

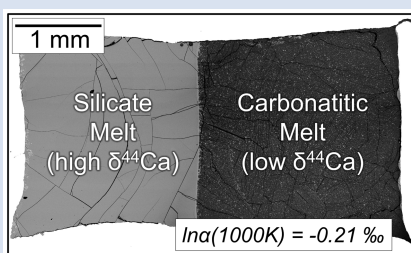
Calcium isotope fractionation during melt immiscibility and carbonatite petrogenesis

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Abstract



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

by fractional crystallisation, carbonatite-silicate melt immiscibility, and calcite/apatite accumulation) that fully explains our natural data (average $\delta^{44}\text{Ca}_{\text{BSE}}$ of -0.30 ± 0.03 ‰) and those from recent studies, without requiring isotopic contributions from recycled marine carbonates. Our results suggest that lighter isotopes of similarly bound cations (*e.g.*, Mg, Fe, Sr, Ba, Zn) should be preferentially incorporated into carbonatitic melts and that calciocarbonatite formation involves melt immiscibility after differentiation of mantle-derived alkaline CO_2 -bearing silicate melts.

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Introduction

Carbonatites are rare igneous rocks that contain large amounts (>50 %) of carbonate minerals and represent the most CO_2 -rich magmas in the geologic record (Yaxley *et al.*, 2022). Although they provide a majority of the world's Rare Earth Elements (REE) and are intimately linked to the deep Earth carbon cycle, their principal formation mechanism(s) are still debated. Possible models of carbonatite formation include (i) exsolution from moderately-to-strongly evolved CO_2 -rich alkaline silicate melts [*i.e.* carbonatite-silicate melt immiscibility (Berkési *et al.*, 2023; Berndt and Klemme, 2022; Brooker and Kjarsgaard, 2011; Guzmics *et al.*, 2015; Weidendorfer *et al.*, 2017)], or (ii) direct partial melting of carbonate-bearing mantle rocks (Harmer and Gittins, 1998; Yaxley and Brey, 2004). There are also significant debates regarding the role of carbonatite magmas within the carbon cycle, with some recent stable isotope studies suggesting that carbonatites may represent the return of subducted marine carbonates back to the surface (Hulett *et al.*, 2016; Amsellem *et al.*, 2020; Banerjee *et al.*, 2021). In contrast, $\delta^{13}\text{C}$ in most carbonatites overlap with those of peridotitic diamonds (Stachel *et al.*, 2022). The carbon in these magmas is thus mantle-derived or, if recycled, could result from a ~4:1 mix between carbonates

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

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

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

Calcium Isotope Fractionation During Carbonatite-Silicate Melt Immiscibility

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

We find that carbonatitic melts always have lower $\delta^{44}\text{Ca}$ than coexisting silicate melts, with the 800 °C (0.8 GPa) experiment yielding $\Delta^{44}\text{Ca}_{\text{carb-sil}}$ of -0.19 ± 0.06 ‰ and the three 1170 °C experiments giving statistically indistinguishable results, regardless of pressure ($\Delta^{44}\text{Ca}_{\text{carb-sil}}$ between -0.08 ‰ and -0.12 ‰; Fig. 1b, Table S-2). Several independent lines of evidence suggest that our experiments achieved Ca isotope equilibrium. Along with the high Ca diffusivities in silicate and carbonatitic melts relative to the length scales and durations of our experiments, the equilibrium fractionation factor [1000ln α ; Fig. 1c] calculated from the lower T experiment (-0.22 at 1000K, using a $10^6/T^2$ law), is strikingly similar to that derived from the average of the higher T experiments (-0.21 at 1000K; Fig. S2). The three different 1170 °C experiments also represent significant variations in the Ca fraction [F(Ca)] in carbonatitic *vs.* silicate melts, yet they yield statistically indistinguishable $\Delta^{44}\text{Ca}_{\text{carb-sil}}$ suggesting closed system equilibrium fractionation (Fig. S-3). Our finding that carbonatitic melts have lower $\delta^{44}\text{Ca}$ than coexisting silicate melts is consistent with predictions for a weaker bonding environment for Ca in ionic carbonatitic melts *vs.* predominantly covalent silicate melts (see Genge *et al.*, 1995).

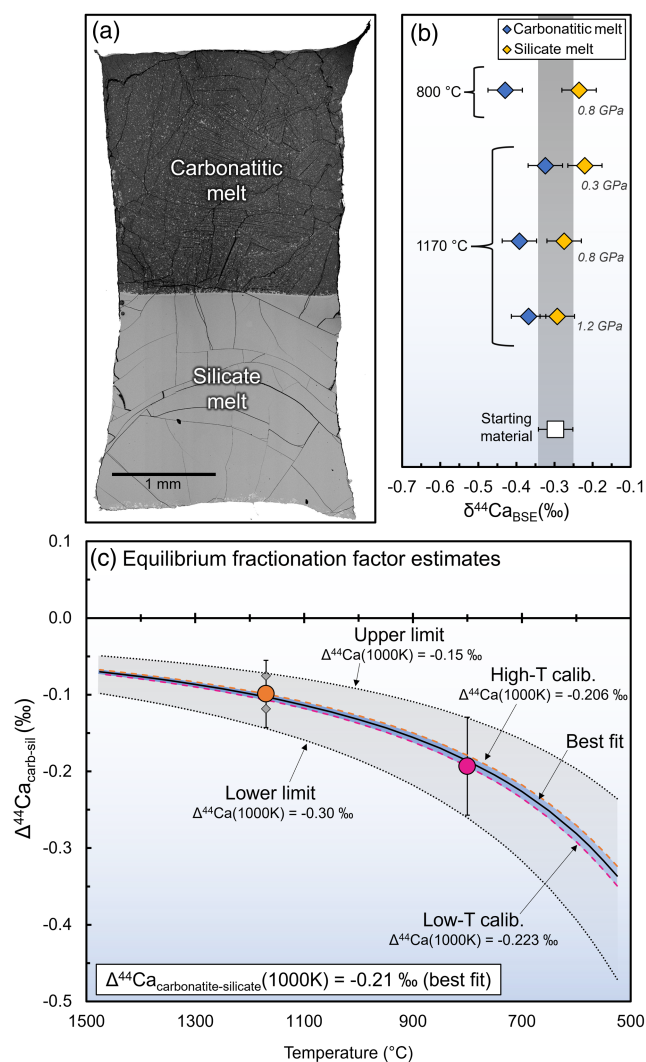


Figure 1 Experimental results of carbonatite-silicate melt immiscibility. (a) Back scattered electron image of an exemplary experimental run product (G58-28) in a welded $\text{Au}_{80}\text{Pd}_{20}$ capsule where the lower density carbonatite melt (dark grey, now quench minerals) migrates to the gravitational top, while the silicate melt (now silicate glass), accumulates at the bottom. (b) Stable Ca isotope results. (c) Estimates of Ca isotope fractionation factor between conjugate carbonatite and silicate melts. Error bars represent 2σ internal uncertainty based on multiple measurements of USGS standards W-2a and COQ-1, where tSE (the t standard error, where 't' is the critical value for a 95% confidence interval in a t-distribution) and 2 s.e. uncertainties both yield similar estimates of ± 0.04 ‰ for $\delta^{44}\text{Ca}$ and ± 0.06 ‰ for $\Delta^{44}\text{Ca}$ (see Supplementary Information). These uncertainty estimates are also similar to our calculated measurement repeatability (± 0.04 ‰, based on the 22 samples measured in duplicate in this work). Long term external reproducibility, which is most important for comparisons of our natural $\delta^{44}\text{Ca}$ data (Fig. 2b) with previous/future work is estimated as ± 0.12 ‰ (2 s.d.) based on 21 measurements of W-2a performed over three years.

Natural and Theoretical Constraints on $\delta^{44}\text{Ca}$ in Carbonatite Minerals

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

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

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

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

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

Four Stage Carbonatite Petrogenesis Model

To evaluate whether incorporation of recycled marine carbonates is required by the $\delta^{44}\text{Ca}$ of carbonatites, we must first evaluate Ca isotope fractionations related to the two foremost models for carbonatite petrogenesis: (i) differentiation of an alkaline CO_2 -rich silicate melt, resulting in carbonatite-silicate melt immiscibility, and (ii) direct formation of carbonatitic melt through partial melting of carbonate-bearing mantle. Given that the latter model (explored in the Supplementary Information; Fig. S-5) is unable to produce calcic carbonatitic melts (Lee and Wyllie, 1998), we focus our main discussion on the first model (Fig. 3). This model consists of four major steps: (i) low degree partial melting of carbon-bearing mantle to form a primitive CO_2 -rich alkaline mafic melt, (ii) fractional crystallisation (mainly of olivine and clinopyroxene) to enrich the differentiated melt in alkalis and reach the carbonatite-silicate melt miscibility gap, (iii) carbonatite-silicate melt immiscibility in the mid-to-lower crust, and (iv) fractionation of calcite (and apatite) from carbonatitic melts to form intrusive (cumulate) calcio-carbonatites in the upper crust.

Partial melting of carbon-bearing garnet lherzolite to form CO_2 -rich ultramafic alkaline melts (Step 1) was explored in a recent study (Antonelli *et al.*, 2023a). Using the fractionation factors and assumptions from that study, we predict $\delta^{44}\text{Ca}$ shifts of -0.13‰ to -0.18‰ (at $1400\text{--}1300\text{ °C}$) for the partial melts.

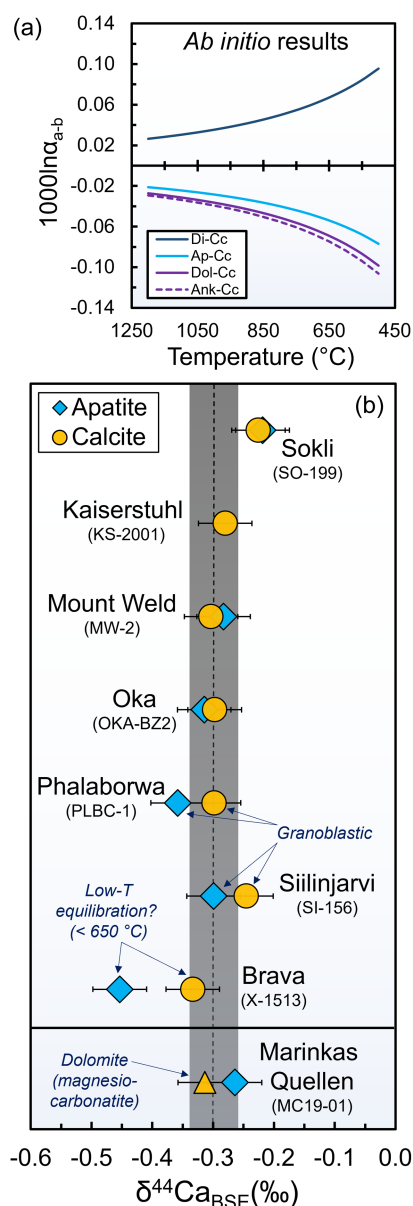


Figure 2 *Ab initio* estimates for equilibrium between various minerals and summary of our $\delta^{44}\text{Ca}$ measurements in calcite and apatite from natural carbonatites. (a) Predicted inter-mineral fractionation factors ($1000\ln\alpha_{\text{mineral-calcite}}$) vs. temperature. (b) $\delta^{44}\text{Ca}$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

Table 1 *Ab initio* results for Ca isotope $1000\ln\beta$ factors ($^{44}\text{Ca}/^{40}\text{Ca}$) in calcite, dolomite, ankerite, diopside, and fluorapatite, along with empirical estimates for melts used in our carbonatite petrogenesis models (preferred values in bold).

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

¹ PBE/GBRV1.4 40–200Ry phonon-based two phonon wave vectors² PBE/GBRV1.4(Ca,C,O)-PSLibrary(Fe) 90–1080Ry Hubbard correction $U = 3.5$ eV phonon-based two phonon wave vectors³ Full C2/c cell with doubled c⁴ Ca1, *7–10th Ca-O neighbours at 2.84Å; Ca2, 5O+1F, and *7th Ca-O bond at 2.80Å

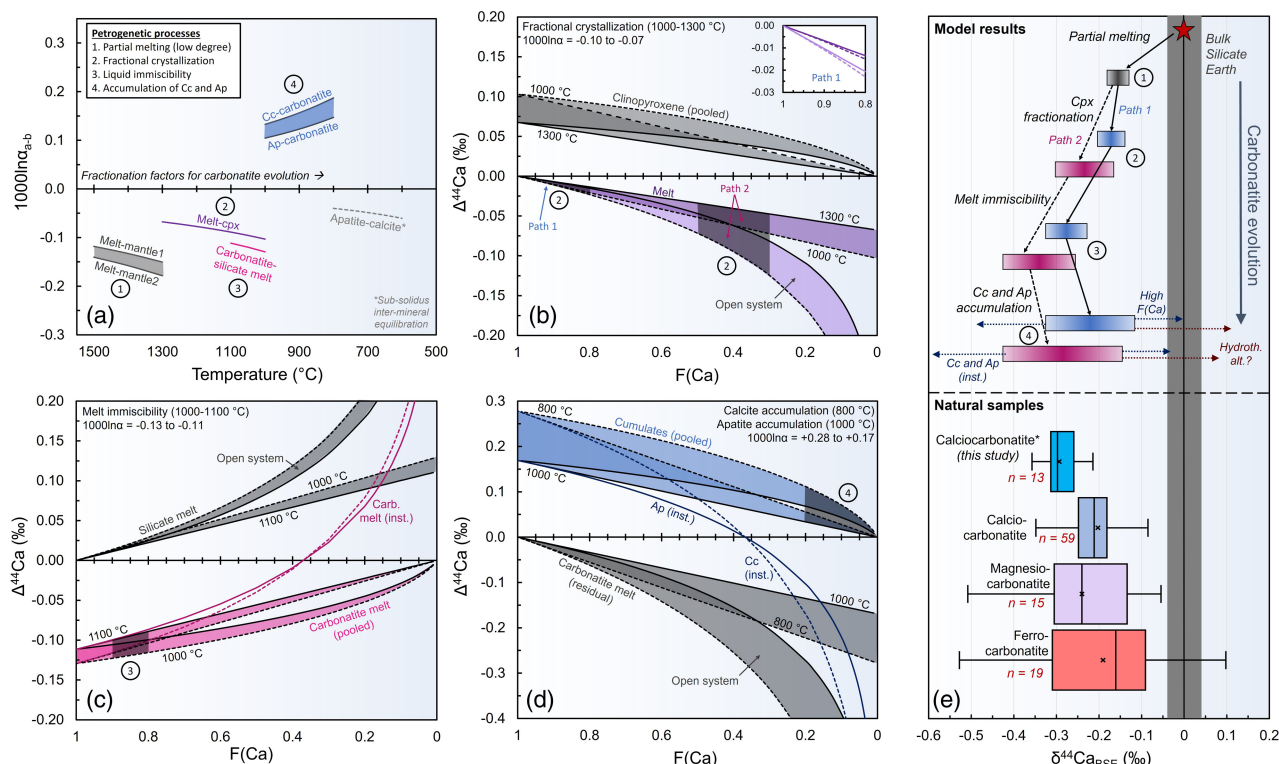


Figure 3 Calcium isotope evolution during the various stages of carbonatite petrogenesis compared to data for carbonatites from this and previous studies. **(a)** Fractionation factors for the four stages: partial melting (Step 1), melt differentiation by crystal fractionation (Step 2), carbonatite-silicate melt immiscibility (Step 3), and accumulation of calcite and apatite (Step 4). Partial melting results (Step 1) come from Antonelli *et al.* (2023a) and encompass the largest and smallest predicted fractionations during melting of carbon-bearing garnet lherzolite at 1400–1300 $^{\circ}\text{C}$. **(b)** Clinopyroxene fractionation from CO_2 -rich alkaline mafic melt (Step 2), showing the two possible paths (nephelinite “path 1” and syenite “path 2”) leading to two-liquid immiscibility. **(c)** Carbonatite-silicate melt immiscibility (Step 3). **(d)** Calcite and apatite accumulation from a carbonatitic melt (Step 4). Shaded regions in **(b-d)** represent predicted F(Ca) values. In **(e)** we show the model results from Step 1 to 4 and compare them with natural carbonatite data (Supplementary Information).

These values agree well with the average $\delta^{44}\text{Ca}_{BSE}$ composition of kimberlites [-0.16 ± 0.03 ‰ (Antonelli *et al.*, 2023a)], which are likely to be similar to the melts generated in the first stages of carbonatite formation. Fractionation of minerals from this melt (Step 2) to reach carbonatite-silicate two-melt immiscibility can occur *via* two different pathways, entailing different amounts of fractional crystallisation, most importantly of clinopyroxene (Supplementary Information). We predict $\delta^{44}\text{Ca}$ shifts of -0.01 ‰ to -0.02 ‰ for CO_2 -rich nephelinitic melts (“path 1”) and of -0.03 ‰ to -0.12 ‰ for CO_2 -rich foid-syenite melts (“path 2”), at temperatures of 1300–1000 $^{\circ}\text{C}$ (Fig. 3b). Carbonatite-silicate melt immiscibility (Step 3) is then assumed to occur at 1100–1000 $^{\circ}\text{C}$ and leads to $\delta^{44}\text{Ca}$ shifts of -0.09 to -0.12 ‰ for carbonatitic melts (Fig. 3c) and relatively little change in the $\delta^{44}\text{Ca}$ of the conjugate silicate melts ($< +0.03$ ‰, because more than ~ 80 % of the total Ca remains in the silicate melts). The final stage, accumulation of calcite and apatite from carbonatitic melt at 1000–800 $^{\circ}\text{C}$ to form an intrusive calciocarbonatite body (Step 4), leads to slight positive shifts in the accumulated minerals (Fig. 3d) relative to the carbonatite melt (ranging from 0.00 to $+0.11$ ‰, depending on the Ca fraction remaining in the melt). This final positive shift in the carbonatite cumulates is of a similar magnitude to the negative shift induced by melt immiscibility, and may explain similar $\delta^{44}\text{Ca}$ in some carbonatites and conjugate silicates (Sun *et al.*, 2021).

Summing the maximum and minimum estimates from the four sequential stages in our model (described in the Supplementary Information; Fig. 3e, Supplementary Data-2) leads to calciocarbonatite cumulates with estimated $\delta^{44}\text{Ca}_{BSE}$

ranging between -0.32 ‰ and -0.12 ‰, for those derived from nephelinites (“path 1”), and from -0.43 ‰ to -0.14 ‰, for those derived from foid-syenites (“path 2”). This four step model can also produce magnesiocarbonatites (once enough calcite precipitates to saturate dolomite), and we predict that these magnesiocarbonatites cumulates would have lower $\delta^{44}\text{Ca}$ (by at least -0.1 ‰) than genetically-associated calciocarbonatite cumulates (Supplementary Information), due to the lower $1000\ln\beta$ of dolomite (relative to calcite) and to open system processes (*i.e.* melt segregation after calcite fractionation). After the final accumulation of calcite (or dolomite) and apatite, sub-solidus equilibration may further shift apatite $\delta^{44}\text{Ca}$ to lower values (*e.g.*, X-1513), but this is unlikely to change the $\delta^{44}\text{Ca}$ of calcite (given that apatite is a relatively minor phase) and cannot change the $\delta^{44}\text{Ca}$ of whole rocks.

Discussion

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



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

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

Conclusions

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

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

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Additional Information

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



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Calcium isotope fractionation during melt immiscibility and carbonatite petrogenesis

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Supplementary Information

The Supplementary Information includes:

- 1. Centrifuging piston-cylinder experiments
- 2. Ca isotope analyses by thermal-ionization mass spectrometry (TIMS)
 - 2a. Radiogenic Ca isotope analyses and implications
 - 2b. Stable Ca isotope analyses
- 3. Density functional theory (ab-initio) estimates
- 4. Natural carbonatite samples
- 5. Two-stage (direct-melting) model for magnesiocarbonatites
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1. Centrifuging piston-cylinder experiments

Experiments on coexisting immiscible carbonatite and nephelinitic alkaline silicate melts were carried out using a centrifuging piston-cylinder apparatus (Schmidt *et al.*, 2006). This apparatus allows for near-perfect physical separation of two immiscible melts (**Fig. 1a, Fig. S-1**). The single-stage piston cylinder has a 14 mm bore, straight graphite heaters, a talc-pyrex-graphite-MgO assemblage, and a B-type Pt-Rh thermocouple. The experiments aim to equilibrate a mixture of a completely depolymerized silicate melt with a carbonatitic melt in order to understand if there would be any Ca isotope fractionation between an at least partly covalent silicate melt and an ionic carbonatic liquid. For the 1170 °C experiments, the starting material is a single bulk

composition corresponding to a 60:40 nephelinite:carbonatite mixture described in (Lee and Wyllie, 1998) and adapted by (Martin *et al.*, 2013), who obtained liquid immiscibility for this composition (**Table S-1**). The 800 °C experimental composition was based on previous work that successfully achieved liquid immiscibility at this temperature (Veksler *et al.*, 2012). The starting powders were dried overnight to remove adsorbed water, following the experimental routine of Martin *et al.* (2013).

Starting powders (~2 g) were made by mixing known quantities of analytical grade SiO₂, Al₂O₃, Al(OH)₃, Fe₂O₃, Fe₂SiO₄, MgO, CaCO₃, Na₂CO₃, Na(OH), K₂CO₃, and NaHPO₄, with bulk compositions corresponding to those reported in **Table S-1** [Note that non-negligible Ca blanks during the experimental preparation procedure would have no bearing on our results because we measured the differences between two immiscible melts that formed from a single homogeneous powder (*i.e.*, the $\delta^{44}\text{Ca}$ difference between the two melts would not be affected if the sample were contaminated with exogenous calcium)]. After thorough homogenization, the powders (~30 mg per capsule) were tightly filled into 4x6 mm Au₈₀Pd₂₀ capsules. After heating to the target temperature (~45 minutes), the two resultant immiscible melts were equilibrated for 6 hours at 1170 °C and at pressures of 0.3, 0.8, and ~1.2 GPa (GS8-32, GS8-33, and GS8-34, respectively), and then mechanically separated by centrifuging at 1000 g for > 2 hours. The lower temperature experiment (GS9-37 at 800 °C, 0.8 GPa) was conducted analogously to the higher temperature experiments.

The experimental temperature gradient between the center and edge of the capsules is less than 6-9 °C (Hin *et al.*, 2012). Given that the temperature gradients are symmetric about the center of the capsule and that we fully dissolved each half (minus the interface and edges), any minor Soret effects (affecting either melt) should be canceled out. This inference agrees with our experimental results, where the 800 °C experiment [which has a smaller temperature gradient between the center and ends of the capsule (due to temperature scaling) compared to the higher temperature experiments] yields essentially the same $1000\ln\alpha_{\text{carb-sil}}$ (1000 K) value (within ~0.01‰) as the 1170 °C experiments.



After quenching, a thin longitudinal slice of the capsule was prepared for imaging (**Fig. S-1**) and major element analyses (**Table S-1**). Most of the near-perfectly separated carbonatitic quench and the silicate glass (*e.g.*, **Fig. 1a**) were mechanically extracted from the remainder of the capsule using a precision diamond wire saw and file, which resulted in two solid blocks (each with silicate glass and quenched carbonatite, to be broken in a tungsten carbide die). The interface between the two melts was removed and discarded, leading to small blocks of silicate glass (1 – 12 mg) and quenched carbonatitic melt (1-8 mg) from each experiment which were then dissolved for Ca isotope analyses by TIMS.

We targeted three different pressures in our 1170 °C experiments to control the amount of Ca in the silicate vs. carbonatite melt $[F(\text{Ca})]$ in order to demonstrate closed-system equilibrium behavior without having to change the composition of the starting materials (**Fig. S-3**). The experimental composition used in our lower-T (800 °C) experiment only produces coexisting immiscible carbonatite and silicate melts in a small P-T window, such that we did not explore pressure variations for the lower T experiment. Our current set of experiments covers the high- and low-temperature limits of carbonatite-silicate melt immiscibility. The observation that we get the same $1000\ln\alpha_{\text{carb-sil}}(1000\text{ K})$ from all four experiments, suggests that the carbonatite-silicate melt Ca isotope fractionation factor is well constrained by the present dataset.

2. Ca isotope Analyses by Thermal-Ionization Mass Spectrometry (TIMS)

The silicate glass samples were dissolved using concentrated HF + 6M HCl (5:2 ratio) and refluxed in Savillex beakers for ~1 week at 130 °C, whereas the carbonatite quench samples were dissolved in 6M HCl for ~24 hours in order to leave behind any silicate glass particles that could have remained in the quenched carbonatite side after centrifugation. We did not, however, observe any visible residues in the carbonatitic samples after dissolution. For one silicate sample (GS9-37-silicate), we observed a slight fizz upon our initial addition of 6M HCl (prior to adding HF), and so we decanted this acid after ~10 minutes (at room temperature) and restarted with fresh HCl three times. No fizzing was observed afterwards, so we then proceeded with our



typical dissolution process for silicates. After evaporation, the samples were redissolved in 3 M HNO₃ for subsequent TIMS analyses using well-established methods (Antonelli *et al.*, 2019c, 2019b, 2023a, 2023b) described below.

2a. Radiogenic Ca isotope analyses

Approximately 30 µg of calcium were separated from dissolved samples using column chemistry methods (DGA resin, 3M HNO₃, and ultrapure H₂O) that are based on extensive previous work (*e.g.*, Antonelli *et al.*, 2019a, 2021a, 2023b). For each analysis, ~5 µg of unspiked Ca (in 3M nitric acid) was loaded onto zone-refined Re filaments, evaporated, coated with ~1-2 µL of 40 % phosphoric acid and heated to a dull red glow in a dark room before loading into the Triton-plus TIMS at ETH-Zurich. We used a double-filament method and heated samples slowly (<50 mA/min) in order to achieve stable ⁴⁰Ca signals of 20-30 volts. ⁴²Ca, ⁴³Ca, and ⁴¹K were measured in faraday cups connected to 10¹³ Ω amplifiers, applying a response-time (Tau) correction, and ⁴⁰Ca and ⁴⁴Ca was measured on 10¹¹ Ω amplifiers. The detailed analytical protocol is reported in Antonelli *et al.* (2021a). Resultant ⁴⁰Ca/⁴⁴Ca ratios were corrected to ⁴²Ca/⁴⁴Ca = 0.31221 with an exponential mass law (Russell *et al.*, 1978) and are reported as ε_{Ca} values {defined as 10,000 x [(⁴⁰Ca/⁴⁴Ca)_{sample}/(⁴⁰Ca/⁴⁴Ca)_{standard} - 1]} relative to bulk-silicate Earth (BSE), which is defined by contemporaneous measurements of the USGS standard W-2a [best-estimated absolute ⁴⁰Ca/⁴⁴Ca = 47.157 (Antonelli *et al.*, 2021a)]. None of the samples had detectable levels of ³⁹K or ⁴¹K after column chemistry.

Within the single analytical session from which all of the radiogenic Ca data in this study were obtained, SRM915a yielded an ε_{Ca}(BSE) value of +1.4 ± 0.4 (n = 1) relative to W-2a (n = 3), in agreement with previous work (**Table S-5**). The ε_{Ca}(BSE) value of carbonatite standard COQ-1 was found to be 0.4 ± 0.4 (n = 3), suggesting that it is indistinguishable from the BSE value and also agreeing with previous work within uncertainty (He *et al.*, 2017; Dai *et al.*, 2022). We also analyzed apatite and calcite separates from two of our carbonatite samples (SI-156 and X-1513) that were explicitly chosen because they represent the highest and



lowest $\delta^{44}\text{Ca}$ values found in our study (*see* **Fig. 2**). We found no resolvable difference in any of their ϵ_{Ca} compositions. Calcite and apatite from SI-156 have $\epsilon_{\text{Ca}}(\text{BSE})$ of 0.4 ± 0.5 ($n = 3$) and those from X-1513 have $\epsilon_{\text{Ca}}(\text{BSE})$ of 0.4 ± 0.3 ($n = 3$). Both of these values are the same as that of COQ-1 and within uncertainty of W-2a.

All of the above-quoted $\epsilon_{\text{Ca}}(\text{BSE})$ uncertainties are a combination of the 2sd measurement uncertainties on both W-2a and on the analyzed sample (square root of the sum of the squared uncertainties). Although it is analytically challenging to distinguish between pure mantle calcium [$\epsilon_{\text{Ca}}(\text{BSE}) = 0$] and calcium that may contain some marine carbonates [average $\epsilon_{\text{Ca}}(\text{BSE}) = 1.1 \pm 0.3$ (Antonelli *et al.*, 2021a)], our radiogenic Ca data are consistent with purely mantle-derived calcium in the sources of carbonatites. The uncertainties are too large, however, for this to be a particularly useful observation (*i.e.* they are within error of up to ~80% average marine carbonate).

2b. Stable Ca isotope analyses

Stable Ca isotope data were obtained by TIMS at the University of Bern, Switzerland (Thermo Scientific Triton plus), using the same dissolved sample solutions as for our radiogenic Ca measurements. The resultant $\delta^{44}\text{Ca}$ data [defined as $(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1$] are reported relative to Bulk Silicate Earth (BSE) in per mil notation (‰), where BSE has a recommended $\delta^{44}\text{Ca}$ value of +0.95 ‰ relative to SRM915a (Antonelli and Simon, 2020).

Column chemistry methods are the same as described for the radiogenic Ca measurements, except that a ^{42}Ca - ^{48}Ca double-spike is added to the dissolved rock solutions prior to Ca separation to monitor potential fractionations during column chemistry and instrumental mass fractionation (IMF). This double spike is well-calibrated and is the same as used in previous stable Ca isotope studies (Antonelli *et al.*, 2019b, 2019c, 2023b). After Ca separation (~30 μg), samples were loaded in the same fashion as for our ϵ_{Ca} measurements but were analyzed at the University of Bern because the TIMS at ETH-Zurich does not have enough low-resistance



amplifiers ($10^{11} \Omega$) to accommodate the enriched ^{42}Ca and ^{48}Ca in the double spike. The TIMS at the University of Bern benefits from an additional cup (L5) that allows for the simultaneous collection of ^{40}Ca ($10^{11} \Omega$), ^{41}K ($10^{12} \Omega$), ^{42}Ca ($10^{11} \Omega$), ^{43}Ca ($10^{12} \Omega$), ^{44}Ca ($10^{11} \Omega$), ^{47}Ti ($10^{12} \Omega$), and ^{48}Ca ($10^{11} \Omega$) in static mode, but we also monitored ^{47}Ti with an electron multiplier in a second line of each measurement. We heated samples slowly to obtain stable (slowly-growing) ^{40}Ca signals of 7-9 volts. All samples [other than MC-1901 (apatite) and KS-2001 (calcite)] were analyzed a minimum of two times. Each analysis consisted of 100 cycles and each cycle consists of ten 1-second integrations (line 1), 5 seconds of downtime, and two 1-second integrations of ^{47}Ti on the SEM (followed by 3 seconds of downtime). We found that none of our analyses required corrections for possible isobaric interferences on ^{40}Ca (from ^{40}K) or ^{48}Ca (from ^{48}Ti).

Our measurements of dolerite standard W-2a and carbonatite standard COQ-1 give $\delta^{44}\text{Ca}_{\text{BSE}}$ values of $-0.13 \pm 0.04\text{‰}$ (2SE, $n = 9$) and $-0.21 \pm 0.03\text{‰}$ (2SE, $n = 5$) in agreement with previously reported values for both standards (Banerjee *et al.*, 2021; Sun *et al.*, 2021; Zhao *et al.*, 2022; Antonelli *et al.*, 2023a, 2023b). Based on our nine W-2a measurements, we thus estimate that our internal 2SE uncertainty on $\delta^{44}\text{Ca}$ is $\pm 0.04 \text{‰}$, which happens to be the same value as our calculated repeatability (average absolute difference between duplicate measurements of 0.042‰) considering the 22 samples that were analysed twice in this study (**Table S-2**).

It has been recently suggested that tSE (rather than 2SE) better represents uncertainties for smaller groups of samples, such as those in typical stable isotope studies (Wang *et al.*, 2023). Our tSE uncertainty for W-2a is $\pm 0.047 \text{‰}$ (8 degrees of freedom at 95 % confidence) and for COQ-1 is 0.041‰ (4 degrees of freedom at 95 % confidence, **Table S-2**). Both of these uncertainties are very similar to our repeatability and to the 2SE uncertainty estimate of 0.04‰ . These values in turn yield an estimated 2σ internal uncertainty of $\pm 0.06 \text{‰}$ for $\Delta^{44}\text{Ca}$ values (square root of the sum of squared uncertainties for $\delta^{44}\text{Ca}$), which agrees well with the highly repeatable $\Delta^{44}\text{Ca}_{\text{carb-sil}}$ values measured in our three high-T (1170 °C) experiments [$\Delta^{44}\text{Ca}$ values of -0.10‰ (0.3 GPa), -0.12‰ (0.8 GPa), and -0.08‰ (1.2 GPa)]. Given their higher degree of accuracy, we



report tSE uncertainties for averages derived from populations with $n > 3$, such as our calculated carbonatite-silicate melt fractionation factor ($n = 4$) and the average values for calcite ($n = 8$), apatite ($n = 7$), and all natural data from this study ($n = 15$), as well as for data from previous studies.

For our individual samples (most of which were analysed twice, as is often done by TIMS), the use of tSE (where $t = 12.71$ for a C.I. of 95 % with 1 degree of freedom) leads to a pronounced over-estimation of our uncertainties that are over an order of magnitude higher (tSE of up to ± 0.65 ‰) than our repeatability. This is likely because each single analysis entails 100 ten-second measurements, for a total of 200 ten-second analyses per sample measured in duplicate (*i.e.*, the effective n is > 2). This same number of analyses is equivalent to what would be referred to as 10 separate measurements by MC-ICP-MS [*e.g.*, for the measurements in (Antonelli *et al.*, 2021b) performed at IPGP], so the decision on what to use as the true number of analyses for calculating tSE (or 2SE) is somewhat subjective and can vary from lab to lab. Thus, we argue that our internal uncertainty estimates for individual samples are best represented by those derived from our repeated standard measurements for W-2a and COQ-1 (where $2SE \approx tSE \approx 0.04$ ‰), which give uncertainties that are highly consistent with our calculated repeatability.

We thus chose these internal uncertainties (± 0.04 ‰ for $\delta^{44}\text{Ca}$ and ± 0.06 ‰ for $\Delta^{44}\text{Ca}$) as the error bars to display in our figures (Fig. 1 and Fig. 2), as they should accurately reflect 2σ uncertainty in the measured isotopic differences between samples. Long-term external uncertainties, as estimated from repeated analyses of USGS standard W-2a by the lead author at the University of Bern over three years ($n = 21$, nine of which are reported in this study), on the other hand, are estimated to be ± 0.12 ‰ (2SD), which should be taken as the conservative uncertainty when comparing our $\delta^{44}\text{Ca}$ results to data from previous and future studies.

In addition to providing stable Ca isotope data, our double-spike Ca isotope analyses also give (isotope-dilution based) Ca concentrations in the analysed samples (**Table S-2**). These results agree quite well with the CaO concentrations determined by EPMA in the various minerals (**Table S-4**) and in the experimental silicate



and carbonatitic melts (**Table S-1**) suggesting that Ca blanks were negligible with respect to the amount of Ca dissolved. Although the dissolved experimental samples in this study provided ample amounts of calcium (62 to 1509 μg) and did not present any significant analytical challenges, we do not have a quantitative measurement of the Ca blanks in the U-Pb lab at ETH-Zurich where the chemical separations were performed. Nevertheless, published and unpublished Ca isotope results from the lab have been verified by five independent labs in a number of previous studies (Antonelli *et al.*, 2019c, 2023b, 2023a). Calcium contamination in our samples would decrease the magnitude of observed isotopic fractionations in our experiments. Given that our isotope-dilution Ca concentration measurements give results in agreement with those measured *in-situ* by EPMA, however, it is considered unlikely that significant Ca contamination occurred.

3. Density functional theory (*ab-initio*) estimates

Mineral structures (displayed in **Fig. S-4**) for calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], and ankerite [$\text{CaFe}(\text{CO}_3)_2$], were modeled using the plane-wave density functional theory package Quantum Espresso (Giannozzi *et al.*, 2009) and pseudopotentials from version 1.5 of the GBRV library [<http://www.physics.rutgers.edu/gbrv/>, (Garrity *et al.*, 2014)]. The fractionation factors were calculated using well-established methods (Schauble *et al.*, 2006), where phonon frequencies for ^{40}Ca and ^{44}Ca -substituted crystals were calculated at non-zero phonon wave vectors and used to estimate reduced partition functions ratios (Urey, 1947). Reduced partition functions ratios (*aka.* ‘RPFR’ or ‘ $1000\ln\beta$ ’) for the three mineral structures (reported in **Table S-3**) were estimated from force constants and determined by numerical differentiation of the energies of perturbed structures in which a Ca atom is slightly displaced from its equilibrium position in three orthogonal directions (Bigeleisen and Mayer, 1947; Schauble, 2011; Antonelli *et al.*, 2019c, 2023b). A vibrational frequency scale-factor of 1.06 was assumed for all models using the PBE functional, based on comparison with phonon frequencies measured at high-symmetry wave vectors in lime



and fluorite (Elcombe and Pryor, 1970; Saunderson and Peckham, 1971). Force constants calculated by displacing Ca-atoms (for calcite and diopside) were scaled by the square of this factor (1.1236) and yield results that are comparable to the phonon-based estimates (*e.g.*, calcite $1000\ln\beta$ of 1.275 and 1.254 at 1000 K, for phonon-based and force-constant estimates, **Table 1**). The values used in our model calculations (force-constant estimates for calcite and diopside, and phonon-based estimates for dolomite and fluorapatite) are displayed in bold font in **Table 1**.

For all estimates, we used a gradient-corrected (GGA) density functional [PBE; (Perdew *et al.*, 1996)], which has been successfully employed in several previous studies (Schauble *et al.*, 2006; Méheut *et al.*, 2007; Griffith *et al.*, 2008; Antonelli *et al.*, 2019c, 2023b). Several other studies have also provided DFT estimates for Ca isotopes in mineral structures (Feng *et al.*, 2014; Huang *et al.*, 2019; Song *et al.*, 2019; Li *et al.*, 2022; Wang *et al.*, 2017a; Xiao *et al.*, 2022), based on local density approximation (LDA) functionals, but these are not directly comparable to the RPFRs used in this study. Nevertheless, LDA-based estimates also give inter-mineral $1000\ln\alpha$ values that are generally consistent with our PBE-based estimates (Wang *et al.*, 2017a; Xiao *et al.*, 2022). Our estimated calcite-dolomite fractionation factor (+0.06 ‰ at 1000 K), for example, generally agrees with (but is slightly smaller than) previous results based on LDA functionals (+0.10 ‰) (Wang *et al.*, 2017a). We find that calcite is slightly lighter than diopside (by -0.06 ‰ at 1000 K) and slightly heavier than fluorapatite (by +0.05 ‰ at 1000 K), in agreement with previous predictions based on LDA functionals (Wang *et al.*, 2017a, 2017b). Note that calcite is predicted to be slightly heavier (+0.03 ‰ at 1000 K) than clinopyroxene, if combining the diopside prediction from (Feng *et al.*, 2014) with the calcite prediction from (Wang *et al.*, 2017a), but predicted to be -0.03 ‰ if using the $1000\ln\beta$ values from (Wang *et al.*, 2017a, 2017b). Our calcite-apatite prediction also compares favorably with previous work [+0.07 ‰ at 1000 K, combining LDA predictions from (Wang *et al.*, 2017a; Xiao *et al.*, 2022)]. Recent work suggests that PBE (and other generalized gradient approximation, GGA) predictions, however, are generally more accurate for estimating Ca isotope fractionation factors, but a correction factor for combining LDA- and PBE-based RPFRs has also



been proposed (Xiao *et al.*, 2022). This correction-dependent combination is not necessary for the study at hand, however, as all the relevant minerals have self-consistent PBE-based predictions from this study and Antonelli *et al.* (2019c, **Table S-3**). Finally, it is important to note that our RPFR estimates for various melt compositions (**Table 1**) are tied to PBE-based *ab-initio* predictions and would need to be adjusted if used in future studies based on different types of *ab-initio* (e.g., LDA) predictions.

In line with previous studies, we assume that the RPFR of CO₂-rich alkaline silicate melt is half-way between diopside and labradorite (Antonelli *et al.*, 2019b, 2021b, 2023a, 2023b; Antonelli and Simon, 2020; ; Zhu *et al.*, 2021; Soderman *et al.*, 2022). For carbonatitic melt, we assume that the RPFR is lower than this melt by -0.21 (**Table 1**), which implies that the RPFR of nephelinite/syenite is the same as for the CO₂-rich precursor melt, prior to carbonatite-silicate immiscibility. We also explored models, however, where the carbonatitic melt has a higher RPFR (lower than the precursor melt by -0.11). Given that the experimentally-constrained carbonatite-silicate melt $1000\ln\alpha(1000\text{ K})$ value is -0.21, this assumption implies that the nephelinite/syenite melts would have a higher RPFR (by approximately +0.11) than the CO₂-rich precursor melts (**Table 1**). This difference, however, does not lead to significantly different results in our four-stage model of carbonatite petrogenesis, because the absolute RPFR value of carbonatitic melt is only required for calculating Ca isotope fractionations during calcite/apatite accumulation (Step 4 in our four-step model). In our direct-melting model for magnesio-carbonatites (see **Section 5** of the Supplementary Information), the differences in our model results for the two carbonatitic melt RPFR estimates are more significant, because the absolute RPFR of carbonatitic melt is required for both stages of the model (partial melting and dolomite/apatite accumulation). This leads, therefore, to relatively larger uncertainties associated with our two-stage (direct-melting) model results (**Fig. S-5**) compared to those from our four-stage model estimates (**Fig. 3**). It should also be noted that additional components (not included in our experiments) could possibly have minor effects on Ca-O bonds in carbonatitic melts. These effects would be largely subordinate, however, to the effects from the carbonate anions that dominate the melt. Typical carbonatites have 1-2 wt. % P₂O₅, so



only a very small fraction of Ca bonding sites would be affected by the presence of phosphate. F has even lower concentrations than P_2O_5 , and Cl is negligible. The experiments contained 1 wt. % H_2O , and it is likely that natural carbonatite and nephelinite melts contain more than this, but this is not currently known.

4. Natural Carbonatite samples and mineral separates

Apatite and calcite were separated from one magnesiocarbonatite and seven calciocarbonatite whole-rock samples from 7 different countries. These rocks were characterized in previous work (Sartori *et al.*, 2023) and include samples from Brava Island (Canary Islands), Sokli and Siilinjärvi (Finland), Phalaborwa (South Africa), Oka (Canada), Mount Weld (Australia), Marinkas Quellen (Namibia), and Kaiserstuhl (Germany). The magnesiocarbonatite sample (Marinkas Quellen) is the only one with disequilibrium calcite-apatite REE distributions (indicative of calcite recrystallization), whereas the calciocarbonatite samples all have equilibrium REE distributions indicative of a primary magmatic nature (Sartori *et al.*, 2023).

Briefly, the Brava island sample (X-1513, sövite dyke) consists of clusters of unaltered nephelinite with calcite and apatite inclusions, as well as clinopyroxene and magnetite in textural equilibrium with the calcite matrix. The Kaiserstuhl sample (KS-2001, olivine-bearing sövite) has decimeter-sized calcite comb-layers ascribed to rapid magmatic crystallization (observed at the outcrop scale). The Mount Weld sample (MW-2, biotite bearing sövite) consists of coarse-grained calcite matrix cross-cut by fine-grained biotite and apatite domains. The Oka sample (OKA-BZ2, niocalite bearing sövite) contains small apatite grains in a coarse calcite matrix. The Phalaborwa sample (PLBC-1) contains large apatite grains in a matrix of calcite, and shows granuloblastic structures in thin section, similar to our sample from Siilinjärvi (SI-156). The Sokli sample (SO-199) contains fresh (idiomorphic) biotite and apatite in a calcite matrix, and our magnesiocarbonatite sample from Marinkas Quellen (MC-19-01, beforsite) is composed almost exclusively of dolomite and minor apatite. Despite having disequilibrium REE signatures indicative of recrystallization in this sample (Sartori *et al.*, 2023), the slightly positive $\Delta^{44}\text{Ca}_{\text{apatite-dolomite}}$ ($+0.05 \pm 0.06 \text{ ‰}$) agrees with our equilibrium predictions



(**Fig. 2a**, **Table 1**). Whole-rock chemical data can be found in **Table S-3**. For more information (and photomicrographs) on these samples, see Sartori *et al.*, (2023).

Mineral separations were performed by hand picking using a binocular microscope, resulting in apatite grains with diameters of 100 to 1000 μm and calcite grains ranging in size from 250 to 1000 μm (**Table S-4**). Prior to dissolution, the mineral separates were weighed on a high-precision microbalance (typically used for weighing zircons at ETH-Zurich) and range from ~ 0.1 to 14 mg for apatite and ~ 2 to 16 mg for calcite (or dolomite, **Table S-2**). Other than for apatite from MC-19-01 (which could not be accurately weighed due to small sample size), the purity of our mineral separates and experimental samples was confirmed by isotope-dilution based Ca concentration measurements (see Section 2, **Table S-2**), which agree very well with *in-situ* measurements performed by EPMA (**Table S-4**).

5. Two-stage (direct-melting) model for magnesiocarbonatites

We chose to evaluate the two principal petrogenetic models of carbonatite formation, namely (i) direct-melting of mantle carbonates and (ii) differentiation of a CO_2 -rich alkaline silicate melt resulting in melt-immiscibility. A third model, which entails continuous differentiation of a CO_2 -rich silicate melt until carbonatitic melt is formed (without any silicate-carbonatite immiscibility) is only applicable to the rare carbonatite bodies that are associated with kimberlites and ultramafic lamprophyres (*e.g.*, Dawson and Hawthorne, 1973; Smith *et al.*, 2013; Tappe *et al.*, 2017; Abersteiner *et al.*, 2019). These carbonatites represent a very small proportion of carbonatites in the world (Woolley and Kjarsgaard, 2008). Extensive differentiation of mantle-derived silicate melts to form carbonatitic melts without carbonatite-silicate liquid immiscibility requires mantle pressures and is considered a rare case not applicable to the vast majority of carbonatites. Due to its complexity (*e.g.*, continuous change of melt $1000\ln\beta$ during evolution from silicate to carbonatitic melt) and rareness, we have chosen to not model this process.



In **Fig. S-5** we show results for our two-stage (direct-melting) petrogenetic model for magnesiocarbonatites (*e.g.*, Harmer and Gittins, 1998; Yaxley and Brey, 2004). Based on observations from carbonated mantle xenoliths [up to 2-3 wt. % carbonates (*e.g.*, Ionov *et al.*, 1996)], we conservatively assume that 1-5 wt. % carbonate (dolomite, 21 wt. % Ca) with $\delta^{44}\text{Ca}_{\text{BSE}}$ of 0 ‰ (\approx BSE, red), -0.35 ‰ [average Phanerozoic marine carbonate (Fantle and Tipper, 2014), orange], or -0.67 ‰ [100-200 Ma marine carbonate average (Banerjee *et al.*, 2021), blue] is first mixed into the mantle source (garnet lherzolite, **Fig. S-5b**). The source then undergoes incongruent partial melting where all the carbonates melt and the generated carbonatitic melt equilibrates isotopically with the residual mantle minerals [using the minimum and maximum $1000\ln\beta$ values for garnet lherzolite mantle sources (Antonelli *et al.*, 2023a)].

The absolute RPFR ($1000\ln\beta$ value) of carbonatitic melt is poorly constrained, so we show model results for $1000\ln\beta$ values of 0.929 (as discussed in the main text, “low melt RPFR”) and of 1.037 (“high melt RPFR”) at temperatures of 950-1050 °C, which is the minimum melting temperature for carbonated mantle lithosphere (Foley and Pintér, 2018). To account for the full range of possible $\delta^{44}\text{Ca}$ values, we (i) pair the maximum mantle-source RPFR with the “low melt RPFR” estimate and lower temperature limit (thus yielding the largest possible fractionations), and (ii) pair the minimum mantle-source RPFR with the “high melt RPFR” estimate and higher temperature limit (yielding the smallest possible fractionations, **Fig. S-5c**).

Given that 100 % of the carbonates melt during partial melting, the $F(\text{Ca})$ value (*i.e.* the Ca fraction retained by the residual mantle minerals after melting) is fully controlled by the amount of carbonates initially added to the mantle source, where greater amounts of incorporated carbonate lead to lower $F(\text{Ca})$ because more carbonatitic melt is generated (**Fig. S-5c**). This behavior, which has not been considered in most previous models, thus serves to *increase* the $\delta^{44}\text{Ca}$ of generated melts when greater amounts of carbonate are present in the mantle source. We find that, if the $\delta^{44}\text{Ca}_{\text{BSE}}$ value of the incorporated carbonates is higher than the predicted negative fractionation factor for partial melting (*e.g.*, carbonates with $\delta^{44}\text{Ca}_{\text{BSE}} > -0.25$ ‰), adding more carbonates into the mantle source actually increases the $\delta^{44}\text{Ca}$ of the directly-generated carbonatitic melts



(through a decrease in $F(\text{Ca})$, as shown in **Fig. S-5c**). This behavior changes when the carbonate $\delta^{44}\text{Ca}_{\text{BSE}}$ value is equal to the fractionation factor for partial melting [yielding melts with invariant composition, regardless of the $F(\text{Ca})$, when assuming closed-system equilibrium], and behaves as expected (*i.e.* lowering the $\delta^{44}\text{Ca}$ of carbonatitic melts) when the carbonate $\delta^{44}\text{Ca}_{\text{BSE}}$ is lower than the melt-mantle fractionation factor. In essence, adding more carbonates to the mantle source only lowers $\delta^{44}\text{Ca}$ of carbonatitic melts *if* the carbonates have $\delta^{44}\text{Ca}_{\text{BSE}} < 1000\ln\alpha_{\text{melt-mantle}}(T)$ (in the closed-system case), otherwise, carbonate addition actually increases the $\delta^{44}\text{Ca}_{\text{BSE}}$ of generated carbonatitic melts through a feedback with $F(\text{Ca})$ during partial melting, even if the incorporated carbonates have nominally lower $\delta^{44}\text{Ca}$ than the mantle.

After partial melting, the equilibrated melt rises into the upper crust and crystallizes dolomite at 1000–800 °C [likely entailing 70–90 % crystallization, where $K_d(\text{Ca})$ for dolomite-melt ≈ 1], leading to slightly heavier $\delta^{44}\text{Ca}$ in the cumulates relative to the carbonatitic melts. As in the first stage of this model, we paired the higher temperature limit for crystallization (1000 °C) with the higher carbonatitic melt RPFR estimate and the lower temperature limit (800 °C) with the lower melt RPFR estimate, in order to recreate the full range of possible values for the dolomite cumulates (+0.01 ‰ to +0.12 ‰ heavier than the carbonatitic melt, **Fig. S-5d**). Note that apatite has essentially the same RPFR as dolomite (**Table 1**), so the estimates would not be noticeably different if apatite is included in the crystallizing mineral assemblage.

The net effect of these two sequential processes leads to predicted magnesiocarbonatite compositions that generally agree with natural data (**Data S-1**), with $\delta^{44}\text{Ca}_{\text{BSE}}$ ranging from -0.41 ‰ to -0.05 ‰ when assuming that the mantle source has 1–5 wt. % dolomite (*e.g.*, Dasgupta and Hirschmann, 2006) with $\delta^{44}\text{Ca}_{\text{BSE}} = 0$ (**Fig. S-5e**). Thus, we predict similar $\delta^{44}\text{Ca}$ ranges for magnesiocarbonatite cumulates that are derived through differentiation of initially calciocarbonatitic melts (*i.e.*, when enough calcite precipitates to saturate dolomite, in our four-stage model) and those that are derived from primary magnesiocarbonatitic melts formed through direct melting of carbonate-bearing mantle.



Using the two lower $\delta^{44}\text{Ca}$ values for carbonates (depicted in orange and blue in **Fig. S-5**) leads to predicted carbonatite values of -0.46 ‰ to -0.15 ‰ (1-5 wt. % dolomite with $\delta^{44}\text{Ca}_{\text{BSE}} = -0.35$ ‰, orange) and -0.55 ‰ to -0.17 ‰ (1-5 wt. % dolomite with $\delta^{44}\text{Ca}_{\text{BSE}} = -0.67$ ‰, blue). Although these estimates have a larger uncertainty than those associated with our four-stage model in the main text (due to the highly variable dolomite mode in mantle sources and that our absolute carbonatitic melt RPF estimate come into play in both the accumulation *and* partial-melting stages), the natural data are best reproduced when using carbonates with $\delta^{44}\text{Ca} = \text{BSE}$. The two lower carbonate $\delta^{44}\text{Ca}$ values considered in our model calculations [-0.35 ‰, corresponding to average Phanerozoic marine carbonates (Fantle and Tipper, 2014), and -0.67 ‰, corresponding to average 100-200 Ma marine carbonates (Banerjee *et al.*, 2021)] lead to predicted magnesiocarbonatite $\delta^{44}\text{Ca}$ compositions that are mostly lower than those observed in nature (**Fig. S-5e**).

6. Four-stage melt-immiscibility model for calciocarbonatites (and magnesiocarbonatites)

The first stage, low-degree partial melting of carbon-bearing garnet lherzolite to form a CO_2 -rich alkaline (ultra)mafic melt, was explored in a recent study (Antonelli *et al.*, 2023a). To remain conservative, we take the minimum and maximum fractionation factors from that study and assume that temperatures for initial partial-melting range between 1400-1300 °C *e.g.*, (Foley and Pintér, 2018). Given that the degrees of melting are very low, the melt compositions can be approximated by the mineral-melt fractionation factors, leading to $\delta^{44}\text{Ca}_{\text{BSE}}$ values between -0.13 ‰ and -0.18 ‰ (**Fig. 3e**), when starting from bulk-mantle with $\delta^{44}\text{Ca}_{\text{BSE}} = 0$ ‰ [equivalent to +0.95 ‰ relative to NIST SRM915a (Antonelli and Simon, 2020)]. These estimates agree very well with the average $\delta^{44}\text{Ca}_{\text{BSE}}$ composition of kimberlites [-0.16 ± 0.03 ‰ (Antonelli *et al.*, 2023a)], which are likely to be similar to the melts generated in the first stages of carbonatite formation.

The second stage, fractionation of minerals from the primitive melt, is then required to reach carbonatite-silicate two-melt immiscibility and can occur via two different pathways (Schmidt and



Weidendorfer, 2018). The first path leads to coexisting carbonatite + nephelinite (or similar) melts (“path 1”), and the second leads to carbonatite + foidic syenite melts (“path 2”). The first path entails 20-30 % fractional crystallization with an olivine to clinopyroxene ratio of 4:1 and temperatures of 1300-1000 °C [estimated from (Weidendorfer *et al.*, 2016)], yielding $F(\text{Ca})$ values of ~ 0.9 [*i.e.* ~ 90 % of Ca stays in the melt, assuming that clinopyroxene-melt $K_d(\text{Ca}) \approx 2$, **Fig. 3b**]. The second path is assumed to occur over the same temperature range but entails 80-90 % fractional crystallization of olivine and clinopyroxene, with some alkali-feldspar in the latest stages (Schmidt and Weidendorfer, 2018), leading to $F(\text{Ca})$ values conservatively ranging between 0.5 and 0.3 (~ 30 wt. % clinopyroxene removal, **Fig. 3b**). We assume that the $1000\ln\beta(1000\text{K})$ of CO_2 -rich alkaline mafic melt is 1.144, as previously inferred for carbonated silicate melts (such as kimberlites, **Table 1**) and typical basaltic melts at lower pressures (Soderman *et al.*, 2022; Antonelli *et al.*, 2023a). The $1000\ln\beta(1000\text{K})$ of diopside is 1.311 (Antonelli *et al.*, 2019c, 2021b; Eriksen and Jacobsen, 2022; Soderman *et al.*, 2022), whereas olivine and alkali-feldspars have insufficient calcium to significantly affect Ca isotopes in the differentiated melt. Clinopyroxene fractionation thus yields estimated $\delta^{44}\text{Ca}$ shifts in the residual melts (considering both closed-system, where the melt and crystals stay in equilibrium, and open-system behaviour, where the crystals are removed from the system) ranging from -0.01 ‰ to -0.02 ‰ for path 1 and from -0.03 ‰ to -0.12 ‰ for path 2 (**Fig. 3b,e**).

The third stage, where the CO_2 -rich silicate melt separates into an immiscible carbonatite and nephelinite or foidic syenite melt, typically leads to ≤ 5 % carbonatite (based on the CO_2 mass-balance during liquid immiscibility – see below). Given the relatively low solubility of CO_2 in alkaline and silica-undersaturated melts (such as nephelinite) at subvolcanic pressure and temperature conditions (Morizet *et al.*, 2014), the likely maximum amount of carbonatitic melt that can be exsolved is ~ 7 wt. %, but may be significantly less when considering the limiting effects of other chemical components. From our experiments and comparisons of average CaO in bulk carbonatites, nephelinites, and syenites from the EarthChem database and previous studies (Supplementary **Data S-3**) typical carbonatite-nephelinite and carbonatite-syenite $K_d(\text{Ca})$



values are 2-4 (Weidendorfer *et al.*, 2016) and 6-20 (Weidendorfer and Asimow, 2022), respectively. CO₂ solubility in syenite melt, on the other hand, is 2-6 times lower than in nephelinite melts at identical pressure (Brooker *et al.*, 2001; Morizet *et al.*, 2002). This suggests that, on average, smaller quantities of carbonatitic melt are exsolved from syenitic vs. nephelinitic melts, which serves to counteract the higher $K_d(\text{Ca})$ for carbonatite-syenite and leads to conservative $F(\text{Ca})$ values of 0.9 to 0.8 for immiscibility stemming from both paths (*i.e.* 10-20 % of the Ca budget goes into the carbonatitic melts, **Fig. 3c**).

Our argument for the relative proportions of carbonatite and conjugate silicate melts formed during immiscibility does not stem from observations of natural outcrops, which are unlikely to mirror primary silicate/carbonatite melt proportions. Carbonatitic melts migrate upward through the crust more effectively than silicate melts (due to high buoyancy and low viscosity compared to silicate melts) and should thus physically decouple from their conjugate silicate melts. The outcrop level of natural carbonatite complexes thus has little bearing on relative magma volumes. To reiterate, our proportion of possible carbonatite stems from the solubility of CO₂ in alkaline silicate melts [*e.g.*, for a syenitic melt this is 0.3-1.0 wt. % CO₂ at 5-15 kbar (Morizet *et al.*, 2002)]. Carbonatites have 30-40 wt. % CO₂ thus suggesting that 1 to 4 wt. % carbonatite would be formed if all CO₂ were to go into a carbonatitic melt. A portion of the CO₂, however, remains in the silicate melt, so only a fraction of this maximum prediction would be formed. For nephelinites, CO₂-solubility at 15 kbar is ~4 times higher than for syenites, so more carbonatitic melt could theoretically be unmixed from nephelinitic melts. This difference is unlikely to significantly affect the predicted $F(\text{Ca})$ values, however, given that the larger quantity of unmixed carbonatite is essentially canceled out by the lower Ca distribution coefficient [$K_d(\text{Ca})_{\text{carb-neph}}$] compared to that for carbonatite-syenite (see above). Our estimate of up to 5 wt. % carbonatitic melt, therefore, represents a number at the uppermost possible end when looking at CO₂ solubility in silicate melts in the middle- to lower-crust. We argue that immiscibility happens in the lower to mid-crust, below the outcrop levels, yet, if immiscibility were to happen at the subvolcanic levels of many carbonatite



outcrops, much less than 1 % of carbonatite would form, as CO₂ solubility in silicate melts at 1-2 kbar is <<1 wt. % (Brooker and Kjarsgaard 2011 *and references therein*).

Taking the best-fit fractionation factor from our experiments (-0.21 ‰ at 1000 K) and assuming temperatures of 1100-1000 °C for immiscibility (Brooker and Kjarsgaard, 2011; Weidendorfer and Asimow, 2022; Berkesi *et al.*, 2023) leads to estimated $\delta^{44}\text{Ca}$ shifts of -0.09 ‰ to -0.12 ‰ in the carbonatitic melt (relative to the parental CO₂-rich alkaline melt from stage 2) when considering both open- and closed-system behaviours (**Fig. 3c**) and regardless of the melt differentiation pathway.

The fourth stage, accumulation of calcite (and apatite) to form calciocarbonatite intrusives, typically occurs at temperatures of ~1000-800 °C and entails 70-90 % crystallization [equivalent to 10-30 wt. % loss of an alkali-rich carbonatitic melt (Sartori and Schmidt, 2023)] with a calcite-carbonatite melt $K_d(\text{Ca})$ of 1.2-1.6 (Weidendorfer *et al.*, 2017). These constraints yield estimated $F(\text{Ca})$ values ranging from approx. 0.2 to 0.0 (*i.e.* 80 to almost 100 % of the total Ca ends up in the cumulates, **Fig. 3d**). The absolute $1000\ln\beta$ of carbonatitic melt, however, cannot be directly constrained from our experiments, as we measure only the difference between carbonatite and nephelinite melts. We assume, therefore, that the nephelinite(/syenite) melts have the same $1000\ln\beta$ as the parental melt (1.144 at 1000 K) and that the carbonatitic melt value is lower by -0.21 [yielding an estimated $1000\ln\beta(1000\text{ K})$ of 0.929, **Table 1**]. Combining the carbonatitic melt estimate with our *ab-initio* calculations (where calcite is slightly heavier than fluorapatite), we find that the predicted $\delta^{44}\text{Ca}$ shift in the pooled cumulates, relative to the initial carbonatitic melt, likely ranges from 0.00 ‰ to +0.11 ‰ (**Fig. 3d**). Given that the absolute $1000\ln\beta$ of carbonatitic melt is poorly constrained, we also evaluated model results using a higher RPFR value {1.037 at 1000 K, which is higher than our preferred estimate by $[0.5 \times 1000\ln\alpha(1000\text{ K})_{\text{carbonatite-silicate}}]}$, but this yields only slightly less positive, yet essentially the same, $\delta^{44}\text{Ca}$ values in the final cumulates ($\Delta^{44}\text{Ca}$ from 0 to +0.08 ‰, for Step 4). This higher β value for carbonatitic melt, however, would also require that the nephelinite melt has a higher β value, such that the $1000\ln\beta$ difference between them stays the same ($1000\ln\alpha$ of -0.21 at 1000 K). We consider this unlikely



because the structure (Ca bonding environment) of the CO₂-depleted nephelinite/syenite melt after immiscibility is probably not drastically different from the Ca bonding environment in the melt prior to immiscibility.

Once enough Ca (roughly estimated as ~80 %) is removed, the differentiated melt becomes sufficiently enriched in Mg to crystallize dolomite (*i.e.* when $F(\text{Ca}) < 0.2$), possibly leading to the formation of differentiated magnesiocarbonatites. Given that residual carbonatitic melt has lower $\delta^{44}\text{Ca}$ after calcite precipitation (**Fig. 3d**) and that dolomite has a slightly lower $1000\ln\beta$ than calcite, we predict that magnesiocarbonatites should have lower $\delta^{44}\text{Ca}$ (by at least ~0.1 ‰) than genetically-related calciocarbonatites.

Although other Ca-bearing minerals have been observed in some carbonatites, garnet is rare in CO₂-rich alkaline precursor magmas that can evolve to silicate-carbonatite melt immiscibility, because garnet crystallization requires high $\text{Al}/(\text{Na}+\text{K})$ while immiscible silicate melts are alkaline. Perovskite is a groundmass phase that crystallizes relatively late in these magmas and only occurs in the most silica-undersaturated cases. If they occur at all, these minerals crystallize mainly as late accessories and would not contain more than ~1 wt. % of the total Ca budget, thus having negligible effects on magmatic Ca isotope compositions of carbonatites. Garnet and perovskite are therefore not considered in our models other than residual garnet during partial melting of garnet lherzolite (stage 1).

Adding together the maximum and minimum $\delta^{44}\text{Ca}$ estimates from the four sequential stages of our model (**Fig. 3e**, Supplementary **Data S-2**) leads to calciocarbonatite cumulates with estimated $\delta^{44}\text{Ca}_{\text{BSE}}$ ranging between -0.32 ‰ and -0.12 ‰, for those derived from nephelinites ('path 1' in **Fig. 3**), and from -0.43 ‰ to -0.14 ‰, for those derived from foid-syenites ('path 2'). In the context of our model, we find that the additional isotopic fractionation resulting from melt-immiscibility (Step 3) can explain calciocarbonatite $\delta^{44}\text{Ca}_{\text{BSE}}$ values < -0.2 ‰ (in nephelinite-derived carbonatites) and < -0.3 ‰ (in syenite-derived carbonatites), suggesting that immiscibility is a key process in the petrogenesis of many carbonatites.



Finally, ferrocarbonatites are thought to be derived from pervasive carbothermal and/or hydrothermal alteration (*e.g.*, Pirajno *et al.*, 2014). Their slightly higher $\delta^{44}\text{Ca}$ values (**Fig. 3e**) suggests that secondary alteration may push $\delta^{44}\text{Ca}$ to heavier values. Whether precipitated kinetically or at isotopic equilibrium, calcite is predicted to be isotopically lighter than aqueous Ca (Tang *et al.*, 2008; DePaolo, 2011; Brown *et al.*, 2013; Fantle and Tipper, 2014; Mills *et al.*, 2021; Watkins and Antonelli, 2021). A positive shift in ferrocarbonatites, therefore, could occur through interactions with evolved fluids (*e.g.*, those that have previously precipitated isotopically light carbonates), but this does not necessarily indicate that hydrothermal alteration always leads to positive $\delta^{44}\text{Ca}$ shifts (*e.g.*, addition of hydrothermally precipitated carbonates could also lower $\delta^{44}\text{Ca}$, depending on reaction rates and on the extents of Ca distilled from the fluids). It must be underlined that, in many carbonatite occurrences, large volumes are affected by carbothermal and hydrothermal alteration (Mitchell and Gittins, 2022). Thus, demonstration that carbonatite samples are truly magmatic (Sartori *et al.*, 2023), is required for meaningful interpretation of magmatic process or mantle-source variations.

7. Comparisons with previous $\delta^{44}\text{Ca}$ data and other isotopic studies

We have shown that Ca isotope variations thus far observed in carbonatites do not require recycled marine carbonates in their mantle sources. This variability can instead be explained through magmatic processes accompanying the various stages of carbonatite petrogenesis, including carbonatite-silicate melt immiscibility, which we have experimentally shown leads to significant Ca isotope fractionation. Although previous work excluded melt-immiscibility as a source of $\delta^{44}\text{Ca}$ fractionations in carbonatites by using mass-balance arguments [which predicted $\delta^{44}\text{Ca}$ values far higher than observed in natural conjugate silicates (Banerjee *et al.*, 2021)], this was based on improbable assumptions, including (i) very low values for $F(\text{Ca})$, equivalent to 70-90% of the Ca going into the carbonatitic melts (*vs.* only 10-20 % in our model, see Fig. 3c) and (ii) that all of the fractionation required to explain the $\delta^{44}\text{Ca}$ of their samples occurred solely during carbonatite-silicate immiscibility (*i.e.*, bulk precursor melts have $\delta^{44}\text{Ca} = \text{BSE}$ when they reach the two-melt stability field).



Previous work looking at seventeen calcite separates in carbonatites (Banerjee *et al.*, 2021) found a significantly larger range of $\delta^{44}\text{Ca}$ values than observed here. The entire range of calcite $\delta^{44}\text{Ca}_{\text{BSE}}$ values that were observed (-0.4 ‰ to +0.3 ‰) can also be found within a single carbonatite complex (Oka, Canada). This strongly suggests that carbonatite $\delta^{44}\text{Ca}$ variations depend on processes, and not solely on their sources. There are several reasons why calcite grains may have a range of $\delta^{44}\text{Ca}$ values, including primary magmatic processes, such as those occurring during step 4 of our model (calcite accumulation). During this accumulation stage, early-formed calcite may have $\delta^{44}\text{Ca}$ values up to approx. +0.3 ‰ higher than its parental carbonatitic melt, and late-formed (instantaneous) calcite may potentially have very negative values at low $F(\text{Ca})$ values (see Fig. 3d). Therefore, these calcite signatures could potentially be manifested through open-system processes such as melt loss. Thus, $\delta^{44}\text{Ca}$ variations, even amongst primary calcite grains, are not unexpected. Secondary alteration processes may also influence calcite and appear to typically push $\delta^{44}\text{Ca}$ to higher values (Banerjee *et al.*, 2021; Sun *et al.*, 2021).

Here, we found only a very limited range of calcite $\delta^{44}\text{Ca}$ values. All of our calcite and apatite samples, other than apatite in one sample (X-1513 from Brava), have $\delta^{44}\text{Ca}_{\text{BSE}}$ values that lie within < 0.1 ‰ of the average of our samples (-0.30 ‰). The primary magmatic nature of our samples has been strongly confirmed by previous work (Sartori *et al.*, 2023). Given that essentially all these samples give the same $\delta^{44}\text{Ca}$, we could claim that this value represents the unaltered signature of primary carbonatites. On the other hand, we have only analyzed minerals from eight samples, so it will be crucial to analyze more thoroughly-characterized mineral separates from fresh carbonatites with primary magmatic signatures in future work to better our understanding of Ca isotope variability in calcite.

By using our experimentally constrained carbonatite-silicate melt fractionation factor and including the effects of both partial melting and fractional crystallization into our four-stage petrogenesis model, we successfully explained the Ca isotope compositions of carbonatites from our study and from previous work, without appealing to mantle source variations. Previous studies modeling Ca isotope fractionations during



carbonatite petrogenesis, however, used significantly different parameters in their models (Banerjee *et al.*, 2021; Sun *et al.*, 2021). For example, Sun *et al.* (2021) assumed a garnet-melt fractionation factor [$1000\ln^{44/40}\alpha$ (1000 K)] of +1.15 ‰ (equivalent to $\Delta^{44/42}\text{Ca}_{\text{grt-melt}} = +0.56$ ‰), whereas Banerjee *et al.* (2021) used a garnet-melt fractionation factor of +0.66 ‰ (1000 K), based on *ab-initio* (LDA-based) estimates for grossular garnet from (Huang *et al.*, 2019). Here, we use *ab-initio* (PBE-based) predictions for pyrope (Antonelli *et al.*, 2019c), as this is the dominant garnet end-member in the mantle, yielding a $1000\ln\alpha_{\text{grt-melt}}$ (1000 K) = +0.89 ‰. This fractionation factor also assumes that the $1000\ln\beta$ value for primordial CO₂-rich silicate melt is half-way between PBE-based *ab-initio* estimates of diopside and plagioclase (An₅₀), as suggested from studies of kimberlites (Antonelli *et al.*, 2023a) and discussed earlier in the supplement. Another notable difference is that the models in Sun *et al.* (2021) assume an initial mantle $\delta^{44}\text{Ca}_{915\text{a}}$ composition of +0.88 ‰ (corresponding to $\delta^{44}\text{Ca}_{\text{BSE}}$ of -0.07 ‰) instead of the generally accepted value of +0.95 ‰ [$\delta^{44}\text{Ca}_{\text{BSE}} = 0$ ‰ (Kang *et al.*, 2017; Antonelli and Simon, 2020)].

Although we successfully explain the $\delta^{44}\text{Ca}$ of carbonatites with sequential equilibrium magmatic processes, it remains possible that the $\delta^{44}\text{Ca}$ of carbonatites could be influenced by high temperature diffusive-kinetic effects [*e.g.*, Zhao *et al.*, 2017; Antonelli *et al.*, 2019b, 2019c, 2023b; Antonelli and Simon, 2020; Kang *et al.*, 2020; Watkins and Antonelli, 2021]. In future studies, triple Ca isotope analyses ($\Delta^{48}\text{Ca}'$) will yield especially important information regarding the Ca isotope fractionation mechanisms (*i.e.*, equilibrium *vs.* diffusive-kinetic effects) that operate during formation of carbonatites. All the processes that we model in this study assume Ca isotope equilibrium between the various minerals and melt phases. Our models would be confirmed, therefore, by $\Delta^{48}\text{Ca}'$ values of ~0 ppm [*i.e.*, confirming adherence to an equilibrium mass law (Antonelli *et al.*, 2019c)]. Triple Ca isotope values ($\Delta^{48}\text{Ca}'$) adhering to an equilibrium mass law would thus be entirely consistent with our model calculations and would have no bearing on the presence of recycled marine carbonates in the sources of carbonatites.



For the reasons made explicit throughout this manuscript, stable Ca isotopes are not ideal tracers of sedimentary carbonates in the mantle. Paired with other geochemical proxies, however, Ca isotopes may be used in future studies to better understand a number of factors (*e.g.*, source-rock mineral assemblage; extents of partial melting, fractional crystallization, and melt-immiscibility) involved in carbonatite formation. Calcium isotopes should also yield similar process-dependent information for carbonatites formed through direct partial melting of mantle carbonates, and potentially on the $\delta^{44}\text{Ca}$ of their carbonate sources, but future efforts need to focus on better understanding the many processes that can undoubtedly modify the $\delta^{44}\text{Ca}$ of mantle-derived magmas.

Beyond Ca isotopes, a number of non-traditional stable isotope systems have been used to help understand the origins of carbonatite magmas, including B (Hulett *et al.*, 2016; Çimen *et al.*, 2018, 2019; Kuebler *et al.*, 2020), Mg (Li *et al.*, 2016; Su *et al.*, 2019), Fe (Johnson *et al.*, 2010), and Ba isotopes (Li *et al.*, 2020). A majority of the studies investigating isotopic variations of the heavier elements (*e.g.*, Mg, Fe, Ba) in carbonatites suggest that isotopic variations can be explained by various magmatic processes, and do not require incorporation of recycled marine carbonates (Johnson *et al.*, 2010; Li *et al.*, 2016, 2020; Su *et al.*, 2019).

The slightly positive boron isotope compositions (*i.e.*, $\delta^{11}\text{B}$ up to approx. +5 ‰ vs. approx. -7 ‰ for the mantle) of < 300 Ma carbonatites, however, have been ascribed to increased recycled marine carbonates in the mantle-sources of carbonatites at this point in Earth history (Hulett *et al.*, 2016). Although the number of data used to draw this conclusion were quite limited [*e.g.*, only five Precambrian data points, two of which actually have the same (slightly high) $\delta^{11}\text{B}$ values as the < 300 Ma carbonatites], subsequent location-specific studies also adopted a similar interpretation (Çimen *et al.*, 2018, 2019; Kuebler *et al.*, 2020). In addition to the lack of heavy carbon isotope signatures in the samples from Hulett *et al.* (which would be expected if marine carbonates were involved), we argue that these slightly heavy boron isotope signatures do not serve as unequivocal evidence for recycled marine carbonates in the sources of carbonatites. Ophiolites, altered oceanic



crust, and serpentinites all have high $\delta^{11}\text{B}$ values of up to +19 ‰, +25 ‰, and +41 ‰, respectively (Smith *et al.*, 1995; Vils *et al.*, 2009; Yamaoka *et al.*, 2012, 2015), and could also impart heavy $\delta^{11}\text{B}$ signatures, along with enriched $^{87}\text{Sr}/^{86}\text{Sr}$ isotope compositions, to carbonatite source rocks. Given that metabasites have been shown to retain essentially MORB-like Ca isotope compositions during prograde metamorphism (Lu *et al.*, 2019), mixing with AOC would be unlikely to significantly change the Ca isotope composition of the mantle-sources of carbonatites, and thus could potentially explain both Ca and B isotope observations (assuming that boron behaves as a perfect tracer). On the other hand, boron is a fluid mobile trace element and is heavily susceptible to fluid exsolution (Marschall, 2018, *and references therein*). It is uncertain, therefore, whether the boron isotope composition of carbonatites can be regarded as that of their original mantle sources, even if the carbonatites are minimally altered. Thus, it will be important for future work to focus on how magmatic processes and fluid exsolution from carbonatites [which can have a wide variety of chemical compositions (Walter *et al.*, 2021)] may influence boron isotope fractionation.

Supplementary Tables

Table S-1 Experimental melt compositions (by EPMA). All concentration data are reported in wt. %.

Sample	Material	T [°C]	P [kbar]	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	FeO	Na ₂ O	MgO	P ₂ O ₅	CO ₂	H ₂ O	TOTAL
GS9	Starting material	-	-	37.96	6.30	4.20	16.29	0.00	13.78	0.72	0.00	19.75	1.00	100.00
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GS9-37	Carb	800	8	0.06	-	7.53	22.45	-	25.43	0.12	-	-	-	55.59
-	-	-	-	0.03	-	0.59	2.95	-	0.86	0.06	-	-	-	-
GS9-37	Sil	800	8	58.21	6.70	4.32	16.74	0.05	11.09	0.83	-	-	-	97.95
-	-	-	-	0.53	1.78	0.47	0.58	0.01	1.17	0.03	-	-	-	-
GS8	Starting material	-	-	18.77	6.91	16.79	1.98	2.96	19.76	7.90	0.01	22.67	2.24	99.99
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-



Table S-1 continued

Sample	Material	T [°C]	P [kbar]	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	FeO	Na ₂ O	MgO	P ₂ O ₅	CO ₂	H ₂ O	TOTAL
GS8-34	Carb	1170	3	3.26	0.25	21.78	3.02	0.61	23.80	5.77	-	38.72	-	97.21
-	-	-	-	0.65	0.13	0.87	0.05	0.07	0.64	0.46	-	-	-	-
GS8-34	Sil	1170	3	32.76	13.09	14.83	1.31	2.67	14.37	8.35	-	6.71	-	94.09
-	-	-	-	10.17	3.65	1.26	0.19	0.20	0.33	0.16	-	-	-	-
GS8-33	Carb	1170	8	5.10	0.63	22.49	1.91	1.89	18.29	8.86	-	35.24	-	94.40
-	-	-	-	1.34	0.40	2.25	0.22	0.41	1.12	2.28	-	-	-	-
GS8-33	Sil	1170	8	38.66	16.26	8.61	1.91	4.07	14.12	4.96	-	14.74	-	103.31
-	-	-	-	0.99	0.41	0.42	0.02	0.06	0.10	0.17	-	-	-	-
GS8-32	Carb	1170	12	4.53	0.75	21.55	1.90	1.51	20.17	8.04	-	35.64	-	94.08
-	-	-	-	2.04	0.68	2.70	0.30	0.52	1.18	2.81	-	-	-	-
GS8-32	Sil	1170	12	39.10	16.14	8.62	1.86	4.30	14.47	5.10	-	6.93	-	96.51
-	-	-	-	1.19	0.26	0.44	0.02	0.10	0.18	0.13	-	-	-	-

Table S-2 Stable Ca isotope data. (Note: 2SD uncertainties reported here are the analytical uncertainties associated with each measurement (100 cycles of ten 1-second integrations per analysis)).

Location	Sample	Type	Dissolved sample (mg)	$\delta^{44}\text{Ca}$ (BSE)	2SD	Average $\delta^{44}\text{Ca}$ (BSE)	Ca (wt. %)	2SD
Natural carbonatites								
Brava island (CV)	X-1513	calcite	9.14	-0.33	0.03	-0.33	40.5	1.0
				-0.33	0.03		40.5	1.0
	X-1513	apatite	1.85	-0.46	0.04	-0.45	39.7	1.0
				-0.45	0.03		39.7	1.0
Sokli (FI)	SO-199	calcite	10.27	-0.23	0.04	-0.23	38.8	0.9
				-0.22	0.04		38.8	0.9
	SO-199	apatite	14.19	-0.27	0.03	-0.22	39.7	1.0
				-0.17	0.03		39.7	1.0
Siilinjarvi (FI)	SI-156	calcite	13.16	-0.23	0.03	-0.25	37.3	0.9
				-0.26	0.03		37.3	0.9
	SI-156	apatite	13.17	-0.28	0.04	-0.30	39.8	1.0
				-0.32	0.03		39.8	1.0



Table S-2 continued

			Dissolved sample (mg)	$\delta^{44}\text{Ca}$ (BSE)	2SD	Average $\delta^{44}\text{Ca}$ (BSE)	Ca (wt. %)	2SD
Location	Sample	Type						
Phalaborwa (SA)	PLBC-1	calcite	3.04	-0.31	0.03	-0.30	38.1	0.9
				-0.29	0.04		38.1	0.9
	PLBC-1	apatite	0.87	-0.40	0.04	-0.36	39.8	1.0
				-0.31	0.04		39.8	1.0
Oka (CA)	OKA-BZ2	calcite	15.90	-0.36	0.04	-0.30	38.9	0.9
				-0.23	0.03		38.9	0.9
	OKA-BZ2	apatite	1.00	-0.30	0.03	-0.31	35.1	0.8
				-0.33	0.04		35.1	0.8
Mount Weld (AUS)	MW-2	calcite	10.84	-0.28	0.04	-0.30	39.0	0.9
				-0.33	0.04		39.0	0.9
	MW-2	apatite	0.65	-0.32	0.04	-0.28	34.7	0.8
				-0.25	0.03		34.7	0.8
Marinkas Quellen (NM)	MC-19-1	dolomite	2.36	-0.28	0.03	-0.31	21.8	0.5
				-0.35	0.03		21.8	0.5
	MC-19-1	apatite	< 0.1	-0.26	0.11	-0.26	-	-
Kaiserstuhl (DE)	KS-2001	calcite	2.87	-0.28	0.03	-0.28	36.9	0.9
Experimental samples								
Starting Materials	GS9-SM	starting mat.	12.83	-0.30	0.03	-0.30	3.0	0.1
	GS8-SM	starting mat.	19.23	-0.32	0.04		11.6	0.3
				-0.27	0.03		11.6	0.3
800°C, 0.8 Gpa	GS9-37-Sil	silicate	12.31	-0.19	0.04	-0.24	2.9	0.1
				-0.28	0.03		2.9	0.1
	GS9-37- Carb	carbonatite	1.16	-0.43	0.03	-0.43	5.4	0.1
				-0.43	0.04		5.4	0.1
1170°C, 0.3 Gpa	GS8-34-Sil	silicate	6.48	-0.22	0.03	-0.22	11.3	0.3
				-0.22	0.03		11.3	0.3
	GS8-34- Carb	carbonatite	2.48	-0.30	0.04	-0.32	15.9	0.4
				-0.35	0.03		15.9	0.4
1170°C, 0.8 Gpa	GS8-33-Sil	silicate	1.11	-0.24	0.03	-0.27	7.3	0.2
				-0.31	0.04		7.3	0.2
	GS8-33- Carb	carbonatite	5.98	-0.40	0.04	-0.39	16.1	0.4
				-0.38	0.03		16.1	0.4
1170°C, 1.2 Gpa	GS8-32-Sil	silicate	2.87	-0.30	0.04	-0.29	6.6	0.2
				-0.28	0.03		6.6	0.2
	GS8-32- Carb	carbonatite	8.48	-0.40	0.04	-0.37	16.0	0.4
				-0.34	0.03		16.0	0.4



Table S-2 continued

Location	Sample	Type	Dissolved sample (mg)	$\delta^{44}\text{Ca}$ (BSE)	2SD	Average $\delta^{44}\text{Ca}$ (BSE)	Ca (wt. %)	2SD
Standards								
Virginia, USA	W-2a	Diabase	-	-0.19	0.04	-	-	-
				-0.04	0.04	-	-	-
				-0.14	0.04	-	-	-
				-0.20	0.03	-	-	-
				-0.06	0.03	-	-	-
				-0.12	0.04	-	-	-
				-0.18	0.04	-	-	-
				-0.19	0.04	-	-	-
				-0.09	0.03	-	-	-
			Average	-0.13				
			2SE	0.041				
			tSE	0.047				
Oka, Canada	COQ-1	Carbonatite	13.93	-0.20	0.03	-	33.6	0.8
				-0.17	0.03	-	33.6	0.8
				-0.21	0.04	-	33.6	0.8
				-0.25	0.03	-	33.6	0.8
				-0.24	0.04	-	33.6	0.8
			Average	-0.21				
			2SE	0.029				
			tSE	0.041				

Table S-3 Natural carbonatite whole-rock chemical compositions.

Table S-3 is available for download from the online version of this article at

<https://doi.org/10.7185/geochemlet.2338>

Table S-4 Natural carbonatite apatite and calcite chemical compositions.

Table S-4 is available for download from the online version of this article at

<https://doi.org/10.7185/geochemlet.2338>



Table S-5 Radiogenic Ca isotope data. All measurements come from the same session (same barrel).

*Combined uncertainties include measurement uncertainty on the samples and on W-2a (square root of the sum squared uncertainties). Corr. = mass-fractionation corrected to $^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$ using an exponential law.

name	$^{40}\text{Ca}/^{44}\text{Ca}$ (corr.)	$^{40}\text{Ca}/^{42}\text{Ca}$ (corr.)	$^{43}\text{Ca}/^{44}\text{Ca}$ (corr.)	$^{42}\text{Ca}/^{44}\text{Ca}$ (raw)	$\epsilon_{\text{Ca}}(\text{BSE})$	2SD (combined)*	$^{40}/^{44}\text{Ca}$ (norm. 47.157)
COQ-1	47.1547	151.0353	0.064883	0.3139	0.52		47.1594
COQ-1	47.1548	151.0356	0.064879	0.3150	0.53		47.1595
COQ-1	47.1536	151.0316	0.064881	0.3152	0.27		47.1583
COQ-1 Mean	47.1544	151.0342	0.064881	0.3147	0.44	0.36	47.1591
2sd	0.0014	0.0044	0.000004	0.0014	0.29		
SI156 - Apatite	47.1555	151.0379	0.064879	0.3138	0.69		47.1602
SI156 - Calcite	47.1542	151.0337	0.064883	0.3100	0.41		47.1589
SI156 - Calcite	47.1533	151.0308	0.064883	0.3138	0.22		47.1580
SI-156 Mean	47.1544	151.0341	0.064881	0.3126	0.44	0.52	47.1591
2sd	0.0022	0.0072	0.000005	0.0044	0.47		
X1513 - Apatite	47.1539	151.0326	0.064880	0.3143	0.34		47.1586
X1513 - Apatite	47.1541	151.0333	0.064880	0.3150	0.38		47.1588
X1513 - Calcite	47.1546	151.0349	0.064882	0.3147	0.49		47.1593
X-1513 Mean	47.1542	151.0336	0.064881	0.3147	0.40	0.26	47.1589
2sd	0.0007	0.0024	0.000003	0.0007	0.16		
SRM915a	47.1588	151.0483	0.064883	0.3100	1.38	0.41	47.1635
W-2a	47.1525	151.0283	0.064885	0.3137	0.05		47.1572
W-2a	47.1526	151.0286	0.064886	0.3144	0.07		47.1573
W-2a	47.1518	151.0258	0.064881	0.3131	-0.12		47.1564
W-2a Mean	47.1523	151.0275	0.064884	0.3137	0.00	0.29	47.1570
2sd	0.0010	0.0031	0.000006	0.0013	0.21		

Supplementary Datasets

Data S-1 Compilation of carbonatite $\delta^{44}\text{Ca}$ data from this and previous studies.

Data S-2 Rayleigh calculation results for carbonatite models.

Data S-3 Earthchem results for CaO in relevant rock-types.

Datasets S-1 to S-3 (.xlsx) are available for download from the online version of this article at <https://doi.org/10.7185/geochemlet.2338>



Supplementary Figures

Figure S-1 Back-scattered electron images of centrifuging piston-cylinder experimental run products. Quenched silicate melt (light grey), quenched carbonatitic melt (dark grey), palladium-gold capsule (white). Although we see a meniscus for other two-liquid immiscibility experiments (*e.g.*, silicate *vs.* metallic melt, silicate *vs.* sulfide melt, and two-silicate melts) performed in the centrifuging piston cylinder apparatus, this is not the case for carbonatite-nephelinite melt experiments. Though speculative, the CO₂-rich nephelinite melt may have too low of a viscosity (or unfavorable wetting properties) for the formation of a meniscus between carbonatite and nephelinite melts.

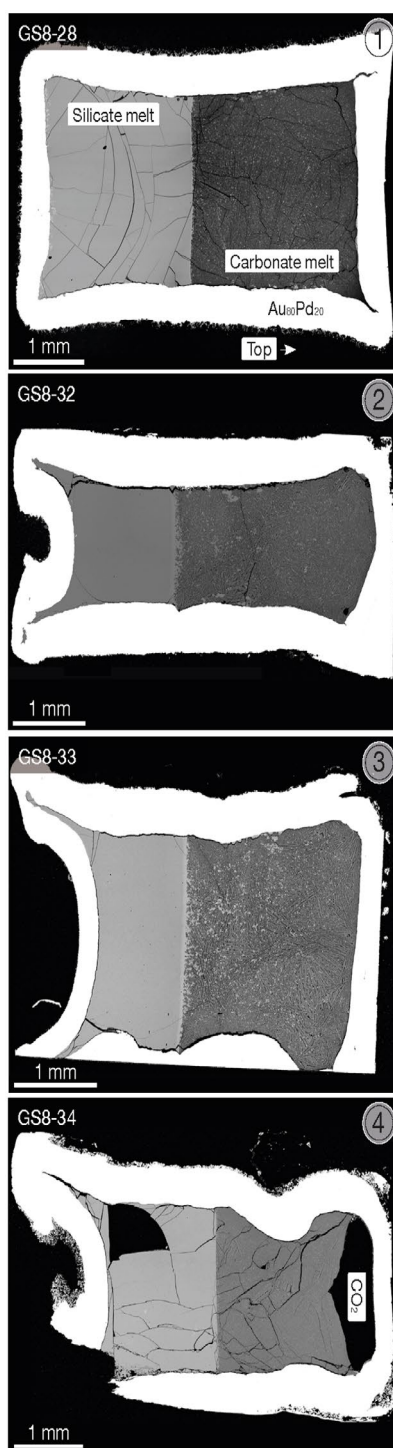


Figure S-2 Experimental melt compositions vs. carbonatite-silicate melt Ca isotope fractionation factors [$1000\ln\alpha$ at 1000 K]. Fractionation factors were calculated using a $10^6/T^2$ law.

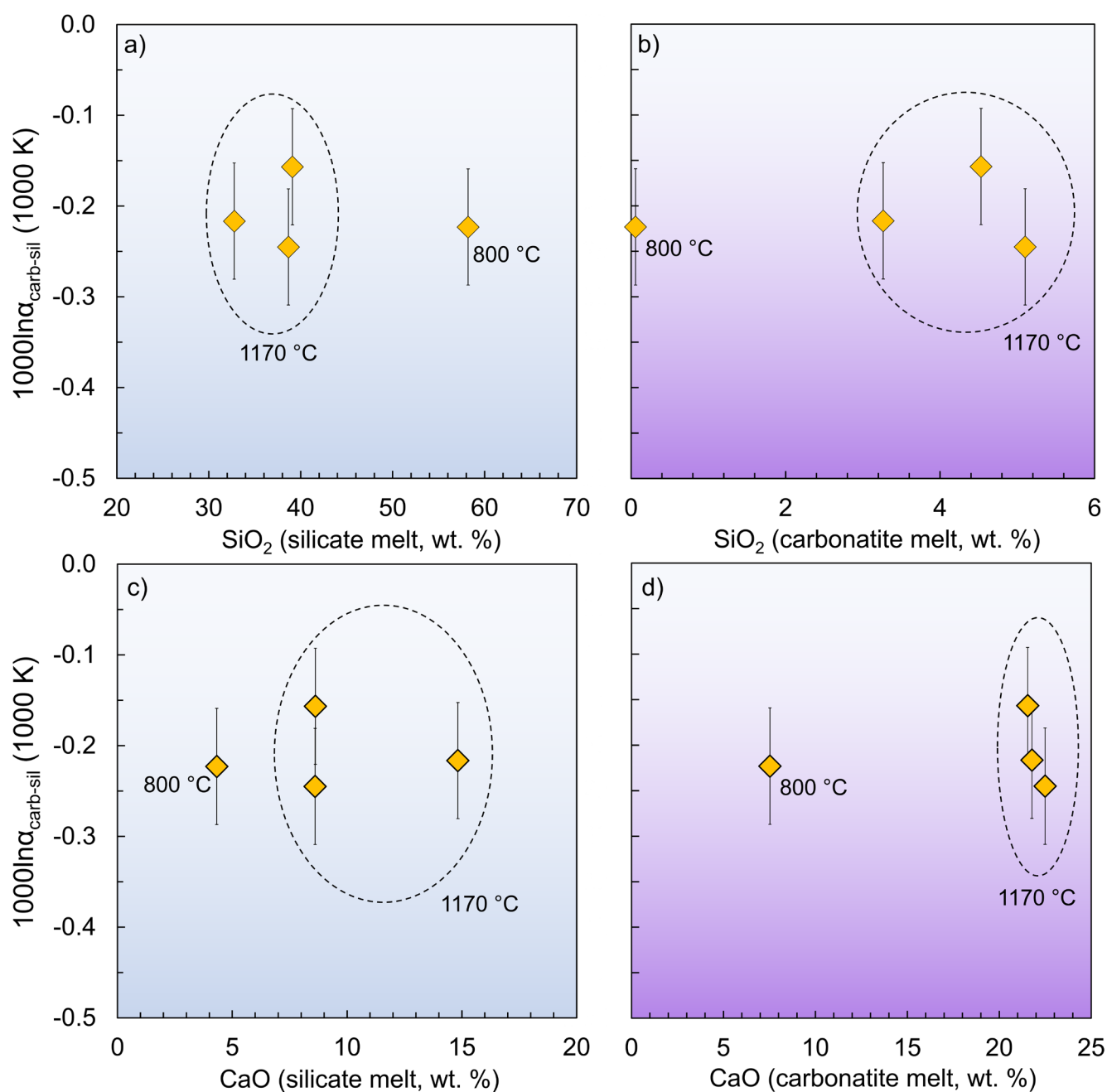


Figure S-3 Experimental $\delta^{44}\text{Ca}$ vs. $F(\text{Ca})$ for the 1170 °C experiments, compared with expected closed-system equilibrium behavior (dashed lines).

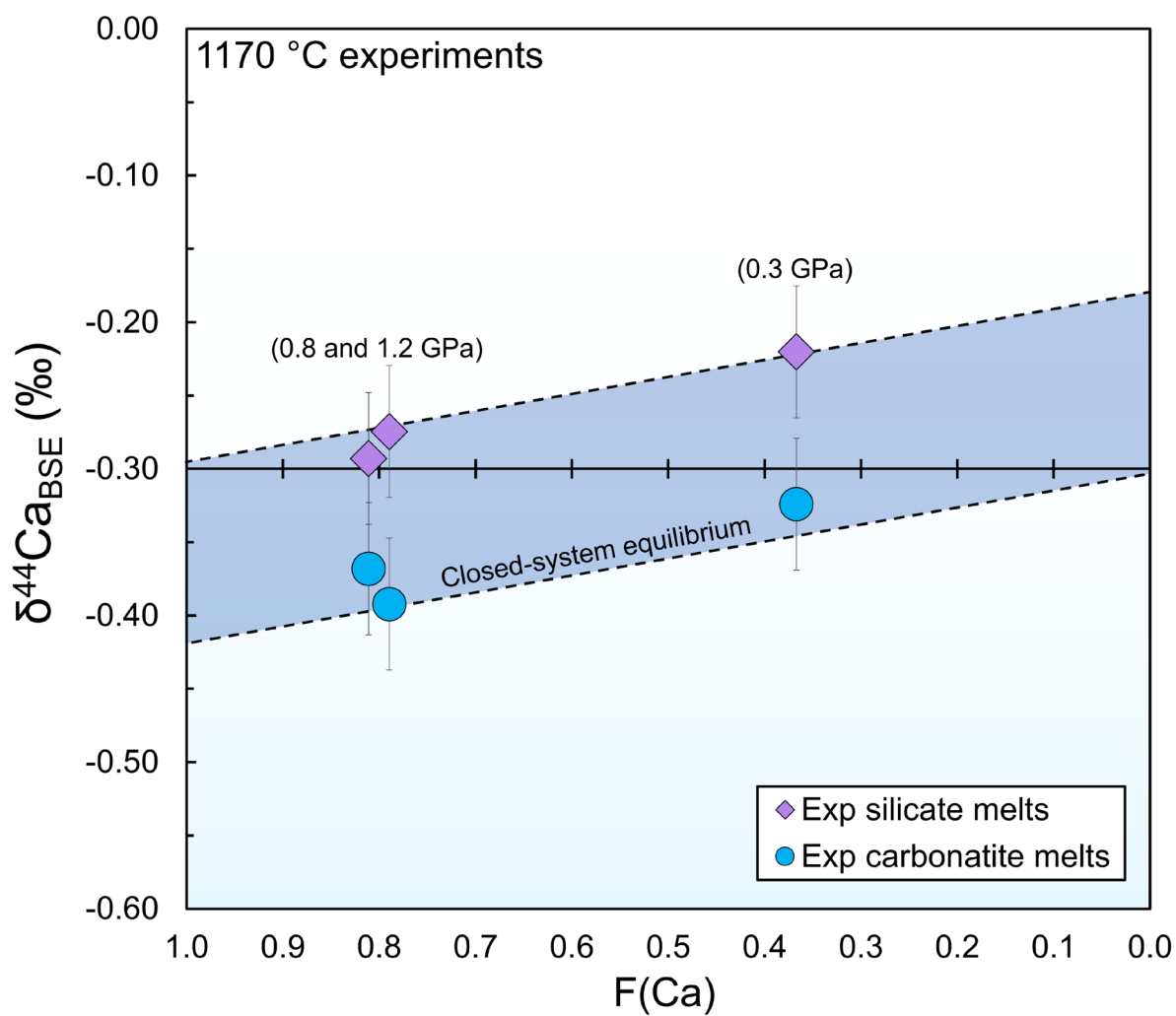


Figure S-4 Mineral structures for **(a)** calcite, **(b)** dolomite, and **(c)** ankerite used in *ab-initio* estimates. Calcium atoms (blue octahedra), magnesium atoms (orange octahedra), iron atoms (brown octahedra), oxygen atoms (red spheres), carbon atoms (dark brown spheres). Images were generated using *Vesta* (Momma and Izumi, 2011). Average Ca-O bond lengths, coordinations, and $1000\ln\beta$ values are reported in **Table 1**.

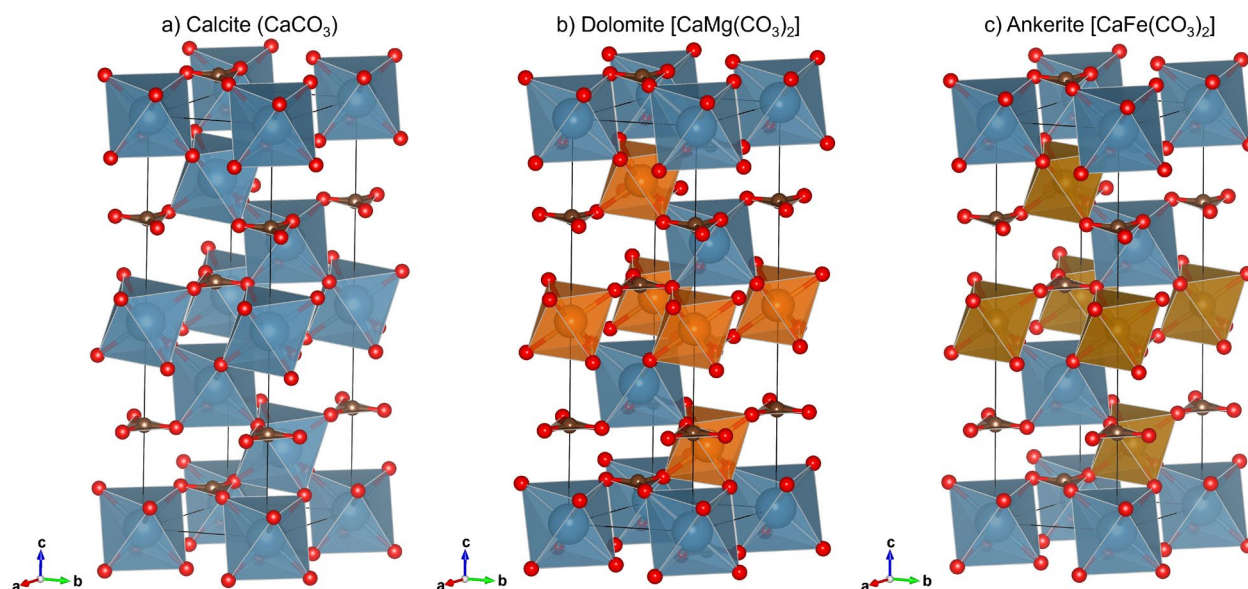
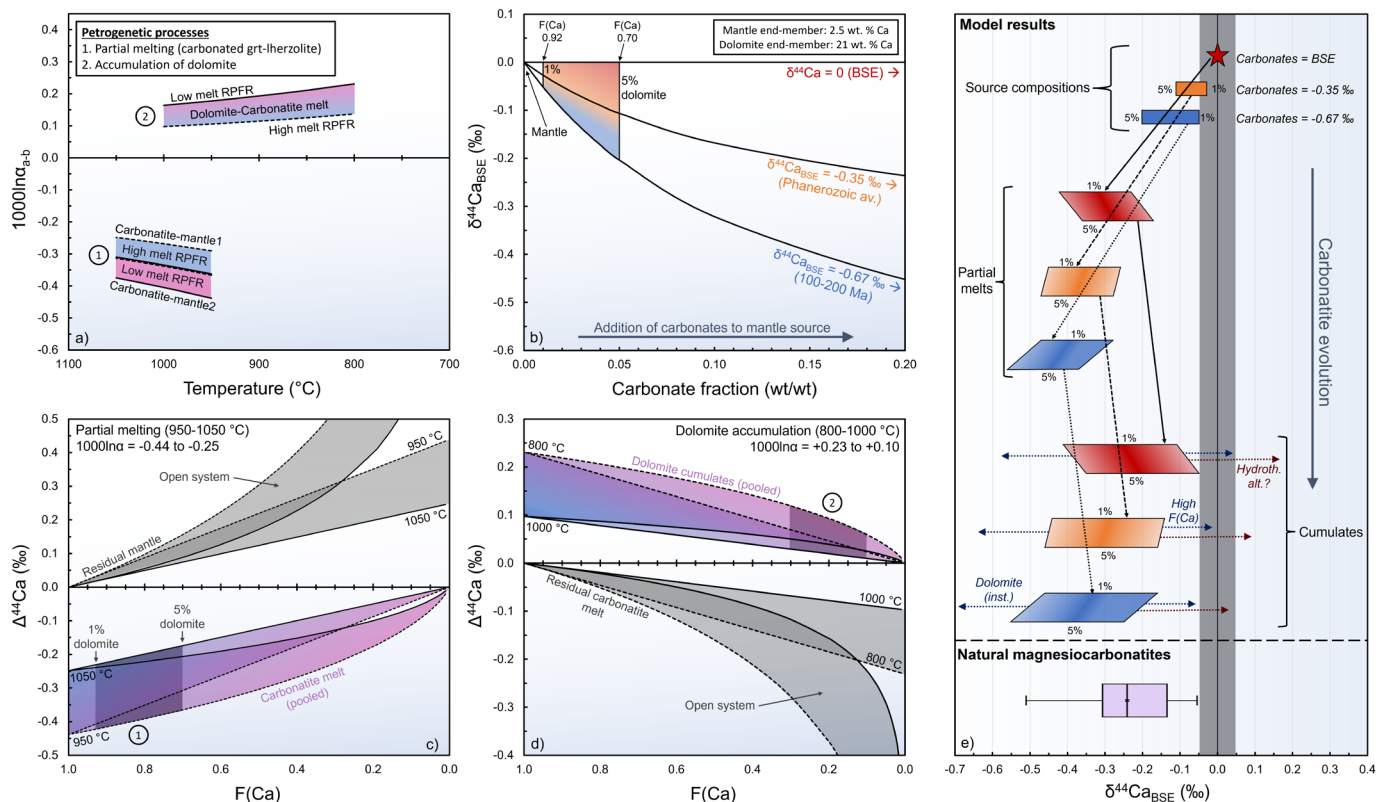


Figure S-5 Two-stage (direct-melting) petrogenetic model for magnesiocarbonatites. **(a)** fractionation factors for partial melting ('1') and dolomite fractionation ('2'). **(b)** Effect of mixing 1-5 wt. % carbonate (dolomite) into the mantle with $\delta^{44}\text{Ca}_{\text{BSE}}$ of 0 ‰ (\approx BSE, red), -0.35 ‰ (orange), or -0.67 ‰ (blue). **(c)** Estimates for Ca isotope fractionation during incongruent partial melting of carbonate-bearing mantle, where $F(\text{Ca})$ is the Ca fraction remaining in the solids. **(d)** Dolomite crystallization from carbonatitic melts at 1000-800 °C, leading to slightly heavier $\delta^{44}\text{Ca}$ in the cumulates, where $F(\text{Ca})$ is the Ca fraction remaining in the carbonatitic melt. Panel **(e)** shows the summative effects of these processes on the various source compositions, leading to predicted magnesiocarbonatite compositions that generally agree with natural data (**Data S-1**).



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