precision Fe/Mn ratios of a suite of picritic basalts and ankaramites from the Ethiopian flood basalt province of NE Africa. These were formed during the initial impact of the Afar mantle plume and prior to the separation of Arabia from Africa. Their compositions reflect melting at considerable depth and at elevated temperatures, consistent with a plume origin and they are characterised by $^3He/^4He$ ratios up to 19 R/R_a (Pik et al., 1998, 2006). Moreover, the Afar plume represents one of the major plumes identified by Courtillot et al. (2003) as originating in the deep mantle, exhibiting four out of their five criteria, and so may be expected to possess a core contribution if such an exchange occurs.

2. Background and samples

The Ethiopian flood basalt province is the earliest surface record of magmatic activity related to the initiation of the Afar mantle plume (Pik et al., 1998). The majority of the picritic and basaltic samples analysed in this study are derived from the Dilb road section, also known as the Chinese Road section, in northern Ethiopia (Fig. 1). The section is located on the eastern escarpment of the northern Ethiopian plateau, adjacent to that part of the Main Ethiopian Rift that broadens into the Afar depression. The lavas are representative of the HT2 series of the Ethiopian flood basalts, as described by Pik et al. (1998), and are capped by an ignimbrite, dated at 30 Ma (Hofmann et al., 1997). The section is characterised by a series of olivine-rich picritic and ankaramitic lavas interbedded with more evolved plagioclase-phyric basaltic lavas. Other samples included in this study are from the petrographically similar sequences that outcrop around Lalibela, some 100 km west of the escarpment. Location information, field and petrographic descriptions are included in the Supplementary Information.

3. Methods

Major elements were determined by standard XRF procedures, using an ARL 8400 instrument at the Open University. Uncertainties in major element abundances as reflected in multiple repeat analyses of in-house and international reference materials are estimated to be better than 2% relative (Ramsey et al., 1995). Trace elements were determined by ICP-MS at the Open University after the method described by Rogers et al. (2006) giving precision and accuracy of $\pm 2\%$ (1σ).

Os isotopes were determined by N-TIMS after the technique described by Schaefer et al. (2002). Long-term $^{187}Os/^{188}Os$ reproducibility is $\leq 0.2\%$ (2 s.d.) as determined from routine measurement of the DTM Os solution ($^{187}Os/^{188}Os = 0.17396 \pm 0.00017$, $n = 140$ over the period when the sample measurements were made). Os isotope ratios are corrected for instrumental mass fractionation using a $^{192}Os/^{188}Os$ ratio of 3.08262. Total procedural blank for Os were consistently <1 pg with an $^{187}Os/^{188}Os$ ratio of 0.17, resulting in blank contributions of $\ll 1\%$ for the Os and $<0.1\%$ for $^{187}Os/^{188}Os$, in samples with >1 ppb Os.

Fe/Mn ratios were determined by quadrupole ICP-MS at the OU using an Agilent 7500 s instrument employing a method similar to that described by Humayun et al. (2004). Details of the analytical procedure are presented in the Supplementary Information and reveal an external reproducibility of $\pm 0.3\%$ (2σ) on repeat analyses of JB-2 while our analyses of BHVO-2 reproduce those reported by Humayun et al. (2004).

4. Results

4.1. Major and Trace elements

Selected major and trace element abundances, $^{187}Os/^{188}Os$ isotope and Fe/Mn ratios are reported in Table 1. Samples vary in composition from Mg-rich picritic basalts and ankaramites to more evolved alkali basalts. MgO varies from 5–20 wt.% but with the majority of samples having >10 wt.% MgO. Mg# values (calculated assuming 10% of total iron as Fe^{3+}) are high and variable, with values of 0.70 in samples with MgO contents of 15 wt.%, indicating that these rocks could represent primary melts (Fig. 2). Samples with MgO >15 wt.% and Mg# values >0.7 are rich in olivine and clinopyroxene and have probably been affected by crystal accumulation. The rocks are unusually Ti-rich with 3–4 wt.% TiO_2 in most samples with 15 wt.% MgO, although some range up to 5.6 wt.%, significantly greater than the compositional range observed by Pik et al. (1998). They are also Al-poor, with Al_2O_3 rising from ~8 wt.% in the most magnesian lavas, to a maximum of 14 in the least magnesian basalts (Fig. 3). $Fe_2O_3^{tot}$ contents at 15 wt.% MgO are between 12 and 14 wt.%, close to the lower limit of 14 wt.% $Fe_2O_3^{tot}$ for ferro-picrites (Gibson et al., 2000; Hanski and Smolkin, 1995).

Compatible trace element abundances reflect the near primary and cumulus-enriched major element composition, but samples with 15 wt.% MgO have Ni ~500 ppm, Cr ~1000 ppm and Co ~75 ppm, all close to values expected for primary melts of a peridotitic source (Hart and Davis, 1978; Korenaga and Kelemen, 2000). Incompatible element abundances are high relative to typical MORB with La >20 ppm in samples with 15% MgO. Mantle-normalised trace element profiles are broadly similar to OIB, although REE fractionation,