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

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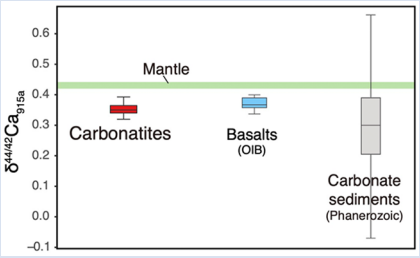
Abstract



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 $\delta^{44/42}$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 $\delta^{44/42}$Ca values of basalts, while non-primary carbonatites show detectable $\delta^{44/42}$Ca variations that are correlated to δ^{13}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 later, 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 $\delta^{44/42}$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 $\delta^{44/42}$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 $\delta^{44/42}$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 $\delta^{44/42}$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 $\delta^{44/42}$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 $\delta^{44/42}$Ca = 0.37 ± 0.01 ‰, 2 s.e., n = 84); while non-primary carbonatites have detectable $\delta^{44/42}$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 processes is fundamental for tracing the carbonatite source using Ca isotopes.

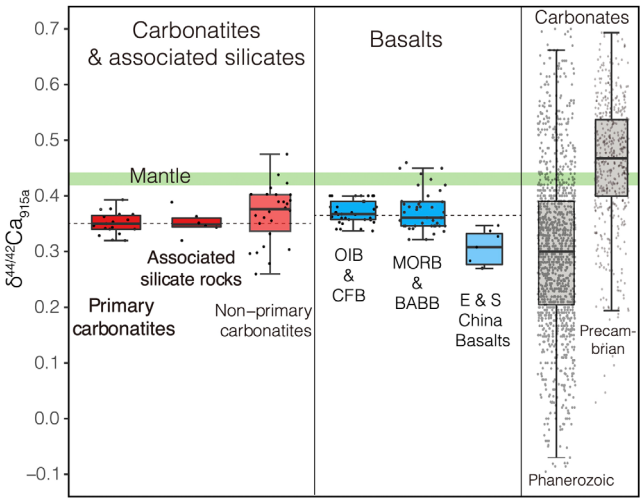

Figure 1 Comparison of $\delta^{44/42}$Ca values between carbonatites, basalts, mantle, and sedimentary carbonates. The dashed lines represent average $\delta^{44/42}$Ca values of carbonatites and basalts, respectively. Data sources are from this study and references (see Tables S-1, S-2; Amini *et al.*, 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).

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 ferrocarbonatites (see descriptions in SI). The rocks of early magmatic stages show homogeneous $\delta^{44/42}$Ca values (around 0.35 ‰), while the later stages exhibit either lower or higher $\delta^{44/42}$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 δ^{18}O values vary significantly, the $\delta^{44/42}$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 $\delta^{44/42}$Ca and δ^{13}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 $\delta^{44/42}$Ca and δ^{13}C values, and a few tend to have lower $\delta^{44/42}$Ca and δ^{13}C values. A δ^{13}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 δ^{13}C-lower $\delta^{44/42}$Ca data, which are not observed (Fig. 2b). Hence, the correlation between

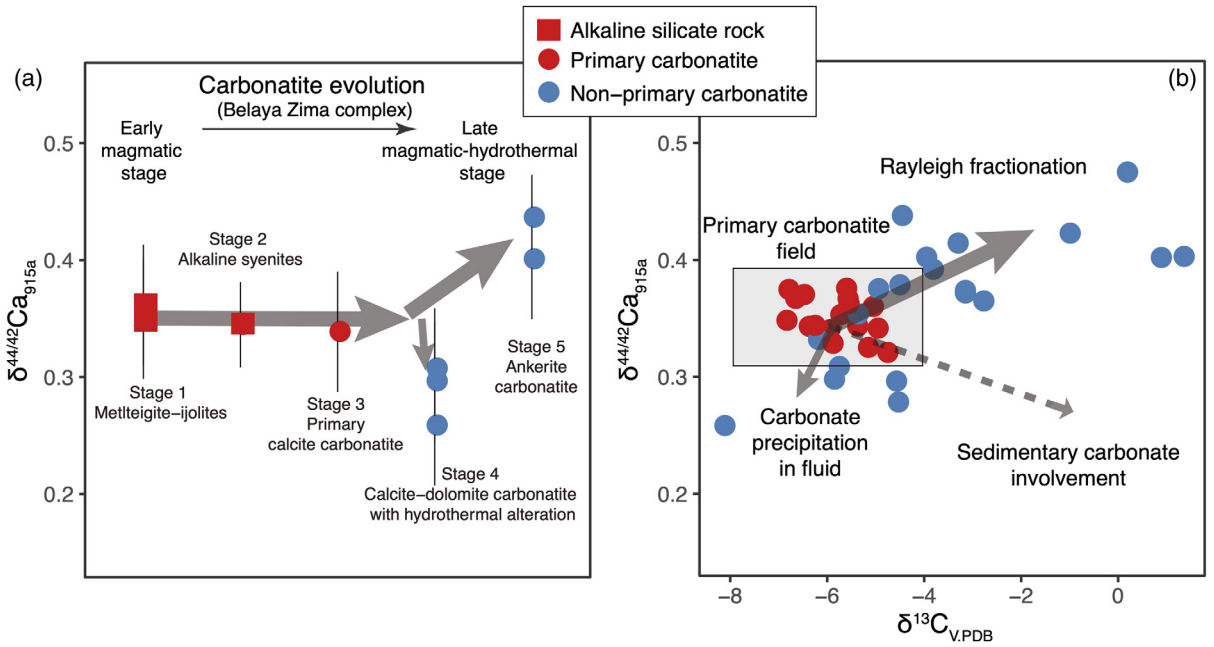

Figure 2 Plots showing $\delta^{44/42}$Ca variation during carbonatite evolution. **(a)** $\delta^{44/42}$Ca for different types of carbonatites and associated silicate rocks from Belaya Zima complex, Russia. **(b)** $\delta^{44/42}$Ca *vs.* δ^{13}C plot for carbonatites. See data sources in Table S-1.

$\delta^{44/42}$Ca and δ^{13}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 $\delta^{44/42}$Ca variation in Belaya Zima and other worldwide 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.*, $\Delta^{44/42}Ca_{calcite\text{-}cpx} < 0.02$ ‰ 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 $\delta^{44/42}Ca = 0.35 \pm 0.01$ ‰ (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 $\delta^{44/42}$Ca due to the temperature effect (Table S-5). Given average $\delta^{44/42}$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 $\Delta^{44/42}Ca_{peridotite\text{-}OIB\ melt} = 0.06$ ‰ and $\Delta^{44/42}Ca_{peridotite\text{-}carbonatite\ melt} = \sim 0.07$–$0.10$ ‰, respectively. Accordingly, the carbonatite melt derived from the normal mantle source is expected to have $\delta^{44/42}$Ca values of ~0.33–0.36 ‰. The $\delta^{44/42}$Ca of carbonatite melts inferred from the measured values of carbonatites (an average of 0.35 ± 0.01 ‰, 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" $\delta^{44/42}$Ca signatures, due to the difference of $\delta^{44/42}$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 $\delta^{44/42}$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 (CaO = 40 %, $\delta^{44/42}Ca = 0.29$ ‰; Fantle and Tipper, 2014) as one end member and a BSE component as another (CaO = 3.65 %, $\delta^{44/42}Ca = 0.43$ ‰; Kang *et al.*, 2017; Simon and DePaolo, 2010). The results show that involvement of the Phanerozoic carbonates would exert a

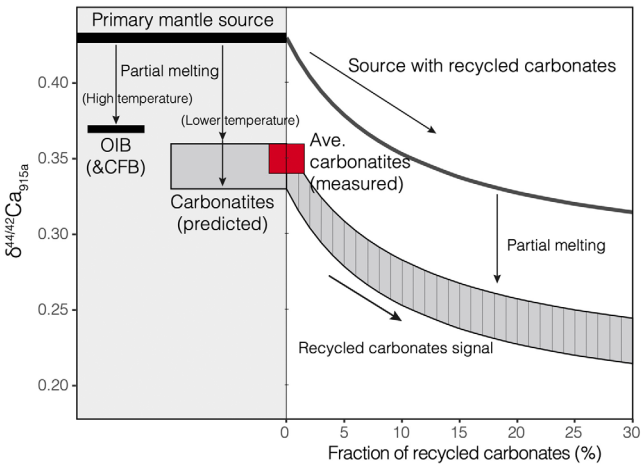

Figure 3 Expected $\delta^{44/42}$Ca values of carbonatites originating from a primary mantle source and mantle sources involved with different fractions of (Phanerozoic) recycled carbonates. The measured $\delta^{44/42}$Ca data for carbonatites is consistent with an origin from the primary mantle source 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 $\delta^{44/42}$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 $\delta^{44/42}$Ca and other proxies (*e.g.*, $^{87}Sr/^{86}Sr$ or $\delta^{13}C$) for mantle-derived rocks. A $\delta^{44/42}$Ca variation correlated to $^{87}Sr/^{86}Sr$ and Sr/Nb signatures has been observed in Hawaiian lavas (Huang *et al.*, 2011). Although "anomalous" $\delta^{44/42}$Ca values, *e.g.*, as low as 0.26 ‰, and correlated $\delta^{44/42}$Ca-$\delta^{13}C$ 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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Supplementary Information

The Supplementary Information includes:

- 1. Ca Isotope Analytical Methods
- 2. Analytical Methods for Major Elements and C-O Isotope Compositions
- 3. Geological Contexts of Carbonatites and Related Alkaline Rocks and Sampling
- 4. Ca Isotope Constraints on the Origin of Ankerite Carbonatite
- Tables S-1 to S-5
- Figures S-1 to S-7
- Supplementary Information References

1. Ca Isotope Analytical Methods

1.1. Sample preparation

Geological reference materials including carbonatite (COQ-1), basalts (BHVO-2, BCR-2, GSR-3), andesite (AGV-2), granite (GSP-2), seawater (IAPSO) and carbonate (NIST SRM 915b), and four carbonatite samples (BR18-A, BR18-E, FZ12-9, FZ12-18) were prepared to validate the Ca isotope analysis. Samples were ground to ~200 mesh in an agate mortar. Silicate rocks were weighed and digested with concentrated HF and HNO_3 at 120 °C for *ca.* 24 h. Carbonatite rocks were digested with dilute HNO_3 or HCl for *ca.* 48 h, which means only the contained carbonate fractions were digested. COQ-1 was also digested with ~6 M HCl and small amount of HF at 120 °C for *ca.* 24 h, to digest the whole rock, for comparison. After digestion, solutions were evaporated and re-dissolved three times to convert to 2 M HCl media. The seawater standard solution was dried and processed with reverse aqua regia at 120 °C for 12 h to remove organic material, before converting to 2 M HCl media. The standard NIST 915b was weighed and digested with ~2 M HCl at room temperature for ~24 h.

1.2. Investigation of matrix effect on Ca isotope analysis using MC-ICP-MS

Prior to Ca isotope analysis for exotic rocks of carbonatites, matrix effects due to elements such as REE were investigated. Artificial solutions of Ca standard solutions doped with different amounts of REE and Y, as well as Al, Ba, Fe, K and Cr elements, were made and measured for their Ca isotope compositions using standard-sample-

standard bracketing method by MC-ICP-MS. The results show that the presence of REE, Y, Cr or Al have detectable effects on the measured Ca isotope ratios when Element/Ca weight ratios are over 0.001 (Fig. S-4 and Table S-3).

1.3. Column Chromatography: one-column Ca-Sr separation

To achieve a highly efficient separation of Ca and avoid any "matrix effect" on Ca isotope analysis for the exotic rocks of carbonatites, a simple and efficient one-column protocol for Ca-Sr separation based on cation exchange resin (AG 50W-X12) was developed in this study, modified from Owen *et al.* (2016) and Nan *et al.* (2015), where nearly all elements (53 elements) present up to ppm levels in natural samples were investigated for their separation efficiency from Ca (Fig. S-5). The column used a 30mL Teflon® micro-column with 6.4 mm ID × 9.6 mm OD (Savillex®), filled with 2 mL AG50W-X12 resin (200-400 mesh, Bio-Rad, USA). Columns were precleaned with 20 mL 6 M HNO_3 and 3 mL 6 M HCl, and then conditioned with 3 mL 18.2 MΩ H_2O, before sample loading. Sample solutions containing ~150 μg Ca were loaded and 19 mL 2 M HCl was used to elute the matrix elements (we find that the measured Ca isotope data become heavier when the Ca load volume is <30 μg, but all within the external reproducibility of Ca isotope composition when Ca load volume is ≥50 μg). Ca was then collected with 18 mL 2 M HCl. Following Ca collection, 2 mL 3 M HCl was used to elute the tailing of trace Ca. (Sr was then collected with 10 mL 3 M HCl.) Collected Ca (and Sr) solutions were dried and redissolved in concentrated HNO_3, further evaporated to dryness three times, and finally dissolved in 0.3 M HNO_3 before isotope analysis. Any matrix element present in the final Ca solution is at a level <0.0001 for element/Ca ratio, and a second pass of the column separation process would be conducted by passing the eluted aliquot through the same column if not. To monitor and assess the Ca recovery and the possible drift of elution curves, both 2 mL aliquots before and after the Ca-cut were collected and measured for their Ca contents. Yields of Ca are normally over 98 % in our protocol. As the isotope fractionation during ion-exchange chromatography is predictable and can be described by "plate theory", effects induced by incomplete Ca recovery on Ca isotope determinations was corrected (Fig. S-6). Compared with that performed with an inadequate column processing, this developed method improves the accuracy of Ca isotope analysis for carbonatite samples (Fig. S-7 and Table S-4).

1.3. Mass spectrometry: MC-ICPMS method

Ca isotope ratios were determined using the HR Nu Instruments MC-ICPMS at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences (CAGS), Beijing, China and at the Department of Earth Sciences, University of Oxford, UK, modified from analytical methods of Halicz *et al.* (1999) and Owen *et al.* (2016). Isotopes of ^{42}Ca, ^{43}Ca and ^{44}Ca were measured at low mass resolution. The standard-sample bracketing (SSB) approach (Belshaw *et al.*, 2000) was used to correct the mass discrimination. The possible interferences for Ca isotope measurements include doubly charged ion interferences from Sr, non-spectral interference arising from scattering of the $^{40}Ar^+$ and $^{40}Ca^+$ ion beams, and various elemental and molecular interferences (*e.g.*, $^{40}Ar^1H_2^+$, $^{12}C^{16}O_2^+$). Sr interferences were corrected by analysing the $^{87}Sr^{2+}$ beam at mass 43.5. The correction was calibrated using a Ca-free Sr solution. Sr content in the final solutions was normally insignificant, with Sr/Ca weight ratio below 0.01 %. Non-spectral interferences and molecular interferences on ^{42}Ca, ^{43}Ca, or ^{44}Ca were unavoidable and the correction for them is critical for data accuracy and precision. A DSN 100 or CETAC Aridus desolvating nebulizer was used and the gas flow rate, RF power and sampling depth were adjusted to reduce and stabilise the interferences (less than 2 mV). They were then determined and corrected by analysing a Ca-free 0.3 M HNO_3 solution, similar to that is performed for the iron isotope measurements at low mass resolution (Belshaw *et al.*, 2000). All samples were normally analysed for 2~5 times for one session.

The accuracy and precision of Ca isotope measurements were estimated using the near-pure carbonate standard reference NIST 915b and a series of geological reference materials. The values are $\delta^{44/42}Ca_{915a} = 0.35 \pm 0.05$ ‰ (2 s.d., n = 21) and $\delta^{43/42}Ca_{915a} = 0.18 \pm 0.06$ ‰ (2 s.d., n = 21) for column processed NIST 915b over a 2-year period. This standard was also measured at Oxford, with $\delta^{44/42}Ca_{915a} = 0.35 \pm 0.07$ ‰ (2 s.d., n = 5) and $\delta^{43/42}Ca_{915a} = 0.19 \pm 0.08$ ‰ (2 s.d., n = 5). Both are in good agreement with published values (Fig. S-2 and Table S-2). The effect of column processing on data quality was assessed by measuring Ca isotope compositions of column-processed NIST 915b related to unprocessed NIST 915b, with the results being $\delta^{44/42}Ca = 0.01 \pm 0.05$ ‰ (2 s.d., n = 21), with the

average value and precision both being consist with the theoretical value of $\delta^{44/42}Ca = 0.00 \pm 0.04$ ‰ (2 s.d.; the long-term precision of mass measurements of 0.04 ‰ is obtained from repeated measurements of unprocessed standard NIST 915b relative to standard NIST 915a). For geological reference samples of carbonatite (COQ-1) and others (basalts of BHVO-2, BCR-2, GSR-3, andesite of AGV-2, granite of GSP-2, seawater of IAPSO and carbonate of NIST SRM 915b), was measured for their Ca isotope compositions, our Ca isotope data are consistent with those reported using high-precision DS-TIMS methods (Fig. S-2 and Table S-2). The long-term external precision for $\delta^{44/42}Ca$, 0.05 ‰ (2 s.d.), for our routine protocol in CAGS, China, is comparable to data obtained by TIMS using double spikes (*e.g.*, He *et al.*, 2017; Liu *et al.*, 2017b).

1.4. Mass spectrometry: Double spike (DS)-TIMS method

To make inter-laboratory comparison, four carbonatite samples were also conducted at the Isotope Geochemistry Laboratory, China University of Geosciences, Beijing (CUGB), following the procedures detailed in (He *et al.*, 2017). An aliquot containing 30-50 μg of Ca was mixed with a ^{43}Ca-^{48}Ca double-spike to have $^{48}Ca/^{40}Ca$ of *ca.* 0.1145. Ca was purified using *ca.* 1.4 ml AG50W- X12 resin (200–400 mesh) using 2.5 N HCl. This column chemistry was repeated twice. The purified solution was then dried down with two drops of concentrated HNO_3 followed by Ca isotopic determination on a Triton Plus thermal ionization mass-spectrometer (TIMS). A Re double filament assemblage was used and about 5μg Ca was loaded using 2 μl 3 % HNO_3. Ionization and evaporation currents were *ca.* 3300 mA and *ca.* 150 mA, respectively, to give a ^{40}Ca signal of *ca.* 20 V. The isobaric interference of ^{40}K was monitored using ^{41}K. Data reduction was conducted offline using an Excel Macro program established by He *et al.* (2017).

Ca isotope results reported in this study are expressed as $\delta^{44/42}Ca$ relative to the standard NIST 915a.

$$\delta^{44/42}Ca\ (‰) = [(^{44/42}Ca)_{sample}/(^{44/42}Ca)_{NIST\ 915a}-1] \times 1000$$

To compare with previous studies, the literature $\delta^{44/40}Ca$ values are converted into $\delta^{44/42}Ca$ following the relationship:

$$\delta^{44/40}Ca \approx 2.048 \times \delta^{44/42}Ca - \varepsilon^{40/44}Ca/10$$

where the $\varepsilon^{40/44}Ca$ denotes the radiogenic excess of ^{40}Ca (from the decay of ^{40}K) relative to NIST SRM 915a (He *et al.*, 2017). $\varepsilon^{40/44}Ca$ of peridotites and basalts, if not available, are assumed to be -0.7 here (He *et al.*, 2017; Mills *et al.*, 2018).

2. Analytical Methods for Major Elements and C-O Isotope Compositions

Major element analysis was undertaken at the ALS Chemex (Guangzhou) Co Ltd., using fusion beads and a X-ray fluorescence (XRF) spectrometer. Carbon and Oxygen isotope analysis of carbonatite samples were carried out at the ALS Chemex (Guangzhou) Co Ltd. Powdered carbonatite sample was digested at temperature of 72 °C with concentrated phosphoric acid, and the evolved CO_2 was measured for C and O isotopes using a MAT Delta^{Plus} Isotope Ratio Mass Spectrometer (CF-IRMS) coupled to a Thermo-Finnigan GasBench. Results are reported relative to the PDB and SMOW standards with an analytical precision of <0.1 ‰ (s.d.) for $\delta^{13}C$ and <0.5 ‰ (s.d.) for $\delta^{18}O$.

3. Geological Contexts of Carbonatites and Related Alkaline Rocks and Sampling

Carbonatite is defined as igneous rock dominated by carbonate (generally >50 vol.%) and may contain variable amounts of silicates (*e.g.* olivine, pyroxene, mica, garnet), oxides (*e.g.* magnetite, pyrochlore, perovskite), sulphides (*e.g.* pyrrhotite, galena, pyrite), and phosphates (particularly apatite). They are divided into groups according to their major mineralogy as calcite-carbonatites, dolomite-carbonatites, ferrocarbonatites and natrocarbonatites (Woolley and Kempe, 1989), with the most common occurrences being calcite-carbonatites. Carbonatite rocks are mineralogically and genetically diverse, subdivided into two broad groups: primary carbonatite of magmatic origin and carbothermal carbonatite that forms from CO_2 or H_2O fluids derived from magma (Mitchell, 2005; Woolley and Kjarsgaard, 2008).

There are also some carbonate-rich rocks formed by pneumatolytic reactions or anatectic melting of crustal rocks, which are not included in this paper. Except a few carbonatites, most are associated with diverse types of igneous silicate rocks, with nephelinite- and melilitite-clan carbonatites representing the most abundant ones (Mitchell, 2005). There are over 500 occurrences of carbonatites with ages from *ca.* 3.0 Ga to modern in the world, but volumetrically minor (Woolley and Kjarsgaard, 2008). Except those in Cape Verde and Canary Islands that occurred in oceanic settings, carbonatites typically occur in continental intraplate settings, with most in rift settings but also a few in collisional settings (Woolley and Kjarsgaard, 2008; Xu *et al.*, 2011).

Representative samples are collected from carbonatite complexes from 15 occurrences globally have been selected for this study: the Oka carbonatite complex in North America, the Brava complex in Cape Verde, the Belaya Zima carbonatite complex in Southern Siberia (Andreeva *et al.*, 2007; Doroshkevich *et al.*, 2016, 2017), the Kovdor phoscorite-carbonatite complex in NW Russia (Veksler *et al.*, 1998; Zaitsev and Bell, 1995), the Mushgai Khudag carbonatite in Mongolia, the Songwe carbonatite complex in Africa (Broom-Fendley *et al.*, 2016), the Moutain Pass in America, the Cataolo in Brazil, the Wajilitage carbonatite in Tarim, NW China (Cheng *et al.*, 2017), the Shaxiongdong and Miaoya carbonatite in South Qinling Orogen carbonatite in Central China (Chen *et al.*, 2018; Ying *et al.*, 2017), the Huanglongpu, Huayangchuan and Caotan carbonatites in the North Qinling Orogen carbonatite in Central China (Xu *et al.*, 2011; Bai *et al.*, 2019; Wei *et al.*, 2020) and the Fengzhen carbonatite-alkaline dyke in North China (Xu *et al.*, 2019). They range from the rift tectonic settings and collisional settings, spanning ages from modern to Mesoproterozoic (Table S-1). Carbonatite varieties include calcite carbonatite, dolomite carbonatite and ferro-carbonatite, and are subdivided into: 1) Primary carbonatites, which are petrologically fresh and unaltered, with no indication of hydrothermal alteration and are C-O isotopically falling in the "primary carbonatite field" defined in the literature. These samples most likely represent magmatic stage products with no post-magmatic hydrothermal alteration, and thus are the best candidates to reveal the primary Ca isotope signals of carbonatite melt. 2) Non-primary carbonatites, which show evidence of hydrothermal alteration either petrologically or with their C-O isotopic values falling outside the "primary carbonatite field". They can be late/post-magmatic hydrothermal stage products (*e.g*, Belaya Zima) or overprinted by secondary low-temperature alteration (*e.g.*, Songwe). Ca isotopic compositions of these samples, as well as elemental and C and O stable isotope compositions are listed in Tables S-1 and are plotted in Fig. 1, 2, S-1, and S-3. Their geological backgrounds have been studied detailed before and are briefly described below.

The **Oka carbonatite complex** is one of series of alkaline intrusions associated with the Monteregian Igneous Province, with an age of *ca.* 120 Ma (Chen and Simonetti, 2015). The complex consists of carbonatite and Si-undersaturated rocks of okaite (melilitite), ijolite, alnoite and jacupirangite, which is a "Melilitite-clan carbonatite" that may be sourced from deeper mantle as compared to "Nephelinite-clan carbonatite" (Mitchell, 2005). Melt inclusions hosted by magnetite in carbonatites are reported (Chen *et al.*, 2013). Sufficiently detailed C-O isotope data shows no evidence for large-scale, hydrothermal circulating systems (Deines, 1989).

The **Belaya Zima plutonic complex** is located in the Tulun district of the Irkutsk region in southern Siberia, with an age of *ca.* 640 Ma, and is related to the Late Riphean Rifting and breakup of Laurasia. It belongs to the nephelinite-clan carbonatites, the most common type of carbonatite, which comprises a suite of alkaline and carbonatite rocks that divide into 5 stages, in sequence: melteigite-ijolites (stage 1), nepheline syenites (stage 2), calcite-carbonatite (stage 3), calcite-dolomite carbonatite (stage 4) and ferrocarbonatite (stage 5). Detailed studies have investigated their petrology, minerology, and elemental and C-O isotope geochemistry. It is demonstrated that the alkaline and carbonatite rocks are comagmatic evolutionary products, generated from either fractional crystallization or liquid immiscibility (Andreeva *et al.*, 2007; Doroshkevich *et al.*, 2016, 2017). Melt inclusions hosted by nepheline and calcite crystals from ijolite series rocks, show that the parental magma corresponds to highly silica-undersaturated Na-rich carbonated nephelinite (Andreeva *et al.*, 2007). The carbonatites comprise those from earlier calcite type (stage 3) to more evolved dolomite (stage 4) and ankerite types (stage 5) that marks the transition from the magmatic to the carbothermal stage. The former is a magmatic product (formed at *ca.* 1100 °C according to melt inclusions) avoiding

alteration while the latter two are characterised by widespread signs of hydrothermal alteration, with mineral-pair O isotope thermometry giving temperatures around 500~350 ℃ (Doroshkevich *et al.*, 2016, 2017).

The **Songwe carbonatite complex** is one of the Early Cretaceous alkaline rocks in Chilwa alkaline province, East Africa (Woolley, 1987). It is shallowly emplaced, and consist of multi-stage carbonatites, including coarse-grained calcite carbonatite, fine-grained calcite carbonatite and ferroan calcite carbonatite. Carbonate C and O isotope ratios show a general trend, from early to late in the evolution, towards higher $\delta^{18}O$ values (*ca.* 8 to *ca.* 20 ‰, VSMOW), with $\delta^{13}C$ (-4 ‰, VPDB) around primary carbonatite values. Carbonatites are interpreted to suffer different degrees of low-temperature alteration by meteoric water (Broom-Fendley *et al.*, 2016).

The **Kovdor alkaline-carbonatite complex** is one of the alkaline massifs in the Kola Peninsula, NW Russia that formed at *ca.* 370 Ma. The massif consists of, from the core to margin, olivinite, olivine-pyroxene rock, melilitolite, and jacupirangite-ijolite series, with various carbonatites and phoscorites occurring at the south-western part (Zaitsev and Bell, 1995). It is also a "Melilitite-clan carbonatite" (Mitchell, 2005). Sr and Nd isotopes show carbonatites and phoscorites are comagmatic evolutionary products (Zaitsev and Bell, 1995). Primary melt inclusions from different varieties record the evolutionary history of the complex, with the parental magmas being silica-undersaturated volatile-rich melts (CO_2-bearing melanephelinite) and calcite-carbonatites likely being calcite cumulates formed from the evolved alkali bearing carbonatite melts (Veksler *et al.*, 1998).

The **Wajilitage carbonatites** are located in the NW part of the Tarim Large Igneous Province, NW China. The region is characterised by diverse rock types including kimberlites (300 Ma), layered mafic-ultramafic intrusions (284-281 Ma), carbonatite, nepheline syenite (273 Ma), diabase and lamprophyre dykes, and nephelinite (268 Ma) (Cheng *et al.*, 2017). The carbonatites occur as dykes, with a width of 0.2~15 m and a length of 10m to > 1km. They are composed predominantly of fine- to medium-grained calcite and dolomite and can be roughly grouped into calcite- and dolomite-carbonatites (Cheng *et al.*, 2017).

The **Shaxiongdong carbonatite complex** is located in the South Qinling Orogen, Central China. Its age is estimated as *ca.* 440 Ma from U-Pb dating of zircons from the syenite, which is older than the collisional age of Qinling Orogen, and it is suggested as forming in a rifting environment. The Shaxiongdong carbonatite complex consists primarily of syenite and carbonatite. Carbonatite occurs as dykes with length of tens to >200 m and dominated by medium to fine-grained euhedral calcite (70-90 vol %). The syenite rock consists mainly of K-feldspar and albite. The C-O isotope compositions of the carbonatites record primary igneous signatures (Chen *et al.*, 2018).

The **Miaoya carbonatite complex** is located in the South Qinling Orogen, Central China. Its age is estimated as *ca.* 440 Ma from U-Pb dating of zircons from the syenite and carbonatite, and is related to the Silurian extension and rifting of the opening of Mianlue Ocean (Ying *et al.*, 2017). Carbonatite occurs as stocks and dykes within the dominant syenite, and it mainly consists of medium- to fine-grained calcite.

The **Huanglongpu and Huayangchuang carbonatites** are located in the North Qinling Orogen, Central China. They have an age of *ca.* 230 Ma and their formations are likely to relate to collision between the North China Craton and the Yangtze Craton during Triassic, with a mantle source affected by recycled surface materials as indicated by Sr-Nd isotope compositions (Bai *et al.*, 2019; Xu *et al.*, 2011). The carbonatites are unusual in that they are composed of calcite and variable amounts of quartz and they contain abundant Mo metals. They occur as dykes and the C-O isotope compositions of the carbonatites record primary igneous signatures (Bai *et al.*, 2019).

The **Caotan carbonatite complex** is located in the North Qinling Orogen, Central China. Its age is possibly *ca.* 230 Ma and their formations are likely to relate to collision between the North China Craton and the Yangtze Craton during Triassic. The carbonatites occur as complexes and dykes, with iron mineralisation locally. There are mainly two types of carbonatites: calcite-carbonatite and dolomite-carbonatite. The former comprises calcite, forsterite and

magnetite, and the latter consists predominantly of dolomite, apatite and magnetite. The C-O isotope compositions of the calcite-carbonatites fall into "primary igneous field" (Wei *et al.*, 2020).

The **Fengzhen carbonatites** are located in North China. They have an age of *ca.* 1.8 Ga and are believed to relate to the Paleoproterozoic collision between the Western and Eastern segments of the North China Craton. Carbonatite, clinopyroxenite and syenite dykes occur in Fengzhen area and their genetic association was suggested by consistent Sr-Nd isotope compositions (Xu *et al.*, 2019).

4. Ca Isotope Constraint on the Origin of Ankerite Carbonatite

The origin of late-stage ankerite carbonatite (ferrocarbonatite) is debated and is explained as either a primary product crystallised from the melt/liquid or a metasomatic product replacing earlier calcite-carbonatite (Barker, 1993; Harmer, 1997). The latter case, where Ca is dissolved and removed, would make the ankerite carbonatite isotopically lighter than or close to the protolith of calcite-carbonatite, as heavier Ca isotopes tend to preferentially incorporate in fluids during dissolution at >100 °C or no Ca isotope fractionation at <100 °C (Perez-Fernandez *et al.*, 2017). This is inconsistent with the observation that highest $\delta^{44/42}$Ca values were exhibited by ankerite carbonatite in Belaya Zima (Fig 2a). Therefore, the Ca isotopic signatures imply that the ankerite carbonatite is of primary origin, i.e. directly crystallised from the melt/liquid.

Supplementary Tables

Table S-1 Major elemental, and C, O and Ca stable isotope compositions of carbonatite and associated alkaline silicate rocks.

The Excel spreadsheet is available for download from the online version of the article at http://www.geochemicalperspectivesletters.org/article2107.

Table S-2 Summary of stable Ca isotope compositions of carbonatite and other geological reference materials from literatures and this study.

Sample Group	Sample ID	Sample Type	Chemistry	Mass	$\delta^{44/40}Ca_{-915a}$-report	$\delta^{44/42}Ca_{-915a}$-report	$\delta^{44/40}Ca_{-915a}$-renorm	$\delta^{44/42}Ca_{-915a}$-renorm	$2SD_{ex}$[1] for $\delta^{44/42}Ca$	$2SE_{ex}$[2]	n[3]	References
1. 915b	**915b**	**Carbonate**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.35**	**0.72**	**0.35**	**0.05**	**0.01**	**21**	**This study**
1. 915b	915b	Carbonate		DS-TIMS	0.72	Not reported	0.72	0.35	0.07	0.01	38	Feng *et al.*, 2017
1. 915b	915b	Carbonate	TIMS-He|Zhang	DS-TIMS	0.79	0.36	0.79	0.36	0.03	0	41	He *et al.*, 2017
1. 915b	915b	Carbonate	TIMS-Hindshaw	DS-TIMS	Not reported	0.35	0.72	0.35	0.07	0.01	46	Hindshaw *et al.*, 2011, 2014
1. 915b	915b	Carbonate		DS-TIMS	0.7	0.35	0.7	0.35	0.11	0.03	19	Lehn and Jacobson, 2015
1. 915b	915b	Carbonate		DS-TIMS	0.72	0.35	0.72	0.35	0.1	0.03	12	Heuser and Eisenhauer, 2008
1. 915b	915b	Carbonate		DS-TIMS	0.73	Not reported	0.73	0.36	0.03	0	135	Jacobson *et al.*, 2015
1. 915b	915b	Carbonate		DS-TIMS	0.81	Not reported	0.81	0.4	0.18	0.06	10	Simon *et al.*, 2017
1. 915b	915b	Carbonate	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.3	0.62	0.3	0.21	0.03	47	Morgan *et al.*, 2011
1. 915b	915b	Carbonate	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.34	0.7	0.34	0.11	0.03	13	Martin *et al.*, 2015
1. 915b	915b	Carbonate	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.35	0.72	0.35	0.07	0.05	2	Colla *et al.*, 2013
1. 915b	915b	Carbonate	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.35	0.72	0.35	0.13	0.07	4	Tacail *et al.*, 2016
1. 915b	915b	Carbonate	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.35	0.72	0.35	0.14	0.04	11	Tacail *et al.*, 2014
1. 915b	915b	Carbonate	Cation exchange	MC-ICPMS	Not	0.35	0.72	0.35	0.14	0.02	40	Owen *et al.*, 2016

			chromatography (AG resin)		reported							
1. 915b	915b	Carbonate	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.34	0.7	0.34	0.07	0.02	15	Harouaka *et al.*, 2016
1. 915b	915b	Carbonate	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.36	0.74	0.36	0.07	0.04	3	Feng *et al.*, 2018
1. 915b	915b	Carbonate	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.36	0.74	0.36	0.07	0.01	67	Li *et al.*, 2018
1. 915b	915b	Carbonate	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.36	0.74	0.36	0.07	0.01	62	Chen *et al.*, 2019
1. 915b	915b	Carbonate	Others	MC-ICPMS	Not reported	0.34	0.7	0.34	0.08	0.02	20	Ionov *et al.*, 2019
2. Seawater	**IAPSO**	**Seawater**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.89**	**1.82**	**0.89**	**0.05**	**0.02**	**5**	**This study**
2. Seawater	Seawater	Seawater		DS-TIMS	1.76	Not reported	1.76	0.86	0.09	0.05	3	Simon *et al.*, 2017
2. Seawater	IAPSO	Seawater		DS-TIMS	1.77	Not reported	1.77	0.86	0.05	0.02	11	Teichert *et al.*, 2009
2. Seawater	Seawater	Seawater		DS-TIMS	1.79	Not reported	1.79	0.87	0.1	0.03	14	Wiegand and Schwendenmann, 2013
2. Seawater	Seawater	Seawater		DS-TIMS	1.8	Not reported	1.8	0.88	0.06	0.02	7	Schmitt *et al.*, 2013
2. Seawater	Seawater	Seawater		DS-TIMS	1.81	0.88	1.81	0.88	0.04	0.04	1	Holmden *et al.*, 2012
2. Seawater	Seawater	Seawater	TIMS-Huang	DS-TIMS	1.9	0.88	1.9	0.88	0.07	0.01	19	Huang *et al.*, 2012
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.81	Not reported	1.81	0.88	0.06	0.02	10	Liu *et al.*, 2015
2. Seawater	IAPSO	Seawater		DS-TIMS	1.82	Not reported	1.82	0.89	0.1	0.01	135	Amini *et al.*, 2009
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.82	Not reported	1.82	0.89	0.06	0	199	Liu *et al.*, 2017b
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.82	Not reported	1.82	0.89	0.06	0.01	17	Liu *et al.*, 2017a
2. Seawater	Seawater	Seawater		DS-TIMS	1.82	Not reported	1.82	0.89	0.06	0.02	6	Schmitt *et al.*, 2009
2. Seawater	IAPSO	Seawater		DS-TIMS	1.83	Not reported	1.83	0.89	0.2	0.05	16	Böhm *et al.*, 2006
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.83	Not reported	1.83	0.89	0.06	0.01	85	Zhu *et al.*, 2018b

2. Seawater	IASPO	Seawater	TIMS-Huang	DS-TIMS	1.84		1.84	0.9	0.08	0.02	15	Huang *et al.*, 2011
2. Seawater	Atalantic SW	Seawater	TIMS-He|Zhang	DS-TIMS	1.89	0.91	1.89	0.91	0.08	0.01	147	He *et al.*, 2017
2. Seawater	Seawater	Seawater		DS-TIMS	1.86	Not reported	1.86	0.91	0.09	0.01	55	Amini *et al.*, 2008
2. Seawater	Seawater	Seawater		DS-TIMS	1.86	Not reported	1.86	0.91	0.12	0.05	6	Gopalan *et al.*, 2006
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.86	Not reported	1.86	0.91	0.06	0.06	1	Zhu *et al.*, 2018a
2. Seawater	Seawater	Seawater		DS-TIMS	1.86	Not reported	1.86	0.91	0.03	0	55	Jacobson *et al.*, 2015
2. Seawater	IASPO	Seawater		DS-TIMS	1.86	0.91	1.86	0.91	0.07	0.03	5	Farkaš *et al.*, 2007
2. Seawater	Seawater	Seawater		DS-TIMS	1.82	0.91	1.82	0.91	0.15	0.07	5	Hippler *et al.*, 2003
2. Seawater	NASS-5 seawater	Seawater		DS-TIMS	1.87	Not reported	1.87	0.91	0.13	0.06	5	Wombacher *et al.*, 2009
2. Seawater	Seawater	Seawater		DS-TIMS	1.88	Not reported	1.88	0.92	0.07	0.01	65	Feng *et al.*, 2017
2. Seawater	Seawater	Seawater		DS-TIMS	1.88	Not reported	1.88	0.92	0.09	0.03	11	Gopalan *et al.*, 2006
2. Seawater	Seawater	Seawater		DS-TIMS	1.88	Not reported	1.88	0.92	0.1	0.1	1	Skulan and DePaolo, 1999
2. Seawater	IASPO	Seawater		DS-TIMS	1.89	Not reported	1.89	0.92	0.05	0.01	20	Farkaš *et al.*, 2007
2. Seawater	Seawater	Seawater		DS-TIMS	1.89	Not reported	1.89	0.92	0.1	0.07	2	Schmitt *et al.*, 2003
2. Seawater	Seawater	Seawater	TIMS-He|Zhang	DS-TIMS	1.89	0.93	1.89	0.93	0.03	0.03	1	Zhang *et al.*, 2018
2. Seawater	IASPO	Seawater	TIMS-Huang	DS-TIMS	1.9	Not reported	1.9	0.93	0.07	0.02	16	Huang *et al.*, 2010
2. Seawater	Seawater	Seawater		DS-TIMS	1.9	Not reported	1.9	0.93	0.16	0.05	9	Scheuermann *et al.*, 2018
2. Seawater	OSIL Atlantic SW	Seawater		DS-TIMS	1.84	0.93	1.84	0.93	0.11	0.02	22	Lehn and Jacobson, 2015
2. Seawater	Seawater	Seawater		DS-TIMS	1.89	0.93	1.89	0.93	0.1	0.03	15	Hippler *et al.*, 2003
2. Seawater	Seawater	Seawater		DS-TIMS	1.91	Not reported	1.91	0.93	0.06	0.02	8	Cobert *et al.*, 2011
2. Seawater	Seawater	Seawater		DS-TIMS	1.88	0.94	1.88	0.94	0.1	0.03	15	Schmitt and Stille, 2005

2. Seawater	Seawater	Seawater		DS-TIMS	1.95	Not reported	1.95	0.95	0.14	0.06	5	Müller *et al.*, 2011
2. Seawater	Seawater	Seawater		DS-TIMS	1.96	Not reported	1.96	0.96	0.05	0.03	3	Kasemann *et al.*, 2005
2. Seawater	Seawater	Seawater	TIMS-Hindshaw	DS-TIMS	1.97	0.96	1.97	0.96	0.07	0.01	45	Hindshaw *et al.*, 2011, 2014
2. Seawater	Seawater	Seawater		DS-TIMS	1.95	0.98	1.95	0.98	0.1	0.05	4	Hippler *et al.*, 2003
2. Seawater	Seawater	Seawater		DS-TIMS	2.01	Not reported	2.01	0.98	0.19	0.05	15	Page *et al.*, 2008
2. Seawater	Seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.88	1.8	0.88	0.14	0.1	2	Tacail *et al.*, 2014
2. Seawater	Seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	1.8	0.88	1.8	0.88	0.11	0.01	54	Wieser *et al.*, 2004
2. Seawater	IAPSO	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.89	1.82	0.89	0.16	0.02	64	Hippler *et al.*, 2013
2. Seawater	Seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.89	1.82	0.89	0.07	0.03	5	Colla *et al.*, 2013
2. Seawater	Seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.9	1.85	0.9	0.11	0.05	5	Martin *et al.*, 2015
2. Seawater	Seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.9	1.85	0.9	0.13	0.06	5	Tacail *et al.*, 2016
2. Seawater	IASPO	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.92	1.89	0.92	0.13	0.13	1	Chang *et al.*, 2004
2. Seawater	Atlantic	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.93	1.91	0.93	0.07	0.03	7	Tipper *et al.*, 2008
2. Seawater	IAPSO	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.97	1.99	0.97	0.21	0.03	61	Morgan *et al.*, 2011
2. Seawater	Mediterranean seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.98	2.01	0.98	0.14	0.06	6	Sime *et al.*, 2005

2. Seawater	Mediterranean seawater	Seawater	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	1.09	2.23	1.09	0.09	0.09	1	Tipper *et al.*, 2006
2. Seawater	Seawater	Seawater	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.91	1.87	0.91	0.07	0.04	4	Feng *et al.*, 2018
2. Seawater	Atlantic Seawater	Seawater	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.94	1.93	0.94	0.07	0.03	5	Harouaka *et al.*, 2016
2. Seawater	IAPSO	Seawater	Others	MC-ICPMS	Not reported	0.89	1.82	0.89	0.08	0.02	17	Ionov *et al.*, 2019
2. Seawater	IAPSO	Seawater	Others	MC-ICPMS	Not reported	0.9	1.85	0.9	0.1	0.02	34	Steuber and Buhl, 2006
2. Seawater	IAPSO	Seawater	Others	MC-ICPMS	Not reported	0.92	1.89	0.92	0.21	0.09	5	Romaniello *et al.*, 2015
2. Seawater	ISPSO	Seawater	Others	MC-ICPMS	Not reported	1.01	2.07	1.01	0.18	0.09	4	Karasinski *et al.*, 2018
3. BCR-2	**BCR-2**	**Basalt**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.40**	**0.82**	**0.40**	**0.05**	**0.04**	**2**	**This study**
3. BCR-2	BCR-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.8	0.38	0.8	0.38	0.03	0.02	4	He *et al.*, 2017
3. BCR-2	BCR-2	Basalt		DS-TIMS	0.79	Not reported	0.79	0.39	0.07	0.01	24	Feng *et al.*, 2017
3. BCR-2	BCR-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.82	Not reported	0.82	0.4	0.06	0.02	12	Liu *et al.*, 2017b
3. BCR-2	BCR-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.82	Not reported	0.82	0.4	0.06	0.02	12	Zhu *et al.*, 2018b
3. BCR-2	BCR-2	Basalt		DS-TIMS	0.87	Not reported	0.87	0.42	0.09	0.09	1	Simon *et al.*, 2017
3. BCR-2	BCR-2	Basalt		DS-TIMS	0.81	Not reported	0.87	0.42	0.1	0.04	6	Amini *et al.*, 2009
3. BCR-2	BCR-2	Basalt		DS-TIMS	0.92	Not reported	0.92	0.45	0.13	0.07	4	Wombacher *et al.*, 2009
3. BCR-2	BCR-2	Basalt		DS-TIMS	0.93	Not reported	0.93	0.45	0.1	0.1	1	Amini *et al.*, 2009
3. BCR-2	BCR-2	Basalt	Cation exchange chromatography (AG resin)	MC-ICPMS	Not reported	0.4	0.82	0.4	0.07	0.04	4	Colla *et al.*, 2013
3. BCR-2	BCR-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.38	0.78	0.38	0.07	0.01	30	Li *et al.*, 2018

3. BCR-2	BCR-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.41	0.84	0.41	0.07	0.04	4	Feng *et al.*, 2018
3. BCR-2	BCR-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.41	0.84	0.41	0.07	0.02	9	Chen *et al.*, 2019
3. BCR-2	BCR-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.43	0.88	0.43	0.09	0.05	3	Valdes *et al.*, 2014
3. BCR-2	BCR-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.45	0.92	0.45	0.09	0.04	5	Amsellem *et al.*, 2017
3. BCR-2	BCR-2	Basalt	Others	MC-ICPMS	Not reported	0.41	0.84	0.41	0.21	0.11	4	Romaniello *et al.*, 2015
4. BHVO	**BHVO-2**	**Basalt**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.36**	**0.73**	**0.36**	**0.05**	**0.04**	**2**	**This study**
4. BHVO	BHVO-1	Basalt	TIMS-He|Zhang	DS-TIMS	0.77	0.36	0.77	0.36	0.03	0.03	1	Zhang *et al.*, 2018
4. BHVO	BHVO-1	Basalt		DS-TIMS	0.76	Not reported	0.76	0.37	0.02	0.01	6	Lehn and Jacobson, 2015
4. BHVO	BHVO-1	Basalt		DS-TIMS	0.77	Not reported	0.77	0.38	0.07	0.04	3	Feng *et al.*, 2017
4. BHVO	BHVO-1	Basalt		DS-TIMS	0.78	0.44	0.78	0.38	0.11	0.04	6	Lehn and Jacobson, 2015
4. BHVO	BHVO-1	Basalt	TIMS-Huang	DS-TIMS	0.96	0.44	0.96	0.44	0.08	0.03	5	Huang *et al.*, 2011
4. BHVO	BHVO-1	Basalt	TIMS-Huang	DS-TIMS	1.04	0.53	1.04	0.53	0.07	0.04	3	Huang *et al.*, 2010
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.8	0.36	0.8	0.36	0.03	0.03	1	Zhang *et al.*, 2018
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.74	Not reported	0.74	0.36	0.06	0.02	10	Liu *et al.*, 2015
4. BHVO	BHVO-2	Basalt		DS-TIMS	0.75	Not reported	0.75	0.37	0.1	0.02	20	Amini *et al.*, 2009
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.8	0.37	0.8	0.37	0.03	0.03	1	Zhang *et al.*, 2018
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.76	Not reported	0.76	0.37	0.06	0.01	19	Liu *et al.*, 2017a
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.79	0.38	0.79	0.38	0.03	0.01	7	He *et al.*, 2017
4. BHVO	BHVO-2	Basalt		DS-TIMS	0.77	Not reported	0.77	0.38	0.07	0.02	12	Feng *et al.*, 2017
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.84	0.39	0.84	0.39	0.03	0.03	1	Zhang *et al.*, 2018
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.8	Not reported	0.8	0.39	0.06	0.02	16	Liu *et al.*, 2017b
4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.8	Not reported	0.8	0.39	0.06	0.01	16	Zhu *et al.*, 2018b

4. BHVO	BHVO-2	Basalt	TIMS-He|Zhang	DS-TIMS	0.84	Not reported	0.84	0.41	0.06	0.06	1	Zhu *et al.*, 2018a
4. BHVO	BHVO-2	Basalt		DS-TIMS	0.9	Not reported	0.9	0.44	0.1	0.1	1	Amini *et al.*, 2009
4. BHVO	BHVO-2	Basalt		DS-TIMS	0.9	Not reported	0.9	0.44	0.05	0.02	5	Magna *et al.*, 2015
4. BHVO	BHVO-2	Basalt	TIMS-Hindshaw	DS-TIMS	Not reported	0.55	1.13	0.55	0.07	0.04	4	Hindshaw *et al.*, 2011
4. BHVO	BHVO-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.35	0.72	0.35	0.07	0.02	12	Chen *et al.*, 2019
4. BHVO	BHVO-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.38	0.78	0.38	0.07	0.01	41	Li *et al.*, 2018
4. BHVO	BHVO-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS		0.4	0.82	0.4	0.09	0.04	6	Amsellem *et al.*, 2017
4. BHVO	BHVO-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.41	0.84	0.41	0.07	0.04	4	Feng *et al.*, 2018
4. BHVO	BHVO-2	Basalt	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.43	0.88	0.43	0.09	0.03	10	Valdes *et al.*, 2014
4. BHVO	BHVO-2	Basalt	Others	MC-ICPMS	Not reported	0.4	0.82	0.4	0.08	0.05	3	Ionov *et al.*, 2019
5. AGV-2	**AGV-2**	**Andesite**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.34**	**0.70**	**0.34**	**0.05**	**0.03**	**3**	**This study**
5. AGV-2	AGV-2	Andesite	TIMS-He|Zhang	DS-TIMS	0.71	Not reported	0.71	0.35	0.06	0.02	8	Liu *et al.*, 2017b
5. AGV-2	AGV-2	Andesite	TIMS-He|Zhang	DS-TIMS	0.75	0.35	0.75	0.35	0.03	0.02	3	He *et al.*, 2017
5. AGV-2	AGV-2	Andesite		DS-TIMS	0.79	Not reported	0.79	0.39	0.07	0.02	9	Feng *et al.*, 2017
5. AGV-2	AGV-2	Andesite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.31	0.64	0.31	0.07	0.04	3	Chen *et al.*, 2019
5. AGV-2	AGV-2	Andesite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.33	0.68	0.33	0.07	0.03	6	Li *et al.*, 2018
5. AGV-2	AGV-2	Andesite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.38	0.78	0.38	0.09	0.05	3	Valdes *et al.*, 2014
6. GSP-2	**GSP-2**	**Granodiorite**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.32**	**0.66**	**0.32**	**0.05**	**0.05**	**1**	**This study**
6. GSP-2	GSP-2	Granodiorite	TIMS-He|Zhang	DS-TIMS	0.3	0.32	0.3	0.32	0.03	0.02	3	He *et al.*, 2017
6. GSP-2	GSP-2	Granodiorite	TIMS-He|Zhang	DS-TIMS	0.25	Not	0.25		0.06	0.02	9	Liu *et al.*, 2017b

						reported						
6. GSP-2	GSP-2	Granodiorite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.27	0.55	0.27	0.07	0.03	6	Chen *et al.*, 2019
6. GSP-2	GSP-2	Granodiorite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.33		0.33	0.07	0.03	5	Li *et al.*, 2018
7. GSR-3	**GSR-3**	**Basalt**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.27**	**0.55**	**0.27**	**0.05**	**0.05**	**1**	**This study**
7. GSR-3	GSR-3	Basalt	TIMS-He|Zhang	DS-TIMS	Not reported	0.27	0.59	0.27	0.03	0.02	2	He *et al.*, 2017
8. COQ-1	**COQ-1**	**Carbonatite**	**Cation exchange chromatography (AG resin)**	**This study**	**Not reported**	**0.35**	**0.72**	**0.35**	**0.05**	**0.04**	**2**	**This study**
8. COQ-1	COQ-1	Carbonatite	TIMS-He|Zhang	DS-TIMS	0.68	Not reported	0.68	0.33	0.06	0.02	8	Liu *et al.*, 2017b
8. COQ-1	COQ-1	Carbonatite	TIMS-He|Zhang	DS-TIMS	0.66	0.34	0.66	0.34	0.03	0.02	4	He *et al.*, 2017
8. COQ-1	COQ-1	Carbonatite		DS-TIMS	0.71	Not reported	0.71	0.35	0.07	0.04	4	Feng *et al.*, 2017
8. COQ-1	COQ-1	Carbonatite	Extraction chromatography (DGA resin)	MC-ICPMS	Not reported	0.35	0.72	0.35	0.07	0.05	2	Li *et al.*, 2018

[1] $2SD_{-ex}$, long-term external two standard deviation.

[2] $2SE_{-ex} = 2SD_{-ex} / \sqrt{n}$.

[3] n, number of measurements.

Table S-3 Effects of matrix elements on Ca isotope analysis.

Sample Name	Matrix elements added	Element/Ca (weight ratio)	$\delta^{44/42}$Ca (relative to pure Ca solution)	2SD$_{ex}$[1]	$\delta^{43/42}$Ca (relative to pure Ca solution)	2SD$_{ex}$[1]	Measured Lab
0.01 % La in Ca solution	La	0.0001	-0.03	0.05	-0.03	0.06	CAGS
0.1 % La in Ca solution	La	0.001	-0.14	0.05	-0.10	0.06	CAGS
1 % La in Ca solution	La	0.01	-0.38	0.05	-0.23	0.06	CAGS
0.01 % Ce in Ca solution	Ce	0.0001	0.01	0.05	0.04	0.06	CAGS
0.1 % Ce in Ca solution	Ce	0.001	-0.02	0.05	0.00	0.06	CAGS
1 % Ce in Ca solution	Ce	0.01	0.13	0.05	0.03	0.06	CAGS
0.01 % Y in Ca solution	Y	0.0001	-0.04	0.05	-0.05	0.06	CAGS
0.1 % Y in Ca solution	Y	0.001	-0.15	0.05	-0.10	0.06	CAGS
RE1_0.0013ppmLa_0.0013ppmCe_0.0013ppmY in 6ppm Ca solution	mix-REE1	0.0008	-0.06	0.07	-0.01	0.08	Oxford
RE2_0.01ppmLa_0.01ppmCe_0.01ppmY in 6ppm Ca solution	mix-REE1	0.006	-0.24	0.07	-0.09	0.08	Oxford
RE3_0.1ppmLa_0.1ppmCe_0.025ppmY in 6ppm Ca solution	mix-REE1	0.045	-0.34	0.07	-0.11	0.08	Oxford
REE_0.2ppmLa_0.1ppmCe_0.01ppmPr_0.05ppmNd_0.01ppmSm in 6ppm Ca solution	mix-REE2	0.074	-0.20	0.07	-0.08	0.08	Oxford
REE2_0.1ppmLa_0.05ppmCe_0.002ppmPr_0.01ppmNd_0.02ppmSm in 6ppm Ca solution	mix-REE2	0.04	-0.09	0.07	0.00	0.08	Oxford
REE3_0.02ppmLa_0.02ppmCe_0.01ppmNd_0.002ppmPr&Sm in 6ppm Ca solution	mix-REE2	0.01	-0.10	0.07	-0.12	0.08	Oxford
0.01 % Al in Ca solution	Al	0.0001	-0.04	0.05	-0.02	0.06	CAGS
0.1 % Al in Ca solution	Al	0.001	-0.13	0.05	-0.10	0.06	CAGS
1 % Al in Ca solution	Al	0.01	-0.08	0.05	-0.03	0.06	CAGS
0.01 % Al in Ca solution (2)	Al	0.0001	-0.04	0.05	-0.08	0.06	CAGS
0.1 % Al in Ca solution (2)	Al	0.001	-0.14	0.05	-0.09	0.06	CAGS
1 % Al in Ca solution (2)	Al	0.01	-0.19	0.05	-0.07	0.06	CAGS
Al_5ppb in 6ppm Ca solution	Al	0.001	-0.06	0.07	0.01	0.08	Oxford
Al_10ppb in 6ppm Ca solution	Al	0.002	-0.06	0.07	-0.04	0.08	Oxford
Al_100ppb in 6ppm Ca solution	Al	0.02	0.02	0.07	0.00	0.08	Oxford
0.01 % Ba in Ca solution	Ba	0.0001	-0.01	0.05	0.00	0.06	CAGS
0.1 % Ba in Ca solution	Ba	0.001	-0.07	0.05	-0.07	0.06	CAGS
1 % Ba in Ca solution	Ba	0.01	0.06	0.05	0.00	0.06	CAGS
Ba_5ppb in 6ppm Ca solution	Ba	0.001	0.00	0.07	0.03	0.08	Oxford
Ba_50ppb in 6ppm Ca solution	Ba	0.01	0.00	0.07	0.02	0.08	Oxford
Ba_100ppb in 6ppm Ca solution	Ba	0.02	0.06	0.07	0.12	0.08	Oxford
0.01 % Cr in Ca solution	Cr	0.0001	0.02	0.05	0.01	0.06	CAGS
0.1 % Cr in Ca solution	Cr	0.001	0.08	0.05	0.07	0.06	CAGS

1 % Cr in Ca solution	Cr	0.01	0.78	0.05	0.34	0.06	CAGS
0.1 % Fe in Ca solution	Fe	0.001	-0.03	0.05	-0.04	0.06	CAGS
1 % Fe in Ca solution	Fe	0.01	0.03	0.05	-0.01	0.06	CAGS
0.1 % K in Ca solution	K	0.001	0.03	0.05	0.05	0.06	CAGS
1 % K in Ca solution	K	0.01	0.02	0.05	-0.01	0.06	CAGS
1 % K in Ca solution	K	0.01	0.13	0.05	0.11	0.06	CAGS
0.1 % K in Ca solution	K	0.001	-0.12	0.05	0.01	0.06	CAGS
0.01 % K in Ca solution	K	0.0001	0.05	0.05	0.06	0.06	CAGS

[1] 2SD-ex, long-term external two standard deviation.

Table S-4 Comparison of measured data between using new developed method and inadequate column processing method.

Sample ID	Sample type	Y/Ca (weight ratio of samples)	$\delta^{44/42}C_{a915a}$	$2SD_{ex}$[1]	$\delta^{43/42}C_{a915a}$	$2SD_{ex}$[1]	$\delta^{44/42}C_{a915a}$	$2SD_{ex}$[1]	$\delta^{43/42}C_{a915a}$	$2SD_{ex}$[1]
			New developed method				Inadequate column processing			
2550	carbonatite	0.00010	0.34	0.05	0.16	0.06	0.34	0.05	0.15	0.06
HLP-3	carbonatite	0.00048	0.32	0.05	0.14	0.06	0.30	0.05	0.16	0.06
HYC-2	carbonatite	0.00043	0.36	0.05	0.19	0.06	0.22	0.05	0.08	0.06
HYC-6	carbonatite	0.00028	0.38	0.05	0.20	0.06	0.22	0.05	0.11	0.06
MY05	carbonatite	0.00024	0.36	0.05	0.18	0.06	0.24	0.05	0.16	0.06
Oka153	carbonatite	0.00005	0.35	0.05	0.16	0.06	0.32	0.05	0.16	0.06
Oka51	carbonatite	0.00010	0.34	0.05	0.18	0.06	0.32	0.05	0.19	0.06
Oka72	carbonatite	0.00011	0.38	0.05	0.16	0.06	0.31	0.05	0.20	0.06
SXD-11c	carbonatite	0.00024	0.36	0.05	0.18	0.06	0.23	0.05	0.08	0.06
SXD-2	carbonatite	0.00022	0.33	0.05	0.16	0.06	0.24	0.05	0.10	0.06
SXD-5	carbonatite	0.00025	0.37	0.05	0.22	0.06	0.27	0.05	0.15	0.06

[1] $2SD_{ex}$, long-term external two standard deviation.

Table S-5 Ca isotope compositions of different experimental partial melts at different temperatures.

The Excel spreadsheet is available for download from the online version of the article at http://www.geochemicalperspectivesletters.org/article2107.

Supplementary Figures

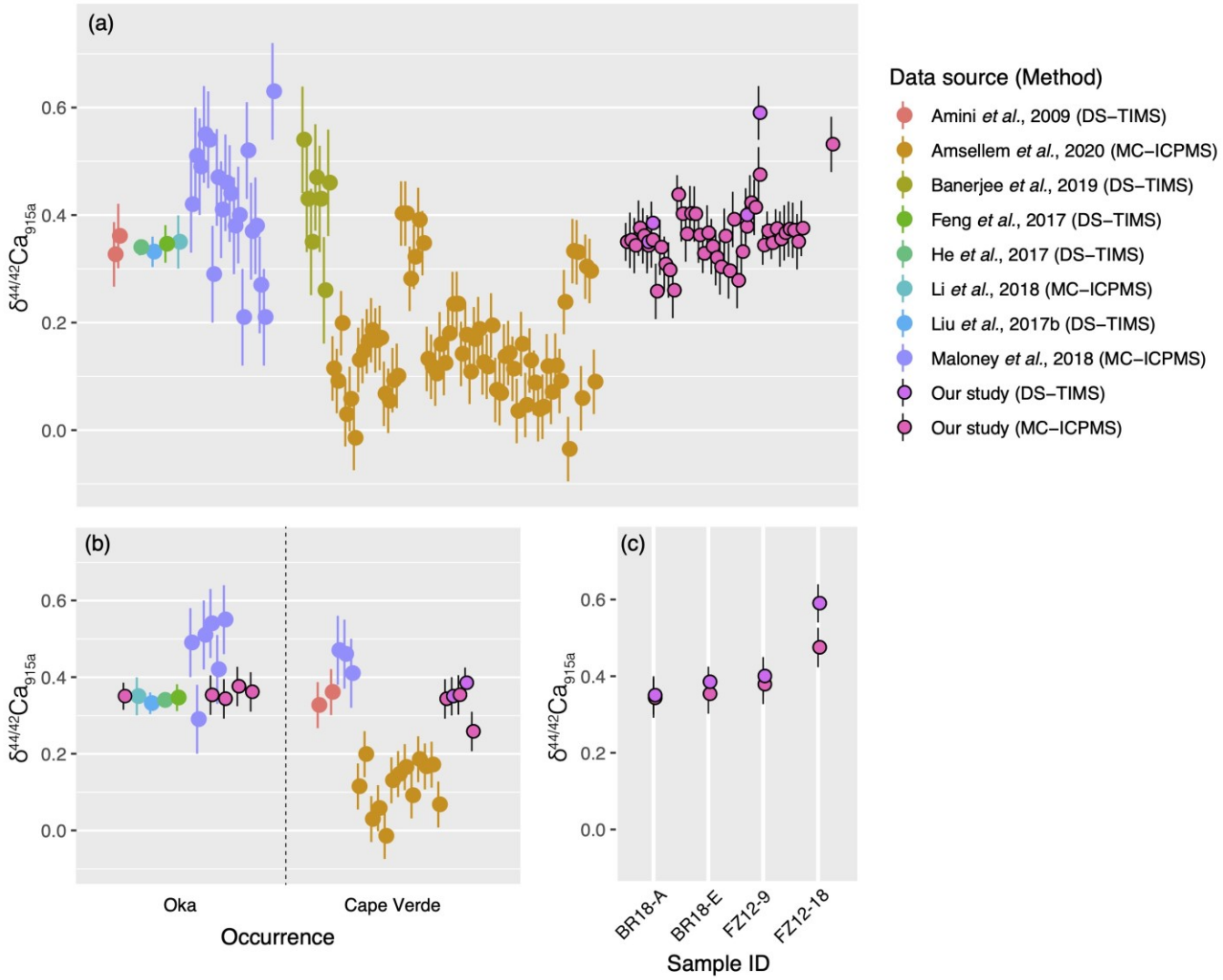

Figure S-1 **(a)** Summary of reported Ca isotope data of carbonatites. **(b)** Reported $\delta^{44/42}$Ca for individual carbonatite occurrences. **(c)** Comparison of $\delta^{44/42}$Ca for individual samples between using MC-ICPMS method performed in CAGS lab and using He *et al.* (2017)'s DS-TIMS method performed in CUGB lab. Range bars represent two standard errors (2 s.e.).

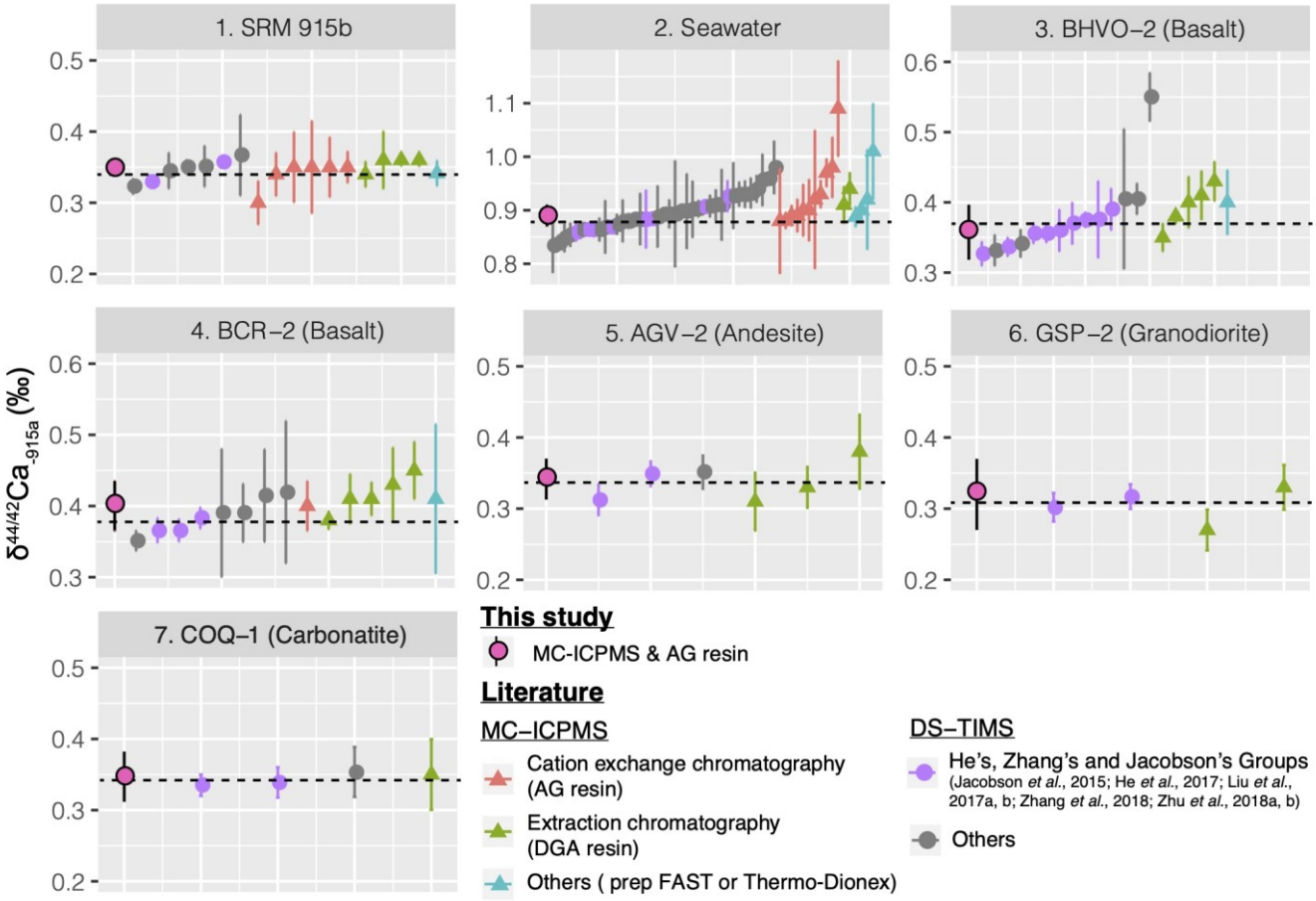

Figure S-2 Summary of stable Ca isotope compositions of geological reference materials. Range bars represent two standard errors (2 s.e.). The dashed line represents the weighted mean of $\delta^{44/42}$Ca values calculated from all reported data. See data sources in Table S-2.

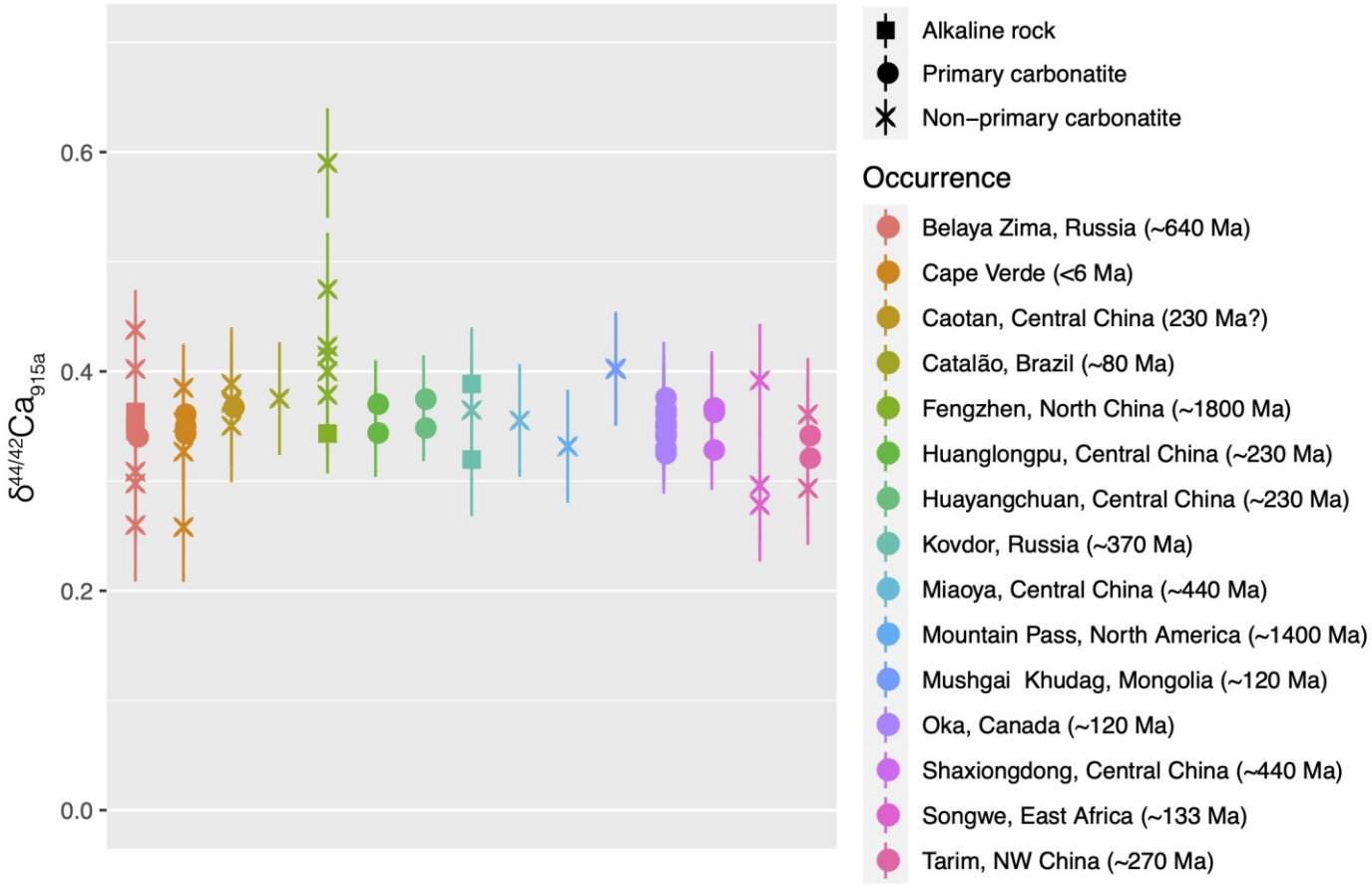

Figure S-3 Summary of refined stable Ca isotope data of worldwide carbonatites. Range bars represent two standard errors (2 s.e.). See data sources in Table S-1.

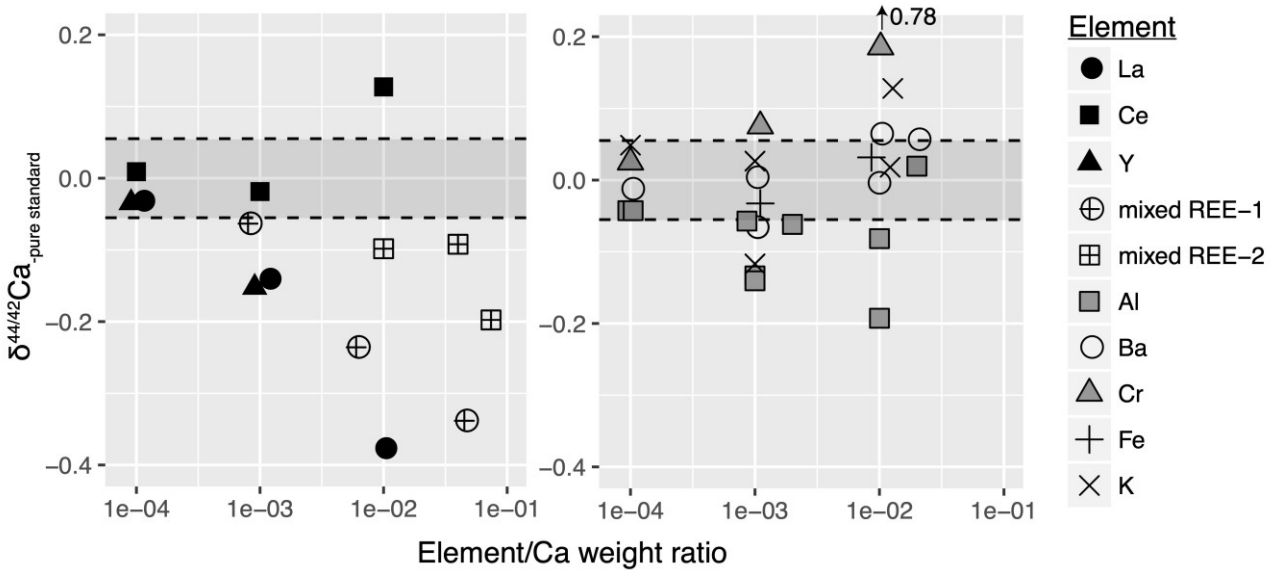

Figure S-4 Plots showing the effects of the presence of REE, Y, Al, Ba, Fe, K and Cr on measured Ca isotope compositions. The "mixed REE-1" is a mixture of La+Ce+Y with Ca solution. The "mixed REE-2" is a mixture of La+Ce+Pr+Sm+Nd with Ca solution. The area within the dash lines represents the external precision at 2σ level for $\delta^{44/42}Ca$. See data sources in Table S-3.

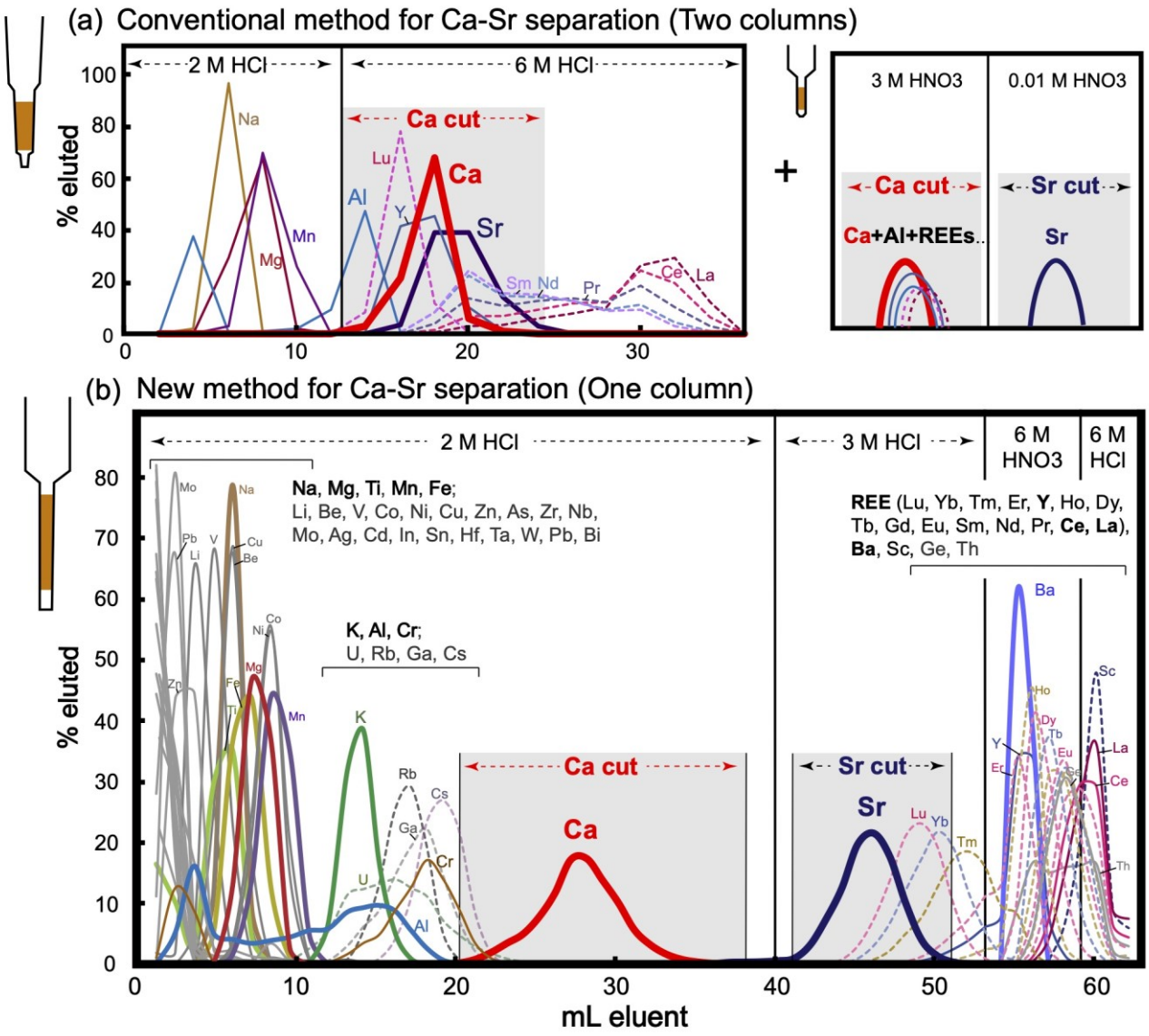

Figure S-5 **(a)** Elution curves for a conventional method using AG 50W-X12 exchange resin (1.6 mL). Note that Sr, Al, Y and some heavy rare earths are overlapped with Ca elute. The elution cures for column 2 is schematic. **(b)** Elution curves for 53 elements including Ca, Sr and other elements using AG 50W-X12 exchange resin (2 mL) for the new developed method.

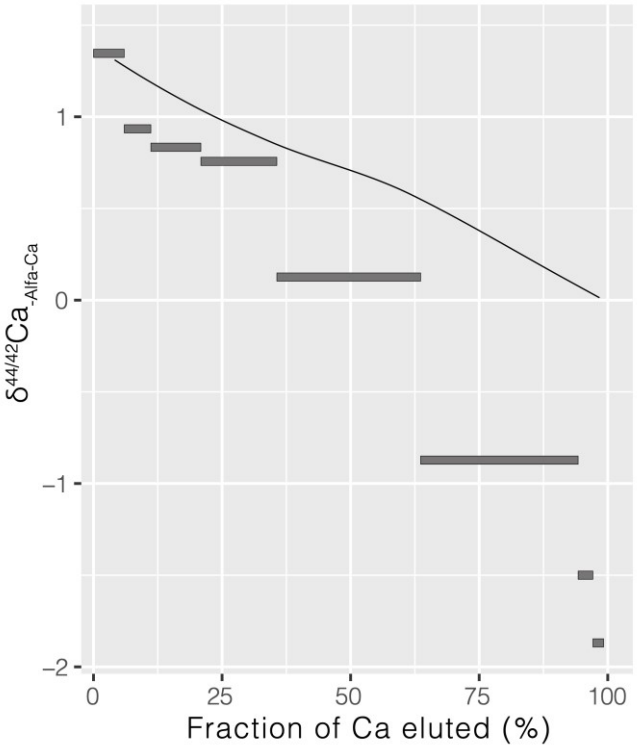

Figure S-6 $\delta^{44/42}Ca_{Alfa\text{-}Ca}$ values of eight Ca subcuts of pure Alfa-Ca solution eluted from the column, showing significant Ca isotope fractionation during ion-exchange chromatography. The cure fits $\delta^{44/42}Ca_{Alfa\text{-}Ca}$ values of accumulated eluted solution.

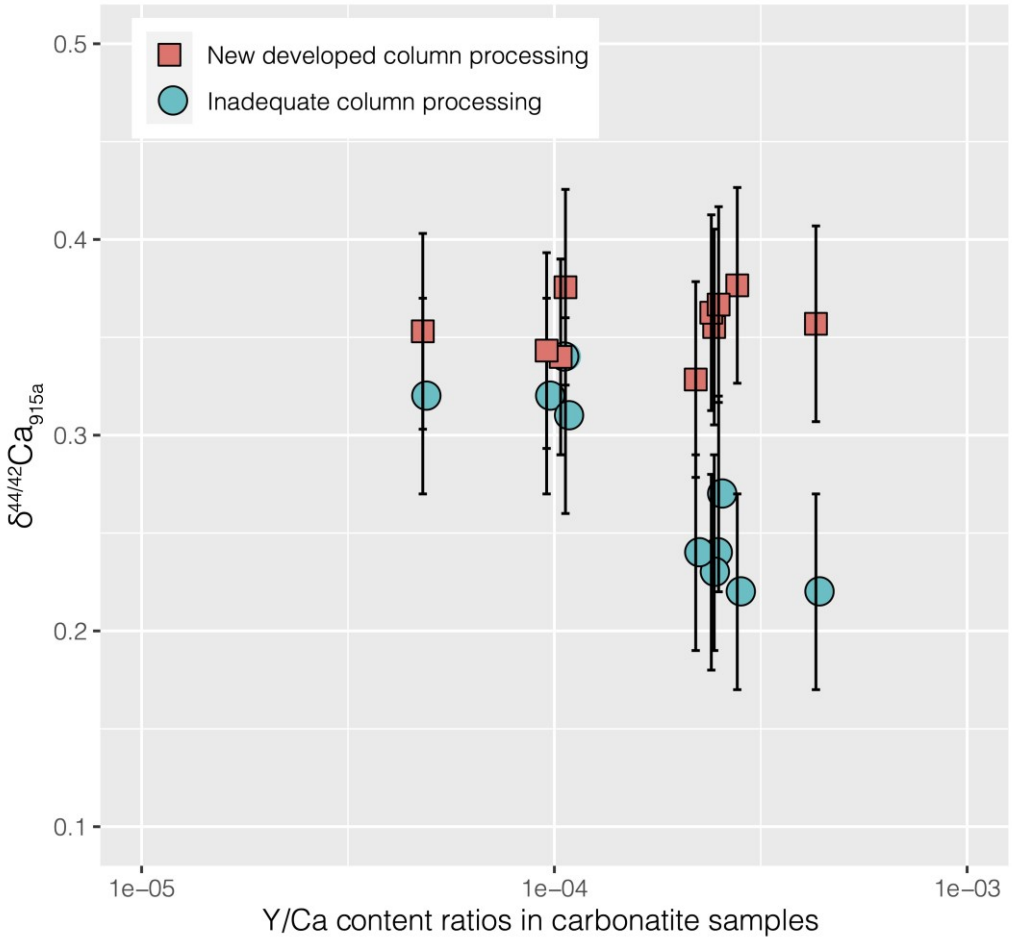

Figure S-7 Comparison of measured $\delta^{44/42}$Ca values for carbonatite samples with new developed column procedure and inadequate conventional column procedure that cannot eliminate Y. For samples with Y/Ca content ratios over 0.0001, the differences in measured $\delta^{44/42}$Ca values between two methods are detectable. See data sources in Table S-4.

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