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Europium and strontium anomalies in the MORB source mantle

Ming Tang *, William F. McDonough, Richard D. Ash

Department of Geology, University of Maryland, College Park, MD 20742, USA

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Abstract

Lower crustal recycling depletes the continental crust of Eu and Sr and returns Eu and Sr enriched materials into the mantle (e.g., Tang et al., 2015, Geology). To test the hypothesis that the MORB source mantle balances the Eu and Sr deficits in the continental crust, we carried out high precision Eu/Eu* and Sr/Sr* measurement for 72 MORB glasses with MgO >8.5% from the Pacific, Indian, and Atlantic mid-ocean ridges. MORB glasses with MgO $\geqslant$ 9 wt.% have a mean Eu/Eu* of 1.025 ± 0.025 (2 σ_m, $n = 46$) and Sr/Sr* of 1.242 ± 0.093 (2 σ_m, $n = 41$) and these ratios are positively correlated. These samples show both positive and negative Eu and Sr anomalies, with no correlations between Eu/Eu* vs. MgO or Sr/Sr* vs. MgO, suggesting that the anomalies are not produced by plagioclase fractionation at MgO >9 wt.% and, thus, other processes must be responsible for generating the anomalies. We term these MORB samples primitive MORBs, as they record the melt Eu/Eu* and Sr/Sr* before plagioclase fractionation. Consequently, the mean oceanic crust, including cumulates, has a bulk Eu/Eu* of ~1 and 20% Sr excess.

Considering that divalent Sr and Eu(II) diffuse faster than trivalent Pr, Nd, Sm, and Gd, we evaluated this kinetic effect on Sm–Eu–Gd and Pr–Sr–Nd fractionations during spinel peridotite partial melting in the MORB source mantle. Our modeling shows that the correlated Eu and Sr anomalies seen in primitive MORBs may result from disequilibrium mantle melting. Melt fractions produced during early- and late-stage melting may carry positive and negative Eu and Sr anomalies, respectively, that overlap with the ranges documented in primitive MORBs. Because the net effect of disequilibrium melting is to produce partial melts with bulk positive Eu and Sr anomalies, the MORB source mantle must have Eu/Eu* $< 1.025 \pm 0.025$ (2 σ_m) and Sr/Sr* $< 1.242 \pm 0.093$ (2 σ_m). Although we cannot rule out the possibility that recycled lower continental crustal materials, which have positive Eu and Sr anomalies, are partially mixed into the upper mantle (i.e., MORB source region), a significant amount of this crustal component must have been sequestered into the deep mantle, as supported by the negative ^{206}Pb/^{204}Pb–Eu/Eu* and ^{206}Pb/^{204}Pb–Sr/Sr* correlations in ocean island basalts.
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Keywords: Eu anomaly; Sr anomaly; Primitive MORB; Disequilibrium melting; Lower crustal recycling

1. INTRODUCTION

Europium is present in two valence states (+2 and +3) in most magmatic systems. Europium(II) behaves like Sr^{2+} due to their similar ionic radii (1.25 vs. 1.26 Angstroms, respectively, Shannon, 1976). In the crust, where plagioclase is stable, Eu(II) and Sr are strongly partitioned into plagioclase and thus fractionated from Sm–Gd and Pr–Nd, respectively. During intra-crustal differentiation, Eu and Sr can be removed from the melt by fractional crystallization of plagioclase or retained in the residual plagioclase at the source. As a consequence, the upper continental crust is distinctly depleted in Eu and Sr while the lower continental crust possesses Eu and Sr excesses. The bulk continental crust likely has negative Eu and Sr anomalies based on observations of crustal samples (Rudnick and Gao,

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* Corresponding author at: Earth Science Department, Rice University, Houston, TX 77005, USA.
E-mail address: tangmyes@gmail.com (M. Tang).

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2014; Tang et al., 2015), and most compositional models for the continental crust have negative Eu and Sr anomalies (Rudnick and Gao, 2014 and the references therein). Such Eu and Sr depletions in the crust likely result from lower crustal recycling.

Niu and O'Hara (2009) observed a positive correlation between Eu/Eu* (Eu/Eu* = Eu_N/sqrt(Sm_N * Gd_N)), Sr/Sr* (Sr/Sr* = Sr_N/sqrt(Pr_N * Nd_N), CI1 normalizing data from Sun and McDonough (1989)) and MgO content in MORB samples from the East Pacific Rise. They also observed that the primitive MORB samples (MgO >9 wt.%) all have positive Eu and Sr anomalies (Eu/Eu* and Sr/Sr* >1), and thus the depleted MORB mantle (DMM, the source region of MORB) might host the Eu and Sr that are missing from the continental crust. More recently, Arevalo and McDonough (2010) failed to reproduce the correlation between Eu/Eu* and MgO in their global MORB dataset, which shows a large variation in Eu/Eu* for MORB samples having MgO contents >9 wt.%. Similarly, both positive and negative Eu and Sr anomalies were observed in global primitive MORB by Jenner and O'Neill (2012a) and Gale et al. (2013). However, none of these studies were dedicated to high precision measurement of Eu/Eu* and Sr/Sr* in MORB. The total variation of Eu/Eu*, in particular, is limited in primitive MORB and requires instrumental fractionation to be well calibrated for accurate measurement of Eu/Eu*. To investigate this issue further, we developed a new LA-ICP-MS method (Tang et al., 2014), and measured Eu/Eu* as well as Sr/Sr* at high precision and accuracy in 72 primitive MORB glasses globally. In contrast to Niu and O'Hara's observations, our data show much reduced average Eu excesses in the primitive MORBs.

Europium and Sr anomalies in mantle partial melts may not be directly used to approximate Eu/Eu* and Sr/Sr* in the source. Experimental studies showed that the divalent Eu and Sr diffuses orders of magnitude faster than the trivalent Pr, Nd, Sm and Gd in clinopyroxene (Sneeringer et al., 1984; Van Orman et al., 2001; Cherniak and Liang, 2007). Disequilibrium melting in the MORB source mantle may result in Eu and Sr enrichments in the partial melts because Eu and Sr are preferentially extracted relative to Pr, Nd, Sm and Gd. In the second part of this work, we evaluate the degrees of Sm–Eu–Gd and Pr–Sr–Nd fractionations and consequent Eu/Eu* and Sr/Sr* generated by partial melting of an anomaly free source. Our calculation suggests that the MORB source mantle may have much less Eu and Sr excesses (permissively no Eu and Sr anomalies) than the primitive MORB.

2. SAMPLES AND ANALYTICAL METHODS

A total of 72 MORB glasses from 21 sites (Fig. 1) were measured for their Eu/Eu*, Sr/Sr* and MgO contents. Of these samples, 28 are from the Pacific, 22 are from the Indian and 22 are from the Atlantic. All samples have MgO contents >8.5%, and are thus relatively primitive. Eu/Eu* and Sr/Sr* were normalized to chondrite values from Sun and McDonough (1989).

The LA-ICP-MS method provides a better approach to evaluate Eu and Sr anomalies in MORB glasses than the solution ICP-MS method in that one can easily detect and avoid micro-crystals within the glass. The plagioclase micro-crystals, either crystalized from or assimilated into the melt, can significantly bias the measurements of Eu and Sr anomalies. The LA-ICP-MS data reduction method in (Tang et al., 2014) was adopted from Liu et al. (2008), and allows simultaneous determination of major and trace element concentrations in volatile-free samples. One of the two basaltic reference materials, KL2-G and BIR-1G, was analyzed after every one or two samples (see Supplementary file for measurements on reference materials). A long-term reproducibility of ~3% (2 SD) was achieved for both Eu/Eu* in KL2-G and BIR1-G. The Eu/Eu* measured in reference materials over a wide range of compositions agree with GeoReM preferred values (http://georem.mpch-mainz.gwdg.de/) within 3%. To avoid potential heterogeneities such as micro-crystals, we measured each glass chip three to four times at different sites (see Supplementary file for data). The uncertainties for BHVO-2G, our calibration standard, are ~2% (2 RSD) for Eu/Eu* and ~8% (2 RSD) for Sr/Sr*. We excluded individual spot analyses having distinct Eu/Eu* (>2 SD reproducibility different from the remainder) or major element composition compared to the remainder of the analyses on the same sample, and took the average values of the remainder as the Eu/Eu* and MgO content for each sample. The Sr/Sr* were measured separately on the same set of samples using BHVO-2G as the calibration standard. Each sample was measured twice. Our repeated measurements of BIR-1G throughout the analytical session gave an average Sr/Sr* of 3.44 ± 0.12 (2 SD, 2 RSD = 3.6%, $n = 15$), which agrees with the GeoReM preferred value within 2%. For Eu/Eu*, twenty-five analyses (marked in red in the Supplementary file) were thus discarded from the total of 320 analyses (7.8% of the population). We compared the long-term reproducibility of the two reference materials, and standard deviation of multiple analyses of each sample, and took whichever is greater as the uncertainty. Nineteen randomly selected samples were re-analyzed on different days to check the reproducibility of Eu/Eu* measurements (see Supplementary file for the plot). One possible caveat with our approach is that our MORB glass chips are small, mostly several mm^3 volumes. How representative are these glass chips compared to those chunks of whole rocks remains to be investigated.

3. RESULTS

The primitive MORB samples we analyzed show both positive and negative Eu (Eu/Eu* = 0.92–1.13) and Sr anomalies (Sr/Sr* = 0.81–1.98) (Fig. 2). No significant correlations between Eu/Eu* (or Sr/Sr*) and MgO when MgO exceeds 8.5%, precluding the extrapolation of Niu and O'Hara's putative trend to higher MgO. Plagioclase saturates at around 9 wt.% MgO (Bender et al., 1984; Niu et al., 2002; Niu and O'Hara, 2009) and its fractional crystallization only happens within the oceanic crust (Wanless and Shaw, 2012). The three ocean basins, Pacific, Indian, and Atlantic, show no discernable difference in their mean Eu/Eu* (1.011 ± 0.013, 1.023 ± 0.020 and 1.030 ± 0.024,