

## GEOCHEMISTRY

## Calcium isotopic evidence for the mantle sources of carbonatites

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The origin of carbonatites—igneous rocks with more than 50% of carbonate minerals—and whether they originate from a primary mantle source or from recycling of surface materials are still debated. Calcium isotopes have the potential to resolve the origin of carbonatites, since marine carbonates are enriched in the lighter isotopes of Ca compared to the mantle. Here, we report the Ca isotopic compositions for 74 carbonatites and associated silicate rocks from continental and oceanic settings, spanning from 3 billion years ago to the present day, together with O and C isotopic ratios for 37 samples. Calcium-, Mg-, and Fe-rich carbonatites have isotopically lighter Ca than mantle-derived rocks such as basalts and fall within the range of isotopically light Ca from ancient marine carbonates. This signature reflects the composition of the source, which is isotopically light and is consistent with recycling of surface carbonate materials into the mantle.

## INTRODUCTION

Carbonatites are highly distinctive igneous rocks, containing more than 50% of carbonate minerals and limited silica. They are often associated with silicate rocks, range in age from 3 billion years (Ga) to present day, and occur on all continents and in at least one modern ocean basin (1). While there is consensus that carbonatites are ultimately derived from Earth's upper mantle, either directly by very low degrees of partial melting or by differentiation of primary carbonated silicate magmas, the ultimate source of the carbon is still unresolved. An origin of carbonatites either from primordial carbon stored long term in the mantle or from crustal carbon recycled through the mantle via subduction on a billion-year or more deep carbon cycle has both been invoked (2–6). Understanding the origin of carbonatites is further complicated by the fact that the only active carbonatitic volcano on Earth, Oldoinyo Lengai in Tanzania, produces unusual Na-rich carbonatitic melts (natrocarbonatites) compared to all other Ca-, Mg-, and Fe-rich carbonatites (calciocarbonatites, magnesiocarbonatites, and ferrocarbonatites). Why Oldoinyo Lengai is chemically different from other carbonatitic occurrences, whether it is a good analog for carbonatites in general, and whether all extrusive carbonatites were originally erupted as natrocarbonatites and subsequently altered to calciocarbonatites are outstanding questions (7–9).

Radiogenic isotopes, including Sr-Nd-Hf-Pb isotope systematics and noble gases, have been widely used to study the composition of the source of the carbonatites, but results appear ambiguous between recycled carbon [e.g., (2, 6, 10)] and primordial carbon (11–13). The enrichment of the light rare earth elements observed in most carbonatites indicates that they likely derive from low-degree partial melting of the mantle. Stable isotopes that are fractionated in low-temperature surface environments are tracers par excellence of the presence of crustal recycled materials in igneous mantle sources, particularly

because their compositions are invariant of age [e.g., (14)]. For instance, oxygen isotopes are often used to trace ocean island basalt mantle sources [e.g., (15)]. A previous study using boron isotopes indicated a contribution of recycled crustal materials in the sources of carbonatites (16). However, B is a trace element that is sensitive to alteration (17). It has been suggested that no significant amount of B is introduced to the upper mantle through subducted slab components (18). In contrast, subducted B has been invoked to explain superdeep diamond growth [type IIB; (19)]; the behavior of B in the mantle is, therefore, still unclear. Calcium is a major element in carbonatites [CaO, >20 weight % (wt %) (20)] and is in higher abundance in marine carbonates (~40 wt %) than in the mantle [~3.5 wt %; (21)]. As marine carbonates [ $\delta^{44/40}\text{Ca}$  down to ~-1 per mil (‰) (22)] are isotopically distinct from the mantle [ $\delta^{44/40}\text{Ca}$  of the bulk silicate earth (BSE), ~0.9; (23, 24)], Ca isotopes are tracers of a subducted sedimentary material that has been recycled into the mantle (25, 26), and so they have the potential to reveal the origin of carbonatites. Seven carbonatites from the Ambadongar complex in India have been studied for Ca isotopes (27), but the complex consists on carbonatites dikes and a massive fluor spar deposit with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and high  $\delta^{44/40}\text{Ca}$ , which could have altered the primary composition of the carbonatites.

## RESULTS

We analyzed 73 carbonatites and associated silicate rocks, including natrocarbonatites from Oldoinyo Lengai, and recent to 24-Ma calciocarbonatites from the ocean islands of Fuerteventura (Canary Islands), Fogo, and Brava (Cape Verde) and 4- to 3000-Ma calciocarbonatites, magnesiocarbonatites, and ferrocarbonatites, mainly associated with rifts, from Germany (Kaiserstuhl), Norway (Fen), Brazil (Jacupiranga), Greenland (Tupertalik and Singertat), and various localities in Africa (tables S1 and S2). All the studied carbonatites, with the exception of natrocarbonatites, are enriched in the lighter Ca isotopes relative to basalts and the mantle [BSE estimates:  $0.88 \pm 0.07\text{‰}$ ,  $0.94 \pm 0.05\text{‰}$ , and  $1.05 \pm 0.04\text{‰}$  (23, 24, 28)], with a mean of  $\delta^{44/40}\text{Ca} = 0.26 \pm 0.25\text{‰}$  (2 SD,  $n = 50$ ) ( $\delta^{44/40}\text{Ca}$  is the ‰ deviation of  $^{44}\text{Ca}/^{40}\text{Ca}$  from the SRM915a standard). The five fresh natrocarbonatite samples from Oldoinyo Lengai are isotopically similar

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to mantle-derived basalts, averaging  $0.71 \pm 0.20\text{‰}$  (2 SD,  $n = 5$ ) (Fig. 1 and table S1). Associated silicate rocks from three units in Brava and two localities in Greenland span a range of  $\delta^{44/40}\text{Ca}$  from  $0.31 \pm 0.02\text{‰}$  to  $1.14 \pm 0.09\text{‰}$ . The  $\delta^{44/40}\text{Ca}$  of all the carbonatites studied remains constant regardless of the emplacement age and mode (i.e., intrusive or extrusive) and the tectonic setting (i.e., oceanic or continental) (Fig. 1). The O and C isotopic compositions of the calcio-carbonatites and the natrocarbonatites are presented in tables S1 to S3.

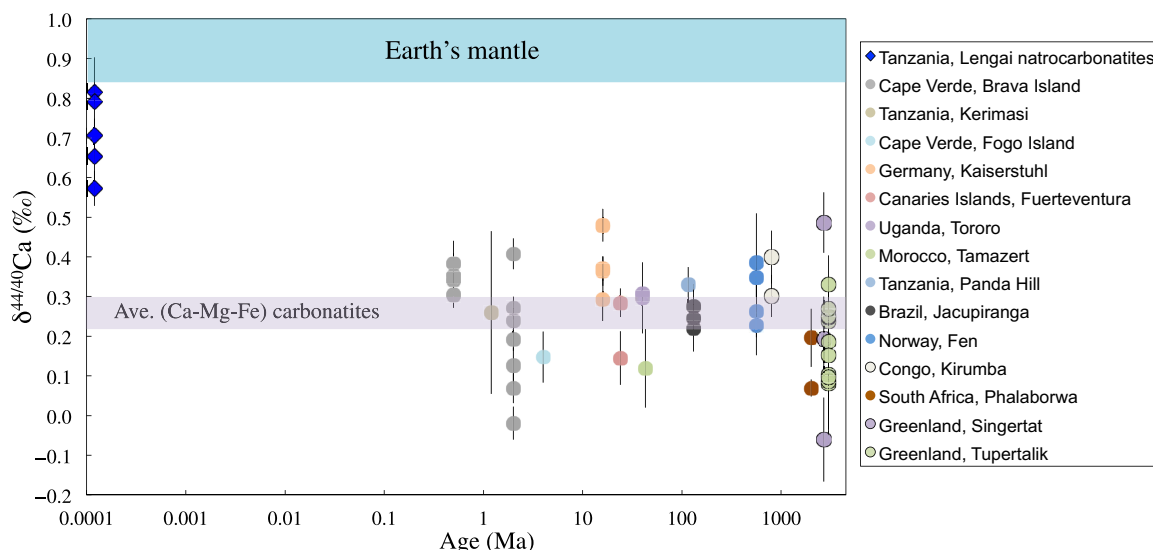
## DISCUSSION

Since Oldoinyo Lengai is the only modern example of carbonatites and represents the only occurrence of natrocarbonatites, it has been suggested that all extrusive carbonatites were erupted Na rich and that secondary processes acted to substitute Na with Ca (7–9). To examine whether calcio-carbonatites are isotopically light due to such Na–Ca substitution, a set of Oldoinyo Lengai natrocarbonatites samples representing various degrees of alteration (9) were analyzed. In general, altered natrocarbonatites do not have significantly lighter Ca isotopic compositions. Their Ca isotopic composition correlates neither with CaO content (Fig. 2A) nor with the carbon isotopic composition, a sensitive parameter to alteration (Fig. 2B) [e.g., (7, 29)]. However, two pirssonite [ $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ ] carbonatites are characterized by low  $\delta^{44/40}\text{Ca}$  signatures and are enriched in metals including Zn (up to 100 times) and Fe (>10 times) (fig. S1 and table S3) and have  $\delta^{18}\text{O}$  5 to 8‰ lower than other pirssonite samples (fig. S2 and table S3).

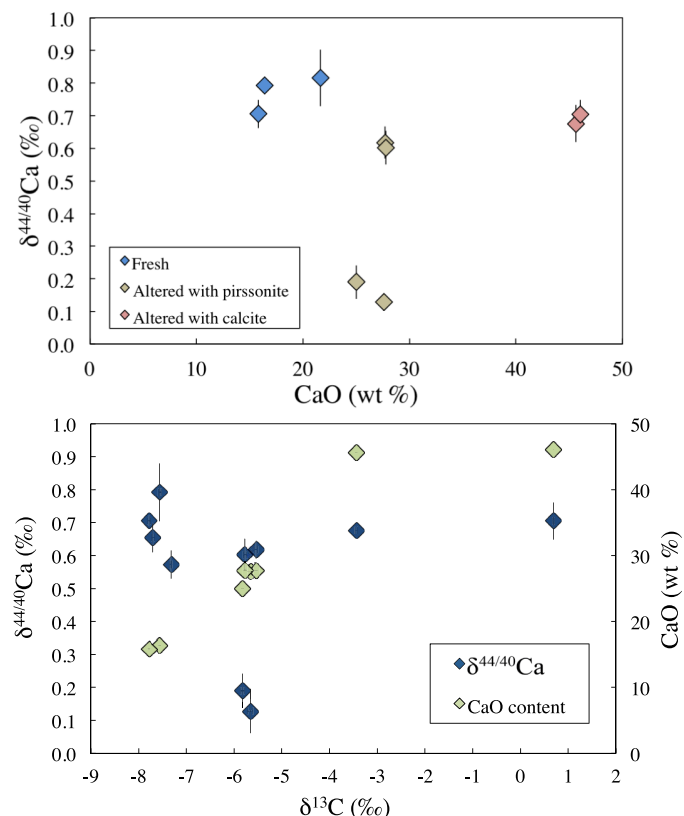
Further evidence that the Ca isotopic composition of calcio-carbonatites is not controlled by alteration is revealed by the similar Ca isotopic compositions of the intrusive BRAV-1 ( $\delta^{44/40}\text{Ca} = 0.34 \pm 0.05\text{‰}$ ) and extrusive BRAV-2 ( $\delta^{44/40}\text{Ca} = 0.35 \pm 0.04\text{‰}$ ) samples that otherwise have different C and O isotopic compositions (BRAV-1,  $\delta^{18}\text{O} = 9.06 \pm 0.06\text{‰}$  and  $\delta^{13}\text{C} = -7.49 \pm 0.11\text{‰}$ ; and BRAV-2,  $\delta^{18}\text{O} = 23.66 \pm 0.06\text{‰}$  and  $\delta^{13}\text{C} = -2.65 \pm 0.05\text{‰}$ ). Furthermore, the absence of correlation between  $\delta^{44/40}\text{Ca}$  and  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  values, and the LOI (loss on ignition) for the Brava and Greenland

carbonatites (figs. S3 to S5) suggests that Ca isotopes are resilient to alteration processes in calcio-carbonatites. The Fen carbonatites present different degrees of metasomatism by alkali-rich fluids; the similarity in their Ca isotopic composition suggests that this metasomatism process does not fractionate Ca isotopes either and confirms the primary signature of Ca.

The origin of the light Ca isotope enrichment of Ca-, Mg-, and Fe-rich carbonatites must be due to either magmatic processes (partial melting or fractional crystallization) or source effects. Orthopyroxene and olivine are isotopically heavier than clinopyroxene in mantle peridotites [e.g., (23, 30)]. The preferential breakdown of clinopyroxene during partial melting would enrich the melt in the lighter isotopes compared to the residual source producing  $\sim 0.3\text{‰}$  lighter basalt compared to peridotite (23, 31). Garnet is also enriched in the heavier Ca isotopes compared to coexisting clinopyroxene (32). Modeling of peridotite partial melting shows that no significant fractionation occurs at <25% melting (24, 33). However, a recent study showed that partial melting of a garnet and jadeite clinopyroxene-rich source (eclogite or pyroxenite) with a starting composition of  $\delta^{44/40}\text{Ca} \sim 0.8\text{‰}$  can fractionate Ca isotopes of about  $\sim 0.2\text{‰}$  (32). Thus, depending on the mantle source composition, partial melting can have a nonnegligible effect on the fractionation of Ca isotopes. This effect is unable to explain the light composition of the carbonatites, which is as much as 0.6‰ lower than the mantle value. There is no evidence for Ca isotopic fractionation during fractional crystallization of silicate melt (34), which is confirmed by the absence of correlation between the CaO, MgO content, or Nb/Th ratio [Nb/Th is used as a proxy for the differentiation of carbonatitic magmas (35)] and  $\delta^{44/40}\text{Ca}$  in a series of the carbonatites from Fen, Kaiserstuhl, and Uganda complexes where we have several samples from the same volcano (Fig. 4 and figs. S6 and S7). Intermineral equilibrium fractionation implying chemical bonding strength could be responsible for the  $^{44}\text{Ca}/^{40}\text{Ca}$  ratio decrease in Ca-, Mg-, and Fe-rich carbonatites relative to basalts. Calcium isotopic fractionation in the mantle peridotites is controlled by the Ca–O bond length in the coexisting minerals, with the heavier isotopes enriched in phases with the shortest bonds (24, 36). In calcite, Ca–O has an intermediary bond



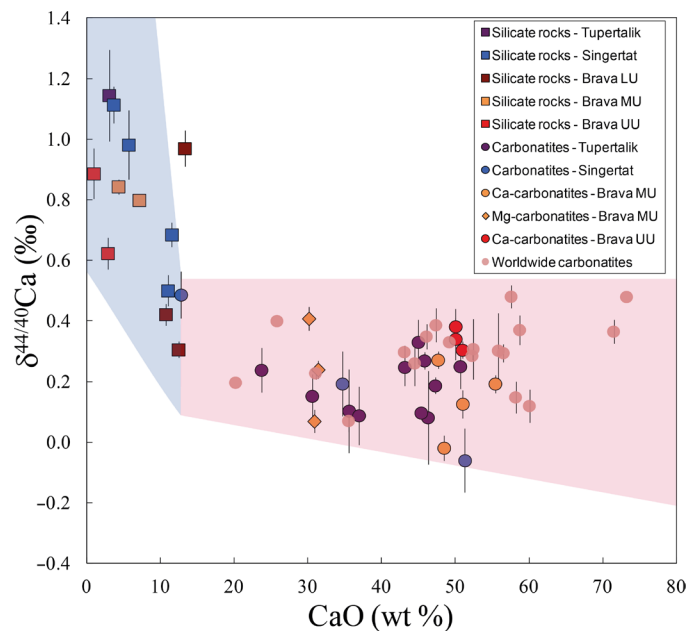
**Fig. 1. Calcium isotopic composition of carbonatites relative to their age.** The bulk silicate earth (BSE) estimate (23) (shaded area) is shown for comparison. All carbonatites are isotopically lighter than basalts and Earth's mantle except for natrocarbonatites, which have isotopic composition that overlaps with basalts.



**Fig. 2. Comparison of fresh and altered natrocarbonatites from Oldoinyo Lengai.** (A) Calcium isotopic composition of fresh and altered natrocarbonatites relative to their CaO content. The absence of correlation between the  $\delta^{44/40}\text{Ca}$  and the alteration degree of the carbonatites suggests that substitution of Na by Ca does not change the composition of the samples. (B) Carbon isotopic composition relative to CaO content and Ca isotopic composition. Processes of alteration tend to enrich in the lighter C isotopes (29).

length compared to Opx and Cpx (37), and therefore, precipitating calcite would not produce the light isotope enrichment observed in carbonatites. Ab initio calculations for silicate and carbonate phases have only been obtained for aqueous solutions (38). Using these calculations as a first approximation to calculate the fractionation between the carbonatitic and the silicate melt during liquid immiscibility or fractional crystallization at 573 K, we show that there should be no fractionation detectable at our level of analytical precision ( $\Delta_{\text{carbonate-silicate}} < 0.05\text{‰}$ ).

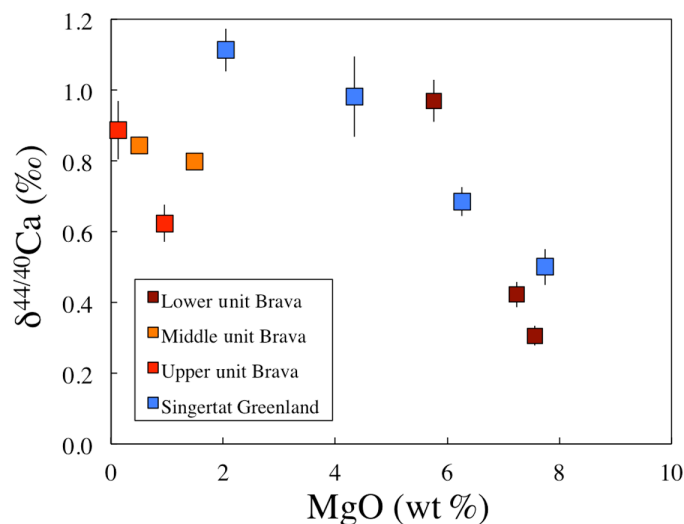
The analysis of silicate rocks associated with carbonatites has the possibility to reveal the behavior of Ca isotopes during silicate and carbonatite magma differentiation and during silicate-carbonatite liquid immiscibility. The Ca isotopic composition of the silicate rocks from Brava (extrusive and intrusive) and Singertat (intrusive) correlates with their CaO and MgO contents (Figs. 3 and 4). These correlations follow the expected differentiation trend for Brava (39). For the Brava's lower unit (submarine sequence), the least evolved sample (foidite) presents the lightest Ca isotopic composition and the highest Ca content. The most differentiated sample (nephelinite) presents the heaviest Ca isotopic composition and the lowest Ca content. Silicate rocks from the lower unit are not associated with carbonatites and, hence, have not experienced carbonatite immiscibility (40). Consequently, the correlation with MgO implies that Ca isotopes fractionated during differentiation of the silicate magma.



**Fig. 3. Ca isotopic composition of carbonatites and silicate rocks associated with Brava and Greenland relative to their CaO content [CaO content from (59) for Brava].**

Unlike tholeiitic silicate magmas where no Ca isotopic fractionation has been observed with magma evolution (34), alkali-rich silicate magmas could present a Ca isotopic fractionation because of the different Ca-bearing phases such as melilite, titanite, combeite, or wollastonite. However, for carbonatite magmas, it is more difficult to infer Ca fractionation during differentiation. The Ca isotopic composition of calciocarbonatites and magnesiocarbonatites is similar, which is at odds with the differentiation trend proposed in the literature (40–42). Most of the carbonatites have similar Ca isotopic composition relative to the wide range of Ca contents. This implies that Ca isotopes may not reveal the differentiation trend of carbonatites. Thus, the different Ca isotopic compositions between carbonatites and some of their associated silicate rocks likely represent the differentiation of the silicate magma. Although carbonatite/silicate immiscibility or crystal fractionation cannot be ruled out as a means for Ca isotope fractionation, there is no need to invoke this process to explain the light Ca isotopic composition of carbonatites. As the less differentiated silicate samples from Brava and Singertat show a similar Ca isotopic composition to the carbonatites (CY-165,  $\delta^{44/40}\text{Ca} = 0.31 \pm 0.03\text{‰}$ ; and 525984,  $\delta^{44/40}\text{Ca} = 0.50 \pm 0.05\text{‰}$ ) and have the highest content of Ca, the mantle source of the silicate rocks should have the same isotopic composition as the source of the carbonatites, confirming the light composition of the source and the enrichment in Ca content. The mantle source could be represented by the intersection between the silicate trend and the carbonatite composition in Fig. 3, with  $\sim 11\%$  of Ca and  $0.31\text{‰} < \delta^{44/40}\text{Ca} < 0.50\text{‰}$ .

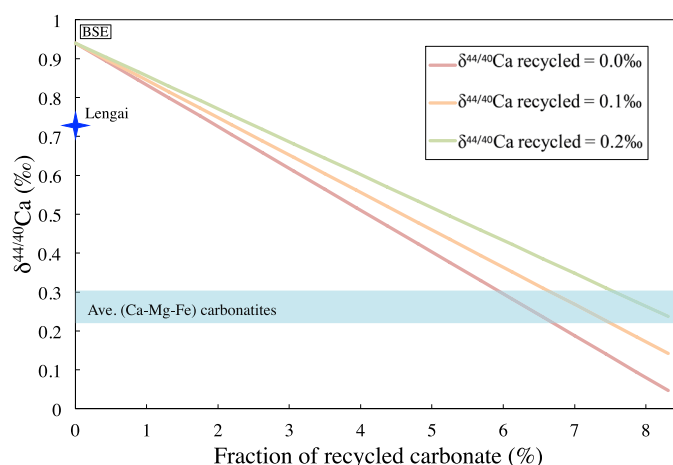
The enrichment in the lightest Ca isotopes in the source might originate either from isotopically light carbonatite metasomatism or from isotopic fractionation during carbonatite metasomatism. In the case of isotopically light carbonatite metasomatism, the metasomatic Ca must have ultimately been derived from isotopically light recycled carbonate. In the case of isotopic fractionation, this would result from percolation of melt within peridotites inducing kinetic



**Fig. 4. Ca isotopic composition of silicate rocks from Brava and Singertat relative to their MgO content [MgO content from (59) for Brava].**

isotopic fractionation via diffusion of Ca from the melt to the crystals, enriching the peridotite in the lightest Ca isotopes. To enrich C and Ca in the carbonatite magma mantle source, the melt must be carbonatitic. This melt may be produced by percolation of carbonatitic melts out of a subducting slab via infiltration of surrounding peridotites (43) or it can also derive deeper in the mantle. For example, mantle carbon (graphite and diamond) can be oxidized and lead to the production of carbonate melt (44). The main issue with kinetic isotopic fractionation is that during this process, there must be an isotopically heavy counterpart that has never been sampled, either among the 62 carbonatites analyzed or in other mantle-derived materials. Furthermore, significant Ca isotopic variability between carbonatites of different ages and localities would be expected, as observed for mantle xenoliths (45, 46).

The enrichment in light Ca isotopes in Ca-, Mg-, and Fe-rich carbonatites likely reflects the incorporation of isotopically light marine carbonates into their mantle sources. Unexpectedly, the carbon isotopic composition of nonaltered carbonatites is close to that of mantle peridotites [clustering at  $\delta^{13}\text{C} \sim -5\text{‰}$  (29)], although marine carbonates are enriched in the heaviest C isotopes clustering at  $\delta^{13}\text{C} \sim 0\text{‰}$ , whereas organic materials are depleted in the heaviest C isotopes. Subducted carbon, including these reservoirs and altered mafic oceanic crust, therefore span a wide range of  $\delta^{13}\text{C}$  (47, 48), making C isotopes a “blunt” tool for tracing recycled subducted materials (49). In contrast, the major output of Ca from the slab is subducted carbonates [which have relatively narrow  $\delta^{44/40}\text{Ca}$  for ancient carbonates (22)], and it has been shown that during subduction processes, the fluids expelled from the slab are enriched in the heavier Ca isotopes relative to the crust, which would further enrich the slab in the lighter Ca isotopes (50, 51). Although the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is commonly used as a tracer of carbonate recycling in the mantle, ancient carbonates have very similar Sr isotopic compositions to present-day mantle values (52). A simple mixing model between a mantle component [CaO abundance = 3.5% (21) and  $\delta^{44/40}\text{Ca} = 0.94$  (23)] and recycled carbonates [CaO = 40% and  $0 < \delta^{44/40}\text{Ca} < 0.2$  (22, 53, 54)] is consistent with the incorporation into the mantle source of carbonatites of  $\sim 7\%$  of recycled marine carbonates (Fig. 5). This is in agreement with the Ce isotopic com-



**Fig. 5. Estimation of the proportion of recycled marine carbonate material added to the mantle sources of carbonatites.** The mantle sources of the (Ca-Fe-Mg) carbonatites contained up to 7% of recycled carbonate materials. The mantle end-member is represented by the BSE value close to Oldoinyo Lengai carbonatite samples.

position of the carbonatites from Cape Verde and the Canary Islands, which indicate a marine carbonate contribution of a few percent (5). The recycled contribution might have undergone multistage processing and mixing with mantle sources, suggesting that carbonatite melts are not direct contributions from recycled carbonate material.

Isotopically light Ca in both oceanic and continental Ca-, Mg-, and Fe-rich carbonatites shows that their sources may contain up to 7% recycled marine carbonate material. Our results confirm the melting of carbonate-bearing peridotite/eclogite as the source of carbonatitic melts, in accordance with high-pressure/temperature experiments (55, 56). The accumulated carbon in cratonic lithosphere beneath rifts is often suggested to link the origin of continental carbonatites with rifting (57, 58). Our results are consistent with the idea that this accumulation could be due to the gradual addition of slab-derived materials. However, at least for the occurrences of Brava Island (Cape Verde), a contribution of primordial carbon cannot be dismissed in the light of relatively high  $^3\text{He}/^4\text{He}$  (up to 15.5 Ra, where Ra is the atmospheric ratio), the higher than atmospheric  $^{129}\text{Xe}/^{130}\text{Xe}$  (up to 6.84) and the very low  $^4\text{He}/^{\text{Ar}^*}$  (down to  $<0.3$ ) measured in these carbonatites (12, 13).

Our results also imply that calcio-carbonatites cannot be derived from natrocarbonatites. The difference of mantle sources between natrocarbonatites and other carbonatites is consistent with the primordial carbon content of the Lengai mantle source [ $<300$  parts per million (11)]. Natrocarbonatites would then be formed by immiscibility from a nephelinite magma at upper crustal pressure (57), with no need of a carbonate-rich source (11). For the origin of the other types of carbonatites (Ca-, Mg-, and Fe-rich), the contribution to the mantle source of recycled carbonate material is needed to explain the isotopically light Ca signatures, yet the involvement of primordial carbon cannot be completely ruled out (see above). The only known example of natrocarbonatite on Earth (Oldoinyo Lengai) has therefore a singular origin compared to all other known worldwide occurrences of carbonatites. Calcium-, Mg-, and Fe-rich carbonatites likely reveal prolonged and continuous addition of subducted marine carbonate into the mantle sources of enriched carbonatites, further confirming their previously suggested HIMU [high  $\mu$  ( $\mu = 238\text{U}/204\text{Pb}$ )]-EM1 (enriched mantle 1) mixing signature (2, 10). Considering the

results presented here for samples as old as 3 Ga, this study provides implications for the recycling of oceanic lithosphere during the Archean, thus providing a minimum age for the onset of plate tectonics.

## MATERIALS AND METHODS

Carbonatite samples used in this study have been previously described and came from the Africa [Morocco, Congo, Uganda, South Africa, and Tanzania (29)], oceanic islands [Cape Verde and Canary Islands (39, 40, 59)], Europe [Germany and Norway (29)] Greenland, and South America (Brazil). Natrocarbonatites came from the Oldoinyo Lengai volcano in Tanzania (9). They span in age from 2 Ga to the present day.

Samples were dissolved in a concentrated HNO<sub>3</sub>/HF mixture (1:3) for 2 days on a hot plate at 120°C, dried, and redissolved in 6 concentrated HCl for 2 days to remove fluorides. After evaporation to dryness, samples were introduced on four- to five-step column chromatography procedure following previously described methods (31). First, Ca and Sr were eluted in concentrated HNO<sub>3</sub> with 1.8 ml of Eichrom DGA resin, and then Ca was further separated from Sr using 200 µl of Eichrom Sr-Spec resin in 3 N HNO<sub>3</sub>. Carbonatites were passed twice through the DGA columns, while natrocarbonatites necessitated a third pass because of their high content of Na. All samples were passed two times through Sr-specific resin.

The Ca isotopic measurements were performed on a Thermo Fisher Neptune multicollector inductively coupled plasma mass spectrometry (ICP-MS) located at the Institut de Physique du Globe de Paris (IPGP). Samples were introduced using an Apex desolvating introduction system. Measurements were made in high resolution to correct for the isobaric interference of <sup>14</sup>N<sub>3</sub><sup>+</sup> on the mass 42. Standard-sample bracketing was used to correct for instrumental drift over time using NIST (National Institute of Standards and Technology) SRM (Standard Reference Materials) 915b as standard. <sup>42</sup>Ca/<sup>43</sup>Ca and <sup>43</sup>Ca/<sup>44</sup>Ca were reported and converted to δ<sup>44/40</sup>Ca after ensuring that the data were mass dependent. Last, all the data are renormalized to SRM 915a to facilitate comparison with literature data. The 2 SE is typically 0.06‰ and replicates are isotopically identical within uncertainty. Major and trace elements measurements were carried out on an Agilent 7900 Quadrupole ICP-MS, with a precision better than 10% for all elements.

Around 1 mg of powdered carbonate sample was digested overnight at room temperature with 100% phosphoric acid in a helium-flushed Exetainer. The evolved CO<sub>2</sub> was then purified through gas chromatography and measured for C and O isotopes using a Thermo Fisher Delta XP coupled to a Finnigan GasBench II at IPGP. External reproducibility is better than 0.2‰ (1 SD) for δ<sup>13</sup>C and 0.3‰ (1 SD) for δ<sup>18</sup>O.

The bulk rock major element compositions for the Greenland samples were determined by WDS XRF (Wavelength Dispersive Spectroscopy X Ray Fluorescence) methods at the University of Johannesburg, and a detailed method description, including the results for certified and in-house reference materials, is given in (60).

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/6/23/eaba3269/DC1>

## REFERENCES AND NOTES

1. A. Woolley, B. A. Kjarsgaard, Paragenetic types of carbonatites as indicated by the diversity and relative abundances of associated silicate rocks: Evidence from a global database. *Can. Mineral.* **46**, 741–752 (2008).
2. K. Bell, G. R. Tilton, Probing the mantle: The story from carbonatites. *Eos, Trans. Am. Geophys. Union* **83**, 273–277 (2002).
3. M. J. Walter, G. P. Bulanova, L. S. Armstrong, S. Keshav, J. D. Blundy, G. Gudfinsson, O. T. Lord, A. R. Lennie, S. M. Clark, C. B. Smith, L. Gobbo, Primary carbonatite melt from deeply subducted oceanic crust. *Nature* **454**, 622–625 (2008).
4. D. S. Barker, Consequences of recycled carbon in carbonatites. *Can. Mineral.* **34**, 373–387 (1996).
5. R. Doucelance, N. Bellot, M. Boyet, T. Hammouda, C. Bosq, What coupled cerium and neodymium isotopes tell us about the deep source of oceanic carbonatites. *Earth Planet. Sci. Lett.* **407**, 175–186 (2014).
6. K. Hoernle, G. Tilton, M. J. Le Bas, S. Duggen, D. Garbe-Schönberg, Geochemistry of oceanic carbonatites compared with continental carbonatites: Mantle recycling of oceanic crustal carbonate. *Contrib. to Mineral. Petrol.* **142**, 520–542 (2002).
7. J. B. Dawson, A supposed sövite from Oldoinyo Lengai, Tanzania: Result of extreme alteration of alkali carbonatite lava. *Mineral. Mag.* **57**, 93–101 (1993).
8. J. Keller, A. N. Zaitsev, Calcicarbonatite dykes at Oldoinyo Lengai, Tanzania: The fate of natrocarbonatite. *Can. Mineral.* **44**, 857–876 (2006).
9. A. N. Zaitsev, J. Keller, Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania. *Lithos* **91**, 191–207 (2006).
10. M. D'Orazio, F. Innocenti, S. Tonarini, C. Doglioni, Carbonatites in a subduction system: The Pleistocene alvikites from Mt. Vulture (southern Italy). *Lithos* **98**, 313–334 (2007).
11. T. P. Fischer, P. Burnard, B. Marty, D. R. Hilton, E. Füri, F. Pahlol, Z. D. Sharp, F. Mangasini, Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature* **459**, 77–80 (2009).
12. J. Mata, M. Moreira, R. Doucelance, M. Ader, M. L. C. Silva, Noble gas and carbon isotopic signatures of Cape Verde oceanic carbonatites: Implications for carbon provenance. *Earth Planet. Sci. Lett.* **291**, 70–83 (2010).
13. C. Mourão, M. Moreira, J. Mata, A. Raquin, J. Madeira, Primary and secondary processes constraining the noble gas isotopic signatures of carbonatites and silicate rocks from Brava Island: Evidence for a lower mantle origin of the Cape Verde plume. *Contrib. Mineral. Petrol.* **163**, 995–1009 (2012).
14. R. Halama, W. F. McDonough, R. L. Rudnick, K. Bell, Tracking the lithium isotopic evolution of the mantle using carbonatites. *Earth. Planeta. Sci. Lett.* **265**, 726–742 (2008).
15. J. M. D. Day, D. G. Pearson, C. G. Macpherson, D. Lowry, J.-C. Carracedo, Pyroxenite-rich mantle formed by recycled oceanic lithosphere: Oxygen-osmium isotope evidence from Canary Island lavas. *Geology* **37**, 555–558 (2009).
16. S. R. W. Hulet, A. Simonetti, E. T. Rasbury, N. G. Hemming, Recycling of subducted crustal components into carbonatite melts revealed by boron isotopes. *Nat. Geosci.* **9**, 904–908 (2016).
17. A. Deyhle, A. J. Kopf, The use and usefulness of boron isotopes in natural silicate-water systems. *Phys. Chem. Earth* **30**, 1038–1046 (2005).
18. A. M. McCaig, S. S. Titarenko, I. P. Savov, R. A. Cliff, D. Banks, A. Boyce, S. Agostini, No significant boron in the hydrated mantle of most subducting slabs. *Nat. Commun.* **9**, 4602 (2018).
19. E. M. Smith, S. B. Shirey, S. H. Richardson, F. Nestola, E. S. Bullock, J. Wang, W. Wang, Blue boron-bearing diamonds from Earth's lower mantle. *Nature* **560**, 84–87 (2018).
20. A. R. Woolley, A. A. Church, Extrusive carbonatites: A brief review. *Lithos* **85**, 1–14 (2005).
21. D. G. Pearson, D. Canil, S. B. Shirey, Mantle Samples Included in Volcanic Rocks: Xenoliths and Diamonds. in *Treatise on Geochemistry* (The Mantle and Core, A. M. Davis Oxford: Elsevier, Ed. 2, 2014), vol. 3, pp. 169–253.
22. M. S. Fantle, E. T. Tipper, Calcium isotopes in the global biogeochemical Ca cycle: Implications for development of a Ca isotope proxy. *Earth-Sci. Rev.* **129**, 148–177 (2014).
23. J.-T. Kang, D. A. Ionov, F. Liu, C.-L. Zhang, A. V. Golovin, L.-P. Qin, Z.-F. Zhang, F. Huang, Calcium isotopic fractionation in mantle peridotites by melting and metasomatism and Ca isotope composition of the bulk silicate earth. *Earth Planet. Sci. Lett.* **474**, 128–137 (2017).
24. S. Huang, J. Farkaš, S. B. Jacobsen, Calcium isotopic fractionation between clinopyroxene and orthopyroxene from mantle peridotites. *Earth Planet. Sci. Lett.* **292**, 337–344 (2010).
25. S. Huang, J. Farkaš, S. B. Jacobsen, Stable calcium isotopic compositions of Hawaiian shield lavas: Evidence for recycling of ancient marine carbonates into the mantle. *Geochim. Cosmochim. Acta* **75**, 4987–4997 (2011).
26. F. Liu, X. Li, G. Wang, Y. Liu, H. Zhu, J. Kang, F. Huang, W. Sun, X. Xia, Z. Zhang, Marine carbonate component in the mantle beneath the southeastern Tibetan Plateau: Evidence from magnesium and calcium isotopes. *J. Geophys. Res. Solid Earth* **122**, 9729–9744 (2017).
27. A. Banerjee, R. Chakrabarti, A geochemical and Nd, Sr and stable Ca isotopic study of carbonatites and associated silicate rocks from the ~65Ma old Ambadongar carbonatite complex and the Phenai Mata igneous complex, Gujarat, India: Implications for crustal contamination, carbonate recycling, hydrothermal alteration and source-mantle mineralogy. *Lithos* **326–327**, 572–585 (2019).
28. J. I. Simon, D. J. DePaolo, Stable calcium isotopic composition of meteorites and rocky planets. *Earth Planet. Sci. Lett.* **289**, 457–466 (2010).

29. F. Pineau, M. Javoy, M. C. J. Allegre, Systematic study of isotopes of oxygen, carbon and strontium in carbonatites. *Geochim. Cosmochim. Acta* **37**, 2363–2377 (1973).
30. J.-T. Kang, H.-L. Zhu, Y.-F. Liu, F. Liu, F. Wu, Y.-T. H. X.-C. Zhi, Z.-F. Zhang, F. Huang, Calcium isotopic composition of mantle xenoliths and minerals from Eastern China. *Geochim. Cosmochim. Acta* **174**, 335–344 (2016).
31. E. Amsellem, F. Moynier, E. A. Pringle, A. Bouvier, H. Chen, J. M. D. Day, Testing the chondrule-rich accretion model for planetary embryos using calcium isotopes. *Earth Planet. Sci. Lett.* **469**, 75–83 (2017).
32. Y. Wang, Y. He, H. Wu, C. Zhu, S. Huang, J. Huang, Calcium isotope fractionation during crustal melting and magma differentiation: Granitoid and mineral-pair perspectives. *Geochim. Cosmochim. Acta* **259**, 37–52 (2019).
33. C. Chen, W. Dai, Z. Wang, Y. Liu, M. Li, H. Becker, S. F. Foley, Calcium isotope fractionation during magmatic processes in the upper mantle. *Geochim. Cosmochim. Acta* **249**, 121–137 (2019).
34. H. Zhang, Y. Wang, Y. He, F.-Z. Teng, S. B. Jacobsen, R. T. Helz, B. D. Marsh, S. Huang, No measurable calcium isotopic fractionation during crystallization of Kilauea Iki Lava Lake. *Geochim. Geophys. Geosyst.* **19**, 3128–3139 (2018).
35. A. V. Lapin, Carbonatite Differentiation Processes. *Int. Geol. Rev.* **24**, 1079–1089 (1982).
36. C. Feng, T. Qin, S. Huang, Z. Wu, F. Huang, First-principles investigations of equilibrium calcium isotope fractionation between clinopyroxene and Ca-doped orthopyroxene. *Geochim. Cosmochim. Acta* **143**, 132–142 (2014).
37. J. R. Smyth, D. L. Bish, *Crystal Structures and Cation Sites of the Rock-Forming Minerals* (Boston Allen & Unwin, 1988), p. 332.
38. F. Moynier, T. Fujii, Calcium isotope fractionation between aqueous compounds relevant to low-temperature geochemistry, biology and medicine. *Sci. Rep.* **7**, 44255 (2017).
39. J. Madeira, J. Mata, C. Mourão, A. B. da Silveira, S. Martins, R. Ramlho, D. L. Hoffman, Volcano-stratigraphic and structural evolution of Brava Island (Cape Verde) based on  $^{40}\text{Ar}/^{39}\text{Ar}$ , U–Th and field constraints. *J. Volcanol. Geotherm. Res.* **196**, 219–235 (2010).
40. C. Mourão, J. Mata, R. Doucelance, J. Madeira, M.-A. Millet, M. Moreira, Geochemical temporal evolution of Brava Island magmatism: Constraints on the variability of Cape Verde mantle sources and on carbonatite-silicate magma link. *Chem. Geol.* **334**, 44–61 (2012).
41. M. J. Le Bas, Carbonatite magmas. *Mineral. Mag.* **44**, 133–140 (1981).
42. N. K. Basu, A. Mayila, Petrographic and chemical characteristics of the Panda Hill carbonatite complex, Tanzania. *J. Afri. Earth Sci.* **5**, 589–598 (1986).
43. A. R. Thomson, M. J. Walter, S. C. Kohn, R. A. Brooker, Slab melting as a barrier to deep carbon subduction. *Nature* **529**, 77–79 (2016).
44. V. Stagno, D. O. Ojwang, C. A. McCammon, D. J. Frost, The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature* **493**, 84–88 (2013).
45. X. Zhao, Z. Zhang, S. Huang, Y. Liu, X. Li, H. Zhang, Coupled extremely light Ca and Fe isotopes in peridotites. *Geochim. Cosmochim. Acta* **208**, 368–380 (2017).
46. D. A. Ionov, Y.-H. Q, J.-T. Kang, A. V. Golovin, O. B. Oleinikov, W. Zheng, A. D. Anbar, Z.-F. Zhang, F. Huang, Calcium isotopic signatures of carbonatite and silicate metasomatism, melt percolation and crustal recycling in the lithospheric mantle. *Geochim. Cosmochim. Acta* **248**, 1–13 (2019).
47. J. C. Alt, E. M. Schwarzenbach, G. L. Früh-Green, W. C. Shanks III, S. M. Bernasconi, C. J. Garrido, L. Crispini, L. Gaggero, J. A. Padrón-Navarta, C. Marchesi, The role of serpentinites in cycling of carbon and sulfur: Seafloor serpentinitization and subduction metamorphism. *Lithos* **178**, 40–54 (2013).
48. J. C. Alt, C. J. Garrido, W. C. Shanks III, A. Turchyn, J. A. Padrón-Navarta, V. L. Sánchez-Vizcaino, M. T. G. Pugnaire, C. Marchesi, Recycling of water, carbon and sulfur during subduction of serpentinites: A stable isotope study of Cerro del Almiraz, Spain. *Earth Planet. Sci. Lett.* **327–328**, 50–60 (2012).
49. T. Hammouda, S. Keshav, Melting in the mantle in the presence of carbon: Review of experiments and discussion on the origin of carbonatites. *Chem. Geol.* **418**, 171–188 (2015).
50. T. John, N. Gussone, Y. Y. Podladchikov, G. E. Bebout, R. Dohmen, R. Halama, R. Klemd, T. Magna, H.-M. Seitz, Volcanic arcs fed by rapid pulsed fluid flow through subducting slabs. *Nat. Geosci.* **5**, 489–492 (2012).
51. C. Chen, Y. Liu, L. Feng, S. F. Foley, L. Zhou, M. N. Ducea, Z. Hu, Calcium isotope evidence for subduction-enriched lithospheric mantle under the northern North China Craton. *Geochim. Cosmochim. Acta* **238**, 55–67 (2018).
52. G. Shields, J. Veizer, Precambrian marine carbonate isotope database: Version 1.1. *Geochem. Geophys. Geosyst.* **3**, 1–12 (2002).
53. J. Farkaš, D. Buhl, J. Blenkinsop, J. Veizer, Evolution of the oceanic calcium cycle during the late Mesozoic: Evidence from  $\delta^{44/40}\text{Ca}$  of marine skeletal carbonates. *Earth Planet. Sci. Lett.* **253**, 96–111 (2007).
54. M. S. Fantle, D. J. DePaolo, Variations in the marine Ca cycle over the past 20 million years. *Earth Planet. Sci. Lett.* **237**, 102–117 (2005).
55. M. E. Wallace, D. H. Green, An experimental determination of primary carbonatite magma composition. *Nature* **335**, 343–346 (1988).
56. G. M. Yaxley, G. P. Brey, Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: Implications for petrogenesis of carbonatites. *Contrib. to Mineral. Petrol.* **146**, 606–619 (2004).
57. S. F. Foley, T. P. Fischer, An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nat. Geosci.* **10**, 897–902 (2017).
58. S. Tappe, R. L. Romer, A. Stracke, A. Steinfeld, K. A. Smart, K. Muehlenbachs, T. H. Torsvik, Sources and mobility of carbonate melts beneath cratons with implications for deep carbon cycling, metasomatism and rift initiation. *Earth Planet. Sci. Lett.* **466**, 152–167 (2017).
59. C. Mourão, J. Mata, R. Doucelance, J. Maderia, A. B. da Silveira, L. C. Silva, M. Moreira, Quaternary extrusive calcio-carbonatite volcanism on Brava Island (Cape Verde): A nephelinite-carbonatite immiscibility product. *J. African Earth Sci.* **56**, 59–74 (2010).
60. A. Dongre, S. Tappe, Kimberlite and carbonatite dykes within the Premier diatreme root (Cullinan Diamond Mine, South Africa): New insights to mineralogical-genetic classifications and magma  $\text{CO}_2$  degassing. *Lithos* **338–339**, 155–173 (2019).

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