

Lithium Isotopic Geochemistry in Subduction Zones: Retrospects and Prospects

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Abstract: Subduction zones involve many complex geological processes, including the release of slab-derived fluids, fluid/rock interactions, partial melting, isotopic fractionations, elemental transporting, and crust/mantle interactions. Lithium (Li) isotopes (^6Li and ^7Li) have relative mass difference up to 16%, being the largest among metal elements. Thus, Li isotopes have advantage to interpret trace various geological processes. Most importantly, during crust/mantle interactions in deep subduction zones, surface materials and mantle rocks usually have distinct Li isotopic compositions. Li isotopes can be potential tracer for subduction processes, from the onset of subduction to the release of Li from subducted slabs and interaction with mantle wedge, as well as the fate of Li in slab-derived fluids and residual slabs. Moreover, the Li isotopic composition of subducting output materials can provide useful information for understanding global Li circulation. With developments in measurement and expansion of Li isotopic database, Li isotopic geochemistry will provide more inference and be a powerful tracer for understanding subduction-related processes. This work retrospected the application of Li isotopes in tracing successive subduction processes, and made some prospects for further studies of Li isotopes.

Key words: subduction zone, Li isotopes, subduction-related processes, Li geological tracer

1 Introduction

Early studies on Li isotopes started in 1930s (Lewis and Macdonald, 1936; Taylor and Urey, 1937, 1938). Li is the lightest lithophile element and its atomic number is 3, with two stable isotopes of ^6Li and ^7Li (terrestrial abundances are 7.5% and 92.5%, respectively). The large relative mass-difference (up to 16%) between ^6Li and ^7Li can generate large isotopic fractionation in various geological processes, making variation of terrestrial $\delta^7\text{Li}$ range from -20‰ to 40‰ (Rudnick et al., 2004). The currently accepted expression of Li isotopic composition is the $\delta^7\text{Li}$ notation: $\delta^7\text{Li}(\text{‰}) = [({}^7\text{Li}/{}^6\text{Li})_{\text{sample}}/({}^7\text{Li}/{}^6\text{Li})_{\text{standard}} - 1] \times 1000$. The Li isotopic standard (L-SVEC) is pure Li_2CO_3 provided by the American national standards institute of technology (NIST), and its value determined by various laboratories is: ${}^7\text{Li}/{}^6\text{Li} = 12.02 \pm 0.03$ (Flesch et al., 1973), 12.039 (Chan et al., 1992), 12.019 (Decitre et al., 2002), or 12.119 (Kobayashi et al., 2004). Concerning the measurement of Li isotopic composition, the development of MC-ICP-MS offers new opportunities for low-Li

materials to be analyzed with high precision of $\pm 0.24\text{‰}$ (Millot et al., 2004), $\pm 0.20\text{‰}$ (Huang et al., 2010), $\pm 0.30\text{‰}$ (Gao and Casey, 2012), $\pm 0.25\text{‰}$ (Lin et al., 2016). In recent years, spectacular progress have been achieved on the studies of Li isotopic composition of various geological reservoirs. In this review, the Li isotopic composition of major geological samples in nature are summarized (Fig. 1).

Li exists in minerals, melt and fluids as 1^+ valence of cation. As a trace element, Li content of most minerals is low, but some minerals such as biotite, cordierite and alkali feldspar have higher Li content (tens to hundreds of ppm); Li even occurs as major elements in certain minerals, like spodumene and petalite. As a medium incompatible element, Li preferentially enters into silicate melt phase over solid phases during partial melting, making Li enrichment in crustal rocks during crust–mantle differentiation (Teng et al., 2008). As a fluid mobile element (FME), Li is preferentially enriched in fluid phases, accompanying significant Li isotopic fractionation when involved fluid activities, e.g., oceanic crust alteration and slab dehydration (Brenan et al., 1998).

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Moreover, Li has high diffusion rates in minerals and melt, with ^6Li diffusing 3‰ faster than ^7Li in melt (Richter et al., 2003). Based on these properties, Li isotopes have been widely applied to tracing continental weathering (Rudnick et al., 2004; Teng et al., 2010; Lechler et al., 2015), hydrothermal system (Henchiri et al., 2014; Pogge von Strandmann et al., 2016), magmatic activities (Gao et al., 2011; Weyer and Seitz, 2012; Sun et al., 2016), various geological processes associated with mantle (Seitz et al., 2004; Aulbach and Rudnick, 2009; Ackerman et al., 2013; Su Benxun et al., 2016). Combining stable isotopes with ore deposit (Pei Yingru et al., 2016; Li Bo et al., 2016), there are several examples of Li isotopic application in the genesis of ore deposit (Chan et al., 2007; Su Yuanna et al., 2011). In addition, Li zoning in minerals can be used as a geospeedometer (Jeffcoate et al., 2007; Gao et al., 2011; Trail et al., 2016). Recently, Li isotopes play a more important role in researches on plate subduction and crust/mantle material cycling processes, e.g., using Li isotopes to trace the evolution of fluids, mass transfer in subduction zones, the recycle of slab-derived materials (Simons et al., 2010; Caciagli et al., 2011), and trace subduction-related water-rock interactions (Chan et al., 2002a; Wunder et al., 2006). In particular, experimental studies on Li isotopic fractionation between mineral phases provide important information for the genesis of Li isotopic compositions of metamorphic rocks in subduction zones.

Previously, there have been a few reviews about progress on the geochemical properties of Li isotopes and the application of Li isotopes in tracing various geological processes. Tomascak (2004) for the first time summed the developments in the understanding and application of Li isotopes in the Earth and Planetary Sciences and the Li isotopic compositions of various geological reservoirs. Combining Li isotopic composition of materials from mantle, Elliot et al. (2004) reviewed the terrestrial Li isotopes cycle and the distribution of recycled materials in mantle and its tracing significance of mantle convection. Afterwards, summary of the application of Li isotopes in tracing various geochemical processes, e.g., continental weathering, crust/mantle recycling, and the convective mantle was made by Tang et al. (2007). There also have been several reviews about the mechanism of Li isotopic fractionation (Tang Yangjie et al., 2009), the characteristics of Li isotopes in subduction zones (Li Zhenzhen et al., 2010), the new progress in geological application of Li isotopes (Qin Delin et al., 2011), and recent reviews about the advances in Li isotopic geochemistry (Tomascak et al., 2016; Penniston-Dorland et al., 2017). These publications have contributed to sketchy understanding of the geochemical features of Li

isotopes, nevertheless most researchers paid attentions to Li geochemical behavior in a single geological process but rarely to a sequential set of subduction processes. This paper aims to make an overview concerning using Li isotopes to trace the successive subduction processes, including the Li isotopic composition of subducted materials, geochemical behavior of Li isotopes during subduction dehydration and interactions involving slab-derived fluids and mantle wedge rocks, Li isotopic composition and its indicative significance of subduction-related metamorphic rocks.

2 Isotopic Characteristics of Li in Oceanic Subduction Zone

Subduction plays an important role in crust/mantle interactions and materials recycling. Based on the nature of subducted plates, subduction zones can be classified into two types: oceanic subduction and continental subduction. The sketchy oceanic subduction processes are: surficial materials (crustal materials and possible hydrated mantle rocks) are drawn into subduction zones and undergo series of metamorphic and chemical alteration at the deep earth; during subduction, fluids (or melts) released from the subducting slab will trigger partial melting and generate arc magmas and ultimately form new continental crust (Taira et al., 1998).

2.1 Oceanic subduction zone

Figure 2 shows the Li isotopic composition of major geological reservoirs involved in oceanic subduction: oceanic sediments, altered oceanic crust, oceanic lithosphere mantle, mantle wedge and continental crust above the subducting slab.

2.1.1 Subducted oceanic sediments

Subducted sediments play an important role in crust-mantle recycling and arc magmatism. Global subducted sediments (GLOSS) are dominated by terrigenous materials (mature continental sources, volcanic sources, organic-rich turbidites) and pelagic sediments (chert, chalk, red clays, hydrothermal clays, mixed lithologies) (Plank and Langmuir, 1998). These sediment types have distinct Li compositions. Pelagic sediments have extremely high Li content while biogenic siliceous rocks and carbonate have relative low Li content (Hoefs and Sywall, 1997); Li content of clay minerals is up to 80 ppm, while that of terrigenous sediments is lower (24 ppm) and of sedimentary carbonates is the lowest (< 5 ppm) (Chan and Hein, 2007). Mineral assemblages may control the bulk Li budget of subducted sediments, especially clay minerals, e.g., Li sorption onto Mn- and

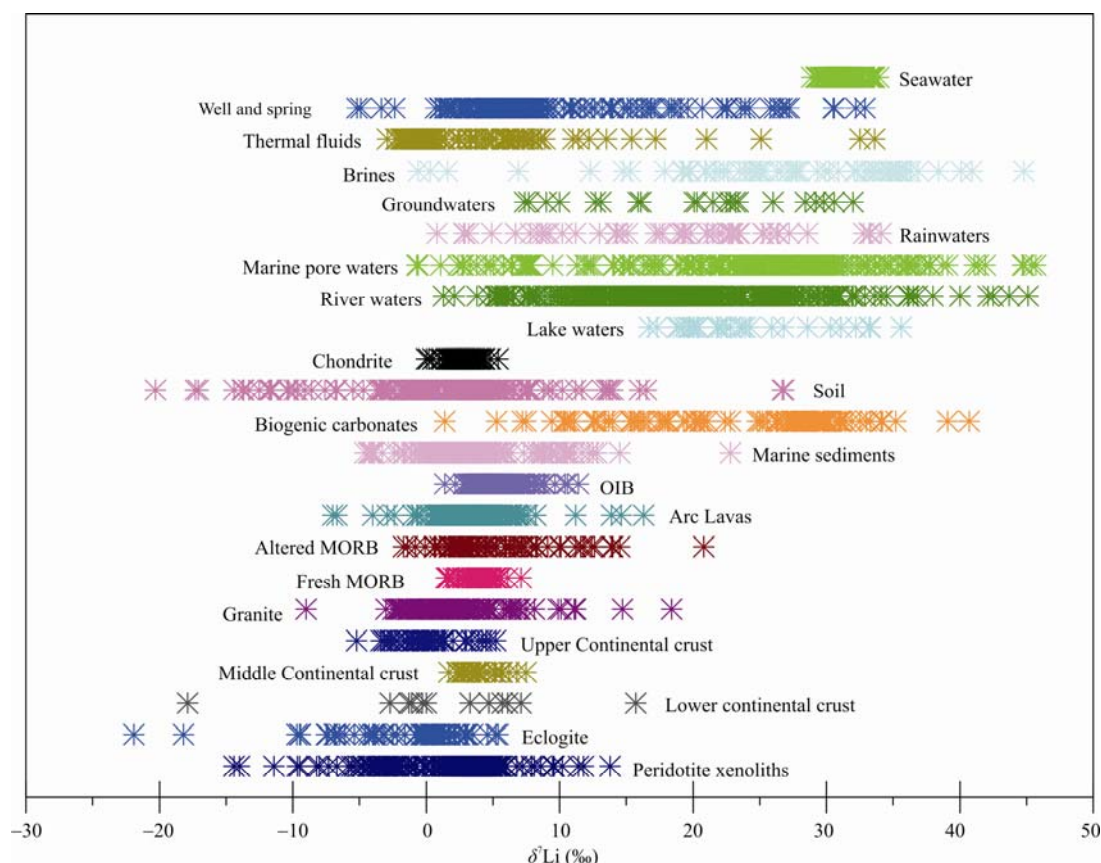


Fig. 1. Li isotopic composition of various reservoirs.

Data sources: Peridotite xenoliths (Not including mineral separates) (Seitz et al., 2004; Brooker et al., 2004; Magna et al., 2006a, 2008; Jeffcoate et al., 2007; Tang et al., 2007; Ionov and Seitz, 2008; Hanama et al., 2009; Kil, 2010; Pogge von Strandmann et al., 2011; Gao et al., 2011; Ackerman et al., 2013; Medaris et al., 2015; Lai et al., 2015); Eclogite (Zack et al., 2003; Marschall et al., 2007b; Penniston-Dorland et al., 2010; Simons et al., 2010; Xiao et al., 2011); Lower crust xenoliths (Teng et al., 2008); Middle crust xenoliths (Teng et al., 2008); Upper crust (Teng et al., 2004, 2008); Granite (Bottomley et al., 2003; Pistiner and Henderdon, 2003; Teng et al., 2004, 2006a, 2009; Kısakürek et al., 2004; Rudnick et al., 2004; Bryant et al., 2004; Marks et al., 2007; Millot et al., 2007b; Magna et al., 2010; Godfrey et al., 2013; Romer and Meixner, 2014); Fresh MORB (Moriguti and Nakamura, 1998b; Chan et al., 1992; Chan and Frey, 2003; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008; Brant et al., 2012); Altered MORB (Chan et al., 1992, 2002b; Bouman et al., 2004; Brant et al., 2012); Arc lavas (Moriguti and Nakamura, 1998b; Tomascak et al., 2000, 2002a; Chan et al., 2002b; Leeman et al., 2004; Moriguti et al., 2004; Magna et al., 2006b; Agostini et al., 2008; Košler et al., 2009; Walker et al., 2009; Janoušek et al., 2010; Tang and Rudnick, 2014a); OIB (James and Palmer, 2000; Pistiner and Henderson, 2003; Chan and Frey, 2003; Kobayashi et al., 2004; Ryan and Kyle, 2004; Nishio et al., 2005, 2007; Chan et al., 2009; Vlastelic et al., 2009; Schuessler et al., 2009; Janoušek et al., 2010; Magna et al., 2011; Krienitz et al., 2012; Genske et al., 2014); Marine sediments (Zhang et al., 1998; James et al., 1999; Chan and Kastner, 2000; Chan et al., 2006; Leeman et al., 2004; Bouman et al., 2004; Tang and Rudnick, 2014a); Marine biogenic carbonates (Huh et al., 1998; Hoefs and Sywall, 1997; Chan and Kastner, 2000; Marriott et al., 2004; Hall et al., 2005; Hathorne and James, 2006); Soil (Pistiner and Henderson, 2003; Chan (unpublished data, 2003); Kısakürek et al., 2004; Rudnick et al., 2004; Huh et al., 2004; Pogge von Strandmann et al., 2012; Ryu et al., 2014; Tsai et al., 2014); Chondrites (James and Palmer, 2000; McDonough, 2003; Sephton et al., 2004, 2006, 2013; Magna et al., 2006a; Seitz et al., 2007; Pogge von Strandmann et al., 2011); Lake waters (Falkner et al., 1997; Chan and Edmond, 1988; Tomascak et al., 2003; Witherow et al., 2010); River waters (Falkner et al., 1997; Hul et al., 1998, 2001; Tomascak et al., 2003; Kısakürek et al., 2005; Pogge von Strandmann et al., 2006, 2010, 2016; Vigier et al., 2009; Wimpenny et al., 2010; Millot et al., 2010c; Witherow et al., 2010; Liu et al., 2011; Liu and Rudnick, 2011; Rad et al., 2013; Henchiri et al., 2014; Bagard et al., 2015; Dellinger et al., 2015; Wang et al., 2015); Marine pore waters (Zhang et al., 1998; James et al., 1999; James and Palmer, 2000; Chan and Kastner, 2000; Scholz et al., 2009, 2010, 2015; Misra and Froelich, 2012; Pogge von Strandmann et al., 2012); Rainwaters (Pistiner and Henderson, 2003; Millot et al., 2010c; Pogge von Strandmann et al., 2006, 2010; Witherow et al., 2010; Clergue et al., 2015); Groundwaters (Tomascak et al., 2003; Hogan and Blum, 2003; Pogge von Strandmann et al., 2006; Bagard et al., 2015); Brines (Bottomley et al., 1999, 2003; Chan et al., 2002b; Scholz et al., 2010; Godfrey et al., 2013); Thermal fluids (Chan et al., 1993; Falkner et al., 1997; Sturchio and Chan, 2003; Foustoukos et al., 2004; Millot et al., 2007b, 2012; Mottl et al., 2011; Henchiri et al., 2014; Bernal et al., 2014); Well and spring (Tomascak et al., 2003; Kısakürek et al., 2005; Kloppmann et al., 2009; Lemarchand et al., 2010; Millot et al., 2010a; Nishio et al., 2010; Pogge von Strandmann et al., 2006, 2010; Rad et al., 2013; Godfrey et al., 2013); Seawater (Chan, 1987; Chan and Edmond, 1988; You and Chan, 1996; Moriguti and Nakamura, 1998a; Tomascak et al., 1999a; James and Palmer, 2000; Pistiner and Henderson, 2003; Bryant et al., 2003; Millot et al., 2004, 2010a; Kısakürek et al., 2004; Bouman et al., 2004; Jeffcoate et al., 2004; Hall et al., 2005; Romer et al., 2005; Wunder et al., 2006; Rosner et al., 2007; Witherow et al., 2010; Choi et al., 2010; Misra and Froelich, 2012; Nishio and Nakai, 2002; Nishio et al., 2010, 2015).

Fe-oxyhydroxide surfaces (Millot et al., 2010b), illite and sericitic muscovite mainly bounding exchangeable Li and chlorite and illite/sericite hosting structurally-bound Li, making chlorite-rich sedimentary rocks have distinctly

high Li contents (Romer and Meixner, 2014). As a whole, average Li content of marine sediments is higher than that of oceanic basalts; the reported highest Li content of subducting oceanic sediments is up to 79.2 ppm (Chan et

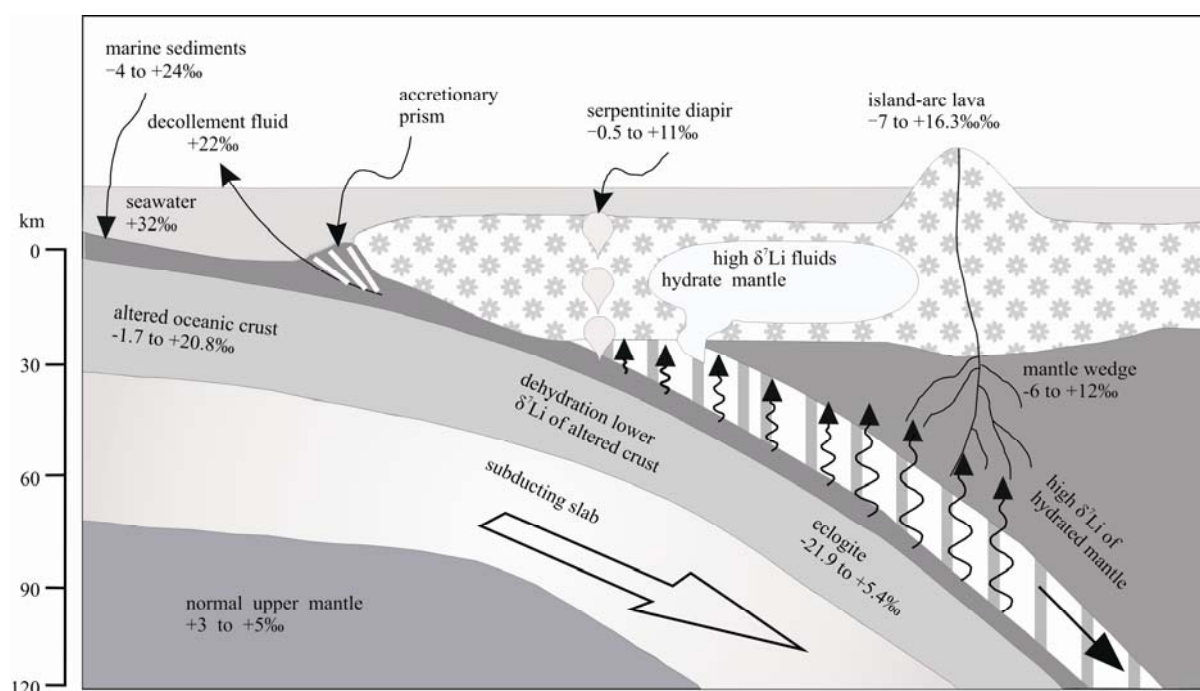


Fig. 2. Schematic illustration of Li isotopic composition in oceanic subduction—zone setting (after Tang et al., 2010).

Data source: Marine sediments, altered oceanic crust, ultramantic mantle, island arc lavas, eclogite (as shown in Fig. 1); Others see Tang et al. (2010).

al., 2006). Meanwhile, the Li isotopic composition of subducting sediments varies largely and is mainly controlled by terrigenous clastic, clay minerals and the relative ratio of marine carbonates. Because terrigenous sediments inherit the Li isotopic characteristics of continental crust rocks, its $\delta^7\text{Li}$ value range from 0 to 6‰; $\delta^7\text{Li}$ of clay minerals and turbidite is lower and ranges from -1.6‰ to 5‰; biogenic materials (mainly biogenic carbonates) have lower Li content but higher $\delta^7\text{Li}$ value (1.4‰–40.7‰); $\delta^7\text{Li}$ of sedimentary carbonates varies largely, ranging from -4.1‰ to 24.3‰ (Table 1). The variations of regional stratigraphy in different oceans may cause geochemical variations among the subducting sediments. In Table 1, we have made a summary of Li content and isotopic composition of subducted lithologies.

Obviously, varying lithological types of subducting sediments results in distinct Li inputs to subduction zones.

2.1.2 Subducted altered oceanic basalts

Compared to fresh MORB ($[\text{Li}] = 2.8\text{--}13.2$ ppm, $\delta^7\text{Li} = 1.5\text{‰--}6.1\text{‰}$), altered basalts have more variable Li contents (0.6–33.1 ppm) and large $\delta^7\text{Li}$ ranges (-2‰–20.8‰) (Table 1). Most previous studies have ascribed these differences to two processes: seawater and hydrothermal alteration. During seawater alteration, uptake of seawater Li into alteration clays results in Li isotopic fractionation between newly formed clay minerals and the seawater, with $\Delta_{\text{clay mineral-seawater}}$ ranging from 16‰ to 19‰ (Chan et al., 2002c). Therefore, $\delta^7\text{Li}$ values of altered oceanic basalts could be largely affected by the

Table 1 The Li content and Li isotopic composition of initial subducting lithologies

Marine sediments			
Sediment types	Li content (ppm)	$\delta^7\text{Li}$ (‰)	Data source
Terrigenous clastic	24	0–6	Chan and Kastner, 2000; Chan et al., 2006; Leeman et al.,2004; Bouman et al., 2004
Clay material	80	−1.6–5	
Sedimentary carbonate	<5	−4.1–24.3	Chan et al., 1997; Hul et al., 2001; Tomascak et al.,2003; Chan et al., 2006; Millot et al., 2007; Négrel et al., 2010; Tsai et al., 2014
Biogenetic material	extremely low	1.4–40.7	Huh et al., 1998; Hoefs and Sywall, 1997; Chan and Kastner, 2000; Marriott et al., 2004; Hall et al., 2005; Hathorne and James, 2006
Fresh and Altered basalts			
Fresh MORB	2.8–13.2	1.5–6.1	Moriguti and Nakamura, 1998; Chan et al., 1992; Chan and Frey, 2003; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008; Brant et al., 2012
Seawater alteration basalts	6.6–33.1	−1.7–20.8	Chan et al., 1992, 2002c; Zack et al., 2003; Bouman et al., 2004; Brant et al., 2012;
Hydrothermal alteration basalts	low to 0.6 ppm	−1.6–4.0	Verney–Carron et al., 2015
Gabbro and Peridotite			
Gabbro	1.5	4.3	Niu et al., 2004; Decitre et al., 2004; Benton et al., 2004; Vils et al., 2008
Peridotite	Altered: 13.7	8	
	Normal: 4	4	

types and amount of the newly formed clay minerals. Moreover, alteration temperature is another key factor: low-T altered oceanic crust with Li content of 6.6 to 33.1 ppm (mostly 10.4–21.8 ppm), higher than that of unaltered basalts (2.8–13.2 ppm); meanwhile, $\delta^7\text{Li}$ values of low-T alteration oceanic basalts (1.7‰–20.8‰) is generally much higher than that of unaltered MORB. In contrast, the influence of high-T alteration on Li content and $\delta^7\text{Li}$ value of basalts is estimated to be less than that of low-T alteration, e.g., $\delta^7\text{Li}$ value of high-T alteration oceanic crust (–2‰–8‰) is significantly lower than that of low-T alteration oceanic basalts (Zack et al., 2003). Consequently, both low-T and high-T alteration may change the Li isotopic composition of oceanic basalts. On the other hand, if oceanic basalts are altered by hydrothermal fluids, both Li content and $\delta^7\text{Li}$ of the rocks would decrease. For example, the Li content of hydrothermally altered basalts is as low as 0.6 ppm (Chan et al., 2002c), and $\delta^7\text{Li}$ value of hydrothermally altered basalt from ODP Site1256 (EPR) varies largely, its $\delta^7\text{Li}$ value is low to –1.6‰ at 1350 mbsf (Gao et al., 2012). However, the water-rock ratio (w/r) together with variation of temperature make the mechanism of hydrothermal alteration complicated. Contrast to previous researches, Verney-Carron et al. (2015) show the $\delta^7\text{Li}$ values of deep high-T (300°C) hydrothermally altered basalts (1.9‰–4.0‰) is similar to that of unaltered

basalts, whereas $\delta^7\text{Li}$ of shallow low-T (150–270°C) hydrothermally altered basalts (1.9‰–3.1‰) is slightly lower (Fig. 3).

2.1.3 Subducted gabbro and peridotite from the bottom of oceanic crust

Main lithological units in the bottom of oceanic crust consist of gabbro and peridotite. The former is more resistant to be affected by seawater alteration than the latter. Researchers usually select alteration-free peridotites to infer the Li composition of the bottom oceanic crust. For example, serpentine-free peridotites from Gakkel Ridge have very similar Li contents (1.6–2.7 ppm) and $\delta^7\text{Li}$ values (3‰–5‰) to reported normal pristine ‘MORB mantle’ values (Gao et al., 2011). Previous studies have shown Li is preferentially incorporated into olivine (1–2 ppm) in mantle peridotites (Seitz and Woodland, 2000), making peridotite being an important carrier of Li during crust-mantle interaction. If peridotite has been modified by Li-rich fluids or melts, its Li contents would increase (up to 18.9 ppm) and $\delta^7\text{Li}$ values might vary largely (–9.7‰–14‰) (Fig. 1 Peridotite xenoliths). For example, when fluids circulate deeply into oceanic crust, serpentine preferentially incorporates lighter Li isotope (^6Li), causing serpentines with relatively low $\delta^7\text{Li}$ values and high Li contents while fluids becoming isotopically heavier (Decitre et al., 2002); meanwhile, at low temperatures, the

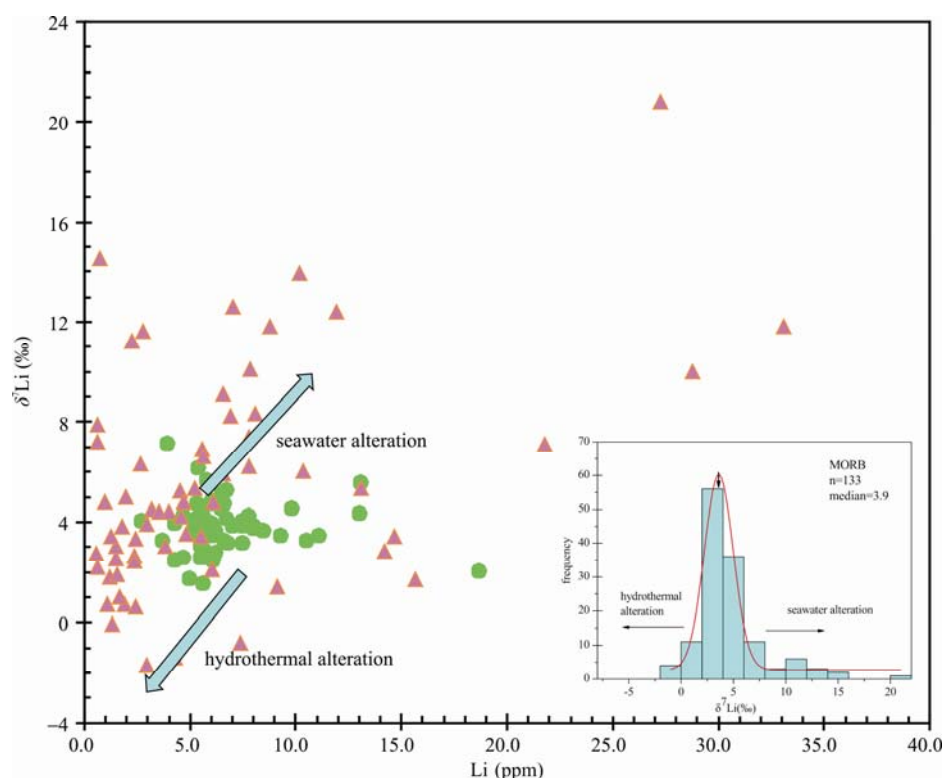


Fig. 3. Li isotopic composition of Fresh and Altered basalts.

The circle symbols represent fresh MORBs and the triangle is altered MORBs, data source is same with MORB in Fig. 1.

uptake of Li by clay minerals may result in a greater range in both Li concentration (0.6–18.9 ppm) and Li isotopic composition (–6.1‰ to 14‰) in bulk serpentinized peridotite (Decitre et al., 2002; Benton et al., 2004). Serpentinized peridotite serve as a key repository and carrier of light elements (Li, B, Be), the fractionation mechanism of Li isotopes during serpentinization needs more attention. Vils et al. (2008) reported that the Li contents of serpentinite depend on the degree of serpentinization and its thickness: if serpentinite forming at relatively old oceanic crust (75 Ma) with rapid expansion, Li contents from serpentinites account for 16% of the whole oceanic lithosphere; If serpentinite forming at young oceanic crust (1 Ma) with fast expansion, its Li contents are minor, so the contribution of Li contents from serpentinites to the whole oceanic lithosphere is negligible; for thinner oceanic crust with slow expansion, Li contents of serpentinites even account for 20% of Li content of the whole oceanic lithosphere. According to these results, peridotites with various extent of serpentinization will carry different amount of Li input to subduction zones.

2.2 Li isotopic characteristics of continental subduction zone

The concept of ‘continental subduction’ was set up much later than oceanic subduction. In the last thirty years, the global discovery of coesite- and/or diamond-bearing UHP terranes in continental collision zones, especially numerous studies on the crust/mantle interaction, the recycling of subducted materials, and the exhumation of subducted continental crust, have greatly contributed to the development of global chemical geodynamics and tectonic theory of continental subduction (Zheng et al., 2012 and references therein). Comparing with oceanic subduction, continental crust was firstly believed to hardly subduct to mantle depths because of its lower density relative to oceanic crust. In addition, continental crust (average 33 km in thickness) is much thicker than oceanic crust and its composition is more complex. Therefore continental subduction geological processes are more complicated. Although Alpine-Himalayan orogenic belt and Dabie-Sulu orogenic belt have been extensively studied, most studies have focused on the oceanic subduction zones but rarely on the continental subduction (Hermann and Rubatto, 2009; Zheng Yongfei et al., 2013).

The continental crust normally consists of three layers from the top down: upper crust (12 km), which mainly consists of surface soil, sedimentary rocks and intrusive granitic rocks; middle crust (11 km) consists of tonalite, granitic gneiss and amphibolite; lower crust (14 km) consists of felsic granulite and mafic granulite. The Li

composition of these three layers of continental crust is slightly different from each other. Firstly, average Li content of upper continental crust is about 35 ppm, and $\delta^7\text{Li}$ is $0\pm 2\text{‰}$ (Teng et al., 2004). Upper crust contacts with various surficial spherical layers (eg., hydrosphere, atmosphere, biosphere), and is easy to be weathered. For example, during continental weathering, ^7Li preferentially entering into fluids results in apparently heavy $\delta^7\text{Li}$ values of river (1.3‰ – 45.1‰) (Fig. 1), however, $\delta^7\text{Li}$ values of rivers may be affected by many factors, such as their bedrocks in drainages, weathering intensity and weathering rates. Accordingly, $\delta^7\text{Li}$ of river waters can provide some information for weathering intensity of continental rocks: relatively low $\delta^7\text{Li}$ values of river waters (4.7‰ – 12.9‰) from Qinghai-Tibet Plateau probably reflect less weathering intensity in this arid and cold region (Liu et al., 2011), $\delta^7\text{Li}$ values of river waters from Rio Negro (1.3‰ – 6.5‰) reflect its seasonal changes (Dellinger et al., 2015). Therefore, constant input of materials with relative high $\delta^7\text{Li}$ value to ocean is an important part of surface geochemical cycle of Li isotopes, and continuing continental weathering leads to $\delta^7\text{Li}$ of continental crust becoming lighter than mantle and oceanic crust. Secondly, Li content of middle crust (12 ppm) is significantly lower than upper crust (Rudnick and Gao, 2003), afterwards, Teng et al. (2008) show the Li content of middle crust vary largely from 5 to 33 ppm, with an average value of 12 ppm; and $\delta^7\text{Li}$ value range from 1.7‰ to 7.5‰ , average $\delta^7\text{Li}$ value is $4.0\text{‰}\pm 1.4\text{‰}$, this limited variation may indicate the Li isotopic composition of middle crust is relative homogeneous. Li content of inclusions from lower crust granulite is about 8 ppm and their $\delta^7\text{Li}$ values range largely from -14.0‰ to 14.3‰ , and average $\delta^7\text{Li}$ value is 2.5‰ (Teng et al., 2008), in contrast to middle crust, this large variation may reflect that the Li isotopic composition of lower crust is heterogeneous, but the reason is still unclear. By weighted average calculation, the average Li content and $\delta^7\text{Li}$ value of continental crust are 18 ppm and 1.2‰ , respectively (Teng et al., 2008); By weighted mean of all granites, the average $\delta^7\text{Li}$ value of the continental crust is 1.7‰ (Teng et al., 2009). Overall, Li isotopic composition of subducted continental crust is greatly different from subducted oceanic crust (Table 2), but both have Li content much higher than the asthenospheric mantle.

Currently, most studies on Li isotopes of continental crust is about the Li isotopic composition of granite. Granite is the most important component of the upper continental crust, they are natural samples to study the interior processes of the earth (Zhang Shanhui et al., 2016; Ma Liyan et al., 2016). And Li isotopic characteristics of granite can provide information for the geochemical behavior of Li during crustal anatexis, magmatic crystallization and

Table 2 The Li isotope system of the earth (After Teng et al., 2008)

Reservoir	Mass (10^{22} kg)	Mass ratio (%)	Li (ppm)	Li (%)	$\delta^7\text{Li}$ (‰)
Continental crust					
Upper crust	0.63	0.16	35	3.4	0
Middle crust	0.59	0.14	12	1.1	4
Lower crust	0.78	0.19	8	1	2.5
Main reservoir of the whole silicate earth					
Hydrosphere	0.2	0.049	0.2	0.006	30
Continental crust	2	0.49	18	5.5	1.2
Oceanic crust	0.6	0.15	10	0.93	5
Hydrosphere+Continentalcrust+Oceanic Crust	2.82	0.7	15	6.4	1.8
Mantle	404.3	99.3	1.5	93.6	4
Silicate earth	407.1	100	1.6	100	3.9

differentiation. They are important samples to reflect 'source regions' features of magmas. For example, Li isotopic compositions of S-Type granites show no obvious variation in $\delta^7\text{Li}$ values (-1.1‰ to -1.4‰), suggesting that isotopic fractionation is less than analytical uncertainty during crustal anatexis and subsequent differentiation (Teng et al., 2004). And isotopically heavier I-Type granites with a narrow range of $\delta^7\text{Li}$ (-1.15‰ to 0.52‰) suggests these rocks most likely have been generated by melting of basic meta-igneous, lower crustal lithologies with limited contribution of mantle-derived magmas; however, S-suite (-2.3‰ to 7.0‰) from the Western Carpathians, Slovakia, displays considerable variability of $\delta^7\text{Li}$ probably resulting from melting of a heterogeneous source dominated by metasedimentary lithologies; Meantime, the West-Carpathian A-Type granites' Li isotopic composition (1.2‰ to 6.8‰) more favour melting of subduction-modified mantle segments but not remelting of granulitic residues, anatexis of felsic-intermediate calc-alkaline meta-igneous crust or extensive fractional crystallization from mantle-derived magmas (Magna et al., 2010). On the other hand, recent studies have indicate crustal anatexis by incongruent melting may result in significant Li isotopic fractionations between the leucogranitic melt and the garnet rich restite, suggesting the complex behavior of Li isotopes in granitic rocks (Sun et al., 2016). Nevertheless, Li isotopic composition of continental crust maybe an important window to get a glimpse of Li composition of deep earth and provide insight to geochemical signature of Li in magmatic processes.

3 Li Isotopic Composition of Slab-Derived Fluids and Residual Slab

During subduction and concomitant dehydration, ^7Li preferentially partitioning into fluids over mineral phases at metamorphic conditions leads to Li isotopic fractionation between slab-derived fluids and residual slab.

3.1 Li isotopic characteristics of slab-derived fluid

When the plates go down beneath deep-sea trenches,

with temperature and pressure increasing, certain hydrous minerals will gradually breakdown. During this process, FMEs will be expelled from subducting slabs and dissolved in aqueous fluid phases. Li has been shown to be a soluble element both naturally (Ryan and Langmuir, 1987, 1993) and experimentally (Brenan et al., 1998). Based on these properties, Marschall et al. (2006) studied the partitioning and budget of Li in high-pressure metamorphic rocks and established sets of inter-mineral partition coefficients for Li among 15 different high-pressure minerals. Combining with Brenan et al. (1998)'s results, they calculated partition coefficients of Li between 15 silicates and fluids. According to their studies, Li is mainly existed in hydrous minerals such as chlorite, glaucophane, clinopyroxene, phengite and phlogopite. Figure. 4a shows the type and proportion of each Li-rich phases change with metamorphic-grade increasing. According to previous studies, the loss of Li amount from a subducting slab maybe mainly controlled by two factors: one is mineralogy of rocks, especially, the stability of Li-rich phases; the other is the potential sequestration of Li released during the breakdown of one phase by a newly formed other phases (e.g., Marschall et al., 2006; Romer and Meixner, 2014). The releasing mechanism of Li is complicated, and some other aspects influencing this process may has not yet been explored by geochemists.

There have been many studies on geochemical behavior of Li isotopes during subduction dehydration (Zack et al., 2003, Marschall et al., 2007b, Xiao et al., 2011; Su Benxun et al., 2016), in particular, on the maximum dehydration depth which directly control the depth of Li released from slabs. The results of hydrothermal experiments show that Li is progressively other than instantaneously released to fluid phases (Chan et al., 1994). Collectively, the amount of Li released from subducted slabs may associate with the amount of sediments being subducted and the thermal structure of subduction zones, eg., cool slabs could transport Li to greater depth (Moriguti and Nakamura, 1998b). Concerning the mobility of Li, Bebout et al. (1991) inferred from studies concerning FMEs that Li is the least

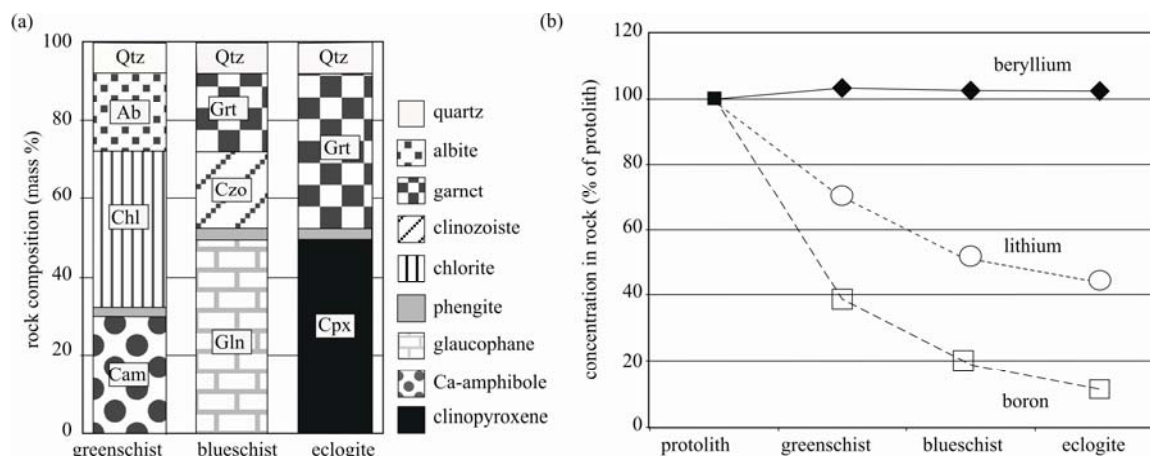


Fig. 4. (a), Mineral composition in different metamorphic facies; (b) The concentrations of Li, Be, B relative to initial value change in different metamorphic stages (After Marschall et al., 2006).

mobile relative to other fluid mobile elements. Experimental studies from Jahn and Wunder (2009) showed that coordination number of Li varies with density of fluids. Subsequent theoretical calculation also confirmed that density of slab-derived fluids changes with increasing depth of subduction (Caciagi et al., 2011). If the Li partition behavior will change with depth, then Li isotopic composition of fluid released from different depth is probable incongruous: $\delta^7\text{Li}$ of fluids released from shallow depths may be higher than that of deeper fluids. Recently, Ryu et al. (2014)'s studies show that Li is less mobile than other alkali metal elements, consisting with early results and leading to selectively retained Li to greater depths than other FMEs (eg., Be, B) (Fig. 4b). Anyway, the geochemical behavior of Li isotopes is very intricate during subducted slab dehydration; up to date, there is yet no consistent cognition about this issue. Further detailed studies are needed in the future.

3.2 Li isotopic characteristics of subducted slab

During progressive dehydration, metamorphism, and possible partial melting in subduction zone, there is no consistent conclusion whether Li isotopic fractionation occurs or not and the fractionation factor is also under discussion. Previous studies have shown the main factors affecting Li isotopic fractionation include temperature, mineral/fluid partition coefficient and diffusion coefficient of Li in rocks or minerals (Seyfried et al., 1998; Brenan et al., 1998; Coogan et al., 2005). Currently, much attention has been paid to Li isotopic fractionation during subduction, which provided important information for us to get understanding of Li isotopic characteristics of the subducted slab (Zack et al., 2003; Marschall et al., 2007b; Xiao et al., 2011; Su Benxun et al., 2016).

Most components (sediments, altered oceanic crust) entering subduction zones have heavy Li isotopic

compositions compared with MORBs. But eclogites, as an analog for subducted oceanic crust because of their similarity in terms of major element fractionation trends and concentration patterns of immobile trace elements (Zack et al., 2002), have significantly lower $\delta^7\text{Li}$ values (-1.7‰) than normal MORB ($3.7\text{‰} \pm 1.0\text{‰}$) (Fig. 1). The pioneer work of Zack et al. (2003) firstly reported eclogites derived from basaltic protoliths have very low $\delta^7\text{Li}$ values (-11‰ to 5‰). By calculated Li concentration and Li isotopic composition of residual slab (eclogite) by the open-system Rayleigh model (Fig. 5a), they concluded Rayleigh distillation during dehydration of chlorite and/or clays can greatly lower the $\delta^7\text{Li}$ values of subducted slab. Thus, aqueous fluid derived from subducted slabs have heavier Li isotopic composition with large range of $\delta^7\text{Li}$, whereas $\delta^7\text{Li}$ of residual plate is lower than its surrounding mantle rocks (Zack et al., 2003). These light recycled slab materials have been traced in some magmatites of mantle origin (Chan and Frey, 2003; Agostini et al., 2008; Tian et al., 2015) and peridotites from worldwide localities (Nishio et al., 2004; Ackerman et al., 2013; Tang Yanjie et al., 2014; Gu et al., 2016) with negative $\delta^7\text{Li}$ values. Even though there have been many studies about geochemical behavior of Li during subduction, whether Li isotopes fractionate significantly or not is still inconclusive. Despite using Rayleigh distillation to model Li isotopic fractionation during dehydration is very simple, it neglects the possibility of kinetic Li isotopic fractionation and only fits for initial shallow low-T dehydration. In deep high-T dehydration processes, more experimentally and naturally evidence are urgently in need.

However, using the experimental parameters of Wunder et al. (2006), Marschall et al. (2007b) simulated geochemical behavior of Li during metamorphic dehydration, finding that the whole metamorphic dehydration processes can only lower the $\delta^7\text{Li}$ values of the subducted slab by a maximum

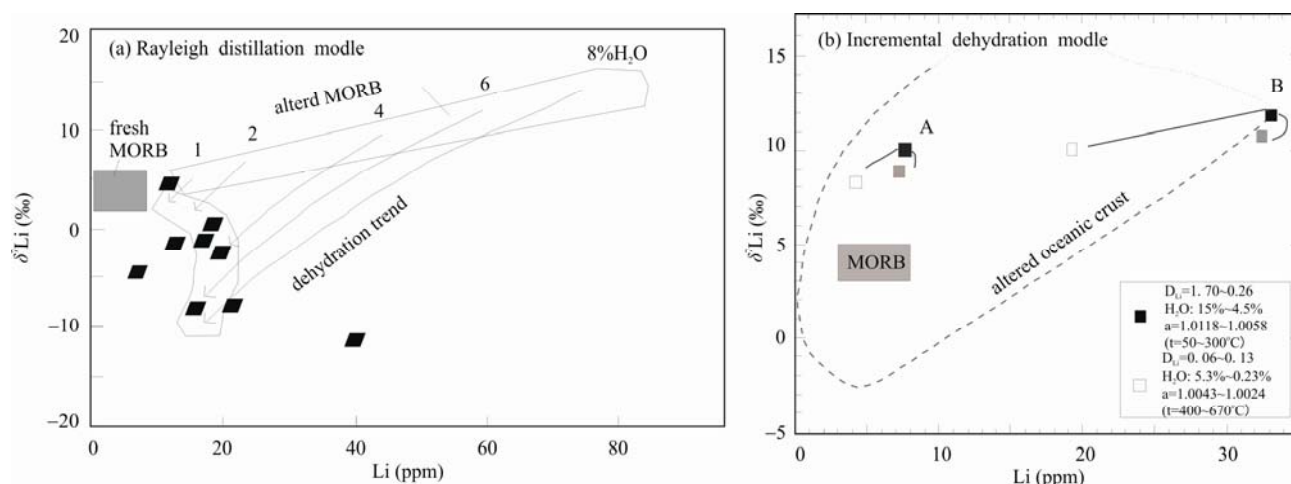


Fig. 5. (a), Rayleigh fractionation model of Li isotope; (b), Dehydration fractionation model of Li isotope under different temperature and pressure (after Marshall et al., 2007b).

of 3‰ (Fig. 5b). That means, if their basaltic protolith having an average $\delta^7\text{Li}$ value of 4‰, $\delta^7\text{Li}$ value of subducted rocks should not be lower than 1‰ after subduction dehydration. Consistently, some recent studies show subducted sedimentary rocks have no major changes in the chemical and Li-isotopic compositions during subduction (Abdelfadil et al., 2014); studies of metamorphic nappes of volcano sedimentary protoliths show $\delta^7\text{Li}$ remains little fractionated by low-grade metamorphism because most Li in sedimentary rocks is structurally bounded (Romer and Meixner, 2014). These studies may further support Marshall et al. (2007b)'s conclusion. Other than dehydration fractionation, because the diffusion rate of ^6Li is 3% to 5% faster than that of ^7Li (Richter et al., 2003), kinetic diffusion fractionation processes may be an alternative explanation for the observed extremely light $\delta^7\text{Li}$ of eclogite representing residual subducted slab (Marshall et al., 2007b). Most importantly, if kinetic diffusion fractionation occurs during subduction, as diffusion rate of Li is highly variable in different minerals and may change with temperature (Coogan et al., 2005; Ionov and Seitz, 2008; Caciagli et al., 2011; Yakob et al., 2012), kinetic diffusion fractionation can lead to significant Li isotopic fractionation at high temperature conditions (800°C–1200°C) (Dohmen et al., 2010). Over all, the Li isotopic characteristics of subducted slab modified by dehydration or kinetic diffusion fractionation is controversial. And the exact mechanism controlling the Li isotopic characteristics of subducted slab is still dubious.

Besides using natural samples to investigate the Li isotopic characteristics of subducted slabs, the theoretical method (ab initio methods) has been applied to compute Li isotopic fractionation between complex minerals and fluids under high P-T conditions (Kowalski and Jahn, 2011). Through theoretically calculates mineral/fluid Li

partition coefficients by intrinsic parameters β of minerals and fluids, this method is potential to predict the direction of equilibrium fractionation of Li isotopes between aqueous fluids and various Li bearing minerals, e.g. staurolite, spodumene and mica. The calculated results are consistent with experimental observation from Wunder et al. (2006, 2007). Hopefully, this method may provide an opportunity to quantitatively compute fractionation factors of Li isotopes at different depths in subduction zones. Moreover, it's applicable to any state without different treatment of crystals or fluids and throws light on Li isotopic fractionation mechanisms on the atomic scale.

The complicated history of subduction makes Li isotopic fractionation very mazy. Up to date, there are still many controversies about Li isotopic fractionation during subduction dehydration and metamorphism. Combining theoretical calculation, experimental observation and natural samples may be a powerful way to understand the Li isotopic composition of subducted slabs. Simultaneously, more experimental verifications are required to confirm theoretical calculation of Li isotopic fractionation in the future.

4 The Fate of Slab-derived Fluids and Residual Subducted Slabs

4.1 The fate of slab-derived fluids: interaction with mantle wedge

Slab-derived Li-rich fluids will interact with mantle wedge when they are transferred through peridotite prior to reaching the ultimate region of melt generation in the sub-arc mantle. During interaction, Li released from the subducted slabs will be extracted from fluids or melts by two ways. Firstly, relatively low temperature and pressure at shallow depth, the shallow mantle wedge rocks in contact

with the slab-derived Li-rich fluids will form alteration products (eg., chlorite, talc, serpentine). These newly formed minerals may remove some Li from slab-derived fluids into mantle wedge; Secondly, with subduction depth increasing, temperature and pressure are beyond the stability of hydrous minerals, Li will be taken away mainly by diffusion. For example, diffusive fractionation model of Li isotopes shows Li isotopes diffuse from slab-derived fluids to mantle wedge (Lundstrom et al., 2005). Some other studies also indicate Li could be diffusively added to or lost from minerals during interaction with fluid or melt prior to eruption (Jeffcoate et al., 2007; Rudnick and Ionov, 2007; Tang et al., 2007, 2011; Gallagher and Elliott, 2009; Aulbach and Rudnick, 2009).

Li⁺ can substitute for Mg²⁺ in Mg-silicates due to their similar radius of ions (Shannon, 1976), making Li be effectively removed during equilibration with sub-arc mantle peridotite (Tomascak et al., 2002a). Because upper mantle is mainly consist of Mg-Silicate minerals (e.g. olivine, enstatite, and diopside), it can store significant amounts of Li (Seitz and Woodland, 2000; Paquin and Altherr, 2002). For example, the fore-arc mantle wedge may be a main sink for the heavy $\delta^7\text{Li}$ component released from the dehydrating subducted oceanic crust (Tomascak et al., 2002a). However, although mantle wedge rocks interact with slab-derived Li-rich fluids, most Li isotopic compositions of arc lavas is similar to that of MORB-Type rocks without modification trace by such heavy Li isotopic slab-derived fluids. There are two explanations for this character: (1) Li carried by slab-derived fluids is much more effectively homogenized in mantle wedge due to effective diffusion coefficients of Li (Qian et al., 2010), making source regions of arc-lavas no longer preserve trace of slab-derived fluids; (2) Li originating from subducted slabs is largely transferred into shallow mantle wedge above the subducting slab other than into source region of arc-lavas (Krienitz and Haase, 2011), so the source regions of arc lavas are hardly affected by such fluids. Contemporarily, it's still hard to precisely understand the quantities and depth of Li released in fore-arc region and the geochemical behavior of Li in mantle wedge.

4.2 The fate of residual subducted slabs

The final fate of oceanic and continental subducted slabs are slightly different. A small part of continental subducted materials will return to surface due to its light density, and the residual subducted slab will subduct into deep mantle. Differently, most part of oceanic subducted materials will insert into deep mantle and recycle. Experiencing dehydration, partial melting, and recrystallization, Fig. 6 shows the Li isotopic composition of subducted slabs significantly differs from the surrounding mantle, and may

affect the Li composition of deep mantle. Materials from the Earth's surface to the mantle by subduction are defined as recycled crustal materials, which have long been invoked to explain compositional heterogeneity in the upper mantle (Allègre and Turcotte, 1986). For instance, Hofmann et al. (2003) ascribed the compositional heterogeneity of convecting mantle inferred from mantle-derived magmas to subduction and recycling of oceanic crust into the deep mantle; $\delta^7\text{Li}$ of glass inclusions from Hawaiian lavas vary from -10.2‰ to 8.4‰ , evidently reflecting recycled materials play an important role in creating geochemical heterogeneity in deep mantle (Kobayashi et al., 2004). Using additional recycled crustal materials to magma source regions to explain the observed Li isotopic composition of mantle-derived samples can be seen in many studies. Such as, Tang et al. (2012) investigated Li isotopic composition of olivines from Longgang harzburgite and cpx-poor lherzolites of North China plate, $\delta^7\text{Li}$ values of these olivines are lower than those published for olivines from worldwide peridotites, suggesting this result from inherent nature of lithospheric mantle beneath Longgang region which is peculiar due to metasomatism by low- $\delta^7\text{Li}$ melt derived from recycled oceanic materials. But whether recycled crustal materials can really have influence on the Li composition of mantle or not, and if so, how long such particular Li isotopic signature can be retained in deep mantle is still under dispute, as discussed by Tang Yanjie et al. (2014).

Subducted oceanic lithosphere will be destroyed into small pieces by later processes and form chemical heterogeneity in deep mantle (Hofmann and White 1982; Allègre and Turcotte, 1986; Elliott et al., 2004). Then diffusive processes may occur due to different Li isotopic composition between subducted lithosphere and ambient mantle. The size of fragments of subducted lithosphere will directly affect the time needed to achieve homogenization. For small scale heterogeneity, Li isotopic heterogeneity can be rehomogenized by diffusion over short geological time due to fast diffusion of Li; For large-scale heterogeneity maybe survives from diffusive homogenization process over long geological time ($>1.5\text{ Ga}$) (Vlastélic et al., 2009). However, at mantle temperature conditions, Li diffusion is sufficiently fast to obliterate isotopic heterogeneities over geologically short time periods over meter to kilometer length scales (Halama et al. 2008). If these heterogeneities caused by subducted materials are perished quickly through diffusion, variations in $\delta^7\text{Li}$ of mantle-derived materials may need other explanation instead of addition of recycled crustal materials, such as diffusive isotopic fractionation in magmatic systems, fractionation associated with shallow-level processes (crustal assimilation, low-Temperature alteration). If Li isotopic heterogeneity of mantle can be

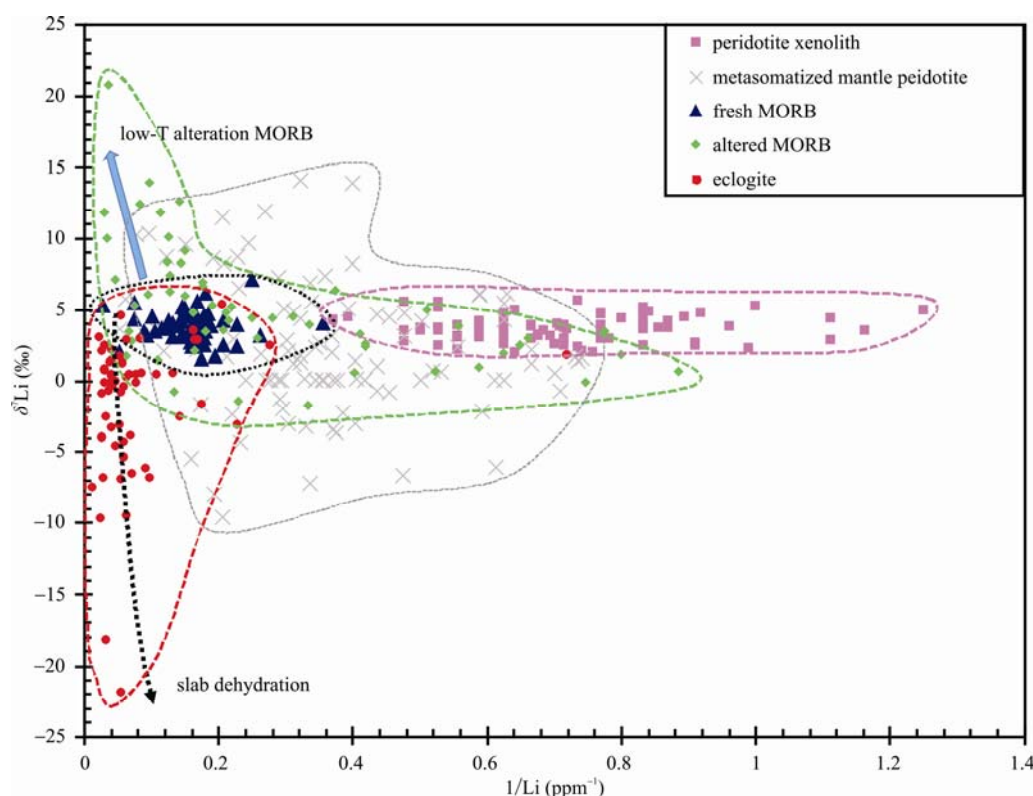


Fig. 6. The $1/\text{Li}$ (ppm^{-1})– $\delta^7\text{Li}$ (‰) diagram of subducted slab and deep mantle components.

Data source: Eclogite, altered MORB, fresh MORB and peridotite xenolith (as Fig.1); metasomatized mantle peridotite (Decitre et al., 2002; Brooker et al., 2004; Seitz et al., 2004; Benton et al., 2004; Kil et al., 2010; Pogge von Strandmann et al., 2011; Ackerman et al., 2013; Lai et al., 2015; Medaris et al., 2015).

retained, additionally, Li isotopes do not fractionate during melting or crystallization at high temperatures (Tomascak et al., 1999b; Jeffcoate et al., 2007), special Li isotopic composition in some igneous rocks should be observed, which can provide some significant constraints on the distribution of recycled material in deep mantle. No matter slab-derived Li isotopic signature is eliminated by later processes or retained in residual slab by significant proportion, subduction process can transfer the heavy Li isotopic composition from the shallow Earth to the deep Earth and be an important part of global Li isotopic cycle.

5 Li Isotopic Composition and Its Use in Tracing Subduction-related Metamorphic Rocks

As the geochemical behaviors of Li is mysterious with P-T conditions changing when subduction continuing, the subduction-related metamorphic rocks can be natural samples to study this issue during different grade of subduction metamorphism.

5.1 Subduction-related low-grade metamorphic rocks

Greenschist and blueschist are typical low-grade metamorphic rocks in subduction zones, and studies about

their Li isotopic composition are relatively scarce now. Our understanding in using Li isotopic composition of subduction-related low-grade metamorphic rocks to trace subduction-related processes is still very limited. Li composition of mudstones experiencing sub-greenschist and greenschist facies metamorphism can provide insights into whether Li isotopes fractionate or not during initial dehydration stage of subducted slabs. Previous studies show barely Li isotopic fractionation during relative low-grade metamorphism. For example, Li isotopic composition of mudrocks from three lower Paleozoic basins in the British Caledonides is mainly controlled by its provenance, implying that sub-greenschist facies metamorphism has negligible effect on Li composition in these low-grade metamorphic rocks (Qiu et al., 2009); Another study about Li isotopic signature of the greenschist from accretionary wedge of New Zealand is similar to their pelitic sedimentary protolith, that is, nearly no Li isotopic fractionation occurs during metamorphism of greenschist facies (Qiu et al., 2011a). Both studies indicate there's no obvious Li isotopic fractionation during the initial stage of subduction-related low-grade metamorphism. Unlike the variation of Li isotopic composition from subgreenschist facies to greenschist facies, Li content shows a decreasing trend, this phenomenon may result from mutual influence of

dilution by intrusion of quartz vein and metamorphic dehydration (Qiu et al., 2011a). As Li-rich Mg-bearing phyllosilicates mainly control the Li composition of both sub-greenschist and greenschist, the Li isotopic signature of these subduction-related low-grade metamorphic rocks may reflect the evolution of Mg-bearing phyllosilicates as a function of metamorphic grade. Furthermore, the activities of slab-derived fluids may be another alternative interpretation for the Li composition of metamorphic rocks. For instance, systematical analysis of Li composition of Catalina Schist, from blueschist to amphibolite facies, Li content (10–50 ppm) and $\delta^7\text{Li}$ value (–2.3‰ to 6.8‰) of metasedimentary rocks have no trend of reducing; Whereas, Li content and $\delta^7\text{Li}$ values of metamafic rocks from the same location decrease from blueschist (25–32 ppm; $\delta^7\text{Li}=0.2\text{‰}–2.4\text{‰}$) to amphibolites (10–16 ppm; $\delta^7\text{Li}=6.7\text{‰}$ to –0.1‰), high Li content of metamafic rocks possibly result from metasomatism by Li-rich fluids other than metamorphic dehydration (Penniston-Dorland et al., 2012). Integrated the above Li isotopic studies of low-grade metamorphic rocks formed in initial dehydration stage of subduction, no apparent Li isotopic fractionation occurs during greenschist and blueschist facies metamorphism. Therefore, temporary conclusion is slab-derived fluids may inherited Li isotopic characteristics of their source rocks during initially shallow subduction dehydration, making low-grade metamorphic have nearly the same $\delta^7\text{Li}$ values with their protolith. In order to clearly ascertain whether Li isotopic fractionation exists or not during these early dehydration stages, accumulating more Li isotopic data of such subduction-related low-grade metamorphic rocks is necessary.

5.2 Subduction-related high-grade metamorphic rocks

Amphibolite and granulite are typically high-grade metamorphic rocks in subduction zones. These high-grade metamorphism often accompany with intense removal of fluid and partial melting even migmatization due to high temperature and pressure. To date, investigations on subduction-related high-grade metamorphic rocks are rare. So far, the only Li isotopic data of amphibolite to granulite facies metapelites from Ivrea-Verbano in Northwest Italy have been investigated by Qiu et al. (2011b). They found the Li content of amphibolite (79 ppm) is higher than that of granulite (8 ppm), the $\delta^7\text{Li}$ values nearly keep unchanged (amphibolites: $\delta^7\text{Li} = -1.4\text{‰}$; granulite: $\delta^7\text{Li} = 0.9\text{‰}$), moreover, $\delta^7\text{Li}$ values of amphibolite and granulite are almost comparative with muddy sediments from other areas. They inferred the Li isotopic characteristics of these metamorphic rocks may inherit from their protolith. Meanwhile, using Li isotopic system to analyze genetic mechanism of leucosomes in amphibolite and granulite

leucosomes maybe another application of Li isotopes. For example, leucosomes in kinzigites (amphibolites facies) had low Li content (13 ppm), and $\delta^7\text{Li}$ value (–1.0‰) was close to the surrounding amphibolites, these leucosomes may precipitate from hydrothermal fluids, which has an average $[\text{Li}] = 13 \pm 2.6$ ppm and isotopically similar to kinzigites ($\delta^7\text{Li} = -1.0\text{‰} \pm 0.2\text{‰}$); leucosomes in stronalites (granulite facies) have lower Li content (3 ± 2.6 ppm) caused by dehydration melting and heavier $\delta^7\text{Li}$ (6.0‰) than that of the stronalites or kinzigites due to fractional crystallization of quartz (Qiu et al., 2011b). According to these studies, we see, Li isotopes can be a useful tool to provide information for small scale fluid-related geochemical processes and relatively large scale metamorphic unit formation.

Eclogites are typically high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic rocks in subduction zones. Most eclogites will enter into mantle together with the residual slab due to their high density, while a fraction of eclogites will return to surface and serve as important samples to study subduction and exhumation processes. In the past decades, Li isotopic composition of eclogites have attracted much attention from geochemists and geologists. At early periods, UHP metamorphic eclogites with extreme low $\delta^7\text{Li}$ values are reported by several researchers (–11‰ by Zack et al. (2003); –21‰ by Marshall et al. (2007b)). The genetic mechanism of these low $\delta^7\text{Li}$ values of eclogite attracts much interest. Recently, Li composition of eclogites and jadeite quartzites from Guatemala and San Francisco add more information, Li content of eclogites (≤ 90 ppm) is much higher comparing to that of normal MORB (2.8–13.2 ppm) but its $\delta^7\text{Li}$ value (–5‰ to 5‰) lower than that of MORB ($3.7\text{‰} \pm 1.0\text{‰}$), simple dehydration model can explain these Li isotopic characteristics (Simons et al., 2010). And Li compositional datas of eclogites from Chinese Continental Scientific Drilling Program (CCSD) (0–2000 m) show the Li content and $\delta^7\text{Li}$ value of these eclogites were 4–29 ppm and –12.4‰ to 3.6‰, respectively (Xiao et al., 2011), researchers also ascribe such Li isotopic character of eclogites to subduction dehydration. Interestingly, some retrograded eclogite with higher $\delta^7\text{Li}$ relative to fresh eclogite, addition of extraneous fluid with high $\delta^7\text{Li}$ value may be responsible for this observation (Xiao et al., 2011). Summing the existing studies, two main interpretation models have been used to interpret the eclogites with extremely low $\delta^7\text{Li}$ values: metamorphic dehydration fractionation model and kinetic diffusion fractionation model. However, both two models still have some limitations. As for metamorphic dehydration fractionation model, Li isotopic fractionation critically depends on fluid-rock fractionation coefficients, meantime, Li fractionation and distribution in mineral-fluid phases during subduction

is a complicated issue (Tomascak et al., 2002a; Lynton et al., 2005; Marschall et al., 2007b; Jahn and Wunder, 2009), and simulation calculation will not be completely identical to actual geological situations. Meanwhile, kinetic diffusion fractionation model alone will be problematical to explain why Li always preferentially diffuse into the eclogites, additionally, there should be complete diffusion profiles if Li isotopes diffuse from surrounding rocks to eclogites, but no such observations have been reported. Above all, to solve the debate about genetic mechanism of extreme low $\delta^7\text{Li}$ values of eclogites from subduction zones still needs further studies on the geochemical behaviors of Li isotopes during subduction dehydration and metamorphism.

6 Li Isotopic Composition and Its Use in Tracing Subduction-related Magmatic Rocks

During subducting, fluids or melts released from subducting slabs flowing into mantle wedge will trigger the generation of arc magmas, and ultimately form a large number of island arc volcano rocks (Taira et al., 1998). Li isotopic composition of subduction-related output rocks including island arc lavas, and oceanic island basalts (OIBs) can be used to trace subduction-related magmatic processes.

6.1 Island arc lavas

Island arc lavas are important samples to trace dehydration processes in subduction zones. So far, there have been lots of studies on arc magmas worldwide, Li isotopic composition of arc lavas from different places vary slightly. We have collected current Li isotopic data of arc lavas and the average $\delta^7\text{Li}$ values of most arc lavas ($3.5\text{‰} \pm 2.4\text{‰}$) is similar to that of min-ocean ridge basalts (MORBs) ($3.7\text{‰} \pm 1.0\text{‰}$), and the average Li content is 9.9 ± 6.3 ppm (Fig. 7a), some extreme Li composition is not included and needs extra explanation.

Pioneer studies of Chan et al. (2002a) found MORB-like $\delta^7\text{Li}$ values (4.5‰) of Nicaragua and Costa Rica series may represent the upper mantle, and correlation between $\delta^7\text{Li}$ range of Costa Rica to Guatemala series (4.5‰ to 6.4‰) and other subduction-related properties (LILEs and FMEs) maybe caused by small additions of slab-derived fluids to either enriched or depleted mantle. Similarly, the $\delta^7\text{Li}$ values of island arc lavas from Kurile arc (2.4‰ to 4.9‰), Sunda arc (2.1‰ to 5.1‰), and Aleutian arc (2.3‰ to 3.9‰) is very homogeneous (Tomascak et al., 2002a), which overlaps the accepted range for MORB ($3.7\text{‰} \pm 1.0\text{‰}$). Combining data from Cascades volcanic arc which also shows MORB-like $\delta^7\text{Li}$ values (2.5‰ to 5‰) (Leeman et al., 2004) and the $\delta^7\text{Li}$ values of lavas from southern

Cascadia subduction zone vary from 0.9‰ to 6.4‰ (Magna et al., 2006b), implies that there's weak slab contributions beneath arc lavas. Now three possible assumption may be responsible for the lack of obvious slab-derived materials contribution to source regions of these arc lavas. Firstly, Li isotopes partition into Mg-silicates during slab-derived fluids transit through peridotite prior to reaching the ultimate region of melt generation in the sub-arc mantle; Secondly, the formation of high Li/B minerals may largely retain Li in the subducting slab; Thirdly, thermal structure of warm subduction zones, slab-derived fluids are reduced extensively before the subducted slabs reach sub-arc depths. Meanwhile, other studies about arc lavas, for example, active arcs like the Northeast Japan arc and the Izu arc both have MORB-like $\delta^7\text{Li}$ values. Interestingly, $\delta^7\text{Li}$ values systematically change across the Izu arc (Moriguti and Nakamura, 1998b), but the Northeast Japan arc shows no such systematic spatial variation (Moriguti et al., 2004). Different arcs with distinct Li isotopic signature may reflect diverse extent of Li isotopic fractionation, which may be influenced by various physical and chemical characteristics, e.g., thermal structure of the subducting slabs, subduction angle, and different chemical composition of subducted materials in each subduction zones.

While most of arc lavas have MORB-like Li composition and no obvious traces of slab-derived fluids in arc lavas, traces of contribution from slab-derived components to source regions of arc lavas can be retained in some unique geodynamic subduction setting. For example, subduction-related volcanic and sub-volcanic rocks of Western Anatolia preserve remarkable Li isotopic variability up to 15‰ , including calc-alkaline volcanic rocks (-4.0‰ to 8.2‰) and potash-rich volcanic rocks (-7.0‰ to 3.1‰) (Agostini et al., 2008), which is greatly distinguishable from other mantle-derived arc lavas. Its low subduction rate and small subduction angle (Doglioni et al., 2002) may make upper mantle wedge be thinner, in some extent, which weaken the leverage of the mantle on heavy Li composition of slab-derived fluids, so late stage C-A and U-K Anatolian lavas with low $\delta^7\text{Li}$ may reflect extensive Li isotope fractionation on the slab or in the mantle. Another recent study on Lesser Antilles lavas from Tang and Rudnick. (2014a) yields an average $\delta^7\text{Li}$ ($1.8\text{‰} \pm 1.3\text{‰}$) that is the first arc lavas with $\delta^7\text{Li}$ systematically lower than MORB, and $\delta^7\text{Li}$ of sediments ($-0.5\text{‰} \pm 1.8\text{‰}$, $-4.4\text{‰} \pm 2.9\text{‰}$) from this subducting slab are the lowest bulk $\delta^7\text{Li}$ seen in subducting sediments from any trenches. In this subducting zone, the special Li isotopic composition of subducted sediments, which is incorporated to a depleted mantle source and reproduce the low Li isotopic signature in the Martinique lavas, is apparent in the lavas. Thus, in these special subduction zones, Li isotopic composition of

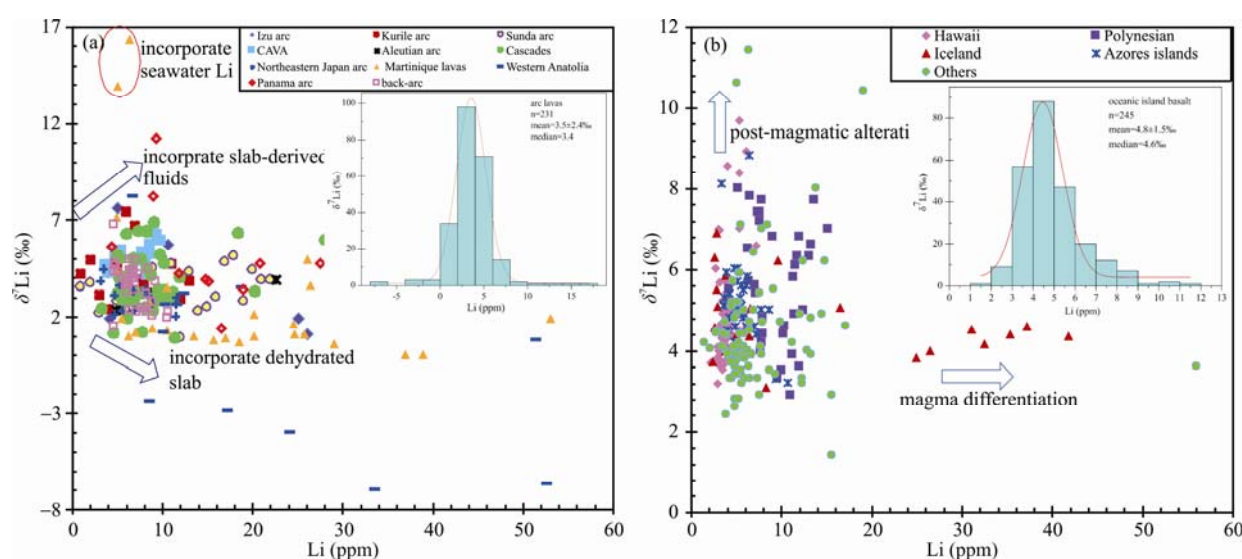


Fig. 7. The Li (ppm)– $\delta^7\text{Li}$ (‰) diagram of worldwide Arc lavas (a) and Oceanic Island Basalt (b).

Data sources: (a), **Arc lavas:** Izu arc lavas from Moriguti and Nakamura (1998b); Kurile arc, Sunda arc, Aleutian arc from Tomascak et al. (2002a); CAVA lavas from Chan et al. (2002b); Cascades lavas from Leeman et al. (2004); Magna et al., 2006b); Northeastern Japan arc from Moriguti et al. (2004); Martinique lavas from Tang and Rudnick, (2014a); Western Anatolia from Agostini et al. (2008); Panama arc from Tomascak et al. (2000); Back-arc (including Lau basin, James Ross Island, Guatemala and western El Salvador, Nicaragua) from Chan et al. (2002b), Košler et al. (2009), Walker et al. (2009), Janoušek et al. (2010); (b), **OIB** Hawaii from James and Palmer (2000), Chan and Frey (2003), Pistiner and Henderson (2003), Kobayashi et al. (2004) Nishio et al., (2007); Iceland from Ryan and Kyle (2004), Schuessler et al. (2009), Magna et al. (2011); Azores from Krienitz et al. (2012), Genske et al. (2014); Polynesian (including Mangaia, Tubuai, Rurutu, Tahiti, Hiva Oa, Ua Pou) from Nishio et al. (2005), Chan et al. (2009), Vlastelic et al. (2009); Others (including Pitcairn, Society, Réunion, St. Helena, Macdonald, Foundation SC, Easter SC, Juan Fernandez, McMurdo, Erebus Lineage, Erebus, Crater Mountains, Pribilof, Réunion–Piton de la Fournaise, Jan Mayen, Rapa, Raivavae) from Ryan and Kyle (2004), Chan et al. (2009), Krienitz et al. (2012).

eruptive products can be a sensitive tool to trace the modification of the mantle by subduction-related material inputs and Li recycling in arcs.

6.2 Oceanic island basalts

Lower mantle is the source region for OIBs, and the Li isotopic composition of OIBs can be a window to study the composition of lower mantle and globally materials recycle. In this paper, we made a summary of Li isotopic data of OIBs worldwide, illustrating a similar mean Li isotopic composition ($4.8\text{‰} \pm 1.4\text{‰}$) to the accepted $\delta^7\text{Li}$ value for MORBs (Fig. 7b). Most OIBs with MORB-like $\delta^7\text{Li}$ values may be a complex offset of highly dehydrated subducted slab with modified sub-arc mantle, or sources of OIB is primitive mantle without contamination by recycled materials, or effective homogenization of Li in the mantle because of the high diffusion rate of Li (Halama et al., 2009). Attractively, some abnormal Li composition of OIB may provide particular insight for us to understand the source regions of these deep mantle-derived rocks. Hofmann and White (1982) firstly report that subducted slabs are finally introduced into deep mantle and then form geochemical anomaly, which could eventually become source regions for mantle plumes expressing at the Earth's surface as OIBs.

On one hand, some OIB samples have relatively light $\delta^7\text{Li}$ values. For example, some ultramafic mantle-derived

xenoliths have extremely light $\delta^7\text{Li}$ values (low to -17‰). Combining with their Sr-Nd isotopic composition, suggesting the source regions of these xenoliths may be EM1 mantle reservoir which is influenced by subducted highly altered basaltic crust as well as pelagic sediments (Nishio et al., 2004). According to their studies, we can get a glimpse of Li isotopic composition of other OIBs originating from EM1 mantle. However, there are scarce reports about OIBs with extremely light Li isotopic composition. Only Ryan and Kyle (2004) reported one lower $\delta^7\text{Li}$ sample which may result from incorporation of deeper, metamorphosed crustal rocks with light Li composition after dehydration (i.e., Zack et al., 2003).

On the other hand, some OIBs have heavier $\delta^7\text{Li}$ values than MORBs. Such as two oceanic island basalts ($\delta^7\text{Li} = 8\text{‰}$, 10‰) indicate their source regions may have been modified by Li enriched slab-derived fluid other than dehydration subducted slab itself (Ryan and Kyle, 2004). Similarly, other increases in $\delta^7\text{Li}$ values, for example, Nishio et al. (2005) presents the first Li isotopic data on HIMU OIBs (5.0‰ to 7.4‰) and they concluded that the Polynesian HIMU source is influenced by the relatively less-altered oceanic crust underlying the highly altered crust. Analogously, olivine from the Cook-Austral Islands lavas with heavy $\delta^7\text{Li}$ values (up to 6.2‰) may be caused by a source region containing recycled dehydrated oceanic crust which may preserve 'heavy' Li isotopic signature

during passing through the subduction factory (Chan et al., 2009). However, not all the heavier Li isotopic signature of OIBs directly result from their source regions. For instance, the variability of $\delta^7\text{Li}$ (3.5‰–8.2‰) in primitive lavas from the western islands of Flores and Corvo is most likely due to contamination by assimilation of hydrothermally altered material other than contributions from recycled materials such as altered MORB or sediments (Genske et al., 2014). The “heavy” Li-isotope signature of altered oceanic crust partially preserved during passage through the subduction factory maybe an explanation for the heavy $\delta^7\text{Li}$ values in HIMU olivines (Chan et al., 2009). However, interpretation of the Li composition of mantle-derived samples have to be treated with care, petrological and radiogenic isotopic characters should be taken into account, eg., two samples from the Cook-Austral Islands with respective $\delta^7\text{Li}$ values 10.6‰ and 11.4‰ are influenced by post-magmatic alteration other than addition of recycled materials into their source regions (Chan et al., 2009). Collectively, as the Li isotopic composition of recycled, dehydrated oceanic crust is currently under debate, interpretation for these heavy $\delta^7\text{Li}$ characteristics of OIBs requires more studies about the Li isotopic composition of recycled, dehydrated oceanic crust.

7 Conclusions

To our knowledge, studies on Li isotopic geochemistry in subduction zones have achieved many cheerful achievements. A large number of natural samples, experimental petrology, theoretical calculation and simulation have greatly promoted our understanding of geochemical properties of Li isotopes and using Li isotopes as tracer of subduction-related processes. However, there's still lots of controversies and more follow-up investigations are urgently required in the future:

(1) The effect of temperature on Li isotopic fractionation: especially, is there any Li isotopic fractionation at middle/high temperature conditions? If it is, what's extent of such Li isotopic fractionation? This will have direct influence on the interpretation of Li isotopic characteristics of magmatic rocks and the difference of Li isotopic fractionation in different subducted slabs with differing thermal structure.

(2) There's still no systematic studies on Li isotopic fractionation of mineral-mineral, and mineral-fluid at different temperature and pressure conditions, especially Li isotopic fractionation between Li-rich mineral and fluid, such as chlorite-fluid and serpentine-fluid. These studies can provide important information to get knowledge of the Li isotopic composition of subducted slabs and slab-derived fluids at various depth.

(3) With temperature changing, how does Li isotopes

redistribute in minerals? This may affect the redistribution of Li isotopes among different minerals during transition of metamorphic phases and exhumation, which may lead to Li releasing from metamorphic rocks (Newly formed minerals can't store these releasing Li when Li-rich minerals break down, or coexist with fluid phase) or absorb additional Li. These study will have great help for us to understand Li composition of metamorphic rocks, and geochemical behavior of Li isotopes during subduction.

(4) The genetic mechanism of eclogites with extremely low $\delta^7\text{Li}$ value is still uncertain. Is it caused by dehydration fractionation during subduction or by kinetic diffusion fractionation during diffusive influx of Li from the country rocks into the exhuming eclogite bodies, or the combine of both processes? If kinetic diffusion fractionation controls the Li isotopic composition of eclogites, does any difference exist between the continuing subducting eclogites and the exhumed eclogites?

(5) In different geological setting, what's the effect of kinetic diffusion fractionation of Li? Whether it control the Li isotopic fractionation of the whole system or just affect the redistribution of Li isotopes in local scale?

(6) How does the thermal structure of subduction zones and mineralogical composition of mantle wedge affect the depth of Li removing from slab-derived fluid and adding to the mantle wedge? This will affect the composition of different depth of mantle wedge modified by slab-derived fluids.

(7) How does the migrating ability of slab-derived fluids change with successive subduction stages? How does the Li isotopic composition of slab-derived fluids change with depth? At different T-P conditions, does it have similar migration mechanism during fluid moving upward and same way of interaction between fluids and mantle wedge?

(8) Will all the slab-derived fluids enter into mantle wedge and trigger partial melting? Whether dehydration fluid will be preserved by deep mantle and traced by OIB or MORB or not?

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