Lithium enrichment and isotopic variation in minerals from peridotite xenoliths from northwestern Ethiopian plateau

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Lithium Enrichment and Isotopic Variation in Minerals from Peridotite Xenoliths from Northwestern Ethiopian Plateau

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ABSTRACT
We report Lithium (Li) concentrations and isotopic compositions for co-existing olivine, orthopyroxene (opx), and clinopyroxene (cpx) mineral separates from depleted and metasomatized peridotite xenoliths hosted by basaltic lavas from northwestern Ethiopian plateau (Gundeweyn area). The peridotites contain five lherzolites and one harzburgite and are variably depleted and enriched in LREE relative to HREE. In both depleted and enriched lherzolites, Li is preferentially incorporated into olivine (2.4-3.3 ppm) compared to opx (1.4-2.1 ppm) and cpx (1.4-2.0 ppm) whereas the Li contents of olivines (5.4 ppm) from an enriched harzburgite are higher than those of lherzolites. Olivines from the samples show higher Li abundances than normal mantle olivines (1.6-1.9 ppm) indicating the occurrence of Li enrichments through melt-peridotite interaction. The average δ7Li values range from +2.2 to +6.0‰ in olivine, from -0.1 to +2.0‰ in opx and from -4.4 to -0.9‰ in cpx from the lherzolites. The Li isotopic composition (3.5%) of olivines from harzburgite fall within the range of olivine from lherzolites but the opx show low in δ7Li (-2.0‰). Overall Li isotopic compositions of olivines from the peridotites fall within the range of normal mantle olivine, δ7Li values of ±1±0±2% within uncertainty, reflecting metasomatism (enrichment) of the peridotites by isotopically heavy Li-rich asthenospheric melt. Li isotope zonation is also observed in most peridotite minerals. Majority of olivine grains display isotopically heavy cores and light rims and the reverse case is observed for some olivine grains. Orthopyroxene and clinopyroxene grains show irregular distribution in δ7Li. These features of Li isotopic compositions within and between grains in the samples reflect the effect of diffusion-driven isotopic fractionation during melt-peridotite interaction and cooling processes.

INTRODUCTION
The continental lithospheric mantle (CLM) beneath Ethiopian plateau and rift zone has experienced depletion and enrichment processes at different scales and periods (Roger et al., 1999; Conticelli et al., 1999; Ayalew et al., 2003; Reisberg et al., 2004). This is shown by the distinct compositions of mantle xenoliths found in the basaltic rocks of plateau and Cenozoic rift (Ferrando et al. 2008; Frezzotti et al. 2010; Meshesha et al. 2011; Beccaluva et al. 2011; Bianchini et al. 2014). Peridotites from the Ethiopian plateau particularly from the Gundeweyn area (Fig. 1) have 0.5-0.9 Ga Lu–Hf depletion and 0.4-0.6 Ga Sm-Nd enrichment ages (Alemayehu et al., 2016c). The Sm–Nd, Lu–Hf and Re–Os isotope systematic of the peridotites indicate that the southern Ethiopian CLM formed between 0.9 to 2.8 Ga (Reisberg et al., 2004; Meshesha et al., 2011; Bianchini et al., 2014), providing strong indication that at least some parts of the lithospheric mantle beneath the southern Ethiopian rift zone were older than the plateau CLM. Many geophysical studies have showed low velocity anomalies related to the presence of anomalously hot and buoyant mantle upwelling beneath various parts of the East African rift including the Ethiopian plateau and rift zone (e.g. Ebinger et al., 1989; Nyblade et al., 2000; Debayle et al., 2001; Benoit et al., 2006). The low velocity anomalies are related to one or two mantle plumes (e.g. Ebinger and Sleep, 1998; George et al., 1998; Rogers et al., 2000) or of mantle upwelling (African super plume, Janney et al. 2002; Furman et al. 2004, 2006b) that triggered lithospheric thinning beneath East African rift (e.g. Ebinger and Casey 2001; Furman and Graham 1999; Rooney 2010). The geophysical investigation integrated with geochemical data of mantle xenoliths from Ethiopian Cenozoic basalts suggest that the present lithosphere is much hotter (60-150 mW/m²; Meshesha et al., 2011; Alemayehu et al., 2016a) than the actual continental lithospheric mantle (40 mW/m²; Pollack and Chapman 1977). Moreover, the investigated physicochemical changes leads to the formation of the Ethiopian CLM during the Pan-African time (e.g. Meshesha et al., 2011; Bianchini et al., 2014) followed by various types of metasomatic processes that have been related to eruption of plateau basaltic lavas connected to plume-related sub alkaline magmatism (Beccaluva et al. 2011). Thus, the Ethiopian xenoliths provide special opportunity to address mantle process and evolution mechanism of modern lithospheric mantle, which is connected with the rising of the Afar plume. It is usually agreed that the Pan-African subduction and Cenozoic East African rift are the two major geological events that affect the CLM beneath Ethiopian plateau and rift zones. The nature of the lithospheric mantle beneath Ethiopia also modified from the typical refractory to fertile (Alemayehu et al., 2016a). However, the processes related to peridotite-melt interaction are still not well constrained.

Many earlier worldwide studies have shown that most of the peridotites are affected by various degrees of peridotite-melt interaction (metasomatism), occurring at different lithospheric levels and causing significant geochemical modifications of the lithospheric mantle (e.g. Piccardo et al., 2007). Peridotite-melt interactions occurring in the Ethiopian CLM have been identified to be the result of multiple metasomatic overprints, that were initially associated with the Pan-African subduction and subsequently caused by small degree partial melts from the asthenospheric mantle or from mantle plume sources during the development of the East African rift system (EARS).
square denote the location of the study area, volcanic rocks in East Africa (Kampunzu and Mohr 1991) and the red isotopes (~16%) cause significant Li (Brenan et al., 1998). The large mass difference between the two Li shown by a cross (+).

Fig. 1. (a) The distribution of Neoproterozoic basement rocks and volcanic rocks in East Africa (Kampunzu and Mohr 1991) and the red square denote the location of the study area, (b) Distribution of Cenozoic volcanic rocks in Ethiopian plateau and rift zone (Ferrando et al. 2008). EVP and MER denote Ethiopian Volcanic Province and Main Ethiopian Rift, respectively. The location of the study area is shown by a cross (+).

Li is a mobile element that preferentially enters the fluid phase during partial melting and fluid/melt-rock reaction processes in mantle (Brenan et al., 1998). The large mass difference between the two Li (\(\text{Li}^{7} \sim 7.59\%\) and \(\text{Li}^{8} \sim 92.41\%\)) isotopes (~16%) cause significant Li isotopic fractionation during geological processes. The Li isotope system has been employed as a potential geochemical tool for tracing various melt/fluid-related geological processes for example continental weathering (Rudnick et al. 2004; Teng et al. 2010), seafloor alteration (Chan et al. 1992; Scholz et al. 2009), crust/mantle recycling (Tomascek et al. 2000; Brooker et al. 2004; Elliott et al. 2006) and peridotite-melt/fluid interactions (Rudnick and Ionov 2007; Zhang et al. 2010; Tanget al. 2011; Su et al. 2012).

In this work, new Li elemental and isotopic data on variably depleted and metasomatized mantle xenoliths entrained in alkaline basalt from northwestern Ethiopian plateau (Gundeweyn area) in order to further explain the characteristics of early and late stage geological processes occurring beneath the area are presented. These new results are integrated with the previous elemental and Sr isotopic studies (Alemayehu et al., 2016a) in order to further explore the compositional modification of CLM beneath Ethiopian plateau.

**GEOLOGICAL SETTING AND ANALYSED SAMPLES**

**Geological setting**

The Ethiopian volcanic province is covered dominantly by Tertiary and Quaternary basaltic rocks, ranging in thickness from 700 to 2000 m. It covers an area of several hundred kilometers across on the plateau, on either side of the Main Ethiopian Rift (MER) and the Afar depression (Berhe et al. 1987; Fig. 1a). The MER, which is bounded by the Ethiopian plateau to the west and Somali plateau to the east, extends northeast to southwest and widens at the Afar depression (e.g. Baker et al., 1972; Fig. 1). Volcanism of the Ethiopian plateau is mainly confined to major deep-seated fractures, which were reactivated during rifting of the EARS. Most eruptions were contemporaneous with the collision of the Arabian and Eurasian plates (Hampton 1987), and took place in northwest to southeast trend.

The thick sequence of late Eocene to early Miocene flood basalts of Ethiopian plateau is overlain by less voluminous late Miocene to Quaternary lavas erupted from several distinct shield volcanoes; their ages vary from <29 to 3 Ma (Kieffer et al., 2004). The shield volcanoes consist of alternating basaltic and rhylolitic lava flows, tufts and ignimbrites. Kieffer et al. (2004) found both tholeiitic and alkaline volcanic rocks from shield volcanoes from northwestern Ethiopian plateau with ages comparable with the flood basalts. They described the large variation in the incompatible element contents of the two volcanic series in terms of differences of source composition and degree of partial melting, and concluded that the lavas from the plateau were formed from a broad region of upwelling mantle, that was thermally and compositionally heterogeneous. Conversely, Tommasini et al. (2005) suggested that plateau mafic lavas are derived from a fertile and vertically zoned enriched CLM with relatively homogeneous lateral continuity at a pressure of about 23.5 GPa. Finally, Furman et al. (2006) reported that the geochemical difference between the Oligocene-Quaternary continental flood basalts of the plateau and the Quaternary rift basalts are probably not related to significant changes in lithospheric source composition but to depth and degree of melting as well as mixing processes involving depleted, moderately enriched and metasomatised mantle domains.

The Gundeweyn volcanic field is located in east Gojam, northwestern Ethiopia plateau and contains mantle xenoliths in the late Miocene alkali basalts dated at 23.1 Ma (Kieffer et al., 2004). The volcanic field is mainly composed of lava flows, trachyte plugs and scoria cones. The pyroclastic and volcanic rocks contain dominantly scoria and olivine-phyric basalts. The basaltic lavas and monogenetic scoria cones enclose various types of fresh mantle xenoliths as described below.

**Analysed Samples**

Six (five lherzolites and one harzburgite) peridotite xenoliths collected from the Gundeweyn volcanic field were studied in this work. The samples are very fresh and, show protogranular and porphyroclastic textures. The primary mineral assemblages are olivine, orthopyroxene, clinopyroxene and spinel with minor amphiboles (Table 1). The minerals vary in size from 1 to 5 mm with subhedral to anhedral profile. A few orthopyroxene contains lamellae of clinopyroxene and vice versa. The olivines have Fo content, which is equivalent to Mg# (= 100 × Mg/(Mg + Fe), in the range from 89.3 to 89.8 with higher values from the harzburgite (Table 1). Based on CI-normalized REE patterns, the clinopyroxene from lherzolites can be classified into two groups (Fig. 2): depleted (GT272, GT278 and GT2716) which are characterized by a distinct depletion in LREE and enriched (GT273 and GT275) which are characterized by enrichment in LREE relative to MREE and HREE. The clinopyroxene from harzburgite (GT2713) is categorized into enriched group with lower MREE-HREE abundances than the lherzolites. Clinopyroxenes from lherzolite have \(^{87}\text{Sr}/^{86}\text{Sr}\) of 0.70227 to 0.70357, \(^{143}\text{Nd}/^{144}\text{Nd}\) of 0.51285 to 0.51346, and \(^{176}\text{Hf}/^{177}\text{Hf}\) of 0.28297 to 0.28360. These values range between depleted mantle and the HIMU mantle end-member. Overall, the petrography combined with detailed major-trace element and Sr–Nd–Hf isotope characteristics of the Gundeweyn peridotites reflect...
the occurrence of variable degree of partial melting and metasomatic overprint at different times (Alemayehu et al. 2016a,c).

**ANALYTICAL METHODS**

Mineral separations and Li elemental and isotope analysis were carried out at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, China. Olivine, orthopyroxene and clinopyroxene separates were handpicked under binocular stereomicroscope. In situ Li concentration and isotope analyses of pyroxenes and olivines on gold coated grain mounts were performed using a Cameca IMS-1280 ion microprobe following the techniques of Zhang et al. (2010) and Su et al. (2012, 2015). A 13 kV, 10-20 nA oxygen primary beam was focused on spot size of 20 µm in diameter. A 60 s pre-sputtering was applied without raster before analysis. A 10 kV was used to accelerate a positive secondary ion, which is measured at medium mass resolution (M/ΔM-M=1100) with 125mm aperture without energy offset. The primary beam position, entrance slits, contrast aperture, magnetic field and energy offset were automatically centered prior to each measurement. Secondary ions were counted on mono-collection pulse counting mode. 30 to 40 cycles were measured with counting time of 12 s for 6Li, 4 s for 7Li and 4 s for background at 6.5 mass. The counting rate on 7Li range from 30,000 to 100,000 cps based on the Li content of the sample and the primary beam intensity. Li isotopic ratios are given in delta units using the δ7Li notation (δ7Li = ([7Li/6Li]sample/ ([7Li/6Li]LSVEC) - 1)*1000 relative to the 7Li/6Li LSVEC Li isotope standard, with 7Li/6LiLSVEC = 12.0192, Flesh et al., 1973)). 06JY31ol for olivine, 06JY31opx for orthopyroxene and 06JY31cpx for clinopyroxene (Su et al. 2015) were used as standards and gave the average values of δ7Li =4.75±0.8‰, -0.24±0.9‰ and -2.47±1.0‰, respectively, which fall in the range of previously published values within analytical uncertainty (δ7Li =-4.51‰, -0.19‰ and -2.37‰, respectively; Su et al., 2015).

**RESULTS**

Olivine, orthopyroxene and clinopyroxene Li abundances and isotope compositions of the peridotite are given in Table 2. Clinopyroxene from the herzolites show negative Li anomaly relative to the neighboring trace elements (Fig. 2). Because limited amount of clinopyroxene, Li content and isotope compositions were not measured from harzburgites. A limited range in Li abundances and large variation in δ7Li values are observed either within or among mineral grains in a sample (Fig. 3a, b). LREE-depleted and enriched samples do not show clear systematic differences in both Li abundances and δ7Li (Fig. 3c, d).

In herzolite, olivine exhibit variable Li abundances and δ7Li values, ranging from 2.4-3.5 ppm and 1.8 to 6.3‰ for depleted and 2.3-2.4 ppm and 2.4 to 4.2‰ for enriched samples (Fig. 4a). With the exception of some grains from GT275 and GT278, some olivines from depleted and enriched samples have higher δ7Li in the cores than in the rims. Olivines from both depleted and enriched sample show higher Li contents relative to mantle olivines (1.6-1.9 ppm; Eggins et al. 1998; Seitz and Woodland, 2000). Olivines reveal negative correlations between Fo content and δ7Li (Fig. 4b). The range of Li contents and isotopic compositions in orthopyroxene of herzolites range from 1.4-2.2 ppm and -1.1 to 1.3‰ for depleted with exception for one core grain of 6.8‰, and 1.3-2.1 ppm and 0.7 to 1.3‰ for enriched samples (Fig.4c). Some orthopyroxenes from depleted and enriched samples have lower δ7Li in the cores than in the rims and some of the grains show irregular distribution in δ7Li, GT273 and GT278 samples. The Li abundance and δ7Li obtained in clinopyroxene from depleted herzolite (1.4-2.0ppm; -5.6 to -0.5‰) is relatively wider compare to enriched one (1.3-1.4ppm; 1.5 to -3.6‰) (Fig.4d). Similar to orthopyroxenes, some clinopyroxenes from depleted and enriched samples have lower δ7Li in the cores than in the rims and some grains show the opposite trend (GT2716). In a harzburgite (GT2713), olivines show homogenous composition and higher Li abundances (5.4-5.5 ppm) than olivines from herzolite. The δ7Li values of olivines vary from 3.2 to 3.8‰ and increase from the core to the rim (Fig. 3b). Orthopyroxenes are also homogeneous in Li contents (1.3-1.4ppm) and variable in δ7Li (-4.3 to -0.4‰) with irregular rim-core-rim zonation.

In general, olivines Li concentration from each depleted and enriched peridotite is usually homogeneous and higher than those of coexisting pyroxenes (Fig. 3c). The clinopyroxenes show more or less similar Li contents with coexisting orthopyroxenes (Fig. 3c). Moreover, olivines δ7Li are mostly higher than those of coexisting pyroxenes with clinopyroxene having lower δ7Li than coexisting orthopyroxenes (Fig. 3d). With some exceptions, most olivines grains show higher Li isotopic compositions in the core than in the rims and the reverse case is observed for some olivine grains. Similarly, some

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**Table 1.** GPS location, modal abundances (vol.%), selected elemental composition and textures of Gundweyn (GT) mantle xenoliths

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mooring course (degree)</th>
<th>Modal mineralogy (Vol. %)</th>
<th>Fo olivine</th>
<th>(La/Yb)N</th>
<th>(Dy/Lu)N</th>
<th>Texture</th>
<th>Rock type</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT272</td>
<td>38.156 10.963</td>
<td>olivine 56</td>
<td>23</td>
<td>18</td>
<td>2</td>
<td>89.6</td>
<td>0.45</td>
</tr>
<tr>
<td>GT273</td>
<td>38.158 10.964</td>
<td>olivine 51</td>
<td>28</td>
<td>19</td>
<td>2</td>
<td>89.5</td>
<td>2.92</td>
</tr>
<tr>
<td>GT275</td>
<td>38.159 10.964</td>
<td>olivine 60</td>
<td>24</td>
<td>15</td>
<td>1</td>
<td>89.3</td>
<td>3.06</td>
</tr>
<tr>
<td>GT278</td>
<td>38.161 10.956</td>
<td>olivine 51</td>
<td>28</td>
<td>19</td>
<td>2</td>
<td>89.6</td>
<td>0.24</td>
</tr>
<tr>
<td>GT2713</td>
<td>38.161 10.951</td>
<td>olivine 69</td>
<td>27</td>
<td>3</td>
<td>1</td>
<td>89.8</td>
<td>34.5</td>
</tr>
<tr>
<td>GT2716</td>
<td>38.163 10.946</td>
<td>olivine 70</td>
<td>19</td>
<td>10</td>
<td>1</td>
<td>89.6</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Fig. 3. Li abundances (a) and isotopic compositions (b) of olivine, orthopyroxene and clinopyroxene core-rim. Comparison of Li abundances (c) and isotopic compositions (d) between depleted and enriched olivine, orthopyroxene and clinopyroxene minerals of Gundeweyn (GT) lherzolites and harzburgite. Triangle, circle and square represent olivine, Opx and Cpx, respectively.

orthopyroxene and clinopyroxene minerals show heavy rims and light cores and in some other grains it is opposite. Among the samples, olivines from the harzburgite and lherzolite show the highest Li abundances and δ\textsuperscript{7}Li, respectively. Compared to most olivines reported from worldwide peridotites, olivines from Gundeweyn harzburgite show higher Li contents (Fig. 4a).

DISCUSSION

Li Elemental Enrichment in Peridotite Xenoliths

Two groups of peridotite xenoliths can be identified from clinopyroxene REE patterns (Alemayehu et al. 2016a; Fig. 2): depleted groups (lherzolites) show low contents of LREE and enriched groups (lherzolite and harzburgite) have relatively high contents of LREE relative to medium and heavy REE. These features are similar to those reported in the most of mantle peridotites worldwide and are generally explained as a result of different degrees of partial melting followed by metasomatic enrichments in incompatible elements (e.g. McDonough and Frey, 1989; Pearson et al. 2003). In general, the contents of compatible and moderately incompatible elements in peridotite series are mainly related to indices of melt extraction whereas those of highly incompatible elements are controlled by style and degree of metasomatic overprint. Li is a mobile and moderately incompatible element that favorably enters to the fluid phase during partial melting and fluid/melt-rock reaction in mantle processes (Brenan et al. 1998). Generally, melt depletion related to partial melting leads to decrease in Li contents in mantle minerals due to the moderate incompatibility of Li whereas melt addition leads to increase in Li contents (e.g. Seitz and Woodland 2000). Most peridotite xenoliths show constant variation of Li content (olivine < orthopyroxene < clinopyroxene) among mantle minerals. This is because of Li diffusion rate in olivine is much slower than in pyroxene under similar environments (Parkinson et al. 2007; Dohmen et al. 2010; Coogan, 2011; Yakob et al. 2012), and on the other hand ///
abundances. Most of the peridotites show generally homogenous Li abundances (Table 2) indicating the occurrence of Li enrichment for longer time to homogenize the Li within the grains. The concentrations of Li in olivines do not correlate well with the modal abundance of olivine (Fig. 5a) and with the degree of LREE enrichment of the peridotites, as measured by the chondrite-normalized (La/Yb)$_N$ ratio of clinopyroxene (Fig. 5b). These features suggest that Li addition and LREE enrichment occur at different times within lithospheric mantle beneath Gundeweyn. Moreover, the Li enrichments do not appear to be correlated with the presence of metasomatic accessory minerals such as amphibole (Table 1). Interestingly, olivines from the enriched harzburgites show Li enrichments (average 5.4 ppm) than those from lherzolites. This characteristic could be related to preferential enrichment of incompatible trace elements including Li in olivine-rich matrices relative to pyroxene (Toramaru et al. 1986; von Bargen et al. 1986; Van Orman et al. 2001; Rudnick et al. 2007).

Another interesting feature is that Li abundance in olivines from harzburgite is higher than most olivines from worldwide peridotites (Fig. 4a). These observations suggest that the lithospheric mantle beneath the Gundeweyn region is influenced by large melt derived from the asthenospheric mantle, probably connected with the rising of the Afar plume which is near northeast of Gundeweyn.

![Table 2: In-situ Li abundance and isotopic compositions of olivine, orthopyroxene and clinopyroxene from Gundeweyn (GT) mantle xenoliths](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
<th>Li (ppm)</th>
<th>2σ</th>
<th>δLi</th>
<th>2σ</th>
<th>Orthopyroxene</th>
<th>Sample</th>
<th>Position</th>
<th>Li (ppm)</th>
<th>2σ</th>
<th>δLi</th>
<th>2σ</th>
<th>Clinopyroxene</th>
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<tbody>
<tr>
<td>GT272Oki @1 rim</td>
<td>2.55</td>
<td>0.05</td>
<td>5.51</td>
<td>0.85</td>
<td>GT272Opx @2 core</td>
<td>2.11</td>
<td>0.04</td>
<td>-0.91</td>
<td>0.96</td>
<td>GT272Cpx @1 core</td>
<td>1.54</td>
<td>0.01</td>
<td>-2.60</td>
</tr>
<tr>
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<td>2.55</td>
<td>0.04</td>
<td>6.34</td>
<td>0.90</td>
<td>GT272Opx @2 core</td>
<td>1.72</td>
<td>0.02</td>
<td>0.02</td>
<td>1.07</td>
<td>GT272Cpx @2 rim</td>
<td>2.19</td>
<td>0.04</td>
<td>0.14</td>
</tr>
<tr>
<td>GT272Oki @3 rim</td>
<td>2.52</td>
<td>0.04</td>
<td>6.09</td>
<td>0.86</td>
<td>GT272Opx @3 core</td>
<td>0.93</td>
<td>0.03</td>
<td>0.03</td>
<td>1.24</td>
<td>GT273Cpx @1 core</td>
<td>0.80</td>
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<td>2.87</td>
<td>0.93</td>
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<td>0.66</td>
<td>1.18</td>
<td>GT273Cpx @2 rim</td>
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<td>1.32</td>
<td>0.03</td>
<td>0.83</td>
<td>1.21</td>
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<td>1.38</td>
<td>0.01</td>
<td>-3.58</td>
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<td>GT273Oki @3 rim</td>
<td>2.39</td>
<td>0.04</td>
<td>2.37</td>
<td>0.88</td>
<td>GT273Opx @3 core</td>
<td>1.40</td>
<td>0.03</td>
<td>0.66</td>
<td>1.18</td>
<td>GT273Cpx @1 core</td>
<td>1.38</td>
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<td>-3.58</td>
</tr>
<tr>
<td>GT275Oki @1 rim</td>
<td>2.44</td>
<td>0.04</td>
<td>4.17</td>
<td>1.00</td>
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<td>0.29</td>
<td>0.04</td>
<td>0.84</td>
<td>1.03</td>
<td>GT275Cpx @1 core</td>
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<td>0.17</td>
<td>0.97</td>
<td>GT275Cpx @1 core</td>
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<td>-2.13</td>
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<tr>
<td>GT275Oki @3 rim</td>
<td>2.52</td>
<td>0.06</td>
<td>6.34</td>
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Fig. 5. Lithium abundances (ppm) in olivine versus (a) modal olivine (vol. %) and (b) LREE normalized (La/Yb)$_N$ in clinopyroxene. The grey field represents range of Li in normal upper mantle (Tilmouth, 2004). Symbols represent data from Alemayehu et al. (2016a, d); van Orman et al. (2001); Rudnick et al. (2007).
orthopyroxene and clinopyroxene show limited range in Li contents (Fig. 4c, d; Table 2). It is understood that olivine crystallizes before pyroxenes at mantle depth and temperature. The higher Li abundance in olivine than pyroxenes (Fig. 3c) indicates that Li is incorporated into mineral in the early stage of melt/magma fractionation at mantle temperature. This is consistent with the earlier experimental and empirical results that Li is moderately compatible element for olivine (Chan et al., 1992; Dohmen et al., 2010; Caciagli et al., 2011).

**Variation of Li Isotope Compositions in Mantle Peridotite**

Diffusion is an essential mechanism for Li isotopic variation in mantle peridotites. The diffusion rate of \(^{6}\text{Li}\) about 2–3% faster than \(^{7}\text{Li}\) (Richter et al. 2003; Coogan et al. 2005; Lundstrom et al. 2005) regardless of other physical factors like temperature and pressure as well as melt composition. On the other hand, the Li diffusion rate is highly variable in different mantle minerals which might be linked to temperature (Wunder et al., 2006; Ionov and Seitz 2008; Dohmen et al., 2010; Caciagli et al., 2011; Coogan, 2011; Yakob et al., 2012). Accordingly, the isotopic fractionation of Li will be accompanied by the preferential incorporation of Li into minerals. Ionov and Seitz (2008) reported that the abnormal and disequilibrated isotopic compositions of Li in peridotite xenoliths might be linked to the re-distribution of Li between minerals, but they attributed it to the post-eruptional cooling process. Minerals from our samples show systematic \(\delta^{7}\text{Li}\) variation (Fig. 3d; Table 2) with olivine (1.8 to 6.3%) > orthopyroxene (-1.1 to 1.3%) > clinopyroxene (-5.6% to 1.5%). The overall decreasing \(\delta^{7}\text{Li}\) value from olivine to both orthopyroxene and clinopyroxene implies that fractional crystallization can result in Li isotopic fractionation of the melts/magmas followed by melt additions into the peridotites. The Li rich and high \(\delta^{7}\text{Li}\) character of olivines in Fe-rich peridotites and the deep-seated garnet-bearing peridotites from Tanzanian are described to be related to a prolonged melt-peridotite interaction event linking to plume related silicate melts connected with the East Africa rift (Aubach et al. 2008). This is consistent with present observations. It is expected that Gundeweyn peridotites, including olivine, have experienced metasomatic overprinting during earlier phases of East Africa rift magmatism, which may be related to Pan-African subduction (Alemayehu et al. 2016a). The Li isotopic compositions of olivines from Gundeweyn peridotites fall within the range of normal mantle olivine, \(\delta^{7}\text{Li}\) values of \(-4.2\pm2\%\) within uncertainty (Fig. 5c), reflecting metasomatism (enrichment) of the peridotites by isotopically heavy Li-rich asthenospheric melt. Moreover, the rough negative correlations between \(\delta^{7}\text{Li}\) and forsterite content in olivine (Fig. 4b) suggest that the peridotites are the results of interaction between lithospheric mantle and isotopically heavy Li rich melt. Comparable interaction between \(\delta^{7}\text{Li}\) depleted lithospheric mantle with a Li rich and isotopically heavy melt has been suggested for south Africa cratonic peridotites (Bell et al., 2005), but it is unclear whether the relatively light Li in ancient refractory mantle is due to earlier melt addition or whether it reflects a secular evolution toward more isotopically heavy mantle due to addition of high \(\delta^{7}\text{Li}\) crustal components (Bell et al. 2005). However, Aubach et al. (2008) infer that the Tanzania peridotites are the results of interaction between isotopically light ancient lithospheric mantle and isotopically heavy Li rich melt. Similar interpretation can be applied for Gundeweyn peridotites that the lithospheric mantle beneath northwestern Ethiopia experienced isotopically heavy Li rich melt-peridotite reactions.

Majority of olivine grains from Gundeweyn peridotite display isotopically heavy cores and light rims and few of the olivine grains show the reverse relation. These indicate that initially the peridotite is metasomatized with isotopically heavy Li-rich melt and later upon cooling the rim becomes low in \(\delta^{7}\text{Li}\) due to diffusion-driven Li isotopic fractionation (e.g. Xiao et al. 2015). It is thus proposed that for the Gundeweyn samples, olivine best records the \(\delta^{7}\text{Li}\) of the metasomatic processes is different from that of the metasomatic processes responsible for LREE enrichment. Even though most of the earlier studies have underlined that Li isotopic disequilibrium could not survive due to the very high diffusion rate of Li (e.g., Jeffcoate et al. 2007; Rudnick and Ionov 2007; Aubach and Rudnick 2009; Halama et al. 2009), Vlaste ‘lic et al. (2009) argued that HIMU mantle has distinctly elevated \(\delta^{7}\text{Li}\) and that Li isotopic heterogeneities could survive diffusion over 1-2 billion years in the mantle. Therefore, it is considered that the disequilibrium of Li isotopes in the mantle peridotites could be preserved for a long period (Tang et al. 2009). The heavy \(\delta^{7}\text{Li}\) values (up to 6.2%) in olivine from the HIMU lavas from the Cook-Austral volcanic chain reported by Chan et al. (2009). As a result, the HIMU-like Li isotopic compositions in some olivine (up to 6.3%) grains indicate that Gundeweyn peridotites most probably experienced metasomatism by fluids/melts possibly derived from HIMU like asthenospheric Afar plume (Beccaluva et al. 2011), which is very near to the study area (Fig. 1). Some orthopyroxene and clinopyroxene also reveal heavy rim and light core Li isotopic compositions and some other pyroxene grains show the reverse. Overall, the three minerals phase does not show systematic regular \(\delta^{7}\text{Li}\) zonation, indicating the presence of complex processes controlling the Li distribution in samples. The irregular variation of \(\delta^{7}\text{Li}\) in core-rim of minerals from depleted and enriched Gundeweyn mantle xenoliths indicate recent diffusive fractionation of Li induced by percolation of metasomatic melt shortly before entrainment, transportation, eruption and cooling. This is consistent with observations reported by Xu et al. (2013).

Many recent studies have suggested that Li diffusion in clinopyroxene is faster than in olivine (Jeffcoate et al. 2007; Rudnick and Ionov 2007; Parkinson et al. 2007). If so, the low \(\delta^{7}\text{Li}\) clinopyroxene relative to \(\delta^{7}\text{Li}\) olivine in the Gundeweyn peridotites (Fig. 3d), coupled with the lack of correlations between \(\delta^{7}\text{Li}\) clinopyroxene and other parameters (5e), may reflect recent diffusion of Li into clinopyroxene and associated kinetic isotope fractionation, possibly during transport in the basaltic host rock. Furthermore, diffusion-driven Li isotopic fractionation will produce lower \(\delta^{7}\text{Li}\) in clinopyroxene than in coexisting olivines (Aubach and Rudnick 2009; Ionov and Seitz 2008; Rudnick and Ionov 2007; Tang et al. 2007) because the diffusivity of Li is much higher in pyroxene (\(\delta^{7}\text{Li}\) diffuses faster than \(\delta^{7}\text{Li}\)) than in olivine (Dohmen et al. 2010; Parkinson et al. 2007). There is no systematic correlation between \(\delta^{7}\text{Li}\) olivine and LREE enrichment and Sr isotope in clinopyroxene (Fig. 5d, e), and oxygen isotope composition in olivine (Fig. 5f). This interpretation is also consistent with the lack of correlation between Li in olivine and (La/Yb)\(_n\) in clinopyroxene and modal abundances of the minerals indicating that diffusion-driven Li isotopic fractionation related to melt-peridotite interaction and incompatible enrichment events occur at different times. The clinopyroxene from Gundeweyn peridotites are fall within the range of the Tanzanian clinopyroxene peridotite in \(\delta^{7}\text{Li}\). This could be related diffusion fractionation \(\delta^{7}\text{Li}\) that can occur during peridotite-melt/fluid interaction before or coincide with the entrainment into host magmas and the transport of the mantle xenolith to the surface. Similar interpretations are also made from worldwide peridotite (e.g. Aubach and Rudnick, 2009; Aubach et al., 2008; Gallagher and Elliott, 2009; Halama et al., 2009; Ionov and Seitz, 2008; Rudnick and Ionov, 2007).

**SUMMARY AND CONCLUSION**

The development of Li elemental and isotope analysis has been used to trace several geological processes related to melt/fluid-rock reaction or metasomatism (Rudnick and Ionov, 2007; Ackerman et al., 2013; Gu et al., 2016), cooling processes upon eruption (Ionov and Seitz, 2008), and the interaction of the peridotite with the host magma during entrainment and ascent (Aubach and Rudnick, 2009).

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Olivines in the Iherzolites and harzburgite from the present samples have generally homogeneous Li contents, higher than mantle olivine (1.6-1.9 ppm; Eggins et al. 1998; Seitz and Woodland 2000), and fall within the range of normal mantle olivine in $\delta$Li (average +2.2 to 6.0‰ in Iherzolites and average 3.5‰ in harzburgite), indicating isotopically heavy Li-rich asthenospheric melt addition to the lithospheric mantle beneath the area. Orthopyroxene and clinoxyroxene show lower Li contents and isotopic composition than coexisting olivine. Most olivine grains display Li isotopic zonation with heavy show lower Li contents and isotopic composition than coexisting lherzolites and average 3.5‰ in harzburgite), indicating within the range of normal mantle olivine in $\delta$Li from core to rim. The observed systematic inter-mineral variations of Li concentrations and isotopic compositions could be combined effects of diffusion-induced fractionation of Li isotopes during melt/fluid-peridotite interactions and cooling, possibly during the transport in the basaltic host rock. Thus, the significant Li enrichment and large isotopic fractionation during melt/fluid-peridotite reactions imply that Li abundance and isotopes may be useful tracers of mantle metasomatic processes. Generally, the large variation in Li isotopic compositions within and between grains in samples reflect the effect of diffusion-driven isotopic fractionation during peridotite-melt interaction and cooling processes.

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