Magnesium isotope fractionation during carbonatite magmatism at Oldoinyo Lengai, Tanzania

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Abstract

To investigate the behaviour of Mg isotopes during carbonatite magmatism, we analyzed Mg isotopic compositions of natrocarbonatites and peralkaline silicate rocks from Oldoinyo Lengai, Tanzania. The olivine melilitites from the vicinity of Oldoinyo Lengai have homogeneous and mantle-like Mg isotopic compositions ($\delta^{26}\text{Mg}$ of -0.30 to -0.26‰), indicating limited Mg isotope fractionation during mantle melting. The highly evolved peralkaline silicate rocks not related to silicate–carbonatite liquid immiscibility, including phonolites from the unit Lengai I, combeite–wollastonite nephelinites (CWNs) from the unit Lengai II A and carbonated combeite–wollastonite–melilite nephelinites (carbCWMNs), have $\delta^{26}\text{Mg}$ values (from -0.25 to -0.10‰) clustered around the mantle value. By contrast, the CWNs from the unit Lengai II B, which evolved from the silicate melts that were presumably generated by silicate–carbonatite liquid immiscibility, have heavier Mg isotopes ($\delta^{26}\text{Mg}$ of -0.06 to +0.09‰). Such a difference suggests Mg isotope fractionation during liquid immiscibility and implies, based on mass-balance calculations, that the original carbonatite melts at Lengai were isotopically light. The variable and positive $\delta^{26}\text{Mg}$ values of natrocarbonatites (from +0.13 to +0.37‰) hence require a change of their Mg isotopic compositions subsequent to liquid immiscibility. The negative correlations between $\delta^{26}\text{Mg}$ values and contents of alkali and alkaline earth metals of natrocarbonatites suggest Mg isotope fractionation during fractional crystallization of carbonatite melts, with heavy Mg isotopes

23 enriched in the residual melts relative to fractionated carbonate minerals.
24 Collectively, significant Mg isotope fractionation may occur during both
25 silicate–carbonatite liquid immiscibility and fractional crystallization of carbonatite
26 melts, making Mg isotopes a potentially useful tracer of these processes relevant to
27 carbonatite petrogenesis.

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30 **Keywords:** magnesium isotopes; isotope fractionation; carbonatite magmatism;
31 liquid immiscibility; Oldoinyo Lengai

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1. Introduction

Magmatism is an important process responsible for chemical differentiation of the Earth. Knowledge on the fractionation behaviour of stable isotopes during magmatic processes is the prerequisite for applying them as tracers of source characteristics or magmatic evolution. Magnesium is the most abundant metallic element in the mantle and, hence, the Mg isotope systematics of mafic and ultramafic igneous rocks have received wide attention. Previous studies demonstrated that Mg isotopic compositions of komatiites, mid-ocean ridge basalts and ocean island basalts ($\delta^{26}\text{Mg}$ of -0.42 to -0.15‰, Teng et al., 2007, 2010; Bourdon et al., 2010; Dauphas et al., 2010) were similar to those of mantle peridotites ($\delta^{26}\text{Mg}$ of -0.48 to -0.06‰, Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Teng et al., 2010; Huang et al., 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013; Lai et al., 2015). This indicates limited Mg isotope fractionation during mantle melting and subsequent basaltic magma differentiation and, hence, Mg isotopic compositions of basalts can be used to constrain those of their mantle sources (Teng et al., 2007, 2010; Bourdon et al., 2010).

Carbonatites are another type of mantle-derived igneous rocks. In contrast to the small equilibrium Mg isotope fractionation between olivine, clinopyroxene and orthopyroxene (Handler et al., 2009; Yang et al., 2009; Huang et al., 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013; Lai et al., 2015), large equilibrium Mg isotope fractionation between olivine and magnesite/dolomite at high

55 temperatures has been revealed by both theoretical calculations (Schauble, 2011) and
56 experimental work (Macris et al., 2013). Such a difference implies the possibility of
57 different behaviour of Mg isotopes between carbonatite magmatism and silicate
58 magmatism, as in the case of Fe isotope systematics (Johnson et al., 2010). Therefore,
59 studies on Mg isotopic characteristics of carbonatites may not only improve our
60 understanding of high-temperature Mg isotope fractionation but also exploit new
61 applications. However, to our knowledge, Mg isotopic data of carbonatites have been
62 reported in only two papers. Sun et al. (2012) found that two carbonatite samples
63 from Bayan Obo, China, had Mg isotopic compositions ($\delta^{26}\text{Mg} = -0.34 \pm 0.11\%$ and
64 $-0.14 \pm 0.18\%$) similar to that of the pristine mantle ($\delta^{26}\text{Mg}$ ranging from -0.48 to
65 -0.06% with an estimated average value of $-0.25 \pm 0.07\%$, 2SD, Teng et al., 2007,
66 2010; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Dauphas et al.,
67 2010; Huang et al., 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013; Lai
68 et al., 2015). Hence, they suggested insignificant Mg isotope fractionation during
69 carbonatite petrogenesis. By contrast, Ling et al. (2013) observed large Mg isotopic
70 variations ($\delta^{26}\text{Mg}$ of -2.28 to +0.23‰) in carbonatite samples from the same area.
71 They explained such variations by mixing various proportions of isotopically heavy
72 crustal materials with an isotopically light carbonatite end-member. However, they
73 didn't provide a genetic interpretation of the isotopically light endmember
74 carbonatite, which was originated from the mantle but had Mg isotopic composition
75 ($\delta^{26}\text{Mg} = -2.28\%$) remarkably different from the average $\delta^{26}\text{Mg}$ value of the pristine
76 mantle ($-0.25 \pm 0.07\%$, 2SD, Teng et al., 2010). These diverging interpretations

underline the importance of a Mg isotope study on a set of carbonatite samples that are well characterized in terms of petrology and geochemistry.

In order to investigate the behaviour of Mg isotopes during carbonatite magmatism, we carried out high-precision Mg isotopic analyses for natrocarbonatites and peralkaline silicate rocks from Oldoinyo Lengai, Tanzania. Our results demonstrate that compositionally variable silicate rocks not related to silicate–carbonatite liquid immiscibility have Mg isotopic compositions clustered around the mantle value, whereas silicate rocks petrogenically associated with liquid immiscibility and natrocarbonatites have heavy Mg isotopic compositions. These observations suggest that significant Mg isotope fractionation may occur during both silicate–carbonatite liquid immiscibility and fractional crystallization of carbonatite melts. Consequently, Mg isotopic compositions of carbonatites may potentially be used to trace processes (i.e., liquid immiscibility and fractional crystallization) relevant to carbonatite petrogenesis.

2. Geological settings and samples

Oldoinyo Lengai is the only active carbonatite volcano on Earth. It lies in the East African Rift Valley in northern Tanzania with volcanological observations more than 100 years (Keller et al., 2010). This volcano consists predominantly (>95 vol.%) of phonolite and nephelinite lavas and pyroclastics, with natrocarbonatite ashes and lavas in the summit area. Klaudius and Keller (2006) defined three major structural

units of Oldoinyo Lengai, namely *Lengai I* (phonolite tuffs and lavas), *Lengai II A* (nephelinite tuffs and lavas) and *Lengai II B* (nephelinite tuffs and lavas as well as natrocarbonatite tuffs and lavas). In addition, ashes, lapilli and scoriae with the unique composition of carbonated combeite–wollastonite–melilite nephelinites (carbCWMNs) were erupted during the 2007–2008 explosive activity (Keller et al., 2010). Although olivine melilitites with high Mg# [molar $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) \times 100$] >50 occur in some monogenetic cones in the vicinity of Oldoinyo Lengai (Dawson et al., 1985; Keller et al., 2006; Mattsson, 2012; Mattsson et al., 2013), rocks of primary magma compositions are absent within the Lengai volcanic edifice itself. Silicate rocks and natrocarbonatites at Oldoinyo Lengai are all peralkaline [molar $(\text{Na} + \text{K})/\text{Al} > 1$, Simonetti et al., 1997; Dawson, 1998; Klaudius and Keller, 2006] and are distinctly of mantle origin as indicated by both Sr–Nd–Pb isotopes (Bell and Simonetti, 1996; Bell and Tilton, 2001) and C–O–Li isotopes (Keller and Hoefs, 1995; Halama et al., 2007). Many previous studies have discussed the petrogenetic relationships between olivine melilitites, phonolites, nephelinites and natrocarbonatites at Oldoinyo Lengai, through investigations of natural samples and/or phase equilibrium experiments. A brief summary is given here (Fig. 1).

Olivine melilitites in the vicinity of Oldoinyo Lengai were formed by small degrees (1–2%) of partial melting of the mantle and were considered to represent the possible primary melts of the Lengai volcano (Peterson and Kjarsgaard, 1995; Keller et al., 2006; Wiedenmann et al., 2010). However, there is a large compositional gap between olivine melilitites ($\text{MgO} > 9$ wt% and $\text{Mg\#} > 50$, Keller et al., 2006;

Mattsson et al., 2013) and the highly evolved phonolites and nephelinites of the units Lengai I and Lengai II ($\text{MgO} < 2 \text{ wt\%}$ and $\text{Mg\#} < 31$, Klaudius and Keller, 2006). Moreover, melilitites and nephelinites/phonolites display different Sr–Nd–Pb isotopic signatures (Keller et al., 2006) and opposite variation trends of some major and trace elements (Mattsson et al., 2013). Therefore, olivine melilitites cannot be related directly to nephelinites/phonolites (Mattsson et al., 2013), and parental magmas of the highly evolved nephelinites/phonolites at Lengai remain unknown.

A widely accepted model for natrocarbonatite petrogenesis at Oldoinyo Lengai is immiscible separation of carbonatite melts from CO_2 -saturated and strongly peralkaline nephelinitic melts (e.g., Peterson, 1990; Church and Jones, 1995; Keller and Spettel, 1995; Kjarsgaard et al., 1995; Dawson, 1998), though other models have been proposed, such as partial melting of fenitized basement (Morogan and Martin, 1985), differentiation from mildly alkalic olivine sövitic magmas (Twyman and Gittins, 1987) and condensation from cognate alkaline fluids (Nielsen and Veksler, 2002). Liquid immiscibility between silicate and carbonatite melts has been directly demonstrated by coexisting silicate and carbonate melt inclusions in nepheline phenocrysts from erupted ashes and in minerals of ijolite xenoliths at Oldoinyo Lengai (Mitchell, 2009; Sekisova et al., 2015). Stratigraphic relationships and Sr–Nd–Pb isotopic data suggest that the combeite- and wollastonite-bearing nephelinites (CWNs) from the unit Lengai II B are petrogenetically related to natrocarbonatites and may represent differentiation products of the conjugate silicate melts from which the original carbonatite melts exsolved (Kjarsgaard et al., 1995;

Bell and Simonetti, 1996; Dawson, 1998; Klaudius and Keller, 2006). By contrast, phonolites from the unit Lengai I, CWNs from the unit Lengai II A and carbCWMNs of the 2007–2008 activity are assumed to represent silicate melts that did not experience liquid immiscibility (Klaudius and Keller, 2006; Keller et al., 2010). Once immiscibility occurred, the original carbonatite melts efficiently segregated from the conjugate silicate melts due to their low viscosity and density. Subsequent carbonatite magma differentiation at Oldoinyo Lengai was dominated by fractional crystallization of nyerereite ($\text{Na}_2\text{Ca}[\text{CO}_3]_2$) and gregoryite ($[\text{Na}, \text{Ca}_x, \text{K}]_{2-x}\text{CO}_3$), generating natrocarbonatites (Peterson, 1990; Kjarsgaard et al., 1995; Gittins and Jago, 1998; Mattsson and Caricchi, 2009).

In this study, Mg isotopes were measured for twenty-two samples, including four olivine melilitites from the vicinity of the Lengai volcano, five phonolites from the unit Lengai I, two CWNs from the unit Lengai II A, three CWNs from the unit Lengai II B, three carbCWMNs of the 2007–2008 activity and five natrocarbonatites. These samples are the same as those studied in previous work (Simonetti et al., 1997; Keller et al., 2006, 2010; Klaudius and Keller, 2006; Halama et al., 2007). Detailed sample descriptions as well as petrological and geochemical aspects of these samples are available therein. As demonstrated in these papers, there is little petrographic evidence for alteration in the investigated samples, except for a few altered combeites in sample OL 804 (Klaudius and Keller, 2006). Both silicate rocks and natrocarbonatites retain their primary igneous mineralogy and do not contain clay minerals. In particular, natrocarbonatites are strongly susceptible to alteration at the

Earth's surface (e.g., Zaitsev and Keller, 2006). However, the natrocarbonatite samples studied here were collected directly after eruption and their C–O–Li isotopic compositions fall into a restricted field within the “primary igneous carbonatites” (Keller and Hoefs, 1995; Halama et al., 2007). Collectively, the effects of alternation on Mg isotopic compositions of the samples investigated here can be excluded.

3. Analytical methods

Magnesium isotopic analyses were performed at the Isotope Laboratory of the University of Arkansas, Fayetteville, following previously established procedures (Teng et al., 2007, 2010, 2015; Yang et al., 2009; Li et al., 2010; Ling et al., 2013; Teng and Yang, 2014). A brief description is given here.

Whole-rock powders were dissolved in screw-top beakers in a combination of concentrated HF–HNO₃–HCl. Separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50W–X8 resin in 1 mol·L⁻¹ HNO₃ media. The Mg column chemistry was performed twice for silicate rocks and four or five times for natrocarbonatites in order to obtain a pure Mg solution for mass spectrometry. The Mg yields through column chemistry, based on analyses of Mg content in the elution collected before and after the Mg cut, were >99.8%. To ensure the efficiency of removing Ca for natrocarbonatites with high CaO/MgO ratios (from 25 to 38, wt/wt), we carried out repeat analyses for natrocarbonatites by using an additional Ca column chemistry with Bio-Rad 200–400 mesh AG50W–X12 resin in

12 mol·L⁻¹ HCl media (Ling et al., 2013) after two or three iterations of Mg column chemistry. The residual content of Ca in the solution after column chemistry was below the detection limit for Ca (~ 10ppb) by inductively coupled plasma mass spectrometry (ICP–MS). Magnesium isotopic compositions were analyzed by the standard-sample bracketing method using a Nu Plasma multi-collector inductively coupled plasma mass spectrometry (MC–ICP–MS).

The results are reported in δ -notation in per mil relative to DSM3: $\delta^X\text{Mg} = [({}^X\text{Mg}/{}^{24}\text{Mg})_{\text{sample}}/({}^X\text{Mg}/{}^{24}\text{Mg})_{\text{DSM3}} - 1] \times 1000$, where X refers to mass 25 or 26. Based on replicate analyses of a seawater sample from Hawaii and an in-house reference solution KH–olivine, the long-term external precision on $\delta^{26}\text{Mg}$ value is $\leq 0.10\text{‰}$ (2SD, Li et al., 2010; Teng et al., 2010, 2015). Both synthetic solutions and reference materials were processed through column chemistry with samples for accuracy check. Multiple analyses of synthetic solutions IL–Mg–1 (concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1) and Carb (concentration ratios of Ca:Mg = 100:1) yielded $\delta^{26}\text{Mg}$ values of -0.05 to -0.01‰ (Table 1), in agreement with the expected true value of 0.00. Magnesium isotopic compositions of seawater, the Allende chondrite and the in-house reference solution KH–olivine analyzed during the course of this study also agree with previously published values (Table 1). These data, combined with the indistinguishable results for repeat analyses of individual samples (Tables 2 and 3), especially of natrocarbonatites that were processed through different column procedures (Fig. 2), assure the accuracy of our data.

4. Results

Magnesium isotopic compositions are reported in Table 1 for synthetic solutions and reference materials, Table 2 for peralkaline silicate rocks, and Table 3 for natrocarbonatites from Oldoinyo Lengai. For reference, some elemental and isotopic data reported in previous studies (Simonetti et al., 1997; Keller et al., 2006, 2010; Klaudius and Keller, 2006; Halama et al., 2007) are also included in Tables 2 and 3. All samples analyzed in this study fall on an isotopic mass-dependent fractionation line with a slope of 0.518 on the Mg three-isotope diagram (Fig. 3). Hence, we only use $\delta^{26}\text{Mg}$ in the subsequent discussions.

Olivine melilitites from the vicinity of Oldoinyo Lengai have homogeneous Mg isotopic compositions ($\delta^{26}\text{Mg} = -0.30$ to -0.26‰ , Table 2). The $\delta^{26}\text{Mg}$ values vary from -0.25 to -0.10‰ in phonolites from the unit Lengai I, from -0.14 to -0.13‰ in CWNs from the unit Lengai II A, and from -0.17 to -0.15‰ in carbCWMNs of the 2007–2008 activity, respectively. The overall variation for these rocks from the Lengai volcano is small and all data cluster around the average $\delta^{26}\text{Mg}$ value of the pristine mantle (Fig. 4). By contrast, the $\delta^{26}\text{Mg}$ values of CWNs from the unit Lengai II B (from -0.06 to $+0.09\text{‰}$) and of natrocarbonatites (from $+0.13$ to $+0.37\text{‰}$) are higher than the pristine mantle value (Fig. 4).

5. Discussion

In this section, we evaluate the behaviour of Mg isotopes during (1) peralkaline

silicate magma differentiation, (2) silicate–carbonatite liquid immiscibility, and (3) carbonatite magma differentiation, respectively.

5.1. Small Mg isotope fractionation during peralkaline silicate magma differentiation

Olivine melilitites in the vicinity of Oldoinyo Lengai were formed by small degrees (1–2%) of partial melting of the mantle (Mattsson et al., 2013). They have variable MgO content and Mg# (from 15 to 10 wt% and 70 to 59, respectively, Table 2) due to the early stages of fractional crystallization of olivine (Keller et al., 2006). However, they have homogeneous and mantle-like Mg isotopic compositions ($\delta^{26}\text{Mg} = -0.30$ to -0.26‰ , Table 2), indicating insignificant Mg isotope fractionation during mantle melting and olivine crystallization. This is consistent with previous suggestions that Mg isotope fractionation during mantle melting and subsequent basaltic magma differentiation is limited (Teng et al., 2007, 2010; Bourdon et al., 2010).

Phonolites from the unit Lengai I, CWNs from the unit Lengai II A and carbCWMNs of the 2007–2008 activity are considered to represent peralkaline silicate melts that did not experience liquid immiscibility (Klaudius and Keller, 2006; Keller et al., 2010). Despite of their variable MgO content (from 2.0 to 0.8 wt%), these rocks display a relatively narrow range in $\delta^{26}\text{Mg}$ (from -0.25 to -0.10‰), barely beyond the average mantle value (Fig. 4). This observation suggests that Mg

isotope fractionation during differentiation of highly evolved peralkaline silicate magma, if any, is small. Hence, the silicate melts before liquid immiscibility at Oldoinyo Lengai probably had Mg isotopic compositions similar to the average mantle value.

5.2. Significant Mg isotope fractionation during silicate–carbonatite liquid immiscibility

Combeite–wollastonite nephelinites from the unit Lengai II B are currently believed to result from differentiation of the silicate melts generated by silicate–carbonatite liquid immiscibility (Kjarsgaard et al., 1995; Klaudius and Keller, 2006). Although the detailed differentiation processes from the conjugate silicate melts at the time of immiscibility to CWNs from the unit Lengai II B remain unknown, they would not affect Mg isotopic composition of the silicate melts since Mg isotope fractionation during highly evolved peralkaline silicate magma differentiation is small. Hence, the $\delta^{26}\text{Mg}$ values of CWNs from the unit Lengai II B (from -0.06 to +0.09‰) are likely to record those of the silicate melts after liquid immiscibility. The difference in Mg isotopic compositions between the silicate melts before and after immiscibility suggests Mg isotope fractionation during liquid immiscibility.

Magnesium isotopic mass balance during silicate–carbonatite liquid immiscibility follows:

275
$$\delta^{26}\text{Mg}_0 = \delta^{26}\text{Mg}_s \times f_{\text{Mg},s} + \delta^{26}\text{Mg}_c \times f_{\text{Mg},c},$$

276 where $\delta^{26}\text{Mg}_0$, $\delta^{26}\text{Mg}_s$ and $\delta^{26}\text{Mg}_c$ are the Mg isotopic composition of silicate melt
 277 before immiscibility and of silicate melt and carbonatite melt after immiscibility,
 278 respectively. The $f_{\text{Mg},s}$ and $f_{\text{Mg},c}$ refer to the fraction of Mg contained in the conjugate
 279 silicate and carbonatite melts ($f_{\text{Mg},s} + f_{\text{Mg},c} = 1$). The heavy Mg isotopic compositions
 280 of CWNs from the unit Lengai II B indicates $\delta^{26}\text{Mg}_s > \delta^{26}\text{Mg}_0$, which in turn implies
 281 $\delta^{26}\text{Mg}_c < \delta^{26}\text{Mg}_0$, i.e., the original carbonatite melts at Lengai were isotopically light
 282 (Fig. 4).

283 The inferred preferential partition of heavy Mg isotopes into silicate melts
 284 relative to carbonatite melts during liquid immiscibility is consistent with the
 285 direction predicted by theoretical and experimental work on equilibrium
 286 inter-mineral Mg isotope fractionation between silicate and carbonate minerals. For
 287 example, theoretical calculations yielded $10^3\ln\alpha_{\text{forsterite-magnesite}}$ of +0.21‰ and
 288 $10^3\ln\alpha_{\text{forsterite-dolomite}}$ of +0.15‰ at 1000 °C (Schauble, 2011), while experimental
 289 measurements yielded $10^3\ln\alpha_{\text{forsterite-magnesite}}$ of $+0.44 \pm 0.10$ ‰ at 600 °C (Macris et
 290 al., 2013). In general, phases with the stronger bonding environment of the cation of
 291 interest favor heavier isotopes when thermodynamic equilibrium is achieved (e.g.,
 292 Bigeleisen, 1965). Hence, the positive $10^3\ln\alpha_{\text{forsterite-magnesite/dolomite}}$ values reflect
 293 stronger Mg–O bonds in forsterite versus weaker bonds in magnesite/dolomite. Such
 294 a difference may also exist between silicate melts and carbonatite melts since they
 295 also use the $[\text{SiO}_4]^{4-}$ tetrahedra and the $[\text{CO}_3]^{2-}$ group, respectively, as their basic
 296 structure units (e.g., Henderson et al., 2006; Vuilleumier et al., 2014). If this is true,

silicate melts are expected to be enriched in heavy Mg isotopes relative to carbonatite melts, though silicate melts and carbonatite melts respectively have homogeneous Mg isotopic compositions due to fast diffusion of isotopes in melts. Such a speculative mechanism of isotope fractionation can be understood on analogy with element partition between immiscible silicate and carbonatite melts, where the concentration of certain elements will be homogeneous among each melt but be different between these two melts due to the different melt structures (e.g., Jones et al., 1995; Martin et al., 2013).

5.3. Significant Mg isotope fractionation during carbonatite magma differentiation

Magnesium isotope fractionation during silicate–carbonatite liquid immiscibility predicts isotopically light original carbonatite melts at Oldoinyo Lengai. However, natrocarbonatite samples have positive $\delta^{26}\text{Mg}$ values (Fig. 4), which requires a change of Mg isotopes of carbonatite melts subsequent to liquid immiscibility. Below, we explore the possible processes responsible for such a change.

One possible process is surface alteration, which can potentially fractionate Mg isotopes. The direction of Mg isotope fractionation during carbonate weathering has been investigated in previous studies on groundwater controlled by dedolomitization reactions and runoff waters draining carbonate bedrocks, which suggested little fractionation between dolomite and water (Jacobson et al., 2010) or the retention of

light Mg isotopes in carbonates (Tipper et al., 2006, 2008; Brenot et al., 2008). Hence, the heavy Mg isotopic compositions of natrocarbonatites cannot be attributed to alteration of samples.

Another process that can also be ruled out is crustal contamination. Due to their low viscosity, carbonatite melts ascend very rapidly and, thus, crustal assimilation during carbonatite volcanism is generally limited. Moreover, assimilation of siliceous sedimentary rocks with heavy Mg isotopes ($\delta^{26}\text{Mg}$ up to +0.92‰, Li et al., 2010) may increase the $\delta^{26}\text{Mg}$ values of carbonatite melts. However, such a process conflicts with the very low SiO_2 content (<0.5 wt%, Table 3) and mantle-like radiogenic and stable isotope characteristics (Keller and Hoefs, 1995; Bell and Tilton, 2001; Halama et al., 2007) of natrocarbonatites.

Diffusion-driven Mg isotope fractionation between ascending carbonate melts and wall rocks is also unlikely to produce the variable and heavy Mg isotopic compositions of natrocarbonatites at Lengai. First, diffusion of isotopes in melts is much faster than that in solids. Therefore, Mg isotopic heterogeneity in melts caused by diffusion will be eliminated quickly, producing isotopically homogeneous carbonatites. Second, light isotopes diffuse faster than heavy ones (e.g., Richter et al., 2008) and, hence, possible diffusion of Mg from wall rocks into the low-Mg natrocarbonatite melts (natrocarbonatites have MgO contents <0.5 wt%, Fig. 4) during magma ascent will result in light Mg isotopes in natrocarbonatites. This is opposite to the positive $\delta^{26}\text{Mg}$ values of natrocarbonatites (Fig. 4).

Carbonatite magma differentiation is another process that may be responsible for

the variable and positive $\delta^{26}\text{Mg}$ values of natrocarbonatites. Fractional crystallization of nyerereite ($\text{Na}_2\text{Ca}[\text{CO}_3]_2$) and gregoryite ($[\text{Na},\text{Ca}_x,\text{K}]_{2-x}\text{CO}_3$) occurred during the carbonatite magma differentiation at Oldoinyo Lengai (Peterson, 1990; Gittins and Jago, 1998; Mattsson and Caricchi, 2009). Both of these two minerals are enriched in alkali and alkaline earth metals. The trends of increasing $\delta^{26}\text{Mg}$ values with decreasing $\text{CaO}+\text{SrO}+\text{BaO}$ and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ contents in natrocarbonatites (Fig. 5) suggest that light Mg isotopes preferentially entered into fractionated nyerereite and gregoryite. Therefore, fractional crystallization of nyerereite and gregoryite may account for the observed Mg isotopic variations ($\delta^{26}\text{Mg}$ of +0.13 to +0.37‰) in natrocarbonatites. The potential processes that drove Mg isotopic shift from the negative $\delta^{26}\text{Mg}$ values ($\leq -0.25\text{‰}$) of the inferred original carbonatite melts to the positive $\delta^{26}\text{Mg}$ values ($\geq +0.13\text{‰}$) of natrocarbonatites (Fig. 4) remain to be defined.

6. Conclusions

This study presents Mg isotopic data for the well-characterized natrocarbonatites and peralkaline silicate rocks from Oldoinyo Lengai, Tanzania. The silicate rocks not related to silicate–carbonatite liquid immiscibility, comprising phonolites from the unit Lengai I, combeite–wollastonite nephelinites from the unit Lengai II A and carbonated combeite–wollastonite–melilite nephelinites of the 2007–2008 activity, have $\delta^{26}\text{Mg}$ values (from -0.25 to -0.10‰) clustered around the mantle value. By contrast, combeite–wollastonite nephelinites from the unit Lengai II B, which

evolved from the silicate melts that were presumably generated by liquid immiscibility, have high $\delta^{26}\text{Mg}$ values of -0.06 to +0.09‰. Such a difference suggests significant Mg isotope fractionation during liquid immiscibility and implies isotopically light original carbonatite melts at Lengai. However, natrocarbonatites have positive $\delta^{26}\text{Mg}$ values from +0.13 to +0.37‰. The negative correlations between $\delta^{26}\text{Mg}$ values and $\text{CaO}+\text{SrO}+\text{BaO}$ and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ contents suggest significant Mg isotope fractionation due to fractional crystallization of nyerereite and grogoryite, with heavy Mg isotopes enriched in the residual melts relative to fractionated carbonate minerals.

The different behaviour of Mg isotopes between silicate magmatism and carbonatite magmatism promises different applications. Previous studies indicate limited Mg isotope fractionation during silicate magma differentiation and, hence, Mg isotopic compositions of basalts and granites can be used to constrain those of their mantle or crustal sources (Teng et al., 2007, 2010; Shen et al., 2009; Bourdon et al., 2010; Li et al., 2010). This study suggests, for the first time, that significant Mg isotope fractionation may occur during both silicate–carbonatite liquid immiscibility and fractional crystallization of carbonatite magmas. Consequently, Mg isotopic compositions of carbonatites may potentially be used to trace processes (i.e., liquid immiscibility and fractional crystallization) relevant to carbonatite petrogenesis. Nevertheless, Mg isotopic data of carbonatites are still very limited. In order to further investigate the magnitude and mechanism of Mg isotope fractionation during carbonatite magmatism and its applications, more comprehensive studies on

carbonatite samples from different localities and of different genesis and evolution
are needed.

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579

Table 1

Magnesium isotopic compositions of synthetic solutions and reference materials.

Standard	$\delta^{26}\text{Mg}$ (‰)	2SD ^a	$\delta^{25}\text{Mg}$ (‰)	2SD
IL-Mg-1 ^b	-0.04	0.07	-0.04	0.04
Replicate ^c	-0.04	0.07	-0.03	0.03
Replicate	-0.01	0.07	0.00	0.05
Replicate	-0.03	0.10	-0.02	0.05
The expected value	0.00	0.07	0.00	0.05
Carb ^d	-0.03	0.04	-0.01	0.04
Replicate	-0.05	0.08	+0.01	0.04
Replicate	-0.03	0.08	-0.04	0.05
Replicate	-0.02	0.08	-0.04	0.05
The expected value	0.00	0.07	0.00	0.05
Seawater	-0.84	0.07	-0.42	0.04
Replicate	-0.86	0.08	-0.42	0.05
Foster et al. (2010)	-0.82	0.05	-0.43	0.05
Ling et al. (2011)	-0.83	0.09	-0.43	0.06
Allende chondrite	-0.34	0.06	-0.19	0.04
Replicate	-0.27	0.12	-0.16	0.06
Schiller et al. (2010)	-0.35	0.13	-0.19	0.07
Pogge von Strandmann et al. (2011)	-0.36	0.06	-0.19	0.05
Wang et al. (2011)	-0.30	0.17	-0.17	0.07
Bouvier et al. (2013)	-0.29	0.05	-0.16	0.03
KH-olivine ^e	-0.33	0.06	-0.18	0.05
Replicate	-0.32	0.07	-0.18	0.05
Replicate	-0.30	0.08	-0.13	0.04
Yang et al. (2009)	-0.32	0.10	-0.19	0.05
Li et al. (2010)	-0.31	0.06	-0.16	0.05
Teng et al. (2015)	-0.27	0.07	-0.14	0.05

^a 2SD = two times the standard deviation of the population of n (n > 20) repeat measurements of the standards during an analytical session.

^b IL-Mg-1 is a synthetic solution with concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1.

^c Replicate = repeat column chemistry and measurements of different aliquots of a stock solution.

^d Carb is a synthetic solution with concentration ratios of Ca:Mg = 100:1.

^e KH-olivine is an in-house reference solution made from the Kilbourne Hole olivine.

Table 2

Magnesium isotopic compositions and selected geochemical parameters of peralkaline silicate rocks from Oldoinyo Lengai.

Sample ID	$\delta^{26}\text{Mg}$ (‰)	2SD ^a	$\delta^{25}\text{Mg}$ (‰)	2SD	SiO ₂ (wt%) ^b	MgO (wt%) ^b	Mg# ^b
Olivine melilitites from the vicinity of Oldoinyo Lengai							
OL198	-0.30	0.08	-0.15	0.05	36.48	13.78	68.7
OL343	-0.26	0.08	-0.12	0.05	36.35	15.04	69.8
OL352	-0.26	0.08	-0.14	0.05	36.38	14.92	70.3
OL12/2K	-0.27	0.08	-0.15	0.05	34.07	9.80	58.7
Phonolites from the unit Lengai I							
OL440	-0.10	0.07	-0.05	0.06	47.94	0.81	20.5
OL442	-0.11	0.07	-0.05	0.08	51.07	0.85	25.2
OL450	-0.08	0.11	-0.03	0.06	52.91	0.74	22.3
Repeat ^c	-0.15	0.07	-0.07	0.06			
OL503	-0.13	0.11	-0.05	0.06	49.34	1.28	27.6
Repeat	-0.17	0.07	-0.06	0.06			
OL822	-0.26	0.08	-0.15	0.05	50.01	0.83	23.6
Repeat	-0.23	0.09	-0.12	0.05			
Combeite–wollastonite nephelinites (CWNs) from the unit Lengai II A							
OL247	-0.17	0.10	-0.10	0.07	41.79	1.95	30.7
Repeat	-0.10	0.07	-0.04	0.06			
OL803	-0.15	0.09	-0.07	0.07	46.32	1.18	24.6
Repeat	-0.10	0.10	-0.05	0.07			
Combeite–wollastonite nephelinites (CWNs) from the unit Lengai II B							
OL624	-0.04	0.09	-0.03	0.07	43.40	1.28	20.6
Repeat	-0.08	0.06	-0.05	0.06			
OL788	+0.11	0.09	+0.08	0.07	44.58	0.93	17.6
Repeat	+0.03	0.11	+0.03	0.06			
OL804	+0.08	0.08	+0.02	0.05	45.51	0.64	12.1
Repeat	+0.10	0.08	+0.03	0.05			
Carbonated combeite–wollastonite–melilite nephelinites (carbCWMNs) of the 2007–2008 activity							
OL835-1	-0.17	0.07	-0.09	0.06	28.54	1.35	30.3
OL836	-0.17	0.09	-0.09	0.07	29.57	1.87	36.5
Repeat	-0.16	0.10	-0.10	0.07			
OL837	-0.15	0.09	-0.07	0.07	25.99	1.63	37.0

^a 2SD = two times the standard deviation of the population of n (n > 20) repeat measurements of the standards during an analytical session.

^b Data are from Keller et al. (2006, 2010) and Klaudius and Keller (2006); Mg# = molar Mg/(Mg + Fe²⁺) × 100.

^c Repeat = repeat dissolution and column chemistry of individual samples.

598 **Table 3**

599 Magnesium isotopic compositions and selected geochemical parameters of natrocarbonatites from Oldoinyo Lengai.

Sample ID	Column procedures ^a	$\delta^{26}\text{Mg}$ (‰)	2SD ^b	$\delta^{25}\text{Mg}$ (‰)	2SD	SiO ₂ (wt%) ^c	MgO (wt%) ^c	Na ₂ O (wt%) ^c	K ₂ O (wt%) ^c	CaO (wt%) ^c	SrO (wt%) ^c	BaO (wt%) ^c	$\delta^{18}\text{O}$ (‰) ^d	$\delta^{13}\text{C}$ (‰) ^d	$\delta^7\text{Li}$ (‰) ^d
OL2	Mg×4	+0.29	0.07	+0.14	0.05	0.21	0.42	30.41	6.66	12.08	1.13	1.50	+9.2	-6.9	+3.6
Replicate ^e	Mg×5	+0.32	0.07	+0.21	0.08										
Repeat ^f	Mg×2+Ca	+0.35	0.10	+0.23	0.08										
Replicate	Mg×3+Ca	+0.29	0.08	+0.10	0.05										
OL7	Mg×4	+0.36	0.07	+0.20	0.05	0.10	0.47	30.85	6.67	11.71	1.10	1.60	+9.3	-7.0	+3.3
Replicate	Mg×5	+0.38	0.07	+0.23	0.08										
Repeat	Mg×2+Ca	+0.37	0.10	+0.19	0.07										
OL123	Mg×4	+0.12	0.06	+0.07	0.05	0.44	0.42	31.92	7.46	15.97	1.41	1.26	+8.6	-7.0	+4.8
Repeat	Mg×2+Ca	+0.23	0.07	+0.10	0.08										
Replicate	Mg×3+Ca	+0.22	0.10	+0.05	0.07										
OL148	Mg×4	+0.18	0.07	+0.10	0.05		0.44	32.57	8.45	14.53	1.35	1.68	+7.4	-7.0	+4.6
Repeat	Mg×2+Ca	+0.11	0.07	+0.10	0.08										
Replicate	Mg×3+Ca	+0.20	0.10	+0.06	0.07										
OL259	Mg×4	+0.12	0.07	+0.10	0.05	0.23	0.43	32.74	8.30	15.11	1.46	1.54	+7.4	-6.9	+5.0
Replicate	Mg×5	+0.15	0.08	+0.04	0.05										
Repeat	Mg×2+Ca	+0.12	0.10	+0.04	0.08										

600 ^a Mg = Mg column chemistry; Ca = Ca column chemistry; the numbers 2, 3, 4 and 5 indicate the repeat times of Mg column chemistry.601 ^b 2SD = two times the standard deviation of the population of n (n >20) repeat measurements of the standards during an analytical session.602 ^c Data are from Simonetti et al. (1997).603 ^d Data are from Halama et al. (2007).604 ^e Replicate = repeat column chemistry and measurement of different aliquots of a stock solution.605 ^f Repeat = repeat dissolution and column chemistry of individual samples.

Figure captions

Fig. 1. Flow chart illustrating the petrogenesis of peralkaline silicate rocks and natrocarbonatites at Oldoinyo Lengai. The magmatic evolution at Lengai includes three main processes: (1) peralkaline silicate magma differentiation, (2) silicate–carbonatite liquid immiscibility, and (3) carbonatite magma differentiation. The parental melts of the Lengai volcano and how the phonolitic and nephelinitic melts evolved from the parental melts are unknown and labeled with question marks. See text for details and related references.

Fig. 2. $\delta^{26}\text{Mg}$ (‰) vs. CaO/MgO (wt/wt) for natrocarbonatites processed through different column procedures (see text for details). The error bar indicates the maximum external precision of $\pm 0.10\text{‰}$ (2SD) on $\delta^{26}\text{Mg}$ during analytical sessions of this study. Data are reported in Table 3.

Fig. 3. Magnesium three-isotope diagram of all samples analyzed in this study. Repeated measurements of individual samples are shown as individual points. The solid line represents the isotopic mass-dependent fractionation line with a slope of 0.518. Error bars represent the 2SD uncertainties of individual samples. Data are reported in Tables 2 and 3.

Fig. 4. $\delta^{26}\text{Mg}$ (‰) vs. MgO (wt%) for peralkaline silicate rocks and

natrocarbonatites from Oldoinyo Lengai. The gray band and horizontal solid line represent the average $\delta^{26}\text{Mg}$ value of the pristine mantle ($-0.25 \pm 0.07\text{‰}$, 2SD, Teng et al., 2010). Three arrows represent (1) peralkaline silicate magma differentiation, (2) silicate–carbonatite liquid immiscibility, and (3) carbonatite magma differentiation, respectively. The dashed diamond represents the inferred “original carbonatite melts” at Lengai, whose $\delta^{26}\text{Mg}$ values and MgO contents are unknown and shown schematically in the diagram. Error bars represent the maximum external precision of $\pm 0.10\text{‰}$ (2SD) on $\delta^{26}\text{Mg}$ during analytical sessions of this study. Data are reported in Tables 2 and 3.

Fig. 5. $\delta^{26}\text{Mg}$ (‰) vs. (a) $\text{CaO}+\text{SrO}+\text{BaO}$ (wt%) and (b) $\text{Na}_2\text{O}+\text{K}_2\text{O}$ (wt%) for natrocarbonatites from Oldoinyo Lengai. The red lines represent linear regressions and the gray arrows represent the assumed general trends for fractional crystallization of nyerereite and gregoryite. Error bars represent the 2SD uncertainties of the population of n ($= 3$ or 4) repeat measurements of individual natrocarbonatite samples. Data are reported in Table 3.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5