Ca isotope systematics of carbonatites: Insights into carbonatite source and evolution

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Abstract

Carbonatite, an unusual carbonate-rich igneous rock, is known to be sourced from the mantle which provides insights into mantle-to-crust carbon transfer. To constrain further the Ca isotopic composition of carbonatites, investigate the behaviour of Ca isotopes during their evolution, and constrain whether recycled carbonates are involved in their source regions, we report $\delta^{44/42}\text{Ca}$ for 47 worldwide carbonatite and associated silicate rocks using a refined analytical protocol. Our results show that primary carbonatite and associated silicate rocks are rather homogeneous in Ca isotope compositions that are comparable to $\delta^{44/42}\text{Ca}$ values of basalts, while non-primary carbonatites show detectable $\delta^{44/42}\text{Ca}$ variations that are correlated to $\delta^{13}\text{C}$ values. Our finding suggests that Ca isotopes fractionate during late stages of carbonatite evolution, making it a useful tool in the study of carbonatite evolution. The finding also implies that carbonatite is sourced from a mantle source without requiring the involvement of recycled carbonates.

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Introduction

Carbonatite is an exotic igneous rock formed predominantly of carbonates and an important host or source of critical metals, including REE and Nb (Woolley and Kempe, 1989; Sun *et al.*, 2013; Verplanck *et al.*, 2016). It is closely related to the deep carbon cycle which can provide insights into mantle-to-crust carbon transfer. Consensus has been made that carbonatite melts are derived from the carbonate-bearing mantle (Dasgupta *et al.*, 2007; Bell and Simonetti, 2010). However, whether the carbon generating the carbonatite was originally sourced from the primitive mantle or a recycled component remains debated (Barker, 1996; Hoernle *et al.*, 2002; Bell and Simonetti, 2010). C and O isotopes are the most direct tracers for recycled carbonates as carbon and oxygen are the major elements in carbonates. However, their primary isotope signatures tend to be fractionated or affected by late stage fluids and magma degassing (Deines, 1989).

Ca is the most common and abundant metal in carbonatites (Woolley and Kempe, 1989). Ca isotopes have emerged as a novel tool for tracing recycled carbonates in the mantle (Huang *et al.*, 2011; Liu *et al.*, 2017). This is because, 1) Ca isotope compositions of surface carbonate and the mantle peridotite are distinct (Fantle and Tipper, 2014; Kang *et al.*, 2017), 2) Ca abundance of the former is nearly one order of magnitude higher than that of the latter, and 3) Ca isotope fractionation is negligible during (basaltic) magmatic differentiation (Zhang *et al.*, 2018; Chen *et al.*, 2019).

Previous studies indicate the potential of Ca isotopes in mantle-derived rocks for tracing recycled carbonates but the Ca isotope composition of carbonatites has remained poorly constrained, and the reported $\delta^{44/42}\text{Ca}$ values are inconsistent among different groups (Amini *et al.*, 2009; Maloney, 2018; Banerjee and Chakrabarti, 2019; Amsellem *et al.*, 2020). Here, based on a refined analytical protocol, the Ca isotope composition of worldwide carbonatites and associated silicate rocks is

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investigated, Ca isotope behaviour during carbonatite evolution is studied, and the role of recycled carbonates in producing carbonatite is assessed.

Basalt-like Ca Isotope Compositions for Carbonatites

Previously reported Ca isotope data of carbonatites have significant $\delta^{44/42}\text{Ca}$ variations and the values are inconsistent among different groups (Fig. S-1). The scatter may partly be related to inter-laboratory bias. Carbonatites are unusual rocks (extremely enriched in critical metals such as rare earth elements), and no analytical method developed specifically for this kind of sample has been reported so far. To ensure the accuracy of Ca isotope measurements using the SSB-MC-ICPMS method, much effort has been spent on methodology in this study. These include: (1) detailed investigation on effects of matrix elements, particularly REE, on Ca isotope analysis, which were largely ignored previously but turn out to be serious, (2) a new protocol of column chemistry developed based on cation ion exchange resin (with higher stability than the DGA extraction resin that is often used), where all possible matrix elements are examined to be sure of being eliminated effectively (to a level of Element/Ca < 0.0001). Any other possible analytical pitfalls, including a “column effect”, Sr effect or “column fractionation”, were avoided (see details of analytical method in SI), (3) inter-laboratory comparison was made by measuring eight standard reference materials and four carbonatite samples both performed in CAGS lab using this rigorous method and performed in CUGB lab using a DS-TIMS method reported by He *et al.* (2017), where all measured $\delta^{44/42}\text{Ca}$ values are consistent within analytical precision (Figs. S-1, S-2, Tables S-1, S-2).

Using the refined Ca isotope analytical method, we analysed 47 samples of carbonatites and associated silicate rocks from 15 occurrences from Canada, America, East Africa, Russia, Mongolia, Brazil and China (see details of sample information and their geological background in SI), along with analyses of their major elements and C-O isotope compositions (see analytical methods in SI). The results of $\delta^{44/42}\text{Ca}$ fall within the range previously reported (Fig. S-1). To avoid any possible inter-laboratory bias and make a better estimate of Ca isotope composition of carbonatites, only those previously reported data sets with their accuracies demonstrated by carbonatite standards/samples and with the analytical precision similar or better than ours are used. The available data (Table S-1) give a range of 0.26 ‰ to 0.47 ‰ for $\delta^{44/42}\text{Ca}$ in carbonatites, with most clustering around 0.35 ‰ (Figs. 1, S-3, Table S-1). Notably, primary carbonatites and associated silicate rocks are homogeneous in Ca isotope composition with an average of 0.35 ± 0.01 ‰ (2 s.e., $n = 30$) (Fig. 1), close to those of worldwide basalts (average $\delta^{44/42}\text{Ca} = 0.37 \pm 0.01$ ‰, 2 s.e., $n = 84$); while non-primary carbonatites have detectable $\delta^{44/42}\text{Ca}$ variations (Figs. 1, S-3). This estimate is significantly different to that made by Amsellem *et al.* (2020), and accordingly leads to a different understanding on the nature of the carbonatite source as discussed below.

Ca Isotope Fractionation during Carbonatite Evolution and Implications for Carbonatite Petrogenesis

The processes relevant to the formation of carbonatite may involve partial melting of the mantle, magmatic differentiation, magmatic-hydrothermal processes and secondary hydrothermal alteration. Understanding Ca isotope behaviour during these

Figure 1 Comparison of $\delta^{44/42}\text{Ca}$ values between carbonatites, basalts, mantle, and sedimentary carbonates. The dashed lines represent average $\delta^{44/42}\text{Ca}$ values of carbonatites and basalts, respectively. Data sources are from this study and references (see Tables S-1, S-2; Amini *et al.*, 2009; Simon and DePaolo, 2010; Fantle and Tipper, 2014; Jacobson *et al.*, 2015; Blättler and Higgins, 2017; Kang *et al.*, 2017; Liu *et al.*, 2017; Zhang *et al.*, 2018; Zhu *et al.*, 2018, 2020; Chen *et al.*, 2019).

processes is fundamental for tracing the carbonatite source using Ca isotopes.

The extent of Ca isotope fractionation during carbonatite evolution is investigated through a suite of carbonatite and associated silicate rocks from the Belaya Zima complex, a typical “nephelinite-clan carbonatite”, the most common carbonatite group worldwide (see details in SI). Associated rocks include early magmatic alkaline silicate rocks and primary calcite carbonatites (both containing melt inclusions) through to more evolved late magmatic-hydrothermal calcite-dolomite carbonatites and ferro-carbonatites (see descriptions in SI). The rocks of early magmatic stages show homogeneous $\delta^{44/42}\text{Ca}$ values (around 0.35 ‰), while the later stages exhibit either lower or higher $\delta^{44/42}\text{Ca}$ values (0.26 ‰ to 0.44 ‰) (Fig. 2a), suggesting that Ca isotopes fractionate insignificantly during magmatic processes but moderately during late stage magmatic-hydrothermal processes.

The extent of Ca isotope fractionation during secondary meteoric alteration is examined from Songwe carbonatite samples that have suffered variable degrees of low temperature meteoric alteration (see descriptions in SI). Although $\delta^{18}\text{O}$ values vary significantly, the $\delta^{44/42}\text{Ca}$ variation is small and falls at the edge of the range of primary carbonatite (Table S-1), implying that Ca isotope fractionation during this process is subtle.

Ca and C are normally associated in carbonatite evolution. Using coupled Ca-C stable isotope data, Ca isotope behaviour during carbonatite evolution is further assessed. In the Ca-C isotope plot, it is interesting to note that there exists a correlation between $\delta^{44/42}\text{Ca}$ and $\delta^{13}\text{C}$ for worldwide carbonatites (Fig. 2b). A “primary carbonatite field” can be defined based on the Ca-C isotope data of primary carbonatites. Most non-primary carbonatites tend to have higher $\delta^{44/42}\text{Ca}$ and $\delta^{13}\text{C}$ values, and a few tend to have lower $\delta^{44/42}\text{Ca}$ and $\delta^{13}\text{C}$ values. A $\delta^{13}\text{C}$ higher than the “mantle values” for carbonatites may result from, (1) Rayleigh fractionation processes in fluid-rich carbonatite magma, and (2) incorporation of sedimentary carbonates before or after carbonatite emplacement. The latter case, however, would result in coupled higher $\delta^{13}\text{C}$ -lower $\delta^{44/42}\text{Ca}$ data, which are not observed (Fig. 2b). Hence, the correlation between

Figure 2 Plots showing $\delta^{44/42}\text{Ca}$ variation during carbonatite evolution. (a) $\delta^{44/42}\text{Ca}$ for different types of carbonatites and associated silicate rocks from Belaya Zima complex, Russia. (b) $\delta^{44/42}\text{Ca}$ vs. $\delta^{13}\text{C}$ plot for carbonatites. See data sources in Table S-1.

$\delta^{44/42}\text{Ca}$ and $\delta^{13}\text{C}$ implies that Ca isotope variation in carbonatites is dominated by Rayleigh fractionation processes in fluid-rich carbonatite magma—a process also resulting in correlated C–O isotope variation in carbonatites (Deines, 1989).

The little $\delta^{44/42}\text{Ca}$ variation in Belaya Zima and other world-wide primary carbonatites and associated silicate rocks suggest that Ca fractionation is negligible during carbonatite magmatic differentiation, as that has been observed for basaltic magmatic differentiation (Zhang *et al.*, 2018; Chen *et al.*, 2019). This is consistent with the theoretical prediction that the equilibrium Ca isotope fractionation between Ca-dominated minerals in high temperature conditions is minimal, *e.g.*, $\Delta^{44/42}\text{Ca}_{\text{calcite-cpx}} < 0.02\text{‰}$ at a temperature over 800 °C (Wang *et al.*, 2017; Chen *et al.*, 2019). Hence, the Ca isotope signature of primary carbonatites and associated silicate rocks reflects the composition of their parental carbonatite melts, which is $\delta^{44/42}\text{Ca} = 0.35 \pm 0.01\text{‰}$ (2 s.e., $n = 30$).

Detectable Ca isotope fractionation during late stages of carbonatite evolution is likely related to the involvement of fluids. Precipitation of carbonate from the CO_2 -fluid-bearing carbonatite melt/liquid likely leads to Ca and C isotope fractionation (possibly kinetic), driving the evolved carbonatite melt/liquid isotopically heavier by Rayleigh fractionation. Ca isotopes are thus a useful tool for studying the petrogenesis of carbonatite and may further provide insights in relevant REE mineralisation with which it is normally associated. For example, Ca isotopes may help to discriminate between magmatic and magmatic-hydrothermal carbonatite, which is a critical for understanding REE mineralisation in carbonatites. It may also help to constrain the origin of late stage ankerite carbonatite (ferrocarbonatite), *i.e.* whether a primary product crystallised from the melt/liquid or a metasomatic product replacing earlier calcite-carbonatite (see details in SI).

No Requirement for Recycled Carbonate in a Carbonatite Source

The source of carbonatite has commonly believed to be carbonate-bearing, but whether the carbon is primitive or recycled surface carbonate remains controversial.

Assuming a carbonatite melt is derived from the “normal” mantle, its expected Ca isotope composition can be modelled and calculated using available equilibrium Ca isotope fractionation factors of minerals in the literature (Table S-5). The partial melting conditions are assumed to OIB-like in pressure but with a lower temperature, as the presence of CO_2 (which is required to generate carbonatite melts) may depress the solidus of peridotite by ~100–400 °C (Dasgupta *et al.*, 2007; Foley and Pintér, 2018). The results show that Ca isotope fractionation during partial melting of carbonatite melt is expected to larger than that of OIB melt by ~0.01–0.04 ‰ in $\delta^{44/42}\text{Ca}$ due to the temperature effect (Table S-5). Given average $\delta^{44/42}\text{Ca}$ values of 0.37 ‰ and 0.43 ‰ for OIB and BSE (Fig. 1 and references therein), Ca isotope fractionation during partial melting of mantle for OIB melts and carbonatite melts is $\Delta^{44/42}\text{Ca}_{\text{peridotite-OIB melt}} = 0.06\text{‰}$ and $\Delta^{44/42}\text{Ca}_{\text{peridotite-carbonatite melt}} = \sim 0.07\text{–}0.10\text{‰}$, respectively. Accordingly, the carbonatite melt derived from the normal mantle source is expected to have $\delta^{44/42}\text{Ca}$ values of ~0.33–0.36 ‰. The $\delta^{44/42}\text{Ca}$ of carbonatite melts inferred from the measured values of carbonatites (an average of $0.35 \pm 0.01\text{‰}$, 2 s.e.; Fig. 1) are in accordance with these predicted values, supporting a normal mantle source for their origin.

If carbonatites are sourced from the mantle involving recycled surface carbonates, they should have “anomalous” $\delta^{44/42}\text{Ca}$ signatures, due to the difference of $\delta^{44/42}\text{Ca}$ between mantle and surface carbonates (Fig. 1). This is observed in Cenozoic basalts from East and South China (Tengchong basalts and Zhangjiakou basalt, GSR-3) (He *et al.*, 2017; Liu *et al.*, 2017), whose sources are commonly believed to involve recycled carbonates (Li *et al.*, 2017), with $\delta^{44/42}\text{Ca}$ (0.31 ‰ on average) lower than those of “normal” global basalts (Fig. 1). The effect of recycled carbonates on the change in the Ca isotope composition of carbonatites is assessed by a simple model using a Phanerozoic carbonate component ($\text{CaO} = 40\%$, $\delta^{44/42}\text{Ca} = 0.29\text{‰}$; Fantle and Tipper, 2014) as one end member and a BSE component as another ($\text{CaO} = 3.65\%$, $\delta^{44/42}\text{Ca} = 0.43\text{‰}$; Kang *et al.*, 2017; Simon and DePaolo, 2010). The results show that involvement of the Phanerozoic carbonates would exert a

Figure 3 Expected $\delta^{44/42}\text{Ca}$ values of carbonatites originating from a primary mantle source and mantle sources involved with different fractions of (Phanerozoic) recycled carbonates. The measured $\delta^{44/42}\text{Ca}$ data for carbonatites is consistent with an origin from the primary mantle source mixed with little (<2 %) recycled carbonates. See detailed description in the main text.

significant effect on the Ca isotope compositions of carbonatite melts (Fig. 3), and that for the studied carbonatites with $\delta^{44/42}\text{Ca}$ values within analytical uncertainty, the contribution of surface carbonates to their sources, if it occurred, would be 2 % at most (Fig. 3). Incorporation of recycled carbonate in the mantle source may also result in a “mixing trend” coupled with $\delta^{44/42}\text{Ca}$ and other proxies (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$ or $\delta^{13}\text{C}$) for mantle-derived rocks. A $\delta^{44/42}\text{Ca}$ variation correlated to $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Nb signatures has been observed in Hawaiian lavas (Huang *et al.*, 2011). Although “anomalous” $\delta^{44/42}\text{Ca}$ values, e.g., as low as 0.26 ‰, and correlated $\delta^{44/42}\text{Ca}$ - $\delta^{13}\text{C}$ variations are observed for carbonatites (including non-primary types), the coupled Ca-C isotope pattern is inconsistent with involvement of sedimentary carbonates (Fig. 2b).

Therefore, Ca isotope data imply that carbonatites originate from a normal mantle source, with no requirement for any contribution of recycled carbonates into their source.

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Author contributions

X-KZ designed the research project. NSB and GMH provided expertise and facility in the establishment of the Ca isotope analytical method. JS, W-JL, B-BC and Z-HL performed the MC-ICPMS-method Ca isotope measurements and YW performed the TIMS Ca isotope measurements. JK, WC, AGD, W-LS, Z-GC and W-JL provided samples. JS and X-KZ interpreted the data and wrote the paper, with additional input from all the co-authors.

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2107>.

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