Barium isotopic composition of the mantle: Constraints from carbonatites

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Abstract

To investigate the behaviour of Ba isotopes during carbonatite petrogenesis and to explore the possibility of using carbonatites to constrain the Ba isotopic composition of the mantle, we report high-precision Ba isotopic analyses of: (1) carbonatites and associated silicate rocks from the only active carbonatite volcano, Oldoinyo Lengai, Tanzania, and (2) Archean to Cenozoic carbonatites from Canada, East Africa, Germany and Greenland. Carbonatites and associated phonolites and nephelinites from Oldoinyo Lengai have similar $\delta^{137/134}$Ba values that range from +0.01 to +0.03‰, indicating that Ba isotope fractionation during carbonatite petrogenesis is negligible. The limited variation in $\delta^{137/134}$Ba values from −0.03 to +0.09‰ for most carbonatite samples suggests that their mantle sources have a relatively homogeneous Ba isotopic composition. Based on the carbonatites investigated in this work, the average $\delta^{137/134}$Ba value of their mantle sources is estimated to be +0.04 ± 0.06‰ (2SD, $n = 16$), which is similar to the average value of +0.05 ± 0.06‰ for mid-ocean ridge basalts. The lower $\delta^{137/134}$Ba value of −0.08‰ in a Canadian sample and higher $\delta^{137/134}$Ba values of +0.14‰ and +0.23‰ in two Greenland samples suggest local mantle isotopic heterogeneity that may reflect the incorporation of recycled crustal materials in their sources.

Keywords: barium isotopes; carbonatites; mantle geochemistry; crustal recycling
1. Introduction

Stable isotopes are powerful tools for identifying crustal recycling into the mantle, primarily due to significant stable isotope fractionation at low temperatures or near the Earth's surface (e.g., Hoefs, 2018). Recent studies have already explored mass-dependent isotopic variations for heavy metals (Fe, Cu, Mo, Hg, U etc.) in different geochemical reservoirs and their use as geochemical tracers for a wide range of geological processes (see Teng et al., 2017). The Ba stable isotope system is potentially a sensitive tracer of crustal recycling because Ba is highly enriched in crustal rocks (average of 456 μg/g for the continental crust; Rudnick and Gao, 2014) and in pelagic and terrigenous marine sediments (average of 786 μg/g for the mean of global subducted sediments; Plank, 2014). By comparison, the depleted mantle (DM) and bulk silicate Earth (BSE) have average Ba contents of 1.2 μg/g (Salters and Stracke, 2004) and 7.0 μg/g (Sun and McDonough, 1989), respectively.

Barium has seven stable isotopes and the percent abundance of these isotopes is as follows: $^{130}$Ba (0.11%), $^{132}$Ba (0.10%), $^{134}$Ba (2.42%), $^{135}$Ba (6.59%), $^{136}$Ba (7.85%), $^{137}$Ba (11.23%), and $^{138}$Ba (71.70%) (Eugster et al., 1969). Recent studies have demonstrated substantial Ba isotope fractionation among terrestrial samples and experimental precipitates (see review of Charbonnier et al., 2018). For example, measurements of granites, loess, glacial diamictites and river sediments show that the upper continental crust has highly variable $\delta^{137/134}$Ba$_{SRM3104a}$ values ($\delta^{137/134}$Ba$_{SRM3104a}$ = $\left[\left(\frac{^{137}}{^{134}}\text{Ba}_{\text{sample}}\right)/\left(\frac{^{137}}{^{134}}\text{Ba}_{\text{SRM3104a}}\right) - 1\right] \times 1000$, where SRM3104a is a pure Ba standard solution from NIST) ranging from −0.47 to +0.35‰ (Nan et al., 2018), and
negative values down to ca. −0.5‰ were reported from marine/diagenetic barite (von Allmen et al., 2010). If Ba isotopes are to be used as possible tracers for crustal recycling, the Ba isotopic composition of the mantle reservoir needs to be defined. To our knowledge, no Ba isotopic data are currently available for mantle peridotites, and Ba isotopic data for mid-ocean ridge basalts (MORBs) have only recently been reported in a single paper, with δ¹³⁷/¹³⁴Ba values that range from +0.02 ± 0.03‰ to +0.11 ± 0.03‰ (Nielsen et al., 2018). The δ¹³⁸/¹³⁴Ba values published by Nielsen et al. (2018) have been recalculated to enable comparison with the δ¹³⁷/¹³⁴Ba values used in this study, i.e. δ¹³⁷/¹³⁴Ba = 0.75 × δ¹³⁸/¹³⁴Ba (Horner et al., 2015). Nielsen et al. (2018) speculated that the limited variability in Ba isotopic composition of MORBs reflects binary mixing between a "depleted MORB (D-MORB) mantle" with δ¹³⁷/¹³⁴Ba = +0.11 ± 0.02‰ and an "enriched MORB (E-MORB) mantle" with δ¹³⁷/¹³⁴Ba = +0.02 ± 0.02‰, where the two end-member components were defined by the samples with the lowest ⁸⁷Sr/⁶⁶Sr (0.7023) and the highest ⁸⁷Sr/⁶⁶Sr (0.7034) ratios, respectively. However, D-MORBs with ⁸⁷Sr/⁶⁶Sr < 0.7024 display δ¹³⁷/¹³⁴Ba values from +0.02 to +0.11‰, overlapping with the range from +0.02 to +0.08‰ of E-MORBs with ⁸⁷Sr/⁶⁶Sr > 0.7030 (Nielsen et al., 2018). This feature suggests that the supposed Ba isotopic difference between the depleted mantle and enriched mantle may not actually exist.

In order to further investigate the Ba isotopic characteristics of the mantle, we focus on igneous carbonatites, i.e. mantle-derived rocks containing >50% carbonate minerals. They are generated through low-degree partial melting of carbonated mantle,
either as primitive melts or as parental carbonated silicate melts that undergo differentiation by liquid immiscibility and/or crystal fractionation (see reviews in Bell et al., 1998; Bizimis et al., 2003). Carbonatites can provide information on mantle geochemistry because: (1) they are widely distributed (>500 occurrences on all continents) with ages ranging from 3 Ga to present (Woolley and Kjarsgaard, 2008), (2) their petrogenesis is now considered by some researches to be closely linked to the global carbon cycle (e.g., Barker, 1996; Hoernle et al., 2002), and (3) they are sensitive indicators of thermal instabilities because they are near-solidus melts and can be associated with dynamic processes in the mantle (e.g., orogenic activity or mantle upwelling including plumes/hot spots; Woolley and Kjarsgaard, 2008; Ernst and Bell, 2010). In terms of isotopes, the radiogenic isotopic data of most young carbonatites (<200 Ma) plot within the fields of some ocean island basalts (OIBs), with values similar to the FOZO (focal zone), HIMU (high μ, where \( \mu = \frac{^{238}\text{U}}{^{204}\text{Pb}} \)) and EM1 (enriched mantle type 1) mantle components based mainly on data from OIBs (Bell and Tilton, 2001). Mixing between two of these components, HIMU and EM1, characterizes many of the carbonatites from East Africa (Bell and Tilton, 2002; Bell and Simonetti, 2010). By contrast, the depleted MORB mantle (DMM) plays little role in forming carbonatites (see figures in Rukhlov et al., 2015). These observations are more consistent with a model involving the generation of carbonatite melts from sub-lithospheric mantle rather than the lithosphere (Bell and Simonetti, 2010). Both the traditional C and O stable isotopes (e.g., Deines, 1989; Keller and Hoefs, 1995; Ray et al., 1999) and the non-traditional Li and B stable isotopes
(Halama et al., 2008; Hulett et al., 2016) have been analyzed in carbonatites to
document isotopic variations of their mantle sources and to monitor their temporal
evolution.

Carbonatites are ideal for investigating the Ba isotopic characteristics of the
mantle because they contain very high abundances of Ba (generally hundreds to tens
of thousands μg/g; e.g., Woolley and Kempe, 1989; Keller and Kraft, 1990). Moreover, the extremely low viscosity (e.g., Genge et al., 1995) leads to rapid
migration of carbonatite melts to the surface, reducing the possible addition of Ba
from crustal assimilation. In this work, high-precision Ba isotopic data were obtained
of 19 well-characterized carbonatites. In addition, ten silicate rocks were analyzed
from Oldoinyo Lengai. The purpose of this work is to illustrate the behaviour of Ba
isotopes during carbonatite petrogenesis, and assess its significance in constraining
the Ba isotopic composition of their mantle sources.

2. Samples

The carbonatite and associated silicate rock samples analyzed in this work are
from Canada, East Africa, Germany and Greenland, with ages that range from the
Archean to present. These samples have been well characterized with respect to
petrological, major and trace element, and Sr-Nd-Pb-Li-B-C-O-Mg isotopic aspects
(Schleicher et al., 1990; Tilton and Bell, 1994; Bell and Simonetti, 1996; Simonetti et
al., 1997; Bell and Tilton, 2001; Halama et al., 2005, 2007, 2008; Klaudius and Keller,
2006; Rukhlov et al., 2015; Hulett et al., 2016; Li et al., 2016). Similar to the majority
of global carbonatites, the carbonatite samples studied here have Sr-Nd isotopic compositions similar to those of OIBs (Halama et al., 2008). Most of the samples have oxygen isotopic compositions that fall into the range of "primary" igneous carbonatites, although some samples show elevated $\delta^{18}O$ values, which are common post-emplacement features in altered carbonatites (Demény et al., 2004). The detailed petrological and geochemical features of the samples have been presented in previous literature (Halama et al., 2007, 2008, and references therein), and only a brief introduction about the samples is given here.

2.1. The 0 Ma carbonatites and silicate rocks from Oldoinyo Lengai, Tanzania

As Oldoinyo Lengai is the only active carbonatite volcano on Earth, it has played a key role in assessing the origin of carbonatite melts (see Bell and Keller, 1995). The generally accepted model for natrocarbonatite petrogenesis at Oldoinyo Lengai involves silicate-carbonatite immiscible separation from a parental carbonated, alkaline silicate melt (e.g., Freestone and Hamilton, 1980; Church and Jones, 1995; Keller and Spettel, 1995; Dawson, 1998; Brooker and Kjarsgaard, 2011). Additional magmatic processes described at Oldoinyo Lengai include fractional crystallization of carbonate minerals nyerereite [Na$_2$Ca(CO$_3$)$_2$] and gregoryite [(Na$_2$, K$_2$, Ca)CO$_3$] (e.g., Peterson, 1990; Gittins and Jago, 1998) as well as phenocryst assimilation and cumulate disruption (Mitchell and Dawson, 2012). Differentiation via carbonate-halide liquid immiscibility may also have occurred during eruption (Potter et al., 2017).
Klaudius and Keller (2006) defined three major structural units of Oldoinyo Lengai (i.e., Lengai I, Lengai II A, and Lengai II B) and discussed the petrogenetic relationship of silicate rocks and natrocarbonatites from each unit. Stratigraphic relationships and Sr-Nd-Pb isotopic data suggest that the combeite–wollastonite nephelinites (CWNs) and natrocarbonatites of Lengai II B are conjugate silicate and carbonatite melts produced by liquid immiscibility, unlike the phonolites of Lengai I and CWNs of Lengai II A (Klaudius and Keller, 2006). Samples studied here include: 1) natrocarbonatites (OL2, OL7, OL123, OL148 and OL259) and the petrogenetically related CWNs (OL624, OL788 and OL804) from the Lengai II B unit, and 2) silicate rocks not generated by liquid immiscibility (including phonolites OL440, OL442, OL450, OL503 and OL822 from the Lengai I unit as well as CWNs OL247 and OL803 from the Lengai II A unit). Li et al. (2016) found that the silicate rocks related to carbonatites by liquid immiscibility have different Mg isotopic compositions to other silicate rocks, implying significant Mg isotope fractionation during silicate-carbonatite liquid immiscibility. Comparison between the Ba isotopic compositions of these two types of silicate rocks can provide constraints on the behaviour of Ba isotopes during the generation of conjugate liquids.

2.2. Archean to Cenozoic carbonatites from Canada, East Africa, Germany and Greenland

The Archean carbonatite samples from the Dolodau and Lac Shorrt occurrences in Canada (2.7 Ga) are biotite-calcite carbonatites (DOD77, LSC20 and LSC108) and an
amphibole-biotite silicocarbonatite (DOD91). Proterozoic carbonatite samples from the Gardar igneous province, South Greenland, are calcite carbonatites (GR46, GR73 and GR74) from the Grønnedal-Ika complex (1.3 Ga). Phanerozoic carbonatite samples consist of a calcite carbonatite sample (K5) from the 17 Ma old Kaiserstuhl complex, Germany, and carbonatites with ages ranging from 138 to 13 Ma from the East African Rift (calcite carbonatites N1295, PH212, PH213, SU103 and HB, and a ferrocarbonatite DU365).

The 29 whole-rock samples investigated here for Ba isotopic compositions are the same powders as those studied previously for radiogenic and Li-C-O isotopic compositions (Halama et al., 2007, 2008, and references therein) as well as Mg isotopic compositions but only for the Oldoinyo Lengai samples (Li et al., 2016). On the basis of petrography and Li-C-O-Mg isotopic data (Halama et al., 2007, 2008; Li et al., 2016), post-emplacement alteration is negligible for all but three of the carbonatite samples from East Africa (i.e., N1295, DU365 and OL804). These three samples show signs of late-stage alteration (e.g., altered minerals or hydrothermal veins), and two of them (N1295 and DU365) have elevated δ18O values (12.4‰ and 15.6‰) that lie outside the range of "primary" igneous carbonatites (see Fig. 5a in Halama et al., 2008).

3. Analytical methods

Barium isotopic analyses were performed at the University of Science and Technology of China, Hefei. All chemical procedures were carried out in an ISO-class
6 clean laboratory. Using screw-top Teflon beakers, the whole-rock powders were
dissolved in a combination of concentrated HF–HNO₃–HCl. Purification of Ba was
achieved by cation exchange chromatography with Bio-Rad 200–400 mesh
AG50W–X12 resin, following established procedures (Nan et al., 2015, 2018).
Sample solutions containing ~2 μg Ba were loaded onto the resin. The Ba recoveries
through column chemistry, based on analyses of Ba content in the elution collected
before and after the Ba cut, were >99%. The procedural blank was 2 ng Ba.

Barium isotopic measurements were carried out on a Neptune Plus multi-collector
inductively coupled plasma mass spectrometer (MC–ICP–MS), and a double-spike
technique was used to correct for instrumental mass bias. An appropriate amount of
the ¹³⁵Ba–¹³⁶Ba double spike with a ratio of 1.72 (m/m; Rudge et al., 2009) was added
to a portion of the purified sample solution containing ~100 ng Ba. The optimal range
of the proportion of double spike in the double spike-sample mixture is 0.43 to 0.60.
The "dry" plasma conditions (Aridus II desolvating nebulizer) were used to increase
sensitivity (~7V/100ng/g for ¹³⁷Ba). Barium isotopic analyses were conducted in a
low-resolution mode, with ¹³⁴Ba, ¹³⁵Ba, ¹³⁶Ba and ¹³⁷Ba collected simultaneously by
the L2, L1, C and H1 Faraday cups, respectively. ¹³¹Xe and ¹⁴⁰Ce were also collected
by the L4 and H3 Faraday cups to correct the effects of isobaric interferences from Xe
and Ce. The background signals for ¹³⁷Ba (<0.005 V) were negligible relative to the
sample signals (~7 V).

The results are reported in δ¹³⁷/¹³⁴Ba values relative to the NIST Standard
Reference Material (SRM) 3104a, i.e. δ¹³⁷/¹³⁴Ba = [(¹³⁷/¹³⁴Ba)sample/(¹³⁷/¹³⁴Ba)SRM3104a −
11 \times 1000. For comparison, all published $\delta^{138/134}\text{Ba}$ values have been recalculated to $\delta^{137/134}\text{Ba}$ values by assuming mass-dependent fractionation following $\delta^{137/134}\text{Ba} = 0.75 \times \delta^{138/134}\text{Ba}$ (Horner et al., 2015). Based on duplicate analyses of two in-house reference solutions USTC-Ba and ICPUS-Ba, the external precision is $\leq 0.04\%$ for $\delta^{137/134}\text{Ba}$ (2SD). The $\delta^{137/134}\text{Ba}$ values yielded in this study for the three USGS reference materials, i.e. BCR-2, BHVO-2 and COQ-1, are in good agreement with previously published values (Table 1).

4. Results

Barium isotopic compositions are reported in Table 2 for the 0 Ma carbonatites and silicate rocks from Oldoinyo Lengai (OL), and in Table 3 for Archean to Cenozoic carbonatites. For reference, Ba concentrations of all samples and Mg isotopic compositions of the OL samples that have been reported in previous studies (Simonetti et al., 1997; Klaudius and Keller, 2006; Halama et al., 2008; Li et al., 2016) are also included in Tables 2 and 3.

Due to the high incompatibility of Ba during mantle melting ($D_{\text{solid/melt}} = 0.00012$; Workman and Hart, 2005), preferential partition of Ba into the carbonatite melt during liquid immiscibility (e.g., $D_{\text{carbonatite liquid/silicate liquid}} = 5.2$; Veksler et al., 1998), and different degrees of enrichment or depletion of Ba during magmatic crystallization, the Ba concentrations of carbonatites investigated here vary considerably over more than two orders of magnitude (Fig. 1). However, regardless of their highly variable Ba concentrations, different localities and different ages, 17 of the 19 carbonatite samples
display $\delta^{137/134}$Ba values that range from $-0.03$ to $+0.14\%$, which are similar, within limits of analytical uncertainties, to the range of MORBs that extends from $-0.01$ to $+0.14\%$ (Nielsen et al., 2018; Fig. 1). The remaining two samples are outside the range of MORBs (Fig. 1), i.e., one carbonatite from Canada (DOD 91) with a lower $\delta^{137/134}$Ba value of $-0.08\%$ and one carbonatite from Greenland (GR74) with a higher $\delta^{137/134}$Ba value of $+0.23\%$. The OL silicate rocks have homogeneous $\delta^{137/134}$Ba values from $+0.01$ to $+0.03\%$ with an average of $+0.02 \pm 0.02\%$ (2SD, $n = 10$), which is identical to that of the OL carbonatites ($+0.02 \pm 0.02\%$, 2SD, $n = 5$).

5. Discussion

5.1. The behaviour of Ba isotopes during carbonatite petrogenesis

Oldoinyo Lengai has been the subject of many studies and most believe that the natrocarbonatites were formed by liquid immiscibility involving a parental peralkaline silicate melt at low pressures (e.g., Freestone and Hamilton, 1980; Church and Jones, 1995; Keller and Spettel, 1995; Dawson, 1998; Brooker and Kjarsgaard, 2011). Li et al. (2016) demonstrated that the OL silicate rocks not generated by immiscibility have mantle-like Mg isotopic compositions, whereas those related to carbonatites by liquid immiscibility have isotopically heavier Mg (Fig. 2a). Such a difference indicates significant Mg isotope fractionation during liquid immiscibility, with heavy Mg isotopes preferentially partitioning into the silicate melts. By contrast, all of the OL silicate rocks analyzed here have homogeneous $\delta^{137/134}$Ba values that range from $+0.01$ to $+0.03\%$, all within the limits of analytical uncertainty (Fig. 2a). In addition,
there is no correlation between the $\delta^{137/134}\text{Ba}$ values and the index of carbonatite magma differentiation marked by a decrease in CaO contents (Gittins and Jago, 1998; Fig. 2b). These findings suggest that even during the complex petrogenetic processes associated with the Oldoinyo Lengai magmatism, such as liquid immiscibility and crystal fractionation, little Ba isotope fractionation has taken place. The exact mechanism for the different behaviour of Mg and Ba isotopes during carbonatite magmatism is currently unclear, but may simply result from the smaller relative mass difference between $^{137}\text{Ba}$ and $^{134}\text{Ba}$ (ca. 2%) than that between $^{26}\text{Mg}$ and $^{24}\text{Mg}$ (ca. 8%).

In addition, because Ba is highly incompatible with an estimated bulk distribution coefficient $D_{\text{solid/melt}}$ of 0.00012 during mantle melting (Workman and Hart, 2005), ~99% of the Ba will enter into the melt after 1% partial melting, implying that the Ba isotopic composition of any partial melts from the mantle, including carbonatitic melts, should reflect the source composition (Nielsen et al., 2018). It thus appears that Ba isotopes remain relatively unaffected during both partial melting and liquid immiscibility, even though the Ba concentrations will be significantly changed during these processes.

5.2. Barium isotopic composition of the mantle

The similarity in $\delta^{137/134}\text{Ba}$ values of most carbonatites investigated here to those of MORBs (Fig. 1) suggests that the mantle sources for both have a relatively homogeneous Ba isotopic composition. In order to estimate the average $\delta^{137/134}\text{Ba}$...
value of the mantle sources of carbonatites, the outliers, if any, are identified through
statistical analysis. Using the box plot method (see NIST/SEMATECH e-Handbook of
Statistical Methods), three samples, i.e., DOD91, GR73 and GR74, are identified as
outliers (Fig. 3a).

Based on our data set, the average $\delta^{137/134}$Ba value of the mantle sources of the
parental melts to carbonatites is estimated to be $+0.04 \pm 0.06\%$ (2SD, $n = 16$; Fig. 3a)
when the three outliers are excluded. Hence, within current analytical uncertainties,
the average $\delta^{137/134}$Ba value of carbonatites is indistinguishable from that of $+0.05 \pm
0.06\%$ for MORBs (recalculated from Nielsen et al., 2018; Fig. 3b). This is in
contrast to the difference in radiogenic isotopic compositions between MORBs and
carbonatites (see figures in Rukhlov et al., 2015). The radiogenic isotopic
characteristics of some carbonatites are more closely related to those of some OIBs
(Bell and Tilton, 2002; Bell and Simonetti, 2010). A similarity may also exist for the
Ba isotope system between carbonatites and OIBs, for which an average $\delta^{137/134}$Ba
value of $0.02 \pm 0.10\%$ has been reported by Huang et al. (2015). Collectively, it
seems that the mantle sources for the parental melts of MORBs, OIBs and
carbonatites may be relatively homogeneous in terms of Ba isotopic compositions.
Such a characteristic implies that the terrestrial differentiation events that generated
the depleted and enriched mantle reservoirs (i.e., a major differentiation event during
the Hadean recorded by the Nd-Hf isotopes and a second one at ~3 Ga recorded by the
Sr-Pb isotopes; Bell and Tilton, 2002; Rukhlov et al., 2015) may not have affected the
Ba isotope system.
Our data demonstrate that the Ba isotopic compositions of the Archean to present-day carbonatites investigated here overlap the range typical for modern mantle-derived rocks (MORBs and OIBs). If the mantle sources of carbonatites are related to subduction and recycling of oceanic lithosphere, as suggested by some studies (Nelson et al., 1988; Hoernle et al., 2002; Hulett et al., 2016), we see no evidence for this in terms of their Ba isotopic composition. This implies that one or both of the following is true: (1) the bulk Ba isotopic composition of subducted materials does not deviate greatly from the average mantle value and/or (2) subducted crustal Ba is effectively homogenized upon subduction into the mantle. The first possibility is in agreement with the observations that the average Ba isotopic compositions of marine sediments (δ137/134Ba = +0.03‰) and altered oceanic crust (δ137/134Ba = +0.07‰) overlap the average values of both carbonatites and MORBs (Fig. 3).

5.3. Local mantle Ba isotopic heterogeneity

While most carbonatites display a limited variation in Ba isotopic composition, there are three outliers (i.e., DOD91, GR73 and GR74; Fig. 3a). Their distinct δ137/134Ba values may not result from surface alteration because these three samples lack petrographic evidence for alteration and have Li-C-O isotopic compositions similar to those of "primary" igneous carbonatites (Halama et al., 2008). In addition, crustal contamination also seems unlikely because of the extremely low viscosity of carbonatite melts (e.g., Genge et al., 1995). We therefore attribute the variable Ba
isotopic compositions of the three carbonatites from Canada and Greenland to local heterogeneities in the mantle.

Isotopic heterogeneity within the mantle is usually related to recycling of oceanic crustal materials (e.g., Hofmann, 2014). Although the data base is relatively small, available data show that marine sediments and altered oceanic crust (AOC) have variable $\delta^{137/134}$Ba values that range from $-0.08$ to $+0.15\%o$ and from $-0.07$ to $+0.25\%o$, respectively (Fig. 3b; Bridgestock et al., 2018, 2019; Nielsen et al., 2018). An even larger $\delta^{137/134}$Ba variation from $-0.17$ to $+0.30\%o$ for AOC has been reported by Nan et al. (2017), and higher $\delta^{137/134}$Ba values than those presently observed in marine sediments could be expected as suspended particles in seawater display high $\delta^{137/134}$Ba values ranging from $+0.19$ to $+0.45\%o$ (Horner et al., 2015; Cao et al., 2016). Hence, incorporation of recycled marine sediments and/or AOC with extreme Ba isotopic compositions in local parts of the mantle might account for the distinct $\delta^{137/134}$Ba values of the three outlier carbonatites from Canada and Greenland. If this is true, Ba isotopes could potentially be a novel tracer of crustal recycling. However, further work is needed to find out an unequivocal explanation of the observed different Ba isotopic composition (Fig. 3a) but similar Li-C-O isotopic compositions (Halama et al., 2008) between the three outliers and the other carbonatites investigated in this study.

6. Conclusions

The main conclusions from this study are:
(1) Carbonatites and associated silicate rocks from Oldoinyo Lengai have homogeneous $\delta^{137/134}$Ba values that range from +0.01 to +0.03‰, indicating insignificant Ba isotope fractionation during both silicate-carbonatite liquid immiscibility and subsequent magma differentiation. Hence, Ba isotopic composition of carbonatites could reflect that of their mantle sources.

(2) Most carbonatites from Canada, East Africa, Germany and Greenland display a limited variation in $\delta^{137/134}$Ba values ranging from −0.03 to +0.09‰, suggesting that the mantle sources of carbonatites have a relatively homogeneous Ba isotopic composition. The spatial distribution of the 16 carbonatites we have measured suggests that their mantle sources have an average $\delta^{137/134}$Ba value of +0.04 ± 0.06‰ (2SD), similar to those of MORBs and OIBs. Therefore, the mantle sources for the parental melts of MORBs, OIBs and carbonatites are likely to be relatively homogeneous in terms of Ba isotopic compositions.

(3) The distinct $\delta^{137/134}$Ba values of the three outlier carbonatites might reflect the incorporation of marine sediments and/or altered oceanic crust with extreme Ba isotopic compositions in their mantle sources. On the basis of these observations, Ba isotopes may potentially be a novel tracer of crustal recycling.

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References


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### Table 1

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
<th>δ(^{137/134})Ba(‰)</th>
<th>2SD(‰)</th>
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<td>0.04</td>
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<td>0.04</td>
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</tr>
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<td>Nan et al. (2018)</td>
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<td>Average</td>
<td>((n = 3))</td>
<td>+0.02</td>
<td>0.03</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+0.05</td>
<td>0.03</td>
<td>Nan et al. (2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+0.05</td>
<td>0.04</td>
<td>Bullen and Chadwich (2016)</td>
</tr>
<tr>
<td>COQ-1</td>
<td>Carbonatite, Oka</td>
<td>+0.06</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Duplicate</td>
<td>complex, Canada</td>
<td>+0.08</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
<td></td>
<td></td>
<td>+0.08</td>
<td>0.04</td>
<td>Zeng et al. (2019)</td>
</tr>
</tbody>
</table>

\(^a\) 2SD = two times the standard deviation of \(n\) repeat measurements.

\(^b\) Duplicate = repeat column chemistry and measurement of different aliquots of a stock solution.
### Table 2

Barium isotopic compositions and selected geochemical parameters of the natrocarbonatites and silicate rocks from Oldoinyo Lengai (OL), Tanzania.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rock type</th>
<th>Ba(μg/g) $^a$</th>
<th>$\delta^{137/134}$Ba(‰)</th>
<th>2SD(‰)$^b$</th>
<th>$\delta^{26}$Mg(‰)$^c$</th>
<th>2SD(‰)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL2</td>
<td>Natrocarbonatite</td>
<td>13,430</td>
<td>+0.03</td>
<td>0.03</td>
<td>+0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>OL7</td>
<td>Natrocarbonatite</td>
<td>14,330</td>
<td>+0.03</td>
<td>0.03</td>
<td>+0.37</td>
<td>0.10</td>
</tr>
<tr>
<td>OL123</td>
<td>Natrocarbonatite</td>
<td>11,280</td>
<td>+0.01</td>
<td>0.03</td>
<td>+0.19</td>
<td>0.10</td>
</tr>
<tr>
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<tr>
<td>OL148</td>
<td>Natrocarbonatite</td>
<td>15,040</td>
<td>+0.01</td>
<td>0.03</td>
<td>+0.16</td>
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</tr>
<tr>
<td>OL259</td>
<td>Natrocarbonatite</td>
<td>13,790</td>
<td>+0.03</td>
<td>0.03</td>
<td>+0.13</td>
<td>0.10</td>
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</table>

**OL silicate rocks not generated by liquid immiscibility**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rock type</th>
<th>Ba(μg/g)</th>
<th>$\delta^{137/134}$Ba(‰)</th>
<th>2SD(‰)$^b$</th>
<th>$\delta^{26}$Mg(‰)$^c$</th>
<th>2SD(‰)$^c$</th>
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</thead>
<tbody>
<tr>
<td>OL247</td>
<td>Nephelinite</td>
<td>1431</td>
<td>+0.02</td>
<td>0.03</td>
<td>−0.14</td>
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<tr>
<td>OL440</td>
<td>Phonolite</td>
<td>1440</td>
<td>+0.03</td>
<td>0.03</td>
<td>−0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>OL442</td>
<td>Phonolite</td>
<td>1669</td>
<td>+0.01</td>
<td>0.03</td>
<td>−0.11</td>
<td>0.07</td>
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<tr>
<td>Duplicate</td>
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<tr>
<td>OL450</td>
<td>Phonolite</td>
<td>1523</td>
<td>+0.01</td>
<td>0.03</td>
<td>−0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>OL503</td>
<td>Phonolite</td>
<td>1614</td>
<td>+0.02</td>
<td>0.03</td>
<td>−0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>OL803</td>
<td>Nephelinite</td>
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<td>+0.02</td>
<td>0.03</td>
<td>−0.13</td>
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<tr>
<td>OL822</td>
<td>Phonolite</td>
<td>1532</td>
<td>+0.03</td>
<td>0.03</td>
<td>−0.25</td>
<td>0.09</td>
</tr>
</tbody>
</table>

**OL silicate rocks related to the carbonatites by liquid immiscibility**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rock type</th>
<th>Ba(μg/g)</th>
<th>$\delta^{137/134}$Ba(‰)</th>
<th>2SD(‰)$^b$</th>
<th>$\delta^{26}$Mg(‰)$^c$</th>
<th>2SD(‰)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL624</td>
<td>Nephelinite</td>
<td>1564</td>
<td>+0.02</td>
<td>0.03</td>
<td>−0.06</td>
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<tr>
<td>OL788</td>
<td>Nephelinite</td>
<td>1970</td>
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<td>0.03</td>
<td>+0.07</td>
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<tr>
<td>OL804</td>
<td>Nephelinite</td>
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<td>0.03</td>
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<td>0.08</td>
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</tr>
</tbody>
</table>

$^a$ Data from Simonetti et al. (1997) and Klaudius and Keller (2006).

$^b$ 2SD = two times the standard deviation of n (n >20) repeat measurements of the in-house reference solutions during an analytical session.

$^c$ Data from Li et al. (2016).

$^d$ Duplicate = repeat column chemistry and measurement of different aliquots of a stock solution.
Table 3

Barium concentrations and isotopic compositions of carbonatites from Canada, East Africa, Germany, and Greenland.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rock type</th>
<th>Age(Ma)</th>
<th>$\text{Ba}(\mu\text{g/g})$</th>
<th>$\delta^{137/134}\text{Ba}(%)$</th>
<th>2SD(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Canada</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DOD77</td>
<td>Calcite carbonatite</td>
<td>2680</td>
<td>985</td>
<td>−0.03</td>
<td>0.04</td>
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<tr>
<td>DOD91</td>
<td>Silicocarbonatite</td>
<td>2680</td>
<td>806</td>
<td>−0.07</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Duplicate</td>
<td></td>
<td></td>
<td>−0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>LSC20</td>
<td>Calcite carbonatite</td>
<td>2680</td>
<td>706</td>
<td>+0.08</td>
<td>0.04</td>
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<tr>
<td></td>
<td>Duplicate</td>
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<td>+0.09</td>
<td>0.04</td>
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<td>LSC108</td>
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<td>1472</td>
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<td><strong>East Africa</strong></td>
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<td>N1295</td>
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<td>PH212</td>
<td>Calcite carbonatite</td>
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<td>PH213</td>
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<td>SU103</td>
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<td>366</td>
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<td>DU365</td>
<td>Ferrocarbonatite</td>
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<tr>
<td>HB</td>
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<td>4454</td>
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<tr>
<td><strong>Germany</strong></td>
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<tr>
<td>K5</td>
<td>Calcite carbonatite</td>
<td>17</td>
<td>1319</td>
<td>+0.03</td>
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<tr>
<td><strong>Greenland</strong></td>
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<tr>
<td>GR46</td>
<td>Calcite carbonatite</td>
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<td>405</td>
<td>+0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>GR73</td>
<td>Calcite carbonatite</td>
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<td>91</td>
<td>+0.13</td>
<td>0.04</td>
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<tr>
<td></td>
<td>Duplicate</td>
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<td></td>
<td>+0.15</td>
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<tr>
<td>GR74</td>
<td>Calcite carbonatite</td>
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<td>66</td>
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<td>+0.23</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Data from Halama et al. (2008) and references therein.

** 2SD = two times the standard deviation of n (n >20) repeat measurements of the in-house reference solutions during an analytical session.

$c$ Duplicate = repeat column chemistry and measurement of different aliquots of a stock solution.
Figure captions

**Fig. 1.** $\delta^{137/134}$Ba vs. Ba (μg/g) for carbonatites from Canada, East Africa (including Oldoinyo Lengai (OL)), Germany and Greenland. Data for silicate rocks from Oldoinyo Lengai are also shown. The gray area marks distribution of data from mid-ocean ridge basalts (MORBs) reported in Nielsen et al. (2018). The $\delta^{138/134}$Ba values reported in Nielsen et al. (2018) have been recalculated here to $\delta^{137/134}$Ba values, i.e. $\delta^{137/134}$Ba = 0.75 × $\delta^{138/134}$Ba (Horner et al., 2015). Error bars represent 2SD uncertainties. Data are from Tables 2 and 3.

**Fig. 2.** (a) $\delta^{137/134}$Ba vs. $\delta^{26}$Mg for silicate rocks from Oldoinyo Lengai (OL); (b) $\delta^{137/134}$Ba vs. CaO (wt%) for carbonatites from OL. Data are from Table 2, and the CaO contents from Simonetti et al. (1997).

**Fig. 3.** (a) Histogram of $\delta^{137/134}$Ba values for carbonatites from Canada, East Africa (including Oldoinyo Lengai), Germany and Greenland. The red circles represent the three outliers identified using the box plot method (see NIST/SEMATECH e-Handbook of Statistical Methods). The gray band and vertical red line represent the range and estimated average $\delta^{137/134}$Ba value for the mantle sources of carbonatites (i.e., $+0.04 \pm 0.06\%$, 2SD), excluding the three outliers. Data are from Tables 2 and 3. (b) Histogram of $\delta^{137/134}$Ba values for MORBs (Nielsen et al., 2018). The black horizontal lines and red vertical lines respectively represent the range and the average of $\delta^{137/134}$Ba values for marine sediments (Bridgestock et al., 2018, 2019;...
Nielsen et al., 2018) and altered oceanic crust (AOC; Nielsen et al., 2018). The published $\delta^{138/134}$Ba values have been recalculated here to $\delta^{137/134}$Ba values, i.e. $\delta^{137/134}$Ba = 0.75 $\times$ $\delta^{138/134}$Ba (Horner et al., 2015).
Fig. 2
Carbonatites
average $\delta^{137/134}$Ba =
$+0.04 \pm 0.06\%$
(2SD, $n = 16$; See text for details)

Marine sediments, $\delta^{137/134}$Ba = $-0.08 - +0.15\%$

Altered oceanic crust (AOC), $\delta^{137/134}$Ba = $-0.07 - +0.25\%$

Mid-ocean ridge basalts
average $\delta^{137/134}$Ba =
$+0.05 \pm 0.06\%$
(2SD, $n = 21$)

Fig. 3