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Calcium isotope fractionation during melt immiscibility and carbonatite petrogenesis

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Stable calcium isotopes have been used to suggest that subducted marine carbonates are frequently involved in the formation of carbonatites. Significant Ca isotope fractionations during carbonatite petrogenesis, however, could lead to a dramatically different picture. We present Ca isotope data for (i) coexisting (immiscible) carbonatite and silicate melts from high temperature centrifuging piston cylinder experiments, (ii) primary apatite and calcite/dolomite from natural carbonatites, and (iii) *ab initio* estimates for equilibrium Ca isotope partitioning in calcite, dolomite, and ankerite. Carbonatitic melts have lower δ^{44} Ca than their conjugate silicate melts, with an equilibrium fractionation factor [1000ln α (1000K)] of -0.21 ± 0.06 (tSE). We develop a quantitative four stage model for carbonatite petrogenesis (partial melting followed

by fractional crystallisation, carbonatite-silicate melt immiscibility, and calcite/apatite accumulation) that fully explains our natural data (average $\delta^{44}Ca_{BSE}$ of $-0.30 \pm 0.03 \ \%$) and those from recent studies, without requiring isotopic contributions from recycled marine carbonates. Our results suggest that lighter isotopes of similarly bound cations (*e.g.*, Mg, Fe, Sr, Ba, Zn) should be preferentially incorporated into carbonatitic melts and that calciocarbonatite formation involves melt immiscibility after differentiation of mantle-derived alkaline CO₂-bearing silicate melts.

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Introduction

Abstract

Carbonatites are rare igneous rocks that contain large amounts (>50 %) of carbonate minerals and represent the most CO₂-rich magmas in the geologic record (Yaxley et al., 2022). Although they provide a majority of the world's Rare Earth Elements (REE) and are intimately linked to the deep Earth carbon cycle, their principal formation mechanism(s) are still debated. Possible models of carbonatite formation include (i) exsolution from moderately-to-strongly evolved CO2-rich alkaline silicate melts [i.e. carbonatite-silicate melt immiscibility (Berkesi et al., 2023; Berndt and Klemme, 2022; Brooker and Kjarsgaard, 2011; Guzmics et al., 2015; Weidendorfer et al., 2017)], or (ii) direct partial melting of carbonate-bearing mantle rocks (Harmer and Gittins, 1998; Yaxley and Brey, 2004). There are also significant debates regarding the role of carbonatite magmas within the carbon cycle, with some recent stable isotope studies suggesting that carbonatites may represent the return of subducted marine carbonates back to the surface (Hulett et al., 2016; Amsellem et al., 2020; Banerjee *et al.*, 2021). In contrast, δ^{13} C in most carbonatites overlap with those of peridotitic diamonds (Stachel et al., 2022). The carbon in these magmas is thus mantle-derived or, if recycled, could result from a ~4:1 mix between carbonates

and organic carbon sources, rendering it indistinguishable from primordial carbon.

Given the uncertainties surrounding the interpretation of δ^{13} C data, stable Ca isotopes have recently gained popularity as a potential tool for tracing subducted marine carbonates in mantle-derived magmas. Their use as a recycled carbonate tracer depends on δ^{44} Ca_{BSE} in marine carbonates (Phanerozoic average of -0.35 ‰) being typically lower than found in mantle rocks [≈0 ‰ (see Antonelli and Simon, 2020)]. Previous studies exploring δ^{44} Ca in carbonatites argue that subducted marine carbonates occur in the sources of essentially all (Amsellem et al., 2020), some (Banerjee et al., 2021), or no (Sun et al., 2021) carbonatites. Amsellem et al. (2020) found ubiquitously low δ^{44} Ca_{BSE} in carbonatites (average of -0.7 ‰), while the two more recent studies found similar average values of approximately -0.2 ‰ (using two different analytical approaches), and argue that the data of Amsellem et al. (2020) were affected by analytical issues (Banerjee et al., 2021; Sun et al., 2021). Nevertheless, the latter two studies disagree on the potential effects of magmatic processes (Supplementary Information) and find significantly different total ranges for carbonatite δ^{44} Ca, where lower values [found in Banerjee *et al.* (2021)] are argued to result from subducted marine carbonates.

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Unlike radiogenic isotope tracers, stable Ca isotope ratios may be significantly affected by magmatic processes that are often poorly constrained and lead to large uncertainties regarding their application as source tracers. To constrain the δ^{44} Ca of carbonatites and their parental melts, we explore δ^{44} Ca variations from experimental, natural, and theoretical perspectives. We first demonstrate that conjugate carbonatite-silicate melts in high pressure, high temperature experiments have significant δ^{44} Ca differences at equilibrium. We then combine these results with novel *ab initio* and empirical constraints to develop quantitative models for Ca isotope fractionation during carbonatite petrogenesis.

Calcium Isotope Fractionation During Carbonatite-Silicate Melt Immiscibility

Although mineral-mineral and mineral-melt equilibrium Ca isotope fractionations are relatively well constrained from both ab initio and empirical investigations (Antonelli and Simon, 2020), Ca isotope fractionation between immiscible melts has not been explored. Constraining this process is of the utmost importance for carbonatite petrogenesis, as direct melts of carbonate-bearing peridotites in the upper mantle are dolomitic and cannot evolve to the calciocarbonatite melt compositions (Lee and Wyllie, 1998) most frequently observed and readily unmixed from silicate melts (Lee and Wyllie, 1998; Brooker and Kjarsgaard, 2011; Martin et al., 2013; Guzmics et al., 2015). To better understand Ca isotope fractionation between immiscible melts, we equilibrated conjugate carbonatite and nephelinitic silicate melts in a centrifuging piston cylinder apparatus at ETH Zurich (Schmidt et al., 2006). This apparatus allows for near-perfect physical separation of two immiscible melts (Figs. 1a, S-1). We conducted experiments at two different temperatures (800 °C and 1170 °C) and also explored the effects of variable pressure (0.3, 0.8, and ~1.2 GPa) in the higher temperature experiments (Supplementary Information). After equilibration and centrifugation, experimental run products were quenched and sectioned lengthwise to allow for both destructive (Ca isotope analyses by TIMS) and non-destructive analyses (e.g., EPMA; Table S-1) of the two melts.

We find that carbonatitic melts always have lower $\delta^{44}\text{Ca}$ than coexisting silicate melts, with the 800 °C (0.8 GPa) experiment yielding $\Delta^{44}Ca_{carb-sil}$ of -0.19 ± 0.06 ‰ and the three 1170 °C experiments giving statistically indistinguishable results, regardless of pressure ($\Delta^{44}Ca_{carb-sil}$ between -0.08 ‰ and -0.12 ‰; Fig. 1b, Table S-2). Several independent lines of evidence suggest that our experiments achieved Ca isotope equilibrium. Along with the high Ca diffusivities in silicate and carbonatitic melts relative to the length scales and durations of our experiments, the equilibrium fractionation factor $[1000 \ln \alpha;$ Fig. 1c] calculated from the lower T experiment (-0.22 at 1000K, using a 10⁶/T² law), is strikingly similar to that derived from the average of the higher T experiments (-0.21 at 1000K; Fig. S2). The three different 1170 °C experiments also represent significant variations in the Ca fraction [F(Ca)] in carbonatitic vs. silicate melts, yet they yield statistically indistinguishable $\Delta^{44}Ca_{carb-sil}$ suggesting closed system equilibrium fractionation (Fig. S-3). Our finding that carbonatitic melts have lower δ^{44} Ca than coexisting silicate melts is consistent with predictions for a weaker bonding environment for Ca in ionic carbonatitic melts vs. predominantly covalent silicate melts (see Genge et al., 1995).



Figure 1 Experimental results of carbonatite-silicate melt immiscibility. (a) Back scattered electron image of an exemplary experimental run product (GS8-28) in a welded Au₈₀Pd₂₀ capsule where the lower density carbonatite melt (dark grey, now quench minerals) migrates to the gravitational top, while the silicate melt (now silicate glass), accumulates at the bottom. (b) Stable Ca isotope results. (c) Estimates of Ca isotope fractionation factor between conjugate carbonatite and silicate melts. Error bars represent 20 internal uncertainty based on multiple measurements of USGS standards W-2a and COQ-1, where tSE (the t standard error, where 't' is the critical value for a 95% confidence interval in a t-distribution) and 2 s.e. uncertainties both yield similar estimates of ±0.04 ‰ for $\delta^{44}\text{Ca}$ and ±0.06 ‰ for $\Delta^{44}\text{Ca}$ (see Supplementary Information). These uncertainty estimates are also similar to our calculated measurement repeatability (±0.04‰, based on the 22 samples measured in duplicate in this work). Long term external reproducibility, which is most important for comparisons of our natural $\delta^{44}\text{Ca}$ data (Fig. 2b) with previous/future work is estimated as ± 0.12 ‰ (2 s.d.) based on 21 measurements of W-2a performed over three years.

Natural and Theoretical Constraints on δ^{44} Ca in Carbonatite Minerals

Most carbonatites represent cumulate rocks (Yaxley *et al.*, 2022). In calciocarbonatites, the Ca budget is dominated by calcite (plus minor apatite \pm diopside), whereas magnesiocarbonatites and ferrocarbonatites are dominated by dolomite and ankerite, respectively. We therefore present novel *ab initio* predictions (PBE functionals) for equilibrium Ca isotope fractionation

between these minerals using the Quantum Espresso software package, following established methods (Antonelli *et al.*, 2019, 2023b) (Supplementary Information; Fig. S-4). At isotopic equilibrium, we find that calcite is slightly lighter than diopside (by -0.06 % at 1000K) and slightly heavier than fluorapatite (by +0.05% at 1000K), in agreement with previous predictions based on LDA functionals (Xiao *et al.*, 2022). Dolomite and ankerite both have lower 1000ln β values, similar to those of fluorapatite (Fig. 2a, Table 1).

To better constrain δ^{44} Ca in natural carbonatite minerals, we extracted pristine calcite (or dolomite) and apatite crystals from seven calcio- and one magnesiocarbonatite that have equilibrium calcite-apatite REE distributions reflecting primary magmatic signatures (in all but one sample), characterised in



Figure 2 Ab initio estimates for equilibrium between various minerals and summary of our δ^{44} Ca measurements in calcite and apatite from natural carbonatites. (a) Predicted inter-mineral fractionation factors (1000ln $\alpha_{mineral-calcite}$) vs. temperature. (b) δ^{44} Ca data for pristine apatite and calcite separated from our carbonatite samples. In panel (b) 2σ uncertainties for δ^{44} Ca are the same as described in the caption of Figure 1.

previous work (Sartori *et al.*, 2023) (Tables S-3, S-4). We chose these minerals to test whether equilibrium was attained between the most abundant Ca minerals in carbonatites, or whether kinetic effects could be leading to some of the observed δ^{44} Ca variability. Along with δ^{44} Ca analyses by TIMS, we also measured radiogenic ⁴⁰Ca abundances in several samples (and carbonatite standard COQ-1; Table S-5), all of which yield ε_{Ca} within error of the BSE value (Antonelli *et al.*, 2021).

We find a relatively restricted δ^{44} Ca_{BSE} range in our calcite separates [-0.33 to -0.23 ‰, average of -0.29 ± 0.03 ‰ (tSE, n = 8)] and slightly larger range (but similar average) in our apatite separates [-0.45 to -0.22 ‰, average of -0.31 ± 0.07 ‰ (tSE, n = 7); Fig. 2b, Table S-2]. In most calciocarbonatite samples, apatite is marginally lighter than calcite, consistent with isotopic equilibrium at temperatures above ~700 °C. One calciocarbonatite sample (X-1513), however, has Δ^{44} Ca_{apatite-calcite} of -0.12 ± 0.06 ‰, potentially suggesting lower temperature inter-mineral equilibration (e.g., <650 °C for a calcite-apatite difference >0.06 %). Dolomite and apatite from our magnesiocarbonatite sample (MC-1901) are also consistent with inter-mineral isotopic equilibrium and have δ^{44} Ca indistinguishable from those of our calciocarbonatites. Overall, our mineral δ^{44} Ca analyses yield results that are slightly lower (Fig. 3e; Supplementary Information, Supplementary Data-1) but generally similar to whole rock calciocarbonatite analyses from recent studies (Banerjee et al., 2021; Sun et al., 2021). Previous work exploring carbonatite calcite separates, however, found a larger range in δ^{44} Ca_{BSE} with a slightly higher average [-0.10 ± 0.08 ‰ (tSE, n = 17)] than found in calciocarbonatite whole rocks (Banerjee et al., 2021), but the primary magmatic nature of the calcite in this data set was not investigated. Despite their subtle differences, all these values are significantly different from the earlier report of ubiquitously low $\delta^{44}Ca_{BSE}$ [average of -0.69 ± 0.04 ‰ (tSE, n = 50)] in carbonatite whole rocks (Amsellem et al., 2020). Additional discussion of our data in the context of previous isotopic studies can be found in the Supplementary Information.

Four Stage Carbonatite Petrogenesis Model

To evaluate whether incorporation of recycled marine carbonates is required by the δ^{44} Ca of carbonatites, we must first evaluate Ca isotope fractionations related to the two foremost models for carbonatite petrogenesis: (i) differentiation of an alkaline CO₂-rich silicate melt, resulting in carbonatite-silicate melt immiscibility, and (ii) direct formation of carbonatitic melt through partial melting of carbonate-bearing mantle. Given that the latter model (explored in the Supplementary Information; Fig. S-5) is unable to produce calcic carbonatitic melts (Lee and Wyllie, 1998), we focus our main discussion on the first model (Fig. 3). This model consists of four major steps: (i) low degree partial melting of carbon-bearing mantle to form a primitive CO2rich alkaline mafic melt, (ii) fractional crystallisation (mainly of olivine and clinopyroxene) to enrich the differentiated melt in alkalis and reach the carbonatite-silicate melt miscibility gap, (iii) carbonatite-silicate melt immiscibility in the mid-to-lower crust, and (iv) fractionation of calcite (and apatite) from carbonatitic melts to form intrusive (cumulate) calciocarbonatites in the upper crust.

Partial melting of carbon-bearing garnet lherzolite to form CO₂-rich ultramafic alkaline melts (Step 1) was explored in a recent study (Antonelli *et al.*, 2023a). Using the fractionation factors and assumptions from that study, we predict δ^{44} Ca shifts of -0.13 % to -0.18 % (at 1400–1300 °C) for the partial melts.

Table 1 Ab initio results for Ca isotope 1000lnβ factors (⁴⁴Ca/⁴⁰Ca) in calcite, dolomite, ankerite, diopside, and fluorapatite, along with empirical estimates for melts used in our carbonatite petrogenesis models (preferred values in bold).

	Reduced partition function ratios, 1000ln(^{44/40} β)									
	From phonons		From force constants							
	PBE - phonon s.f. 1.06		PBE - scale factor 1.06 ²		LDA - unscaled		Best estimate		Moon bond	
	298.15K	1000K	298.15K	1000K	298.15K	1000K	1000K	Coord.	length (Å)	Reference
Carbonate Minerals Calcite (primitive) Calcite (rhombohedral, doubled cell) Dolomite [CaMg(CO ₃) ₂] ¹ Ankerite [CaFe(CO ₃) ₂] ²	13.774 - 12.890 12.876	1.275 - 1.195 1.191	- 14.027 - -	- 1.254 - -	- 13.869 - -	- 1.240 - -	- - -	- 6 6 6	- 2.3847 2.4026 2.3942	This study This study This study This study
Other Minerals Diopside ³ Fluorapatite ⁴	- 13.101	- 1.208	14.653 -	1.311 -	-	-	- -	8 6	2.5290 2.4205	Antonelli <i>et al</i> . (2019) Antonelli <i>et al</i> . (2019)
Melts (empirical estimates) silicate melts Carbonatitic melt (low RPFR) Carbonatitic melt (high RPFR)	- - -	- - -	- - -	- - -	- - -	- - -	1.144 0.929 1.037	- - -	- - -	Antonelli <i>et al</i> . (2023a) This study This study

PBE/GBRV1.4 40-200Ry phonon-based two phonon wave vectors
PBE/GBRV1.4(Ca,C,O)-PSLibrary(Fe) 90-1080Ry Hubbard correction U=3.5 eV phonon-based two phonon wave vectors
Full C2/c cell with doubled c
Ca1, *7-10th Ca-O neighbours at 2.84Å; Ca2, 5O+1F, and *7th Ca-O bond at 2.80Å





Figure 3 Calcium isotope evolution during the various stages of carbonatite petrogenesis compared to data for carbonatites from this and previous studies. (a) Fractionation factors for the four stages: partial melting (Step 1), melt differentiation by crystal fractionation (Step 2), carbonatite-silicate melt immiscibility (Step 3), and accumulation of calcite and apatite (Step 4). Partial melting results (Step 1) come from Antonelli *et al.* (2023a) and encompass the largest and smallest predicted fractionations during melting of carbon-bearing garnet lherzolite at 1400–1300 °C. (b) Clinopyroxene fractionation from CO₂-rich alkaline mafic melt (Step 2), showing the two possible paths (nephelinite "path 1" and syenite "path 2") leading to two-liquid immiscibility. (c) Carbonatite-silicate melt immiscibility (Step 3). (d) Calcite and apatite accumulation from a carbonatitic melt (Step 4). Shaded regions in (b-d) represent predicted F(Ca) values. In (e) we show the model results from Step 1 to 4 and compare them with natural carbonatite data (Supplementary Information).

These values agree well with the average $\delta^{44}Ca_{BSE}$ composition of kimberlites $[-0.16 \pm 0.03 \%$ (Antonelli *et al.*, 2023a)], which are likely to be similar to the melts generated in the first stages of carbonatite formation. Fractionation of minerals from this melt (Step 2) to reach carbonatite-silicate two-melt immiscibility can occur via two different pathways, entailing different amounts of fractional crystallisation, most importantly of clinopyroxene (Supplementary Information). We predict δ^{44} Ca shifts of -0.01 %to -0.02 ‰ for CO2-rich nephelinitic melts ('path 1') and of -0.03 ‰ to -0.12 ‰ for CO₂-rich foid-syenite melts ('path 2'), at temperatures of 1300-1000 °C (Fig. 3b). Carbonatite-silicate melt immiscibility (Step 3) is then assumed to occur at 1100 -1000 °C and leads to δ^{44} Ca shifts of -0.09 to -0.12 ‰ for carbonatitic melts (Fig. 3c) and relatively little change in the δ^{44} Ca of the conjugate silicate melts (<+0.03 ‰, because more than ~80 % of the total Ca remains in the silicate melts). The final stage, accumulation of calcite and apatite from carbonatitic melt at 1000-800 °C to form an intrusive calciocarbonatite body (Step 4), leads to slight positive shifts in the accumulated minerals (Fig. 3d) relative to the carbonatite melt (ranging from 0.00 to +0.11 ‰, depending on the Ca fraction remaining in the melt). This final positive shift in the carbonatite cumulates is of a similar magnitude to the negative shift induced by melt immiscibility, and may explain similar δ^{44} Ca in some carbonatites and conjugate silicates (Sun et al., 2021).

Summing the maximum and minimum estimates from the four sequential stages in our model (described in the Supplementary Information; Fig. 3e, Supplementary Data-2) leads to calciocarbonatite cumulates with estimated $\delta^{44}Ca_{BSE}$ ranging between -0.32 % and -0.12 %, for those derived from nephelinites ('path 1'), and from -0.43 % to -0.14 %, for those derived from foid-syenites ('path 2'). This four step model can also produce magnesiocarbonatites (once enough calcite precipitates to saturate dolomite), and we predict that these magnesiocarbonatites cumulates would have lower δ^{44} Ca (by at least -0.1 %) than genetically-associated calciocarbonatite cumulates (Supplementary Information), due to the lower 1000ln β of dolomite (relative to calcite) and to open system processes (*i.e.* melt segregation after calcite fractionation). After the final accumulation of calcite (or dolomite) and apatite, sub-solidus equilibration may further shift apatite δ^{44} Ca to lower values (*e.g.*, X-1513), but this is unlikely to change the δ^{44} Ca of calcite (given that apatite is a relatively minor phase) and cannot change the δ^{44} Ca of whole rocks.

Discussion

As shown in Figure 3e, our four stage carbonatite petrogenesis model accounts for the δ^{44} Ca variability observed in our samples and in recent previous studies (Banerjee *et al.*, 2021; Sun *et al.*, 2021) without requiring any variability in mantle source compositions (*i.e.* δ^{44} Ca_{BSE} \approx 0 ‰). Ca isotope ratios lower than predicted in our models (*e.g.*, 3 samples with δ^{44} Ca_{BSE} down to -0.53 ± 0.06 ‰) have only been found in magnesio- and ferrocarbonatites (Banerjee *et al.*, 2021). Given that we predict lower δ^{44} Ca (by <-0.1‰; Supplementary Information) in magnesiocarbonatite cumulates (relative to calciocarbonatite cumulates) these values are also well explained by our four stage model.

Our two stage model for direct partial melting of carbonated garnet lherzolite (which cannot produce calciocarbonatitic melts; Supplementary Information) followed by dolomite accumulation, yields δ^{44} Ca_{BSE} ranging from -0.41 ‰ to -0.05 ‰ (assuming 1-5 wt. % carbonates in the mantle, with BSE-like δ^{44} Ca) at temperatures of 1050–950 °C for partial melting (Foley and Pintér, 2018) and of 1000-800 °C for dolomite accumulation (Fig. S-5). This predicted range also agrees well with δ^{44} Ca in magnesiocarbonatites (Banerjee *et al.*, 2021). Using δ^{44} Ca_{BSE} significantly lower than BSE for the carbonates [e.g., -0.35 ‰, Phanerozoic average marine carbonates, see Antonelli and Simon (2020) and references therein], however, yields carbonatite compositions that are mostly lower than observed in nature (Fig. S-5). Thus, if recycled marine carbonates are involved in the sources of some magnesiocarbonatites, they most likely have $\delta^{44}Ca_{BSE} \approx 0$ ‰ [the average value of Precambrian carbonates (Blättler and Higgins, 2017)] and are thus isotopically indistinguishable from the mantle.

Ca isotope ratios higher than predicted in our models, on the other hand, could result from several processes, including late stage alteration (Mitchell and Gittins, 2022), and it is well established that ferrocarbonatite formation involves secondary alteration. Given that δ^{44} Ca in ferrocarbonatites range to slightly higher values than other types (Fig. 3e), this suggests that carbohydrothermal alteration is a mechanism that may potentially push δ^{44} Ca to more positive values (Supplementary Information).

Conclusions

We experimentally determined that carbonatite-silicate melt immiscibility leads to significantly lower δ^{44} Ca in carbonatitic melts [1000ln α of -0.21 ± 0.06 (tSE, n = 4) at 1000K] and does not produce particularly high δ^{44} Ca in conjugate silicates. Our finding of lower δ^{44} Ca in carbonatitic *vs.* silicate melts at equilibrium is consistent with empirical predictions for Mg and Fe isotopes (Johnson *et al.*, 2010; Li *et al.*, 2016) and indicates a weaker Ca bonding environment in carbonatitic melts compared to silicate melts. In turn, this suggests that lighter isotopes of other similarly bound and coordinated cations (*e.g.*, Mg, Fe, Sr, Ba, Zn) should also be preferentially partitioned into carbonatitic melts during liquid immiscibility.

Although direct melting of carbonate-bearing mantle with $\delta^{44}Ca_{BSE} \approx 0$ can produce $\delta^{44}Ca$ values that agree with natural magnesiocarbonatite data, without requiring melt immiscibility, this process cannot produce calciocarbonatites (Lee and Wyllie, 1998). Building on our best current understanding of carbonatite petrogenesis (Weidendorfer and Asimow, 2022; Yaxley et al., 2022; Berkesi et al., 2023; Sartori and Schmidt, 2023), we combined our experimental constraints on melt immiscibility with ab initio and empirical predictions to develop a four stage Ca isotope fractionation model that successfully explains natural δ^{44} Ca variations in essentially all primary carbonatites, including those from this study. Although subducted marine carbonates have been invoked to explain δ^{44} Ca in carbonatites (Amsellem et al., 2020; Banerjee et al., 2021), we have shown that magmatic processes can generate the entire range of observed δ^{44} Ca, without requiring any mantle-source variations. Carbonatitic melts, therefore, do not necessarily require the isotopic signature of subducted marine carbonates in their mantle sources at any point in Earth history.

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Additional Information

Supplementary Information accompanies this letter at https:// www.geochemicalperspectivesletters.org/article2338.



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