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 (δ^{26}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 δ^{26}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 (δ^{26}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 δ^{26}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 δ^{26}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

enriched in the residual melts relative to fractionated carbonate minerals.

Collectively, significant Mg isotope fractionation may occur during both silicate–carbonatite liquid immiscibility and fractional crystallization of carbonatite melts, making Mg isotopes a potentially useful tracer of these processes relevant to carbonatite petrogenesis.

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 (δ^{26}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 (δ^{26}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

temperatures has been revealed by both theoretical calculations (Schauble, 2011) and

experimental work (Macris et al., 2013). Such a difference implies the possibility of

different behaviour of Mg isotopes between carbonatite magmatism and silicate

magmatism, as in the case of Fe isotope systematics (Johnson et al., 2010). Therefore,

studies on Mg isotopic characteristics of carbonatites may not only improve our

understanding of high-temperature Mg isotope fractionation but also exploit new

applications. However, to our knowledge, Mg isotopic data of carbonatites have been

reported in only two papers. Sun et al. (2012) found that two carbonatite samples

from Bayan Obo, China, had Mg isotopic compositions (δ^{26}Mg = -0.34 ± 0.11‰ and

-0.14 ± 0.18‰) similar to that of the pristine mantle (δ^{26}Mg ranging from -0.48 to

-0.06‰ with an estimated average value of -0.25 ± 0.07‰, 2SD, Teng et al., 2007,

2010; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Dauphas et al.,

2010; Huang et al., 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013; Lai

et al., 2015). Hence, they suggested insignificant Mg isotope fractionation during

carbonatite petrogenesis. By contrast, Ling et al. (2013) observed large Mg isotopic

variations (δ^{26}Mg of -2.28 to +0.23‰) in carbonatite samples from the same area.

They explained such variations by mixing various proportions of isotopically heavy

crustal materials with an isotopically light carbonatite end-member. However, they

didn't provide a genetic interpretation of the isotopically light endmember

carbonatite, which was originated from the mantle but had Mg isotopic composition

(δ^{26}Mg = -2.28‰) remarkably different from the average δ^{26}Mg value of the pristine

mantle (-0.25 ± 0.07‰, 2SD, Teng et al., 2010). These diverging interpretations

77   underline the importance of a Mg isotope study on a set of carbonatite samples that

78   are well characterized in terms of petrology and geochemistry.

79   In order to investigate the behaviour of Mg isotopes during carbonatite

80   magmatism, we carried out high-precision Mg isotopic analyses for

81   natrocarbonatites and peralkaline silicate rocks from Oldoinyo Lengai, Tanzania.

82   Our results demonstrate that compositionally variable silicate rocks not related to

83   silicate–carbonatite liquid immiscibility have Mg isotopic compositions clustered

84   around the mantle value, whereas silicate rocks petrogenically associated with liquid

85   immiscibility and natrocarbonatites have heavy Mg isotopic compositions. These

86   observations suggest that significant Mg isotope fractionation may occur during both

87   silicate–carbonatite liquid immiscibility and fractional crystallization of carbonatite

88   melts. Consequently, Mg isotopic compositions of carbonatites may potentially be

89   used to trace processes (i.e., liquid immiscibility and fractional crystallization)

90   relevant to carbonatite petrogenesis.

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92   **2. Geological settings and samples**

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94   Oldoinyo Lengai is the only active carbonatite volcano on Earth. It lies in the

95   East African Rift Valley in northern Tanzania with volcanological observations more

96   than 100 years (Keller et al., 2010). This volcano consists predominantly (>95 vol.%)

97   of phonolite and nephelinite lavas and pyroclastics, with natrocarbonatite ashes and

98   lavas in the summit area. Klaudius and Keller (2006) defined three major structural

99   units of Oldoinyo Lengai, namely *Lengai I* (phonolite tuffs and lavas), *Lengai II A*

100   (nephelinite tuffs and lavas) and *Lengai II B* (nephelinite tuffs and lavas as well as

101   natrocarbonatite tuffs and lavas). In addition, ashes, lapilli and scoriae with the

102   unique composition of carbonated combeite–wollastonite–melilite nephelinites

103   (carbCWMNs) were erupted during the 2007–2008 explosive activity (Keller et al.,

104   2010). Although olivine melilitites with high Mg# [molar $Mg/(Mg + Fe^{2+}) \times$

105   100] >50 occur in some monogenetic cones in the vicinity of Oldoinyo Lengai

106   (Dawson et al., 1985; Keller et al., 2006; Mattsson, 2012; Mattsson et al., 2013),

107   rocks of primary magma compositions are absent within the Lengai volcanic edifice

108   itself. Silicate rocks and natrocarbonatites at Oldoinyo Lengai are all peralkaline

109   [molar (Na + K)/Al >1, Simonetti et al., 1997; Dawson, 1998; Klaudius and Keller,

110   2006] and are distinctly of mantle origin as indicated by both Sr–Nd–Pb isotopes

111   (Bell and Simonetti, 1996; Bell and Tilton, 2001) and C–O–Li isotopes (Keller and

112   Hoefs, 1995; Halama et al., 2007). Many previous studies have discussed the

113   petrogenetic relationships between olivine melilitites, phonolites, nephelinites and

114   natrocarbonatites at Oldoinyo Lengai, through investigations of natural samples

115   and/or phase equilibrium experiments. A brief summary is given here (Fig. 1).

116   Olivine melilitites in the vicinity of Oldoinyo Lengai were formed by small

117   degrees (1–2%) of partial melting of the mantle and were considered to represent the

118   possible primary melts of the Lengai volcano (Peterson and Kjarsgaard, 1995; Keller

119   et al., 2006; Wiedenmann et al., 2010). However, there is a large compositional gap

120   between olivine melilitites (MgO >9 wt% and Mg# >50, Keller et al., 2006;

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121 Mattsson et al., 2013) and the highly evolved phonolites and nephelinites of the units

122 Lengai I and Lengai II (MgO <2 wt% and Mg# <31, Klaudius and Keller, 2006).

123 Moreover, melilitites and nephelinites/phonolites display different Sr–Nd–Pb

124 isotopic signatures (Keller et al., 2006) and opposite variation trends of some major

125 and trace elements (Mattsson et al., 2013). Therefore, olivine melilitites cannot be

126 related directly to nephelinites/phonolites (Mattsson et al., 2013), and parental

127 magmas of the highly evolved nephelinites/phonolites at Lengai remain unknown.

128   A widely accepted model for natrocarbonatite petrogenesis at Oldoinyo Lengai is

129 immiscible separation of carbonatite melts from CO_2-saturated and strongly

130 peralkaline nephelinitic melts (e.g., Peterson, 1990; Church and Jones, 1995; Keller

131 and Spettel, 1995; Kjarsgaard et al., 1995; Dawson, 1998), though other models have

132 been proposed, such as partial melting of fenitized basement (Morogan and Martin,

133 1985), differentiation from mildly alkalic olivine sövitic magmas (Twyman and

134 Gittins, 1987) and condensation from cognate alkaline fluids (Nielsen and Veksler,

135 2002). Liquid immiscibility between silicate and carbonatite melts has been directly

136 demonstrated by coexisting silicate and carbonate melt inclusions in nepheline

137 phenocrysts from erupted ashes and in minerals of ijolite xenoliths at Oldoinyo

138 Lengai (Mitchell, 2009; Sekisova et al., 2015). Stratigraphic relationships and Sr–

139 Nd–Pb isotopic data suggest that the combeite- and wollastonite-bearing nephelinites

140 (CWNs) from the unit Lengai II B are petrogenetically related to natrocarbonatites

141 and may represent differentiation products of the conjugate silicate melts from which

142 the original carbonatite melts exsolved (Kjarsgaard et al., 1995; Bell and Simonetti,

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143   1996; Dawson, 1998; Klaudius and Keller, 2006). By contrast, phonolites from the

144   unit Lengai I, CWNs from the unit Lengai II A and carbCWMNs of the 2007–2008

145   activity are assumed to represent silicate melts that did not experience liquid

146   immiscibility (Klaudius and Keller, 2006; Keller et al., 2010). Once immiscibility

147   occurred, the original carbonatite melts efficiently segregated from the conjugate

148   silicate melts due to their low viscosity and density. Subsequent carbonatite magma

149   differentiation at Oldoinyo Lengai was dominated by fractional crystallization of

150   nyerereite $(Na_2Ca[CO_3]_2)$ and   gregoryite $([Na,Ca_x,K]_{2-x}CO_3)$,   generating

151   natrocarbonatites (Peterson, 1990; Kjarsgaard et al., 1995; Gittins and Jago, 1998;

152   Mattsson and Caricchi, 2009).

153   In this study, Mg isotopes were measured for twenty-two samples, including four

154   olivine melilitites from the vicinity of the Lengai volcano, five phonolites from the

155   unit Lengai I, two CWNs from the unit Lengai II A, three CWNs from the unit

156   Lengai II B, three carbCWMNs of the 2007–2008 activity and five natrocarbonatites.

157   These samples are the same as those studied in previous work (Simonetti et al., 1997;

158   Keller et al., 2006, 2010; Klaudius and Keller, 2006; Halama et al., 2007). Detailed

159   sample descriptions as well as petrological and geochemical aspects of these samples

160   are available therein. As demonstrated in these papers, there is little petrographic

161   evidence for alteration in the investigated samples, except for a few altered

162   combeites in sample OL 804 (Klaudius and Keller, 2006). Both silicate rocks and

163   natrocarbonatites retain their primary igneous mineralogy and do not contain clay

164   minerals. In particular, natrocarbonatites are strongly susceptible to alteration at the

165   Earth's surface (e.g., Zaitsev and Keller, 2006). However, the natrocarbonatite

166   samples studied here were collected directly after eruption and their C–O–Li isotopic

167   compositions fall into a restricted field within the "primary igneous carbonatites"

168   (Keller and Hoefs, 1995; Halama et al., 2007). Collectively, the effects of alternation

169   on Mg isotopic compositions of the samples investigated here can be excluded.

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3. Analytical methods

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173   Magnesium isotopic analyses were performed at the Isotope Laboratory of the

174   University of Arkansas, Fayetteville, following previously established procedures

175   (Teng et al., 2007, 2010, 2015; Yang et al., 2009; Li et al., 2010; Ling et al., 2013;

176   Teng and Yang, 2014). A brief description is given here.

177   Whole-rock powders were dissolved in screw-top beakers in a combination of

178   concentrated $HF–HNO_3–HCl$. Separation of Mg was achieved by cation exchange

179   chromatography with Bio-Rad 200–400 mesh AG50W–X8 resin in $1 \ mol·L^{-1} \ HNO_3$

180   media. The Mg column chemistry was performed twice for silicate rocks and four or

181   five times for natrocarbonatites in order to obtain a pure Mg solution for mass

182   spectrometry. The Mg yields through column chemistry, based on analyses of Mg

183   content in the elution collected before and after the Mg cut, were >99.8%. To ensure

184   the efficiency of removing Ca for natrocarbonatites with high CaO/MgO ratios (from

185   25 to 38, wt/wt), we carried out repeat analyses for natrocarbonatites by using an

186   additional Ca column chemistry with Bio-Rad 200–400 mesh AG50W–X12 resin in

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187   12 mol·L^{-1} HCl media (Ling et al., 2013) after two or three iterations of Mg column

188   chemistry. The residual content of Ca in the solution after column chemistry was

189   below the detection limit for Ca (~ 10ppb) by inductively coupled plasma mass

190   spectrometry (ICP–MS). Magnesium isotopic compositions were analyzed by the

191   standard-sample bracketing method using a Nu Plasma multi-collector inductively

192   coupled plasma mass spectrometry (MC–ICP–MS).

193   The results are reported in δ–notation in per mil relative to DSM3: $\delta^X Mg =$

194    $[(^X Mg/^{24} Mg)_{sample}/(^X Mg/^{24} Mg)_{DSM3}$ - 1] $\times$ 1000, where X refers to mass 25 or 26.

195   Based on replicate analyses of a seawater sample from Hawaii and an in-house

196   reference solution KH–olivine, the long-term external precision on δ^{26}Mg value is

197   ≤0.10‰ (2SD, Li et al., 2010; Teng et al., 2010, 2015). Both synthetic solutions and

198   reference materials were processed through column chemistry with samples for

199   accuracy check. Multiple analyses of synthetic solutions IL–Mg–1 (concentration

200   ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1) and Carb (concentration ratios of

201   Ca:Mg = 100:1) yielded δ^{26}Mg values of -0.05 to -0.01‰ (Table 1), in agreement

202   with the expected true value of 0.00. Magnesium isotopic compositions of seawater,

203   the Allende chondrite and the in-house reference solution KH–olivine analyzed

204   during the course of this study also agree with previously published values (Table 1).

205   These data, combined with the indistinguishable results for repeat analyses of

206   individual samples (Tables 2 and 3), especially of natrocarbonatites that were

207   processed through different column procedures (Fig. 2), assure the accuracy of our

208   data.

4. Results

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Magnesium isotopic compositions are reported in Table 1 for synthetic solutions

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and reference materials, Table 2 for peralkaline silicate rocks, and Table 3 for

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natrocarbonatites from Oldoinyo Lengai. For reference, some elemental and isotopic

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data reported in previous studies (Simonetti et al., 1997; Keller et al., 2006, 2010;

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Klaudius and Keller, 2006; Halama et al., 2007) are also included in Tables 2 and 3.

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All samples analyzed in this study fall on an isotopic mass-dependent fractionation

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line with a slope of 0.518 on the Mg three-isotope diagram (Fig. 3). Hence, we only

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use $\delta^{26}Mg$ in the subsequent discussions.

218

Olivine melilitites from the vicinity of Oldoinyo Lengai have homogeneous Mg

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isotopic compositions ($\delta^{26}Mg$ = -0.30 to -0.26‰, Table 2). The $\delta^{26}Mg$ values vary

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from -0.25 to -0.10‰ in phonolites from the unit Lengai I, from -0.14 to -0.13‰ in

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CWNs from the unit Lengai II A, and from -0.17 to -0.15‰ in carbCWMNs of the

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2007–2008 activity, respectively. The overall variation for these rocks from the

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Lengai volcano is small and all data cluster around the average $\delta^{26}Mg$ value of the

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pristine mantle (Fig. 4). By contrast, the $\delta^{26}Mg$ values of CWNs from the unit

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Lengai II B (from -0.06 to +0.09‰) and of natrocarbonatites (from +0.13 to +0.37‰)

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are higher than the pristine mantle value (Fig. 4).

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5. Discussion

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

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

233   carbonatite magma differentiation, respectively.

234

235   **5.1. Small Mg isotope fractionation during peralkaline silicate magma**

236   **differentiation**

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238   Olivine melilitites in the vicinity of Oldoinyo Lengai were formed by small

239   degrees (1–2%) of partial melting of the mantle (Mattsson et al., 2013). They have

240   variable MgO content and Mg# (from 15 to 10 wt% and 70 to 59, respectively, Table

241   2) due to the early stages of fractional crystallization of olivine (Keller et al., 2006).

242   However, they have homogeneous and mantle-like Mg isotopic compositions (δ^{26}Mg

243   = -0.30 to -0.26‰, Table 2), indicating insignificant Mg isotope fractionation during

244   mantle melting and olivine crystallization. This is consistent with previous

245   suggestions that Mg isotope fractionation during mantle melting and subsequent

246   basaltic magma differentiation is limited (Teng et al., 2007, 2010; Bourdon et al.,

247   2010).

248   Phonolites from the unit Lengai I, CWNs from the unit Lengai II A and

249   carbCWMNs of the 2007–2008 activity are considered to represent peralkaline

250   silicate melts that did not experience liquid immiscibility (Klaudius and Keller, 2006;

251   Keller et al., 2010). Despite of their variable MgO content (from 2.0 to 0.8 wt%),

252   these rocks display a relatively narrow range in δ^{26}Mg (from -0.25 to -0.10‰),

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253 barely beyond the average mantle value (Fig. 4). This observation suggests that Mg

254 isotope fractionation during differentiation of highly evolved peralkaline silicate

255 magma, if any, is small. Hence, the silicate melts before liquid immiscibility at

256 Oldoinyo Lengai probably had Mg isotopic compositions similar to the average

257 mantle value.

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5.2. Significant Mg isotope fractionation during silicate–carbonatite liquid

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260 **immiscibility**

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262 Combeite–wollastonite nephelinites from the unit Lengai II B are currently

263 believed to result from differentiation of the silicate melts generated by silicate–

264 carbonatite liquid immiscibility (Kjarsgaard et al., 1995; Klaudius and Keller, 2006).

265 Although the detailed differentiation processes from the conjugate silicate melts at

266 the time of immiscibility to CWNs from the unit Lengai II B remain unknown, they

267 would not affect Mg isotopic composition of the silicate melts since Mg isotope

268 fractionation during highly evolved peralkaline silicate magma differentiation is

269 small. Hence, the δ^{26}Mg values of CWNs from the unit Lengai II B (from -0.06 to

270 +0.09‰) are likely to record those of the silicate melts after liquid immiscibility. The

271 difference in Mg isotopic compositions between the silicate melts before and after

272 immiscibility suggests Mg isotope fractionation during liquid immiscibility.

273 Magnesium isotopic mass balance during silicate–carbonatite liquid

274 immiscibility follows:

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$$\delta^{26}Mg_0 = \delta^{26}Mg_s \times f_{Mg,s} + \delta^{26}Mg_c \times f_{Mg,c},$$

where $\delta^{26}Mg_0$, $\delta^{26}Mg_s$ and $\delta^{26}Mg_c$ are the Mg isotopic composition of silicate melt

before immiscibility and of silicate melt and carbonatite melt after immiscibility,

respectively. The $f_{Mg,s}$ and $f_{Mg,c}$ refer to the fraction of Mg contained in the conjugate

silicate and carbonatite melts ($f_{Mg,s} + f_{Mg,c} = 1$). The heavy Mg isotopic compositions

of CWNs from the unit Lengai II B indicates $\delta^{26}Mg_s > \delta^{26}Mg_0$, which in turn implies

$\delta^{26}Mg_c < \delta^{26}Mg_0$, i.e., the original carbonatite melts at Lengai were isotopically light

(Fig. 4).

The inferred preferential partition of heavy Mg isotopes into silicate melts

relative to carbonatite melts during liquid immiscibility is consistent with the

direction predicted by theoretical and experimental work on equilibrium

inter-mineral Mg isotope fractionation between silicate and carbonate minerals. For

example, theoretical calculations yielded $10^3\ln\alpha_{forsterite-magnesite}$ of +0.21‰ and

$10^3\ln\alpha_{forsterite-dolomite}$ of +0.15‰ at 1000 ℃ (Schauble, 2011), while experimental

measurements yielded $10^3\ln\alpha_{forsterite-magnesite}$ of +0.44 ± 0.10‰ at 600 ℃ (Macris et

al., 2013). In general, phases with the stronger bonding environment of the cation of

interest favor heavier isotopes when thermodynamic equilibrium is achieved (e.g.,

Bigeleisen, 1965). Hence, the positive $10^3\ln\alpha_{forsterite-magnesite/dolomite}$ values reflect

stronger Mg–O bonds in forsterite versus weaker bonds in magnesite/dolomite. Such

a difference may also exist between silicate melts and carbonatite melts since they

also use the $[SiO_4]^{4-}$ tetrahedra and the $[CO_3]^{2-}$ group, respectively, as their basic

structure units (e.g., Henderson et al., 2006; Vuilleumier et al., 2014). If this is true,

297 silicate melts are expected to be enriched in heavy Mg isotopes relative to

298 carbonatite melts, though silicate melts and carbonatite melts respectively have

299 homogeneous Mg isotopic compositions due to fast diffusion of isotopes in melts.

300 Such a speculative mechanism of isotope fractionation can be understood on analogy

301 with element partition between immiscible silicate and carbonatite melts, where the

302 concentration of certain elements will be homogeneous among each melt but be

303 different between these two melts due to the different melt structures (e.g., Jones et

304 al., 1995; Martin et al., 2013).

305

306 **5.3. Significant Mg isotope fractionation during carbonatite magma**

307 **differentiation**

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309   Magnesium isotope fractionation during silicate–carbonatite liquid immiscibility

310 predicts isotopically light original carbonatite melts at Oldoinyo Lengai. However,

311 natrocarbonatite samples have positive δ^{26}Mg values (Fig. 4), which requires a

312 change of Mg isotopes of carbonatite melts subsequent to liquid immiscibility.

313 Below, we explore the possible processes responsible for such a change.

314   One possible process is surface alteration, which can potentially fractionate Mg

315 isotopes. The direction of Mg isotope fractionation during carbonate weathering has

316 been investigated in previous studies on groundwater controlled by dedolomitization

317 reactions and runoff waters draining carbonate bedrocks, which suggested little

318 fractionation between dolomite and water (Jacobson et al., 2010) or the retention of

319　light Mg isotopes in carbonates (Tipper et al., 2006, 2008; Brenot et al., 2008).

320　Hence, the heavy Mg isotopic compositions of natrocarbonatites cannot be attributed

321　to alteration of samples.

322　　　Another process that can also be ruled out is crustal contamination. Due to their

323　low viscosity, carbonatite melts ascend very rapidly and, thus, crustal assimilation

324　during carbonatite volcanism is generally limited. Moreover, assimilation of

325　siliceous sedimentary rocks with heavy Mg isotopes (δ^{26}Mg up to +0.92‰, Li et al.,

326　2010) may increase the δ^{26}Mg values of carbonatite melts. However, such a process

327　conflicts with the very low SiO_2 content (<0.5 wt%, Table 3) and mantle-like

328　radiogenic and stable isotope characteristics (Keller and Hoefs, 1995; Bell and Tilton,

329　2001; Halama et al., 2007) of natrocarbonatites.

330　　　Diffusion-driven Mg isotope fractionation between ascending carbonate melts

331　and wall rocks is also unlikely to produce the variable and heavy Mg isotopic

332　compositions of natrocarbonatites at Lengai. First, diffusion of isotopes in melts is

333　much faster than that in solids. Therefore, Mg isotopic heterogeneity in melts caused

334　by diffusion will be eliminated quickly, producing isotopically homogeneous

335　carbonatites. Second, light isotopes diffuse faster than heavy ones (e.g., Richter et al.,

336　2008) and, hence, possible diffusion of Mg from wall rocks into the low-Mg

337　natrocarbonatite melts (natrocarbonatites have MgO contents <0.5 wt%, Fig. 4)

338　during magma ascent will result in light Mg isotopes in natrocarbonatites. This is

339　opposite to the positive δ^{26}Mg values of natrocarbonatites (Fig. 4).

340　　　Carbonatite magma differentiation is another process that may be responsible for

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341 the variable and positive $\delta^{26}Mg$ values of natrocarbonatites. Fractional crystallization

342 of nyerereite ($Na_2Ca[CO_3]_2$) and gregoryite ($[Na,Ca_x,K]_{2-x}CO_3$) occurred during the

343 carbonatite magma differentiation at Oldoinyo Lengai (Peterson, 1990; Gittins and

344 Jago, 1998; Mattsson and Caricchi, 2009). Both of these two minerals are enriched

345 in alkali and alkaline earth metals. The trends of increasing $\delta^{26}Mg$ values with

346 decreasing $CaO+SrO+BaO$ and Na_2O+K_2O contents in natrocarbonatites (Fig. 5)

347 suggest that light Mg isotopes preferentially entered into fractionated nyerereite and

348 gregoryite. Therefore, fractional crystallization of nyerereite and gregoryite may

349 account for the observed Mg isotopic variations ($\delta^{26}Mg$ of +0.13 to +0.37‰) in

350 natrocarbonatites. The potential processes that drove Mg isotopic shift from the

351 negative $\delta^{26}Mg$ values ($\leq$-0.25‰) of the inferred original carbonatite melts to the

352 positive $\delta^{26}Mg$ values ($\geq$+0.13‰) of natrocarbonatites (Fig. 4) remain to be defined.

353

354 **6. Conclusions**

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356 This study presents Mg isotopic data for the well-characterized natrocarbonatites

357 and peralkaline silicate rocks from Oldoinyo Lengai, Tanzania. The silicate rocks not

358 related to silicate–carbonatite liquid immiscibility, comprising phonolites from the

359 unit Lengai I, combeite–wollastonite nephelinites from the unit Lengai II A and

360 carbonated combeite–wollastonite–melilite nephelinites of the 2007–2008 activity,

361 have $\delta^{26}Mg$ values (from -0.25 to -0.10‰) clustered around the mantle value. By

362 contrast, combeite–wollastonite nephelinites from the unit Lengai II B, which

18

363 evolved from the silicate melts that were presumably generated by liquid

364 immiscibility, have high $\delta^{26}Mg$ values of -0.06 to +0.09‰. Such a difference

365 suggests significant Mg isotope fractionation during liquid immiscibility and implies

366 isotopically light original carbonatite melts at Lengai. However, natrocarbonatites

367 have positive $\delta^{26}Mg$ values from +0.13 to +0.37‰. The negative correlations

368 between $\delta^{26}Mg$ values and $CaO+SrO+BaO$ and Na_2O+K_2O contents suggest

369 significant Mg isotope fractionation due to fractional crystallization of nyerereite and

370 grogoryite, with heavy Mg isotopes enriched in the residual melts relative to

371 fractionated carbonate minerals.

372 The different behaviour of Mg isotopes between silicate magmatism and

373 carbonatite magmatism promises different applications. Previous studies indicate

374 limited Mg isotope fractionation during silicate magma differentiation and, hence,

375 Mg isotopic compositions of basalts and granites can be used to constrain those of

376 their mantle or crustal sources (Teng et al., 2007, 2010; Shen et al., 2009; Bourdon et

377 al., 2010; Li et al., 2010). This study suggests, for the first time, that significant Mg

378 isotope fractionation may occur during both silicate–carbonatite liquid immiscibility

379 and fractional crystallization of carbonatite magmas. Consequently, Mg isotopic

380 compositions of carbonatites may potentially be used to trace processes (i.e., liquid

381 immiscibility and fractional crystallization) relevant to carbonatite petrogenesis.

382 Nevertheless, Mg isotopic data of carbonatites are still very limited. In order to

383 further investigate the magnitude and mechanism of Mg isotope fractionation during

384 carbonatite magmatism and its applications, more comprehensive studies on

19

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

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579

580 **Table 1**

581 Magnesium isotopic compositions of synthetic solutions and reference materials.

Standard	δ^{26}Mg (‰)	2SD[a]	δ^{25}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

582 [a] 2SD = two times the standard deviation of the population of n (n >20) repeat measurements

583 of the standards during an analytical session.

584 [b] IL–Mg–1 is a synthetic solution with concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti =

585 1:1:1:1:1:1:0.1.

586 [c] Replicate = repeat column chemistry and measurements of different aliquots of a stock

587 solution.

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

589 [e] KH–olivine is an in-house reference solution made from the Kilbourne Hole olivine.

590 **Table 2**

591 Magnesium isotopic compositions and selected geochemical parameters of

592 peralkaline silicate rocks from Oldoinyo Lengai.

Sample ID	$\delta^{26}Mg$ (‰)	2SD[a]	$\delta^{25}Mg$ (‰)	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

593 [a] 2SD = two times the standard deviation of the population of n (n >20) repeat measurements

594 of the standards during an analytical session.

595 [b] Data are from Keller et al. (2006, 2010) and Klaudius and Keller (2006); Mg# = molar

596 $Mg/(Mg + Fe^{2+}) \times 100$.

597 [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]	$\delta^{26}Mg$ (‰)	2SD[b]	$\delta^{25}Mg$ (‰)	2SD	SiO_2 (wt%)[c]	MgO (wt%)[c]	Na_2O (wt%)[c]	K_2O (wt%)[c]	CaO (wt%)[c]	SrO (wt%)[c]	BaO (wt%)[c]	$\delta^{18}O$ (‰)[d]	$\delta^{13}C$ (‰)[d]	$\delta^{7}Li$ (‰)[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. δ^{26}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 ±0.10‰ (2SD) on δ^{26}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. δ^{26}Mg (‰) vs. MgO (wt%) for peralkaline silicate rocks and

628   natrocarbonatites from Oldoinyo Lengai. The gray band and horizontal solid line

629   represent the average δ^{26}Mg value of the pristine mantle (-0.25 ± 0.07‰, 2SD, Teng

630   et al., 2010). Three arrows represent (1) peralkaline silicate magma differentiation,

631   (2) silicate–carbonatite liquid immiscibility, and (3) carbonatite magma

632   differentiation, respectively. The dashed diamond represents the inferred "original

633   carbonatite melts" at Lengai, whose δ^{26}Mg values and MgO contents are unknown

634   and shown schematically in the diagram. Error bars represent the maximum external

635   precision of ±0.10‰ (2SD) on δ^{26}Mg during analytical sessions of this study. Data

636   are reported in Tables 2 and 3.

637

638   **Fig. 5.** δ^{26}Mg (‰) vs. (a) CaO+SrO+BaO (wt%) and (b) Na_2O+K_2O (wt%) for

639   natrocarbonatites from Oldoinyo Lengai. The red lines represent linear regressions

640   and the gray arrows represent the assumed general trends for fractional

641   crystallization of nyerereite and gregoryite. Error bars represent the 2SD

642   uncertainties of the population of n (= 3 or 4) repeat measurements of individual

643   natrocarbonatite samples. Data are reported in Table 3.