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Calcium isotope constraints on recycled carbonates in subduction-related magmas

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	which isotopically heavy Ca-bearing fluids have been lost. The decoupled signatures between trace elements and their radiogenic isotopes and those recorded by calcium isotope data are important because they likely reflect different sources and processes, and demonstrate that sediment subduction is not a bulk mixing process.

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Abstract

Calcium isotope ratios are readily mass-fractionated by low-temperature depositional processes that can be recorded in sedimentary rocks and, therefore, have the potential to track distinct geochemical signatures of recycled materials in mantle-derived igneous rocks. In this study, I report calcium isotopic compositions for well-characterized lavas from the Central American volcanic arc that exhibit a range of trace element and radiogenic isotope signatures that have been used to indicate variable amounts of subducted marine carbonate and hemipelagic sedimentary rocks, fresh carbonatite lavas from Oldoinyo Lengai Volcano, Tanzania, and an intrusive carbonatite clast erupted 12.8 ka from the Laacher See Volcano, Germany. I observed no calcium isotope evidence for recycled sedimentary rocks in the Central American arc magmas or in the Oldoinyo Lengai carbonatite volcanic rocks. They all exhibit isotopic compositions similar to rocks dominated by a primitive, mantle-like, bulk silicate Earth (BSE) composition. The exception in this work is the calcium isotope composition measured in the intrusive Laacher See carbonatite that is resolvable from BSE ($\delta^{44}Ca$ = 0.0). Although this calcium isotopic signature might be related to ancient carbonate recycling, the magnitude and relatively light calcium isotopic composition ($\delta^{44}Ca$ = -0.4) of this carbonatite could also reflect an origin that involved partial melting of altered lithospheric mantle from which isotopically heavy Ca-bearing fluids have been lost. The decoupled signatures between trace elements and their radiogenic isotopes and those recorded by calcium isotope data are important because they likely reflect different sources and processes, and demonstrate that sediment subduction is not a bulk mixing process.

Introduction

Understanding the fluxes of carbonate sediment between subducting plates and the overlying mantle wedge and magmatic arc is important because sediment fluxes control mantle heterogeneity

and influence the global carbon cycle. In particular, when large amounts of CO_2 (as carbonate) are subducted, they affect Earth's climate (DePaolo, 2004). In this study, I use calcium isotopes to track recycled carbonates in subduction-related magmas because the global calcium and carbon cycles are linked through carbonate formation.

Traditionally, insights into the differentiation history of the mantle come from radiogenic isotope measurements of oceanic basalts, e.g., DePaolo and Wasserburg (1977), Lassiter et al. (1996), and Stille et al. (1983). These observations can be used to study the origin and evolution of compositionally distinct mantle reservoirs. Subduction processes play an important role in the differentiation of the mantle as they can transport distinct materials into Earth's interior. In fact, geochemical and isotopic systems (e.g., Sr, Nd, Pb) have been used to suggest that subducted marine sediments are important to the petrogenesis of ocean island basalts, even when far from any existing plate margin, e.g., Blichert-Toft et al. (1999), Cabral et al. (2013), Castillo et al. (2018), and Huang and Frey (2005). Accurate interpretation of these mantle signatures is complicated by the fact that both changes in source composition and time can lead to isotopic heterogeneity.

Mass-dependent stable isotope compositions complement radiogenic isotope signatures because they are not affected by age. Calcium isotope measurements of primitive igneous rocks have the potential to provide a powerful tool to test ideas about the various possible sources of mantle heterogeneity. This is because both radiogenic and stable calcium isotopes can be measured, e.g., DePaolo (2004), Huang et al. (2010; 2011), Simon and DePaolo (2010), and Simon et al. (2009). Furthermore, significant stable mass-dependent calcium isotope variability is not expected to originate at mantle solidus temperatures under which oceanic basalts have been generated (>1200-1500°C), e.g., Putrika (2005). This is understood implicitly by the growing number of studies based on mantle-derived rocks that exhibit a similar calcium isotopic composition, e.g., Amini et al. (2009), Amsellem et al. (2019), Antonelli and Simon (2020), Chen et al. (2019a,b), DePaolo (2004), Huang et al. (2010; 2011), Jochum et al. (2006), Kang et al. (2017), Simon and DePaolo (2010), and Wombacher et al. (2009).

Subduction and recycling of sediments, in particular marine carbonates, could introduce distinctive calcium isotopic variations within the mantle because marine carbonates generally have lower values, i.e., lighter isotopic compositions than most igneous rocks by up to several per mil (De La Rocha & DePaolo, 2000; DePaolo, 2004; Fantle & DePaolo, 2005; Farkas et al., 2007; Griffith et al. 2008; Heuser et al., 2005; Kasemann et al., 2005; Watkins et al., 2017; Zhu & MacDougall, 1998). This isotopically light signature is commonly understood to reflect mass-dependent biological fixation of Ca^{2+} into the carbonate sediments, which is a function of seawater temperature and growth kinetics, but also depends on the calcium isotopic composition of seawater that can fluctuate because of calcium input to the ocean from weathering of continental rocks and ocean floor basalt (De La Rocha & DePaolo, 2000; DePaolo, 2004; Nielsen Lammers et al. 2020). Relatively light calcium isotope ratios in Hawaiian basalts and some other mafic igneous rocks have been attributed to crustal recycling (Banergee & Chakrabarti, 2019; Chen et al. 2018; Huang et al., 2011; Kang et al., 2016, 2017; Liu et al., 2017), but the interpretation of the results is debated (Ionov et al., 2019; Antonelli et al., 2019a).

In order to help evaluate the role that carbonate recycling plays for the evolution of Earth's atmosphere and to explain isotopic heterogeneity in mantle-derived rocks, I have measured the mass-dependent calcium isotope compositions of modern arc basalts from Central America. In these lavas, more traditional geochemical signatures of carbonate sediment recycling have been observed, including enrichments in large ion lithophile and fluid-mobile incompatible trace elements, short-lived ^{10}Be abundances, heavy stable Li isotopes, and radiogenic isotopes (Chan et al., 2002, 2006; Feigenson et al., 2004; Leeman et al., 1994; Morris et al., 1990; Nyström et al., 1988; Patino et al., 2000; Sadofsky et al. 2008). Likewise, I report mass-dependent calcium isotope measurements for young carbonatite magmas (Oldoinyo Lengai, Tanzania and Laacher See, Germany) to further test the role that subducted sediment might have on the heterogeneity of the mantle and to address the active debate as to whether such exotic carbonatite magmas originate from low degree partial melting of a primitive mantle source or from recycling of carbonate-rich surface material through subduction, e.g., Bell and Tiltonm (2002), and Walter et al. (2008).

Analytical Methods and Samples

Double-spike thermal ionization mass spectrometry calcium isotope measurements

The approach and analytical methods employed in this work are identical to those described in Simon and DePaolo (2010) and analyses were made during the same period of time as this earlier study. Briefly, bulk rock powders (~25 mg) were dissolved in a mixture of mineral acids and combined with a ^{42}Ca-^{48}Ca spike prior to chemical separation. Calcium was purified on cation exchange columns (AG-50 W-X8). A ^{43}Ca single spike was used to determined column blanks and yields, which were ~10-15 ng and ~99.5%, respectively. About 3 μg of purified calcium was loaded in dilute HNO_3 onto rhenium filaments with dilute H_3PO_4 for each mass spectrometric analysis. Calcium isotope ratios were measured with a Thermo-Finnigan Triton thermal ionization multi-collector mass spectrometer (TIMS) at the University of California in the Center for Isotope Geochemistry (Table 1). The ^{39}K, ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{48}Ca, and ^{49}Ti ion beams were measured in a multi-step static cup configuration. The magnitude of mass interference from ^{40}K and ^{48}Ti was monitored and found to be insignificant; no corrections for ^{40}K and ^{48}Ti were applied. The ^{42}Ca-^{48}Ca double spike method, e.g., Russell et al. (1978), was employed to correct for instrumental mass-fractionation. The tracer ^{42}Ca/^{48}Ca ratio of 0.8364±29 used in this study was determined by isotopic measurements of tracer–standard mixtures, and by assuming that the ^{42}Ca/^{44}Ca ratio of the calcium standard is 0.31221, the value obtained by Marshall and DePaolo (1982) and Russell et al. (1978). Due to the higher abundances of ^{40}Ca (96.94%) and ^{44}Ca (2.09%) stable calcium isotope variations are commonly reported as $\delta^{44}Ca = (^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{standard} - 1)\cdot 1000$, where it is important to note that the most abundant isotope, ^{40}Ca, can also be produced by the radioactive decay of ^{40}K (half-life of ~1.25 Ga). This is typically not a concern for young mafic rocks, but in old rocks, stable calcium isotope variations (δ^{44}Ca) must be corrected for potential radiogenic ingrowth of ^{40}Ca.

More than four different reference materials are currently used to define δ^{44}Ca (see inter-conversions in Antonelli and Simon, 2020). These are igneous samples that represent BSE, e.g., unmetamorphosed peridotites, komatiites, and basaltic rocks from Earth and other terrestrial planets, carbonate standard SRM915a, synthetic carbonate standard SRM915b, and modern seawater. In this study, reported values assume BSE=0.0‰ (reported as deviations from ^{44}Ca/^{40}Ca=0.0212094±3 and ^{43}Ca/^{40}Ca=726.840±45—see Simon and DePaolo, 2010). This follows the approach of DePaolo (2004). When multiple measurements were made, the values

listed in Table 1 are weighted means with uncertainties of 2 standard errors in the mean and are corrected for age and/or intrinsic $^{44}Ca/^{40}Ca$ ratio based on measurements reported by Simon et al. (2009). The reported uncertainties are typically less than the 2SD long-term reproducibility of the SRM915a standard, which is ±0.14 and ±0.20‰ for $\delta^{44}Ca$ and $\delta^{43}Ca$, respectively. Based on my experience, this is the current resolution of the technique and, therefore, I focus on $\delta^{44}Ca$ differences that are greater than ~0.15‰. When only an individual measurement is reported I assign the 2SD reproducibility of the SRM915a standard.

Measured values of SRM915a were $\delta^{44}Ca = -0.97‰$ and $\delta^{43}Ca = -0.77‰$. Correcting for their intrinsic $^{44}Ca/^{40}Ca$ ratio that is slightly higher than most planetary materials (see Mills et al. 2018; Simon et al. 2009), shifts the values to $\delta^{44}Ca = -0.88‰$ and $\delta^{43}Ca= -0.68‰$. All data in Table 1 and the electronic supplement are reported corrected to the value of SRM915a ($\delta^{44}Ca$ = -0.95‰) as recommended by Antonelli and Simon (2020). For reference, the measured difference between the average of repeat analyses of the well-known SRM915a standard and estimates of the BSE for this work ($\Delta^{44}Ca_{BSE\text{-}RM915a}$ = 0.97±0.07‰, 2σ, n=11) is similar to the difference found elsewhere, e.g., Table 2.

Igneous samples characterized for calcium isotope composition

Four Central American arc basalts were selected for this study. The recent volcanism along the Central American volcanic arc results from subduction of the Cocos Plate beneath the Caribbean Plate (Figure 1) and consists of two regions of magmatism, the volcanic front and back-arc volcanism (Carr et al., 1990). Three of the studied arc samples come from the volcanic front and one is from a back-arc volcano. From north to south the samples include: Atitlan volcano, Guatemala (AT-50), back-arc Yohoa volcano, Honduras (YO1), San Cristobal volcano, Nicaragua (SC2), and Telica volcano, Nicaragua (TE1). Trace elements ratios (e.g., Ba/La, Ba/Th, Sr/Nb, U/Th) measured in bulk samples and in olivine-bearing melt inclusions for these samples exhibit a significant amount of the geochemical variation seen both locally and regionally along the volcanic arc that is thought to reflect the influence of subducted sediments (Figure 2; Patino et al., 2000; Sadofsky et al. 2008). Characterization of sedimentary core sampled off the coast at Deep Sea Drilling Program Site 495 indicates early carbonate deposition followed by later hemipelagic deposition involving large differences in incompatible elements and element ratios (e.g., Ba/Th).

These differences can be used to identify sediment contribution and even possibly to distinguish between carbonate deposition and hemipelagic deposition (see Figure 2). In particular, the carbonate sediments are believed to provide a distinctive geochemical signature that has been used to track the flux of sedimentary addition to the arc magmas (Patino et al., 2000). Bulk powders of the samples were obtained from M. Carr. Their major, trace element, and isotopic compositions have been reported by Bolge et al. (2009), Carr et al. (1990), Feigenson (1986), Leeman et al. (1994), and Patino et al. (1997; 2000), see electronic supplement.

Two fresh carbonatite lavas, collected immediately after eruptions in 2007 and 2008, from Oldoinyo Lengai volcano, Tanzania were also selected for this study. Oldoinyo Lengai is located on the eastern branch of the East African Rift Valley and is the only modern extrusive carbonatite locality (Figure 1). The sample from 2007 (OL lava 2007) is representative of the large volumes of rare, relatively Na-rich (natro-) carbonatite lavas extruded until August 2007. The younger lava (OL lava 4-7-08) was extruded at a time when Oldoinyo Lengai was erupting more silicic ashes (Fischer et al., 2009). Both samples were provided to me by T. Fisher.

The final sample was a clast of intrusive carbonatite from the Laacher See volcano, Germany. Laacher See volcano is located in the Late Pleistocene East Eifel Volcanic Field that is part of a series of intra-plate volcanic fields in Central Europe (Figure 1). The carbonatitic ejecta clast was extruded ~12.9 ka as part of the most recent episode of highly alkalic and silica-undersaturated magmas (Schmitt et al., 2010; references therein). The material analyzed comes from a rounded nearly 100% sövite domain (~cm in size) associated with coarse-grained calcite. The sample was provided by A. Schmitt who conducted an accessory mineral uranium-series dating study to address the magmatic longevity of the most recent period of subvolcanic magmatism (Schmitt et al., 2010).

Results

All but one of the studied samples have $\delta^{44}Ca$ values that are similar to the "normal" BSE composition (~0‰), Figure 3 and Table 1. Their calcium isotopic compositions are similar to the compositions of clinopyroxene-rich and/or unmelted and unmetasomatized peridotites (Huang et

al., 2010; Kang et al., 2017; Simon & DePaolo, 2010) and well-studied oceanic and continental basalts, e.g., Bermingham et al. (2018), Huang et al. (2011), Simon and DePaolo (2010), and Simon et al. (2017), Table 1. Honduran sample YO-1, which has MORB-like Sr and Nd isotope and LILE/HFSE trace element ratios, exhibits a $\delta^{44}Ca$ (-0.16±0.14‰ (2σ)) that is similar to the samples from Nicaragua, TE1 ($\delta^{44}Ca$ = -0.12±0.14‰ (2σ)) and SC2 ($\delta^{44}Ca$ = 0.06±0.05‰ (2σ)) that have the most obvious trace element and radiogenic isotope signatures for sediment subduction (Figure 4; Carr et al., 1990; Patino et al., 2000). The final Central American arc sample from Guatemala exhibits a similar calcium isotopic composition ($\delta^{44}Ca$ = -0.08±0.14‰ (2σ)). Likewise, both fresh Oldoinyo Lengai carbonatites OL lava 2007 ($\delta^{44}Ca$ -0.13±0.14‰ (2σ)) and OL Lava 4-7-08 ($\delta^{44}Ca$ = 0.05±0.13‰ (2σ)) have calcium isotope compositions that are similar to BSE. The exception in this study is the clast of intrusive carbonatite from the Laacher See volcano. The carbonatitic ejecta clast has a value that is lighter than BSE ($\delta^{44}Ca$ = -0.39±0.14‰ (2σ)).

Discussion

Calcium isotopic record of marine carbonates

Calcium isotope measurements of carbonates are generally light by up to several per mil (De La Rocha & DePaolo, 2000; DePaolo, 2004; Fantle & DePaolo, 2005; Farkas et al., 2007; Griffith et al., 2008; Heuser et al., 2005; Kasemann et al., 2005; Watkins et al., 2017; Zhu & MacDougall, 1998) when compared to unmelted/non-metasomatized peridotites (Kang et al., 2017), komatiites (Amsellem et al., 2019), and most igneous rocks (e.g., Antonelli & Simon, 2020; Chen et al. 2019; Schiller et al., 2016; Simon & DePaolo, 2010), as shown in Figure 3. It is possible that the marine carbonate record may have evolved over time towards higher $\delta^{44}Ca$ values (Farkas et al., 2007). The notion that marine carbonates had light calcium isotope in the distant past has been challenged recently by Blattler and Higgins (2017), who report that, on average, Precambrian carbonates (n=505) are indistinguishable from BSE ($\pm$ 0.24‰). All carbonate sediments undergo an extended diagenetic evolution after deposition. However, the effects of recrystallization involving pore fluids on the calcium isotopic composition in modern carbonates are minor compared to the magnitude of their light calcium isotope compositions (Fantle & DePaolo, 2005; 2007). Whether Precambrian carbonates were deposited with light calcium isotope compositions and subsequently

modified to heavy calcium isotope compositions remains to be shown, but some modification might be expected due to isotopic exchange with heavy seawater and/or relatively heavy Ca-bearing fluids derived from a silicate mantle or crustal reservoir (i.e., John et al. 2012). Nevertheless, detailed work of Fantle and DePaolo (2005) and Griffith et al. (2008) followed up by the compilation of data from over 70 studies included in Fantle and Tipper (2014) shows that over at least the last ~20-30 Ma there has been a significant difference between "lighter" carbonate and "normal" silicate calcium reservoirs.

Calcium isotopic record of mantle-derived rocks

Most mantle-derived rocks and peridotites studies report calcium isotope compositions similar to BSE (e.g., Amsellem et al., 2019; Ionov et al., 2019; Kang et al., 2017; Simon & DePaolo, 2010). There are reports of mantle rocks including peridotites that have distinctly heavy $\delta^{44}Ca$ isotopic compositions, e.g., Amini et al. (2009), Lu et al. (2019), Huang et al. (2010), and Kang et al. (2017) and a few that are distinctly light, e.g., Amsellem et al. (2019) and Zhao et al. (2017). In order to investigate this variability Huang et al. (2010) measured mineral separates from mantle rocks and found that $\delta^{44}Ca$ in orthopyroxenes (opx) are significantly heavier than their associated clinopyroxenes (cpx) by 0.36-0.75‰. The magnitude and sign of the measured differences are generally consistent with first principles equilibrium inter-mineral isotope fractionation calculations that fundamentally depend on calcium concentration (i.e., Ca—O bond strength) and temperature (Wang et al., 2017; Antonelli et al., 2019a). In detail, calcium isotope fractionation between opx and cpx ($\Delta^{44/40}Ca_{opx\text{-}cpx}$) less than ~0.26‰ and greater than ~0.60‰ is likely related, at least in part, to disequilibrium calcium isotopes effects such as metasomatic metamorphism (Zhao et al., 2017). Disequilibrium effects have also been reported for volcanic settings during rapid crystal growth (Antonelli et al., 2019b) and between opx and cpx and with other minerals during granulite facies and ultrahigh-temperature metamorphism (Antonelli et al., 2019a). In these cases, calcium concentration likely plays an important role, i.e., it is lower by ~1/32 in opx as compared to cpx, and may be more easily affected by isotope fractionation governed by diffusive loss (or gain) of calcium. This would explain why cpx tends to have compositions closer to BSE but why opx compositions can vary wildly—opx as high as $\delta^{44}Ca$ ~6 has been found in mafic granulite samples (Antonelli et al 2019a). Interestingly, a recent investigation using calcium isotope signatures of carbonatite and silicate metasomatism and melt percolation found little

evidence for calcium isotopic heterogeneity and concluded that metasomatism tends to decrease $\delta^{44}Ca$ values of metasomatized mantle materials, but that its effects are usually limited ($\leq 0.3‰$) (Ionov et al., 2019).

Calcium isotopes exhibit no evidence for carbonate sediment recycling at subduction zones

In the studied Central American arc magmas, I found no evidence for calcium isotopic heterogeneity and thus no evidence for carbonate recycling or any isotopic fractionation related to subduction. This is the case despite the fact that I selected rocks that have both little to no geochemical evidence for sediment subduction, i.e., YO1 has MORB-like trace element signatures and depleted mantle (DM) radiogenic isotope compositions, and rocks with strong trace element and radiogenic isotope signatures for carbonate sediment subduction (Figure 2).

To date, resolvable radiogenic calcium isotopic signatures have not been observed in any oceanic or arc basalts (Huang et al., 2011; Marshall & DePaolo, 1989; Simon et al., 2009). This might not be surprising given the work of Caro et al. (2010) who, despite finding well-defined excesses of ^{40}Ca in some river waters draining into the ocean, report that no discernable effects of ^{40}K decay, to within their reported analytical precision (~0.4 epsilon units, 2σ), exist in marine carbonate samples ranging in age from Archean to recent.

There have been recent studies of mantle-derived rocks that find little evidence that recycling of carbonates affects the calcium isotope values of the mantle on a global or regional scale (Ionov et al., 2019; Antonelli et al. 2019a). However, other calcium isotope studies of primitive igneous rocks report evidence for recycling, e.g., Banergee and Chakrabarti (2019), Chen et al. (2018), Huang et al. (2011), Kang et al. (2016, 2017), and Liu et al. (2017). My results are significant since the trace element and radiogenic isotope signatures (e.g., high Ba/La, Ba/Th, $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, see Figs. 2 & 4) of Central American lavas suggest a significant contribution from subducted carbonates (Patino et al., 2000; Sadofsky et al., 2008). The geochemical decoupling reported herein contrasts with the signatures reported for the ocean island basalts studied by Huang et al. (2011). In the Huang et al. (2011) study, stable mass-dependent calcium isotope signatures vary and correlate with other geochemical parameters (i.e., Sr/Nb and $^{87}Sr/^{86}Sr$) used to support the interpretation that Hawaiian lavas represent recycling of ancient calcium bearing surface materials.

All samples from the volcanic front (VF) are interpreted to be elevated in their Pb and Sr radiogenic isotopes above values for back-arc lavas (BA) by the addition of a sedimentary subducted component (see Figure 4; Carr et al., 1990; Feigenson & Carr, 1986; Feigenson et al., 2004; Patino et al. 1997, 2000). Back-arc lavas including YO1 remain within the mantle field, reflecting mixtures of MORB-like depleted mantle (DM) and enriched mantle (HIMU). The potential sedimentary contribution to the arc magmas is believed to be uniform from Guatemala through northern Costa Rica and the sedimentary sequence has been well-documented by the Deep Sea Drilling Program (DSDP), see Patino et al. (2000). The lower section of the sedimentary sequence consists of middle-lower Miocene chalky carbonate ooze and manganiferous chalk and chert that are on average ~50 wt. % CaO (von Huene et al., 1982).

Subducted carbonate sediments along the Central American trough have compositions (Ba/La_{avg} = 244, Sr/Nb_{avg} = 3418, $^{87}Sr/^{86}Sr_{avg}$ = 0.7086) that can produce a distinct signature in the arc basalts (Patino et al., 2000; Sadofsky et al. 2008). The calcium isotopic composition of this sediment has not been measured, but modern carbonate ooze (DSDP 590B) has a $\delta^{44}Ca$ = -0.36±0.15‰ (2σ) (Fantle & DePaolo, 2005), similar to the modern riverine inputs to the oceans (DePaolo, 2004), see Figure 3. The calcium isotope homogeneity among the studied arc magmas is particularly notable when one considers the fact that they exhibit a large range in their sediment contribution signatures. They exhibit compositions that range from non-existent levels typical of MORB up to those near BSE in these sediment signatures (e.g., Ba/La varies from ~4 to 117, Figure 2, Sr/Nb varies from 16-328, and $^{87}Sr/^{86}Sr$ varies from 0.7029-0.7041, Figure 4) as compared to the more limited range recorded by the Hawaiian tholeiites (Sr/Nb = 25-55, $^{87}Sr/^{86}Sr$ = 0.7035-0.7042), considered by Huang et al. (2011) to reflect ancient carbonate recycling. These observations imply that some traditional geochemical signatures for carbonate sediment subduction in arc magmas are at odds with their calcium isotopic signatures.

There are several ways to explain the decoupling of the calcium isotopes and the more traditional geochemical carbonate sediment signatures. First, the calcium isotope compositions of the subducted carbonates could have had little mass-fractionated calcium (i.e., Farkas et al., 2007; Blattler & Higgins, 2017) or their original light calcium isotopic signatures could have been

311 modified, perhaps during diagenesis, prior to subduction and therefore have had limited effect on
312 the calcium isotope composition of the studied arc magmas. I rule this out because it is unlikely
313 that modern (≤ 35 Ma) subducted carbonate sediments had BSE-like calcium isotope
314 compositions, as shown by the work of Fantle and Tipper (2014; references therein). Likewise,
315 even while the enhanced reaction in young carbonates increases the diagenetic effects, and
316 therefore their $\delta^{44}Ca$, the maximum effect (<0.15‰) of diagenesis is not large enough to erase the
317 ≥ 0.3‰ light isotope effects typical of the carbonates, see Fantle and DePaolo (2007).
318
319 Second, it is possible that the flux of subducted sediment to the arc, and in particular marine
320 carbonate, is overestimated. Despite the large volumes (100's m thick) of carbonate inferred from
321 the DSDP drill cores from the subducting sediment sequence along the volcanic front, it is
322 unknown how much sediment-derived calcium is hybridized within the source reservoir(s) of the
323 arc magmas. On average CaO is 4-5x more enriched in the carbonate sediment than the arc
324 magmas. MORB-like magmas have CaO contents that are the same or slightly higher than
325 comparable primitive arc basalts (Patino et al. 1997; Presnall & Hoover, 1987). So, unlike Pb, Sr,
326 and Nd that are found in relatively low abundances in the mantle, and therefore must come from a
327 subducted component, perhaps sediments, to explain the elevated abundances in the arc basalts,
328 all of the CaO needed in the arc basalts can be potentially provided by the mantle. For the most
329 part these trace elements also behave incompatibly and will preferentially contribute, along with
330 H_2O and other fluid mobile LILE, to the arc flux. In contrast, calcium acts compatibly. Therefore,
331 any process that creates new Ca-bearing phases, such as the "reaction pyroxenite" described by
332 Straub et al. (2008; 2011), would effectively trap sediment-derived Ca. As this material sinks into
333 the mantle, this may help explain why some or most subducted carbonate calcium is added to long,
334 deep mantle convection cycles contributing to the formation of ocean island basalts as suggested
335 by Huang et al. (2011) (and possibly the carbonatites discussed in the following section), rather
336 than the arc.
337
338 Third, the calcium isotope signatures may reflect a scenario in which the light calcium isotopic
339 signatures of the subducted sediment are diluted by mixture with relatively heavy calcium
340 reservoir(s), i.e., seawater and/or crustal rocks with BSE calcium isotopic compositions. Clear
341 evidence of sediment subduction in the Central American arc is complicated by the fact that the

radiogenic isotope compositions of the subducted sediments are relatively unradiogenic for marine sediments (cf. Feigenson et al., 2004). The exception may be Guatemalan lava AT-50, but notably its Nd-Sr isotopes could also reflect addition of crust and not necessarily subducted sediment (Figure 4). Some of the trace element variability used as evidence for subducted sediment (Ba/Th) could also be explained by the mobilization of Ba over Th in fluids derived from subducted altered oceanic crust (Figure 4) as seen in oceanic island arc basalts (Turner et al., 1996; Hawkesworth et al., 1997). Moreover, calcium mobilized in fluids extracted via deserpentinization reactions, as subducted rocks rise in temperature and pressure, might buffer the light carbonate signatures. It has been reported that subducted fluids could evolve isotopically during transport and fluid-rock interaction, becoming enriched in heavy isotopes as they rise through the slab into the subvolcanic arc (John et al., 2012). It follows that mixing with isotopically heavy altered oceanic crust could offset the effects of the calcium from carbonate sediment which is isotopically light and produce BSE calcium isotope compositions for the arc lavas.

Mantle source(s) of calcium in carbonatite magmas

The similar $\delta^{44}Ca$ of the studied Oldoinyo Lengai carbonatite lavas and terrestrial basalts (i.e., BSE composition) suggests a mantle-source for their calcium. This interpretation is consistent with the general consensus that carbonatites originate from low-degrees of partial melting of the mantle (see Bell & Tiltonm, 2002; Walter et al., 2008). It is also consistent with studies that conclude carbonatite volcanoes extrude primordial volatiles (CO_2, He, N_2 and Ar) that are indistinguishable from those emitted along mid-ocean ridges despite the fact that Oldoinyo Lengai carbonatites occur in a setting far removed from oceanic spreading centers (Fisher et al. 2009). It is possible that Oldoinyo Lengai lavas, which are natrocarbonatite, are not representative of more Ca-rich carbonatite magmas. Extruded carbonatites, being composed largely of soluble carbonates, are easily weathered and therefore unlikely to be preserved in the geological record. The question of why this volcano extrudes lavas that are chemically different to older carbonatite centers, and whether ancient carbonatites were all originally natrocarbonatites and subsequently altered to calciocarbonatites remains unanswered (Dawson et al., 1987; Zaitsev & Keller, 2006).

Origin of the light calcium isotope composition of Laacher See and other intrusive carbonatites

The distinctly light calcium isotope signature ($\delta^{44}Ca$ = -0.39±0.14‰ (2σ)) of the intrusive Laacher See carbonatite is the sole outlier in this study, and is distinct from what is found in most igneous samples (see compilations in Antonelli & Simon, 2020; Schiller et al., 2016). It is possible that the mass-dependent calcium isotopic deficit seen in Laacher See carbonatite is an artifact produced by relatively large (~4 epsilon-unit) radiogenic ^{40}Ca effects, as can be seen in Precambrian samples (e.g., Antonelli et al., 2019c; Mills et al., 2018; Simon et al., 2009). This is unlikely given the fact that the carbonatite clast studied was cogenetic with its ~12.9 ka phonolite host, which exhibits negligible evidence for assimilation, and contained zircons that range from 32.6 ± 4.1 ka to near-eruption in age (Schmitt et al., 2010).

The calcium isotope composition of the Laacher See carbonatite could originate from recycling of isotopically light marine carbonate as suggested recently for other carbonatites (Amsellem et al., 2020). This would involve carbonate subduction through a long deep convection cycle, which is required given the fact that the East Eifel Volcanic Field is in Central Europe far from a modern subduction zone. Amsellem et al. (2020) recently reported light calcium isotope data for a large number of Ca-, Mg-, and Fe-rich carbonatites spanning from ~3 Ga to ~1 Ma (Amsellem et al., 2020). Their findings are important because they may provide timing constraints for the onset of plate tectonics and subduction of marine sediments. Furthermore, their conclusions imply that since at least 3 Ga there has been relatively similar levels of marine biomineralization, seawater conditions, and continental weathering to produce isotopically light marine carbonate. This does not appear to be true, however, as over approximately the same timespan (~3.0 to 0.7 Ga) there is little evidence for isotopically light marine carbonate in the geologic record (Blatter & Higgins, 2017). In fact, the extensive Precambrian carbonate record reported by Blatter and Higgins (2017) is dominated by BSE calcium isotope compositions. This record poses a serious problem for the interpretations of Amsellem et al. (2020), which necessitate that ancient carbonatites form from recycled light marine carbonates.

The Laacher See carbonatite is notable, in part, because it is the youngest intrusive carbonatite example known on Earth. It may also be important that it is an intrusive rather than an extruded sample. Another significant characteristic of the Laacher See carbonatite is that its oxygen isotopic composition is similar to the relatively narrow range ($\delta^{18}O_{SMOW}$ = 5-8‰) exhibited by mantle-

derived mafic rocks (Schmitt et al. 2010; Taylor et al., 1967). In general, more silicic igneous rocks and most metamorphic and sedimentary rocks exhibit higher $\delta^{18}O$ values. This similarity has been used to suggest a possible genetic relationship between the Laacher See carbonatites and rocks that are commonly believed to originate in the lower crust or upper mantle. Because oxygen is a major component of the studied materials, their oxygen isotopic composition has been used to argue that it is difficult for the Laacher See carbonatites to have formed by addition of any significant sedimentary carbonate component, which generally have much higher oxygen isotope compositions ($\delta^{18}O_{SMOW}$ = 15-25‰; Taylor et al., 1967). It follows, therefore, that its CO_2, and perhaps calcium, is likely also primary and not due to marine carbonate recycling. Taylor et al. (1967) do point out, however, that the Laacher See carbonatites could form from assimilation of carbonate if these materials had undergone recrystallization and oxygen exchange with primary igneous rocks. It should also be noted that despite the fact that a large number of carbonatite complexes around the world do exhibit mantle-like C and O isotopic signatures, some exhibit much heavier oxygen isotope compositions than the Laacher See carbonatites. These heavy oxygen isotope values are consistent with what might be produced by assimilation of sedimentary carbonate country rock (e.g., Santos and Clayton, 1995; Wei et al., 2020). Consequently, the relatively constant $\delta^{44}Ca \sim -0.4$ values seen in carbonatites, over the past 3 Ga, probably reflect a more universal mass-fractionation process rather than the incorporation of a relatively constant amount (6-7%) of recycled marine carbonate sediment into their mantle sources (cf. Amsellem et al., 2020).

Laacher See carbonatite has had a protracted sub-solidus history as an intrusive rock and has a calcium isotopic composition that is similar in magnitude and sign to the mass-fractionation seen for carbonatite metasomatism (Ionov et al. 2019). Therefore, the most likely explanation for its calcium isotopic composition is that its formation included fluid-alteration and/or a partially dehydrated source rock from which isotopically heavy Ca-bearing fluids have been lost, analogous to that reported by John et al. (2012) for metasomatism in subduction zones. Given that a majority of carbonatites have a similar light calcium isotopic composition, and yet marine carbonates may not have had isotopically light calcium isotope compositions in the past, there is no simple scenario in which marine carbonate recycling is the dominate explanation for their calcium isotopic composition.

Conclusions

Studied Central American arc magmas have no calcium isotope evidence for carbonate recycling. This is observed even for magmas with strong trace element and radiogenic isotope signatures indicating sediment subduction. The decoupled signatures are important because they likely reflect different sources and processes, and demonstrate that sediment subduction is not a bulk mixing process. Fresh Oldoinyo Lengai carbonatites also have $\delta^{44}Ca$ values that are similar to unmelted peridotites, komatiites, and most basalts, which again implies a primitive mantle-derived calcium source. The possible exception comes from the intrusive Laacher See carbonatite. Its calcium isotopic signature could be related to carbonate sediment recycling in a long deep convective cycle. Alternatively, the relatively light calcium isotopic composition ($\delta^{44}Ca$ = -0.39) measured in the Laacher See carbonatite, and recently found in other carbonatites, may be associated with a process in which an isotopically heavy Ca-bearing fluid was extracted during dehydration of its lithospheric mantle source, mass-fractionating its original BSE calcium isotopic composition.

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Table 1. Mass-dependent calcium isotope compositions of igneous rocks and standards.

Table 2. Difference between igneous rocks used to estimate $\delta^{44}Ca$ of BSE and SRM915a standard for various research laboratories.

Figure 1. Maps of Central America, Eastern Africa, and Europe showing location of the studied samples. The location of the DSDP Site 495, off the coast of Guatemala, is also indicated (Central American map modified from Patino et al. 2000).

Figure 2. Regional variations in trace element ratios along the Central American volcanic arc. MORB-like Ba/La and Ba/Th values occur in Honduras volcanoes whereas maximum values, believed to be tracers of hemipelagic sediment and marine carbonate, respectfully, occur in western Nicaraguan volcanoes (data from Patino et al., 1997; 2000).

Figure 3. Calcium isotopic composition of Central American volcanic arc magmas (this study), extrusive Oldoinyo Lengai carbonatite lavas (this study), and intrusive Laacher See carbonatite clast (this study). Values for unmelted/unmetamorphosed peridotites, komatiites, terrestrial basalts, seawater, marine carbonates, SRM915a carbonate, and the effect of metasomatism shown for reference (Antonelli et al. 2019a; Amsellem et al., 2019; Bermingham et al., 2018; Fantle & DePaolo, 2005; Huang et al., 2010, 2011; Ionov et al., 2019; Kang et al., 2017; Simon & DePaolo, 2010; Simon et al., 2017). Not shown are the Precambrian carbonate data of Blattler and Higgins (2017) that exhibit an average $\delta^{44}Ca$ that is indistinguishable from BSE calcium isotope composition.

Figure 4. Ba/Th-$^{87}Sr/^{86}Sr$ (a), $^{143}Nd/^{144}Nd$-$^{87}Sr/^{86}Sr$ (b), and $^{206}Pb/^{204}Pb$-$^{87}Sr/^{86}Sr$ (c) diagrams for Central American volcanic arc lavas. All samples from the volcanic front (VF) have geochemical signatures interpreted to be elevated above values for back-arc lavas (BA) by the addition of a sedimentary subducted component, e.g., enriched in $^{87}Sr/^{86}Sr$. Back-arc lavas including YO1 remain within the mantle field, reflecting mixtures of MORB-like depleted mantle and HIMU, enriched mantle (data and illustrative mixing curves from Carr et al., 1990; Feigenson & Carr, 1986; Feigenson et al., 2004; Patino et al. 1997; 2000). Orange and gray squares represent hemipelagic and carbonate DSDP 495 sediment compositions, respectively.

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Table 1. Mass-dependent calcium isotope compositions of igneous rocks and standards.

Sample	Age (Ma)	$\delta^{44}Ca/^{40}Ca$	2σ	$\delta^{43}Ca/^{40}Ca$	2σ	n	Source
BSE							
Peridotite (avg)		0.01	0.04	-0.05	0.07	2	Simon and DePaolo (2010)
Peridotite (avg)		0.00	0.05	-	-	14	Kang et al. (2017)
Komatiite (avg)		-0.02	0.16	-	-	7	Amsellem et al. (2019)
Basalts							
BCR-1	15	-0.08	0.04	-0.05	0.07	2	Simon and DePaolo (2010)
BCR-2	15	-0.09	0.06			1	Simon et al. (2017)
OIB (avg)	1	0.00	0.04	-	-	7	Huang et al. (2010)
Koolau OIB (avg)	1	-0.15	0.06	-	-	6	Huang et al. (2011)
Mahukona OIB (avg)	1	-0.02	0.19	-	-	2	Huang et al. (2011)
Manua Kea OIB (avg)	1	-0.02	0.02	-	-	2	Huang et al. (2011)
BHVO-1 OIB	1	0.01	0.05	-	-	1	Huang et al. (2011)
BHVO-2 OIB	1	-0.05	0.05	-	-	1	Bermingham et al. (2018)
average		*-0.05*	*0.02*				
Arc Lavas							
AT-50		-0.08	0.14	-0.01	0.10	1	
YO1		-0.16	0.14	-0.18	0.11	1	
TE1		-0.12	0.14	-0.15	0.10	1	
SC2		0.06	0.05	0.07	0.05	4	Simon and DePaolo (2010)
average		*-0.07*	*0.05*	*-0.07*	*0.06*		
Carbonatites							
Laacher See 129	0.012900	-0.39	0.14	-0.27	0.25	1	
OL lava 2007	0.000013	-0.13	0.13	-0.06	0.10	2	
OL lava 4-7-08	0.000011	0.05	0.14	0.06	0.10	1	
Standards							
SRM915a		-0.95	0.04	-0.77	0.06	11	Simon and DePaolo (2010) = this study
Seawater (IAPSO)		0.81	0.16	-	-		Simon et al. (2017)
Seawater (GeoB 9506-4)		0.94	0.04	-	-	1	Bermingham et al. (2018)

*All reported where difference between BSE to SRM915a is 0.95 (Antonelli and Simon, 2020), cf. Simon and DePaolo (2010) saw an intrinsic effect in SRM915a, which leads to ~0.1 per mil increase in measured values reported relative to SRM915a (see text).

Table 2. Difference between igneous rocks used to estimate $\delta^{44}Ca/^{40}Ca$ of BSE and SRM915a standard for various laboratories.

Lab Facilities	Method	$\Delta^{44}Ca/^{40}Ca_{BSE\text{-}SRM915a}$	2σ	Source
Center for Isotope Geochemistry, University of California at Berkeley	DS-TIMS	0.97	0.07	Simon & DePaolo (2010); this work
Center for Isotope Cosmochemistry & Geochronology, NASA Johnson Space Center	DS-TIMS	0.96	0.04	Simon et al. (2017)
Isotope Research Geo- and Cosmochemistry Group, Harvard University	DS-TIMS	0.97	0.04	Huang et al. (2011)
State Key Laboratory of Isotope Geochemistry, Guangzhouz Institute of Geochemistry, Chinese Academy of Sciences	DS-TIMS	0.94	0.04	Kang et al. (2017)
Institut für Mineralogie, WWU Münster*	DS-TIMS	0.91	0.03	Bermingham et al. (2018)
IFM-GEOMAR Leibniz-Institut fur Meereswissenschaften, Keil, Germany & University of Saskatchewan Isotope Laboratory, Department of Geological Sciences, University of Saskatchewan, Canada	DS-TIMS	0.93	0.17	Amini et al. (2009)
Institut de Physique du Globe de Paris	MC-ICP-MS	0.90	0.08	Valdes et al. (2014)
Institut de Physique du Globe de Paris	MC-ICP-MS	1.00	0.10	Amsellem et al. (2019; 2020)
Princeton University**	MC-ICP-MS	0.99	0.14	Blattler & Higgins (2017)
Arizona State University**	DS-MC-ICP-MS	0.85	0.16	Ionov et al. (2019)
State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan**	MC-ICP-MS	1.03	0.14	Chen et al. (2018; 2019a,b)

$\Delta^{44}Ca/^{40}Ca_{BSE\text{-}SRM915a} = \delta^{44}Ca/^{40}Ca_{BSE} - \delta^{44}Ca/^{40}Ca_{SRM915a}$

MC-ICP-MS methods obtain $\delta^{44}Ca/^{40}Ca$ by multiplying $\delta^{44}Ca/^{42}Ca$ by a scaling factor. If not stated standard errors are estimated by multiplying those reported by 2.049.

*Value estimated by comparison of reported $\delta^{44}Ca/^{40}Ca$ of BHVO-2 to that of Huang et al. (2011)

**Value estimated by comparison of reported $\delta^{44}Ca/^{40}Ca$ of SRM915b to that of Simon et al. (2017)

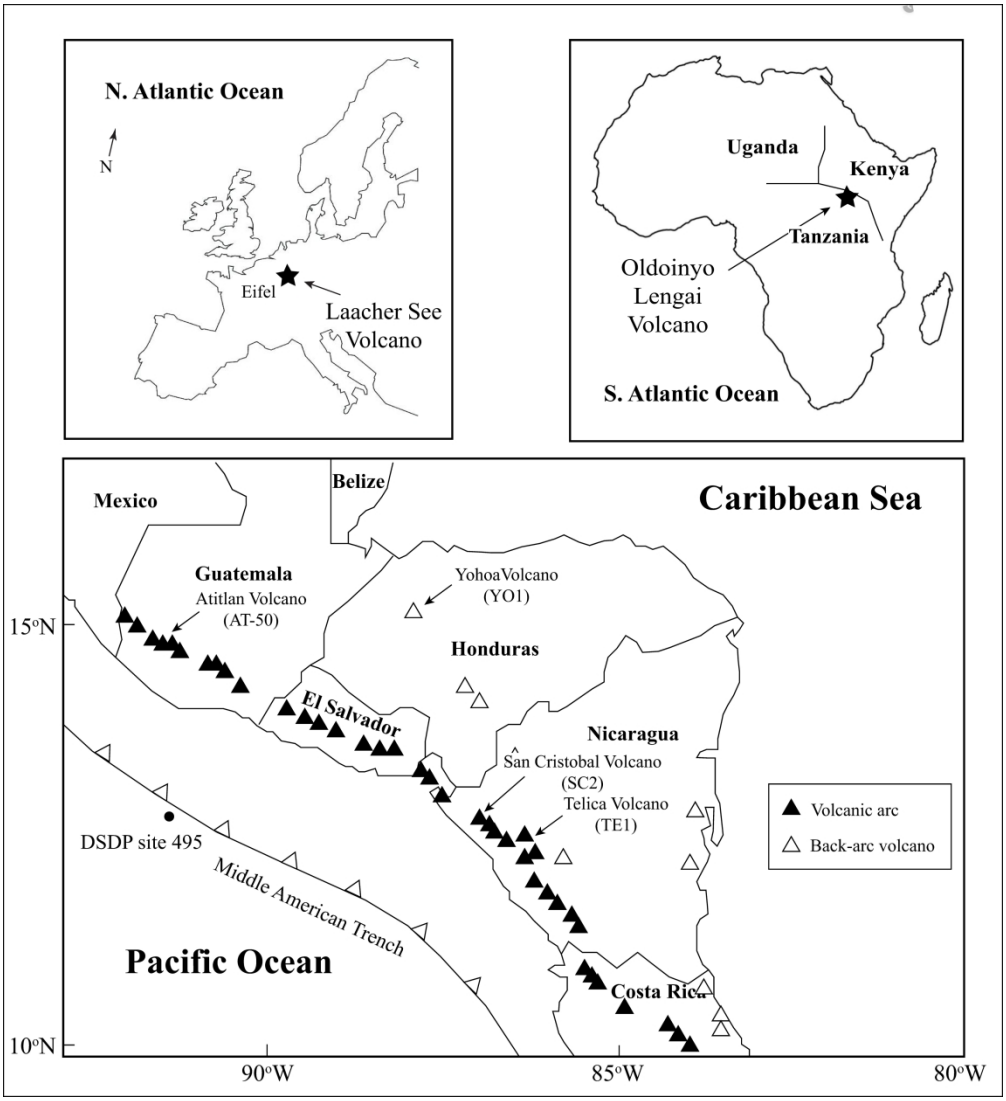


Figure 1. Maps of Central America, Eastern Africa, and Europe showing location of the studied samples. The location of the DSDP Site 495, off the coast of Guatemala, is also indicated (Central American map modified from Patino et al. 2000).

357x390mm (300 x 300 DPI)

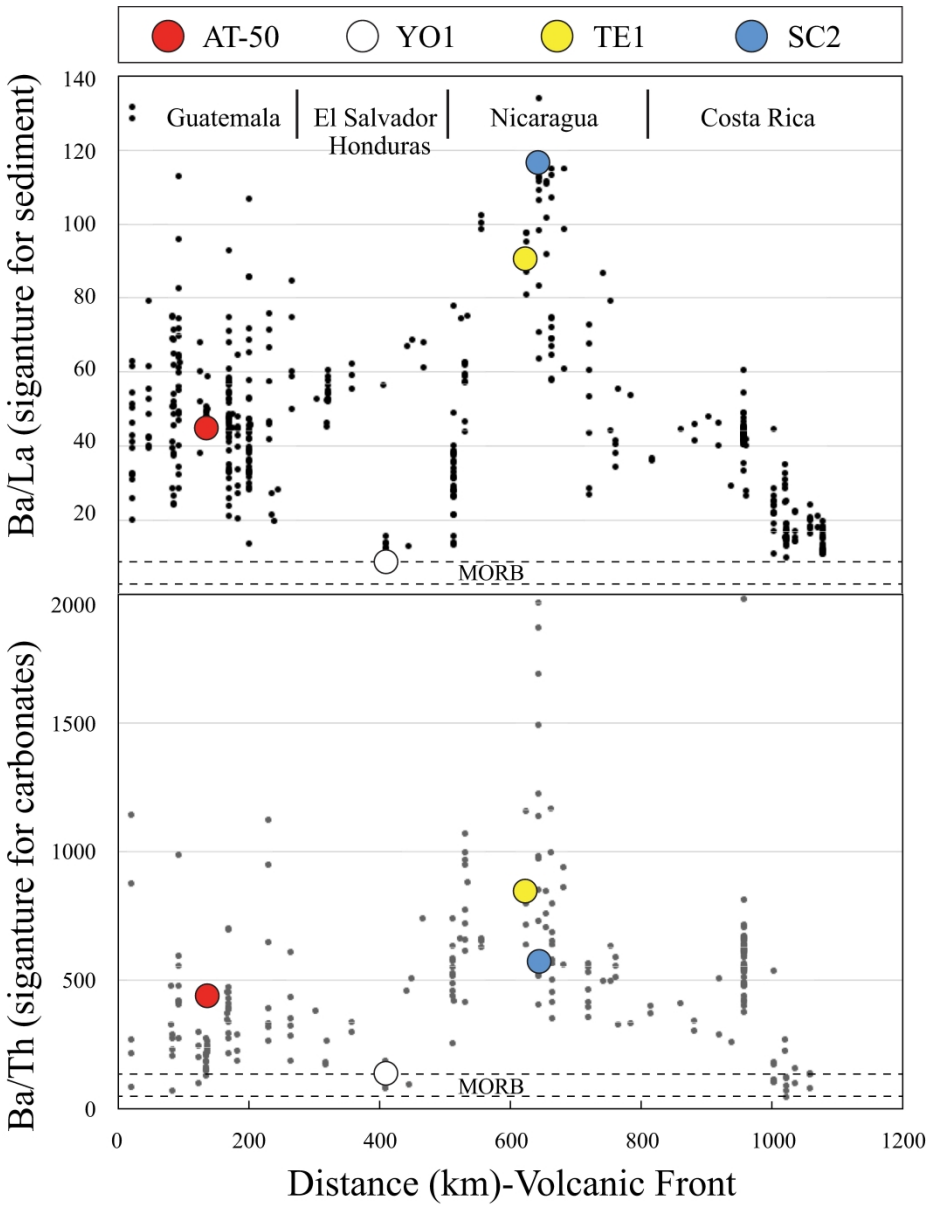


Figure 2. Regional variations in trace element ratios along the Central American volcanic arc. MORB-like Ba/La and Ba/Th values occur in Honduras volcanoes whereas maximum values, believed to be tracers of hemipelagic sediment and marine carbonate, respectfully, occur in western Nicaraguan volcanoes (data from Patino et al., 1997; 2000).

259x336mm (600 x 600 DPI)

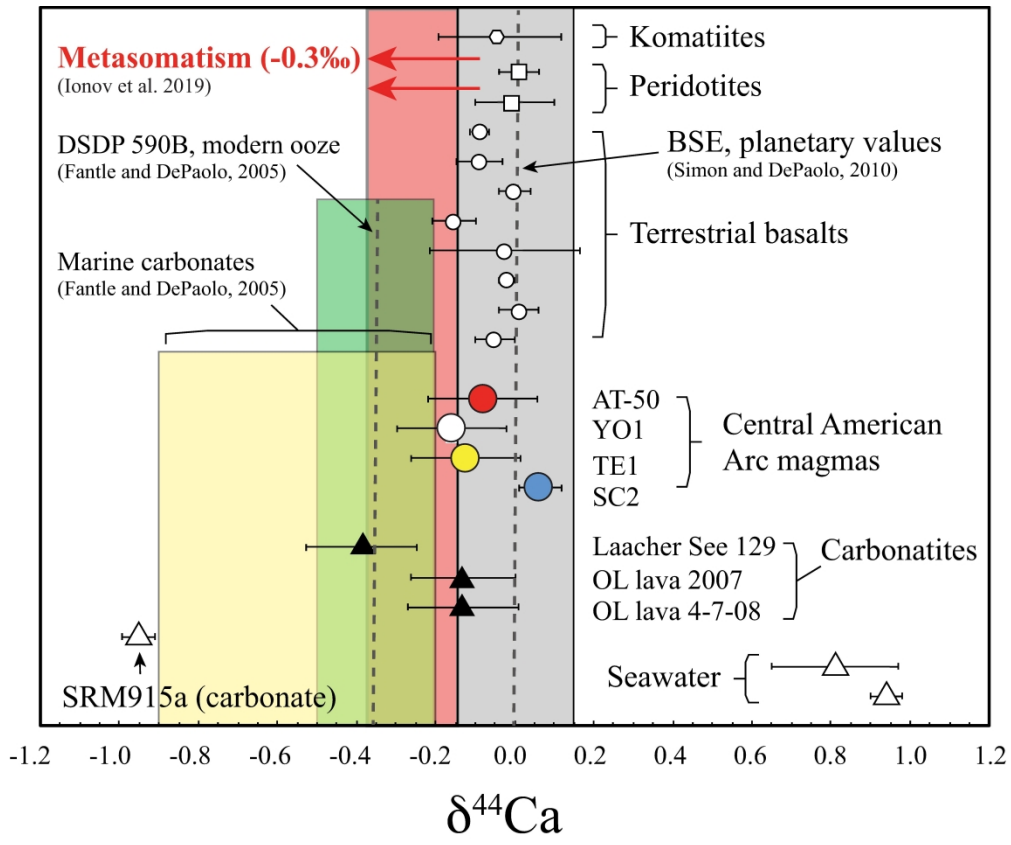
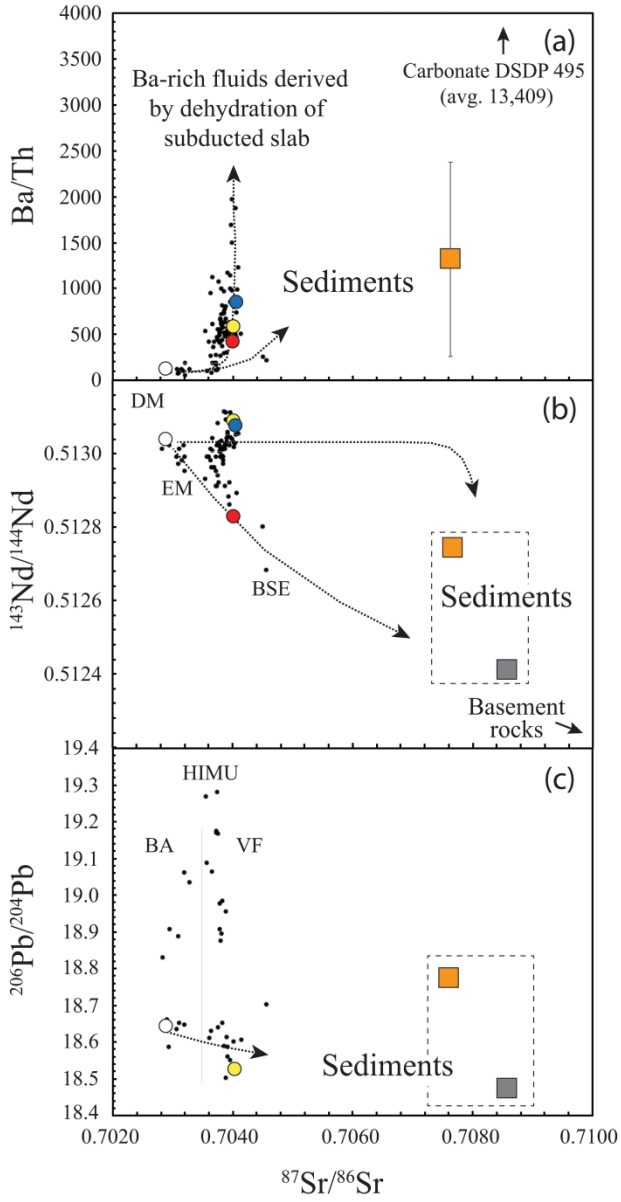


Figure 3. Calcium isotopic composition of Central American volcanic arc magmas (this study), extrusive Oldoinyo Lengai carbonatite lavas (this study), and intrusive Laacher See carbonatite clast (this study). Values for unmelted/unmetamorphosed peridotites, komatiites, terrestrial basalts, seawater, marine carbonates, SRM915a carbonate, and the effect of metasomatism shown for reference (Antonelli et al. 2019a; Amsellem et al., 2019; Bermingham et al., 2018; Fantle & DePaolo, 2005; Huang et al., 2010, 2011; Ionov et al., 2019; Kang et al., 2017; Simon & DePaolo, 2010; Simon et al., 2017). Not shown are the Precambrian carbonate data of Blattler and Higgins (2017) that exhibit an average □44Ca that is indistinguishable from BSE Ca isotope composition.

237x200mm (600 x 600 DPI)



Ba/Th-87Sr/86Sr (a), 143Nd/144Nd-87Sr/86Sr (b), and 206Pb/204Pb-87Sr/86Sr (c) diagrams for Central American volcanic arc lavas. All samples from the volcanic front (VF) have geochemical signatures interpreted to be elevated above values for back-arc lavas (BA) by the addition of a sedimentary subducted component, e.g., enriched in 87Sr/86Sr. Back-arc lavas including YO1 remain within the mantle field, reflecting mixtures of MORB-like depleted mantle and HIMU, enriched mantle (data and illustrative mixing curves from Carr et al., 1990; Feigenson & Carr, 1986; Feigenson et al., 2004; Patino et al. 1997; 2000). Orange and gray squares represent hemipelagic and carbonate DSDP 495 sediment compositions, respectively.

249x478mm (300 x 300 DPI)