Europium anomalies constrain the mass of recycled lower continental crust

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ABSTRACT
Statistical analyses of Sm-Eu-Gd concentrations in more than 3000 samples from the upper, middle, and lower continental crust reveal that the enrichment of Eu in the lower continental crust cannot compensate for the Eu deficit in the upper and middle continental crust, leaving the bulk continental crust with a significant negative Eu anomaly. Because the building blocks of the continental crust (mantle-derived basaltic or tonalitic slab melts) do not possess a negative Eu anomaly, removal of Eu-enriched lower continental crust is required. Using Sm-Eu-Gd systematics and a mass conservation model, at least 2.9 ± 0.3 (95% confidence) crustal masses (~6 × 10²² kg) appear to have been lost to the mantle over Earth’s history via lower crustal recycling. Such a lower crustal component in the mantle may reappear in some ocean island basalts that have positive Eu anomalies and unradiogenic Pb isotopes.

INTRODUCTION
The compositional differences within the continental crust are manifestations of intracrustal differentiation (Taylor and McLennan, 2008), which may occur in mature continental crust or precursor arc crust. It is widely accepted that the composition of the bulk continental crust is anesitic and is too evolved to be derived directly from the mantle (Arculus, 1981; Green et al., 2014; Rudnick, 1995). To explain the evolved crust composition, recycling of mafic to ultramafic lower crust has been proposed to occur through processes such as density foundering (Arndt and Goldstein, 1989; Kay and Mahlburg-Kay, 1991; Rudnick, 1995; Jull and Kelemen, 2001; Davidson and Arculus, 2005), subduction erosion (Clift et al., 2009; Lee, 2014, and references therein), or crustal subduction followed by re-melting (Hacker et al., 2011).

Lower crustal recycling is poorly documented due to its non-observable nature in most circumstances (Taylor and McLennan, 2008). The geochemical evidence provided here supports the hypothesis that intra-crustal differentiation followed by lower crustal recycling is important in crustal evolution. Although lower crustal recycling is mostly studied in Phanerozoic arc systems (e.g., Greene et al., 2006; Jagoutz and Schmidt, 2013), it may also occur in cratons (e.g., Gao et al., 2004). Our geochemical approach using Sm-Eu-Gd systematics constrains the total mass of recycled lower continental crust (LCC) throughout Earth history, independent of the tectonic environments, processes, and timing of recycling.

Sm-Eu-Gd SYSTEMATICS IN THE CONTINENTAL CRUST
Europium is present in two valence states (+2 and +3). During intracrustal differentiation, Eu is fractionated from Sm and Gd, as Eu²⁺ substitutes for Ca²⁺ and Na⁺ in feldspar (Ren, 2004), which is stable under crustal pressure-temperature (P-T) conditions. The magnitude of Eu enrichment or depletion in a sample is calculated as a “Eu anomaly” relative to the neighboring rare earth elements Sm and Gd:

\[
\frac{\text{Eu}}{\text{Eu}^*} = \frac{\text{Eu}_N}{\sqrt{\text{Sm}_N/(\text{Gd}_N)}}
\]

where the subscript N indicates normalization to chondritic values (Sun and McDonough, 1989). Feldspar left behind in the LCC during intracrustal differentiation causes a Eu deficit in the upper continental crust (UCC) and enrichment in the LCC (Taylor and McLennan, 2008). Alternatively, whether the current deep crustal reservoir compensates the Eu deficit in the UCC is unclear. Among the published compositional models for the bulk continental crust (BCC) (plotted in Appendix 1 in the GSA Data Repository), all but one have negative Eu anomalies of varying magnitude (0.78–0.97), while only Taylor and McLennan (2008) proposed Eu/Eu⁺ = 1 for the BCC.

Here we evaluate Eu/Eu⁺ in the UCC, middle continental crust (MCC), and LCC using an updated data compilation following that of Huang et al. (2013). This data set has three subsets: high-P granulate facies rocks, amphibolite facies rocks, and shales + loess + tillites. For simplicity, we assume that the bulk compositions of samples in the three data sets represent those of the LCC, MCC, and UCC, respectively. We have applied no weighting of samples based on their bulk compositions nor have we used any geophysical information regarding the bulk composition of the deep crust. For our calculations, we used only samples that have Sm, Eu, and Gd concentration data, comprising 970 samples from the LCC, 1702 samples from the MCC, and 411 samples from the UCC. The amphibolite and granulate facies data compilations include samples having both meta-sedimentary and meta-igneous protoliths. We excluded 10% of the samples with high and low Sm and Gd concentrations (removing 2.5% from the top and bottom of the Sm concentration distribution, then repeating the process for Gd), and then removed another 10% of samples with high and low Eu/Eu⁺. This double filter, which eliminates 20% of the samples, helps to reduce the chance of incorporating atypical samples or bad analyses without shifting the results significantly (>10%).

Table 1 lists the mean Sm, Eu, and Gd concentrations in UCC, MCC, and LCC, the number of samples that went into the calculations after filtering, the values from Rudnick and Gao (2003), and the calculated mean concentrations of Sm, Eu, and Gd in the BCC, which are made using a bootstrap method with 100,000 times resampling of the compositional data set. This technique allows estimation of the bulk composition and associated uncertainties with all samples taken into account. The mass proportions of UCC, MCC, and LCC are based on global seismic data, as described by Huang et al. (2013), and the uncertainties were simulated using a Monte Carlo scheme (details in Appendix DR1). Uncertainties or biases associated with the sampling of the UCC, MCC, and LCC were not taken into account in these calculations. Although there are fewer UCC samples than MCC and LCC samples, sediments are powerful predictors of the bulk rare earth element (REE) composition of the UCC, as REEs are insoluble and are transported quantitatively from the site of weathering to the site of deposition (Taylor and McLennan, 2008).

Our results, along with previous estimates tabulated here, suggest that the average UCC and MCC have negative Eu anomalies, while the average LCC has a small positive Eu anomaly. To reconcile the Eu/Eu⁺ mass balance in the absence of lower crustal recycling, the Eu/Eu⁺ of the modern LCC would need to be at least ~1.7 (using our estimated Sm-Eu-Gd concentrations in the BCC and Sm-Gd in the LCC), and this seems unlikely in light of the existing data (Fig. 1). Although one could argue that the data compiled here may be biased toward lower Eu/Eu⁺ relative to the true com-

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position of the LCC, we note that as Eu/Eu* increases in granulites, Eu concentration decreases (Fig. 2), so a more mafic (higher Mg#) lower crust with higher Eu/Eu* would have less leverage on the overall Eu/Eu* of the crust due to its lower REE concentration (see Appendix DR1 for sensitivity tests of assumed LCC composition). That is probably the reason that the Rudnick and Gao (2003) BCC, which incorporates a relatively mafic, high-Eu/Eu* LCC, still has a significant negative Eu anomaly (Table 1).

THE Eu DILEMMA

We assume, as many have (e.g., Taylor and McLennan, 2008; Gao et al., 1998), that the original crust produced by mantle melting has Eu/Eu* = 1. However, rather than possessing no Eu anomaly, the modern BCC shows significant Eu depletion relative to Sm and Gd (Table 1). These observations require that materials with positive Eu anomalies be transferred from the continental crust to the mantle. Our observations cannot constrain these processes, but can provide limits on the composition and mass of the recycled crust.

CALCULATING THE MASS OF THE RECYCLED LOWER CRUST

Generally, crustal recycling takes two forms: sediment subduction and LCC recycling (via gravitationally driven processes, e.g., density foundering, subduction erosion, relamination, etc.). Sediment subduction returns upper crustal materials to the mantle. Terrigenous sediments, which dominate the REE budget of global subducting sediments (Plank, 2014), have negative Eu anomalies, and thus cannot account for the Eu deficit in the continental crust. By contrast, recycling of the LCC is a plausible mechanism for decreasing the bulk crust Eu/Eu*, as the LCC is observed to be enriched in Eu.

In our modeling, we make the following assumptions. (1) The present-day bulk continental crust has the composition provided in Table 1 and discussed herein. (2) Juvenile crust has a Eu/Eu* = 1.0. (3) The loss of upper crustal mass due to sediment subduction removes material with Eu/Eu* < 1.0 from the continental crust. (4) The Eu/Eu* of recycled lower crust can be characterized using the following four compositional models: (1) an estimate of recycled intra-oceanic arc lower crust (Jagoutz and Schmidt, 2013; (2) an estimate of high-density cumulates in arc lower crust (Kelemen et al., 2014); (3) an estimate of the recycled LCC from this study. Kernel density is an estimate of probability mass proportion of recycled LCC relative to present-day continental crust. JS13—Arc delaminants from Jagoutz and Schmidt (2013), K14—Talkeetna arc lower crustal cumulates from Kelemen et al. (2014), RG03—LCC from Rudnick and Gao (2003). *Mass proportions of the UCC, MCC, and LCC are from Huang et al. (2013). †Concentrations given in ppm by weight. **Means of granulite facies samples with Mg# > 50 and SiO2 < 54%.

Figure 1. Histogram showing the distribution of Eu/Eu* values in granulite facies samples (n = 970), compared with the Eu/Eu* of lower continental crust (LCC) required to make the bulk continental crust Eu/Eu* = 1 (black assuming the LCC has the Sm and Gd concentrations from this study). Inset shows chondrite-normalized rare earth element patterns for the upper continental crust (UCC, solid gray curve), middle continental crust (MCC, dashed gray curve), and LCC (black curve) from Rudnick and Gao (2003).

Figure 2. Correlations between Eu/Eu*, Eu concentration and Mg# in granulite facies samples. The mean Eu/Eu*, Eu concentration and Mg# represent incremental averages. Each increment consists of 100 samples. High-Mg# samples have high Eu/Eu* but low Eu concentrations.

### Table 1. Mean Concentrations of Sm, Eu, and Gd in the Continental Crust and Candidates of Recycled Lower Continental Crust

<table>
<thead>
<tr>
<th></th>
<th>UCC</th>
<th>MCC</th>
<th>LCC</th>
<th>BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>35.9 ± 6.0</td>
<td>33.5 ± 4.3</td>
<td>30.6 ± 3.4</td>
<td>100</td>
</tr>
</tbody>
</table>

This work:

<table>
<thead>
<tr>
<th>n</th>
<th>328</th>
<th>1362</th>
<th>776</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>5.3 ± 0.2</td>
<td>4.1 ± 0.1</td>
<td>3.6 ± 0.2</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>Eu</td>
<td>1.08 ± 0.03</td>
<td>1.13 ± 0.03</td>
<td>1.22 ± 0.04</td>
<td>1.14 ± 0.03</td>
</tr>
<tr>
<td>Gd</td>
<td>4.5 ± 0.1</td>
<td>4.1 ± 0.1</td>
<td>3.7 ± 0.1</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>0.67 ± 0.01</td>
<td>0.84 ± 0.01</td>
<td>1.02 ± 0.02</td>
<td>0.82 ± 0.04</td>
</tr>
</tbody>
</table>

Rudnick and Gao (2003):

| Sm | 4.7 ± 0.3 | 4.6 | 2.8 | 3.9 |
| Eu | 1 ± 0.1 | 1.4 | 1.1 | 1.1 |
| Gd | 4 ± 0.3 | 4 | 3.1 | 3.7 |
| Eu/Eu* | 0.72 | 0.96 | 1.14 | 0.89 |

** Candidates for Recycled LCC**

<table>
<thead>
<tr>
<th></th>
<th>JS13</th>
<th>K14</th>
<th>RG03</th>
<th>This study**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>1.04</td>
<td>1.03</td>
<td>2.8</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>Eu</td>
<td>0.55</td>
<td>0.47</td>
<td>1.1</td>
<td>1.0 ± 0.06</td>
</tr>
<tr>
<td>Gd</td>
<td>1.77</td>
<td>1.09</td>
<td>3.1</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>1.24</td>
<td>1.36</td>
<td>1.14</td>
<td>1.10 ± 0.03</td>
</tr>
<tr>
<td>(m_{recycled LCC}/m_{BCC})</td>
<td>2.6</td>
<td>2.0</td>
<td>1.9</td>
<td>2.9 ± 1.1/0.9</td>
</tr>
</tbody>
</table>

Note: The estimates of Rudnick and Gao (2003) are listed for comparison. The uncertainties in the estimates from this work are at the 95% confidence level. The uncertainties in the upper continental crust (UCC) values recommended by Rudnick and Gao (2003) are 1σ standard deviation. MCC—middle continental crust; LCC—lower continental crust; BCC—bulk continental crust. m_{recycled LCC}/m_{BCC}—mass proportion of recycled LCC relative to present-day continental crust. JS13—Arc delaminants from Jagoutz and Schmidt (2013), K14—Talkeetna arc lower crustal cumulates from Kelemen et al. (2014), RG03—LCC from Rudnick and Gao (2003). *Mass proportions of the UCC, MCC, and LCC are from Huang et al. (2013). †Concentrations given in ppm by weight. **Means of granulite facies samples with Mg# > 50 and SiO2 < 54%.
(1) Arc lower crustal delaminates. Jagoutz and Schmidt (2013) calculated the composition of missing negatively buoyant cumulates from the crustal section of the Kohistan arc using a major element mass balance approach.

(2) Arc lower crustal cumulates. Kelemen et al. (2014) calculated the average composition of Talkeetna arc high density lower crustal cumulates that may be subject to foundering.

(3) Mafic LCC granulites. We estimate the Sm-Eu-Gd composition of recycled lower crust based on the average compositions of granulates with Mg# > 50 (Mg# = molar ratio of Mg to Mg + Fe) and SiO2 < 54% (double filter applied, as described here), which limits the recycled component to mafic compositions. The density of these mafic granulites, with an average SiO2 and Mg# of 48% and 64, respectively, can increase by ~10% during eclogitization (Austrheim, 1987) and exceed that of the underlying mantle (Krystopowicz and Currie, 2013). Although high-Mg# granulites, on average, have more positive Eu anomalies (Fig. 2), this is counterbalanced by the fact that high-Mg# granulites have low average Eu concentrations (Fig. 2).

(4) We also considered the LCC composition of Rudnick and Gao (2003) as an end member scenario.

The mass of recycled LCC is calculated using mass conservation equations for Sm-Eu-Gd (i.e., the Eu/Eu* in modern BCC + recycled LCC = bulk juvenile crust) (Appendix DR1). Using the Sm-Eu-Gd compositions for the BCC estimated in this work, we calculated the mass of the recycled LCC to be at least 2.9±0.1 (95% confidence) times the mass of the modern continental crust (Table 1; and Fig. 3). The results are not significantly different whether using the recycled lower crust compositions of arc cumulates (Jagoutz and Schmidt, 2013; Kelemen et al., 2014) or the Rudnick and Gao (2003) LCC (Fig. 3). Such consistency is not surprising given the anti-correlation between Eu/Eu* and Eu concentration in various estimates of the recycled LCC (Table 1), similar to the observation in granulites (Fig. 2). This trade-off between Eu/Eu* and Eu concentration makes the model relatively insensitive to the type of samples one chooses to calculate the composition of the recycled LCC. Our model is sensitive to the composition of BCC, which is subject to the uncertainties in sampling of deep crust. However, we show in Appendix DR1 that the BCC Eu/Eu* is insensitive to the greatest unknown; i.e., the LCC composition.

The recycled LCC/BCC mass fraction required by our results over Earth history is within uncertainty of most previous estimates, all but one of which are based on regional case studies. Using Eu/Eu* and Sr/Nd, Gao et al. (1998) estimated 1–2 crustal masses (37–82 km) of LCC were recycled in central east China. In the Mesozoic Sierra Nevada (California, USA) continental arc, 60%–75% of the original juvenile basalt (i.e., 1.5–3.0 crustal masses) is estimated to have been removed from the arc lower crust (Lee et al., 2007). This same ratio calculated by Jagoutz and Schmidt (2013) for the Kohistan arc ranges from 1.3 to 2.4 crustal masses.

The composition of the recycled LCC is difficult to assess except that these components may be denser than bulk crust, and possibly mantle peridotite (a density greater than peridotite is not a precondition for recycling, as mafic granulites may transform to high-density eclogite upon subduction or during crustal thickening), given their mafic to ultramafic bulk compositions. We therefore used four different lower crustal compositional estimates as candidates for the recycled lower crust (Table 1):
A somewhat lower estimate of recycled lower crust (25%–60% by mass) foundering of arc lower crust, which translates into > 0.3–1.5 modern crustal masses) was obtained by Plank (2005) using Th/La systematics of modern arcs and average continental crust composition. However, as she pointed out, this range is a minimum estimate.

The recycled LCC mass (~6 × 10^23 kg) may form a significant reservoir within the mantle. It has a positive Eu anomaly and low 306Pb/204Pb (e.g., Kramers and Tolstikhin, 1997), unradiogenic Sr and Nd isotopes, and radiogenic Os isotopes (e.g., Lee, 2014). Average ocean island basalts (OIBs) also have a bulk positive Eu anomaly (Fig. 4A), which correlates negatively with 206Pb/204Pb (Fig. 4B). This negative correlation may reflect mixing between mantle components and recycled LCC with positive Eu anomalies and low 206Pb/204Pb. Recycled LCC has been suggested to explain the geochemical characteristics of EM I type (enriched mantle I) OIB, typified by Kerguelen Plateau samples (e.g., Frey et al., 2002), which show pronounced positive Eu anomalies (mean Eu/Eu* = 1.12) and unradiogenic Pb isotopes (mean 206Pb/204Pb = 18.3). The recycled LCC, together with the modern continental crust, may balance the depleted mantle in the Sr and Nd isotope systems if the recycling occurred relatively early in Earth’s history.

**CONCLUDING REMARKS**

Using available REE data for upper, middle, and lower crustal samples, we show that the bulk continental crust has a significant negative Eu anomaly (Eu/Eu* = 0.82 ± 0.04, 95% confidence), a result consistent with most previous estimates of Eu/Eu* in the continental crust. Assuming that the original crust extracted from the mantle has no Eu anomaly, recycling of Eu-enriched LCC (mass proportion, m_{recycled LCC} / m_{BCC} of 2.9_{-1.9}^{+1.9} 95% confidence) is required to account for the Eu deficit.

These findings affirm the important roles that intra-crustal differentiation and lower crustal recycling play in the formation and evolution of the continental crust. Moreover, they characterize the mass and composition of a component in the mantle (which could be spatially dispersed or concentrated) that plays a significant role in the chemical budget of the bulk silicate Earth. Consequently, models of growth of the continental crust (mass versus time) must consider that the total original crustal mass fraction could be a factor of greater than the present mass of continental crust.

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