The distribution of lithium in nature and the application of lithium isotope tracing

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Abstract In recent years, with the advancement of isotope analysis methods, lithium isotopes have been widely used in tracing geological processes. This article introduces the unique geochemical properties of lithium and the lithium content and isotope characteristics in all kinds of natural geological reservoirs, and analyzes the fractionation mechanism of lithium isotope in the geological process which happened on the surface and the inner part of the earth. Further, this article summarizes and analyzes the application of lithium isotopes in tracing continental chemical weathering and slab subduction process, and discusses the distribution of lithium among various reservoirs in the light of the material circulation process on the surface and underground.

Keywords: Geological storage reservoir; lithium content; lithium isotope; tracer; continental weathering; oceanic crust subduction

1. Introduction
Lithium is the lightest metal element, it has two stable isotopes (\textsuperscript{7}Li and \textsuperscript{6}Li), the large quality difference between these two isotopes is the main factor leading to the significant difference in Li isotope ratios in various natural systems. Due to the valence state characteristic, the fractionation of lithium isotopes is not affected by redox reactions (Faure and Mensing, 2005). Lithium is not an element necessary for life, creature activities have no effect on lithium isotope fractionation (Clergue et al., 2015). Lithium has a long residence time in the ocean (3Myr), which is much longer than the mixing time of ocean water (1000y) (Henchiri et al., 2014). These special geochemical properties of lithium make it an effective tracking element of continental weathering (Huh et al., 2001), oceanic crust alteration (Chan et al., 2002), slow crust material circulation (Zack et al., 2003) as well as other important geological process, the study of lithium isotope has become a hotspot in the geoscience research during these years.

Lithium isotope fractionation is restricted by two fractionation mechanisms: thermodynamic equilibrium fractionation and kinetic fractionation. Lithium is a moderately incompatible element and rather active during fluid migration process. During fluid-related processes such as continental weathering, oceanic crust alteration, and plate subduction, Lithium is preferentially enriched in the fluid phase, resulting in lithium isotope differences among various geological environments. Studies
have shown that low-temperature systems, such as oceanic crust dehydration alteration (Chan and Edmond, 1988), mantle rock hydration (Agostini et al., 2008), slate garnet pyroxenation (Zack et al., 2003) and so on, are under the control of thermodynamic equilibrium fractionation, which result the significant changes in Li isotopic composition. On the contrary, during the high temperature (T>350°C) process, such as magmatic activity, Li isotopes do not undergo obvious thermodynamic fractionation, so the characteristics of Li isotopes in the lava can be used to trace the nature of the magma source (Wunder et al. 2006). Due to the large quality difference between lithium isotopes, the diffusion rate of $^6$Li is much faster than that of $^7$Li, and the diffusion efficiency is more significant under high temperature conditions. Therefore, the kinetic fractionation caused by the difference in diffusion capacity is the main controlling factor for the fractionation of lithium isotopes under high temperature conditions (Teng et al., 2006).

2. Lithium content and isotopic characteristics of various reservoirs on the earth

2.1 Lithium content and isotopic composition of the mantle

Fresh mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) are representative of the upper mantle material. Among them, the mid-ocean ridge basalt (MORB) is the product of decompression melting of mantle rocks under the tension environment of the mid-ocean ridge, and its lithium isotopic composition is relatively uniform ($\delta^7$Li=+2~+7‰, average about +4‰) (Tang et al., 2007). The ocean island basalt (OIB) represented by Hawaii is considered to be the product of hotspots activity, and its material originates from the mantle plume that reaches the core-mantle boundary. Studies have shown that ocean island basalt has a uniform lithium isotope composition ($\delta^7$Li=+2~+8‰, with an average of about +4‰), and is similar to MORB lithium isotope composition (Tomascak et al., 2002). In addition, studies on the lithium isotopes of igneous carbonates from the deep mantle show that the lithium isotopic composition is similar to MORB and OIB, about +3.3~+5.1‰ (Halama et al., 2008), reflecting that the lithium isotopic composition of the upper mantle is generally uniform.

![Fig. 1 Li isotopic composition of various reservoirs](image)

However, studies on mantle peridotite enclaves have shown that the lithium isotope composition of mantle peridotite in some areas varies a lot. As reported by Nishio et al. (2004), the $\delta^7$Li value of mantle peridotite samples can be as low as -17‰. Also, the lithium isotope composition of molten inclusions in Hawaiian volcanic peridotite reported by Beck et al. (2004) shows a large range of $\delta^7$Li value variation (-11~+5‰). These studies have shown that the mantle fluid activity, in some extent, lead to the inhomogeneous characteristics of lithium isotopic composition within certain geological body.

2.2 Lithium content and isotopic composition of the crust

2.2.1 Lithium content and isotopic composition of oceanic crust

From surface to deep underground, the oceanic lithosphere section is composed of oceanic sediments,
altered basalt, gabbro and peridotite.

Studies have shown that oceanic sediments have a high lithium content and a large $\delta^7\text{Li}$ variation range ($-4.3$ to $+24.5\%$) (Leeman et al., 2004). Oceanic sediments are mainly composed of terrigenous clastics (turbidite, clay rock, volcanic clastic rock), pelagic sediments, deep-sea ooze, and carbonates. The composition of lithium isotopes is controlled by the relative proportions of debris, clay minerals and marine carbonates. The lithium content of these three materials is gradually decreasing from clay minerals (80ppm) to terrigenous debris (24ppm) to carbonates (<5ppm). In terms of isotopic composition, terrigenous clastic materials inherited the lithium isotope characteristics of continental crust rocks ($\delta^7\text{Li}=0$ to $+6\%$). Clay minerals and turbidites are more likely to absorb $^6\text{Li}$, which lead to the lighter lithium isotope characteristics ($\delta^7\text{Li}=+1.6$ to $+5\%$), the lithium isotope composition of marine carbonate is heavier and has a wide range of variation ($\delta^7\text{Li}=+1.6$ to $+25\%$) (Bouman et al., 2004).

Research on core samples of ocean drilling (DSDP, ODP, IOPD) shows that compare to the fresh mid-ocean ridge basalts, the low-temperature altered basalt have higher lithium content and heavier lithium isotopic composition. (Bouman et al., 2004) While the lithium content and $\delta^7\text{Li}$ value of high-temperature altered basalt are lower than that of low-temperature altered basalt (Zack et al., 2003). In the process of oceanic crust alteration, the lithium isotope composition of oceanic crust rocks is affected by the lithium isotope composition of seawater and new-born clay minerals at the same time. Gabbro and peridotite are representative of rocks from the deepest part of oceanic crust. Compared with peridotite, gabbro is more stable and less susceptible to alteration. Its lithium content and isotopic composition are equivalent to the mantle value (1.5ppm, +4.3\%) (Gao et al., 2012). Lithium in mantle peridotite is mainly found in olivine minerals. Since $^7\text{Li}$ is easier to accumulate in the fluid phase than $^6\text{Li}$, during the subduction of the oceanic crust, olivine is under the influence of fluid, the lithium content gradually decreases, and the lithium isotopic composition becomes lighter. As the metasomatism progressing, the peridotite serpentinized, and the $^6\text{Li}$ in the fluid entered the serpentinite in the form of clay minerals constituent, resulting in an increase in the lithium content and isotope ratio of the serpentinite. Because the rock composition of oceanic crust from different areas varies, the lithium isotopes of oceanic crust rocks in different regions are affected by the degree of serpentinization of oceanic crust rocks and the relative thickness of each component rock. For example, the study of lithium geochemical characteristics during the serpentinization process of ocean peridotite conducted by Decitre et al. (2002) showed that due to the different alteration degrees, the lithium isotope composition in the serpentinite varies greatly ($\delta^7\text{Li}=+2.9$ to $+14.2\%$). The oceanic crust of the slow expansion zone is thin, and the lithium contained in the serpentinite accounts for a high proportion of the total lithium content of the oceanic lithosphere (about 20%). The rapid expanding young oceanic crust (about 1 Ma) has a thicker oceanic crust and a low degree of serpentinization. The lithium content in the serpentinite is negligible. As to the rapid expanding ancient oceanic crust (about 75 Ma), the lithium content can account for 16% of the entire oceanic lithosphere.

2.2.2 Lithium content and isotopic composition of continental crust

The continental crust can be divided into upper, middle and lower three layers according to different rock facies. The upper crust is mainly composed of surface soil, sedimentary rocks, and granitic intrusive rocks. The middle crust is mainly composed of tonalite, diorite, granitic gneiss and amphibolite. The lower crust is mainly composed of felsic or mafic granulite. At present, the research on the lithium geochemistry of continental crust mainly focuses on the content and isotopic characteristics of eclogite in the orogenic belt.

The study of the upper crust rock samples such as shale, loess, granite from all over the world (North America, China, Europe, Australia, New Zealand, etc.) shows that the continental upper crust has a relatively high lithium content and a large isotope variation range (The average lithium content is about 35ppm, $\delta^7\text{Li}=0\%$) (Teng et al., 2004). Compared with the mantle and oceanic crust, the lithium isotope composition of the upper crust is significantly lighter, which is believed to be caused by the migration of $^7\text{Li}$ with river water and other fluids during continental weathering. Rivers with heavy
lithium isotopes flow into the ocean and become an important part of the lithium cycle on the earth's surface. Teng et al. (2008) analyzed the geochemistry of lithium in the middle and lower crust with the Archean metamorphic rocks in eastern China and the granulites in Hannuoba, Damaping, Mcbride, North Queensland and other places in Australia. It shows that the lithium content of the middle crust varies greatly, and the isotopic composition is more uniform ($\delta^7$Li=$+1.7$~$+7.5\%$), while, the lower crust has low lithium content and strong heterogeneity ($\delta^7$Li=$-14$~$+14.3\%$).

In general, from bottom to top, the lithium content of continental crust is gradually increasing (the average lithium content in the lower crust is $8\times10^{-6}$, the middle crust is $12\times10^{-6}$; and the upper crust is $35\times10^{-6}$). Compare with the middle crust, the lithium isotopes of the upper crust and lower crust vary greatly. The heterogeneity of the upper crust is mainly caused by the difference in the weathering degree of the continental crust in different regions and different rock types. The reason for the inhomogeneity of the lower crust is still unclear. Teng et al. (2008) used the weighted average method to calculate the average lithium content of the entire continental crust, which is about 18ppm, and $\delta^7$Li is about $+1.2\%$o. It can be seen that the lithium isotope composition of continental crust is significantly different from that of oceanic crust and mantle.

2.3 Lithium content and isotopic composition of the hydrosphere

As mentioned earlier, $^6$Li is apt to enter the fluid phase than $^7$Li, leading to a decrease in the lithium content and $\delta^7$Li value in weathered products and a heavy lithium isotopic characteristic in surface fluids such as river. Research on the current lithium isotope composition of river water in the world shows that the lithium isotope composition of river water varies in a wide range ($\delta^7$Li=$+6$~$+40\%$o, mean value $+23\%$o) (Vigier et al., 2008). In contrast, the lithium isotopic composition of seawater is more uniform ($+29.3$~$+33.3\%$o, mean $+31\%$o) (James et al., 2000). In the submarine hydrothermal system, the submarine hydrothermal fluid continuously leaches the oceanic crust basalt and has a high lithium isotope content (about 60ppm). Because the lithium isotope composition of oceanic basalt is uniform, and the fractionation behavior of the lithium isotope is relatively fixed during the water-rock interaction under high temperature conditions, the seabed hydrothermal fluid has a relatively uniform lithium isotope composition ($\delta^7$Li=$+6.5$~$+11.5\%$o, mean $+8\%$o) (Foustoukos et al., 2004). River water and submarine hydrothermal fluids merge into the ocean. Theoretically, the isotopic composition of ocean water should be an average reflection of the isotopic characteristics of each end member of the ocean. However, unlike the composition characteristics of radioisotopes such as Sr and Os and stable isotopes such as O, C, and Mg, the $\delta^7$Li value of ocean water bodies is significantly higher than the $\delta^7$Li value of each sink. According to the research (Rudnick et al., 2004), oceanic crust rocks such as oceanic basalt undergo dehydration and alteration during the subduction process, forming a large amount of clay minerals, while $^6$Li in seawater is easily enriched in newly formed clay minerals, which leads to the increase of ocean water bodies $\delta^7$Li.

3. The use of lithium isotopes in tracing continental weathering Process

The continental weathering process is an important link between the atmosphere and hydrosphere and the earth’s external environment and the earth’s continental rocks. It plays an important role in shaping the surface morphology, controlling CO$_2$ capture, regulating atmospheric CO$_2$ content and the long-term evolution of the earth’s climate. In all geological processes, the fractionation of Li isotopes mainly occurs in the process of continental weathering. Over 80% of the fractionation of Li isotopes that has been observed in nature occurs in the surface/shallow surface environment (Millot et al., 2010). Therefore, $^6$Li and $^7$Li, which share relatively large atomic mass difference, have the potential to trace continental weathering. The content of Li in carbonate is very low. The weathering process of carbonate will not affect the composition of lithium isotopes in the ocean, so the sea ocean and river lithium isotope system are only sensitive to the silicate weathering process. The chemical weathering of silicate is considered to be the most important carbon sink process on the geological time scale. Therefore, the lithium isotope composition of seawater can be used to trace the continental weathering process during the geological history. The intensity and flux of silicate weathering can be used to trace the circulation of crustal material and the global CO$_2$ burial.
The factors that control the fractionation of Li isotopes in the continental weathering process are the key issues that most weathering crusts and water bodies studies trying to solve. The formation of weathering crust is controlled by many geological processes such as long-term weathering of rocks/minerals, formation of secondary minerals, groundwater leaching, etc. The composition of rocks and minerals of different weathering crusts is complex, and the main factors that control the changes of chemical composition are different. As a result, the main controlling factors of isotope fractionation varies in different lithium profiles. However, on the whole, during the chemical weathering of the continent, the lithium content and isotopic characteristics of the weathering crust are mainly controlled by the dissolution of minerals as well as the formation and dissolution of secondary minerals. In the process of mineral dissolution, $^7\text{Li}$ is more likely to enter the fluid phase when compared with $^6\text{Li}$, and during the formation of clay and other secondary minerals, $^6\text{Li}$ is prone to enter the clay mineral lattice.

The predecessors also did a lot of work on the lithium content and isotopic characteristics of river water. Taken together, the lithium isotopic composition of river water in major river basins around the world has changed dramatically ($\delta^7\text{Li}=+6\text{ to }+40\‰$, average $+23\‰$). In contrast, the $\delta^7\text{Li}$ value of river suspended matter is relatively uniform ($\delta^7\text{Li}=-6.8\text{ to }+9.5\‰$). Figuring out the source of Li in river water and the controlling factors of lithium isotope fractionation are key issues in using river water to trace continental weathering process. The dissolution of silicate minerals and the formation of secondary clay minerals are important processes in the continental chemical weathering process. They not only control the lithium geochemical characteristics of the weathering crust, but are also the main factors affecting the lithium content and isotopic composition characteristics of river water systems. However, Pogge von Straudmann (2017) studied the lithium geochemical characteristics of hydrothermal hot springs and river water in tectonic activity zones, and believed that silicate weathering is not the only factor that restricts the lithium content and isotopic characteristics of river water. We cannot assess the silicate weathering intensity only under the light of $\delta^7\text{Li}$. For example, in areas where evaporites and volcanic activity are developed, hydrothermal Li will also have a significant impact on the Li content in river systems (Wang et al., 2015). In addition, studies have shown that the Ph value of river water (Dellinger et al., 2015) and the climatic conditions of the river basin (rainfall, atmospheric dust fall, etc.) (Godfrey et al., 2013) also exert effects on the lithium isotopic composition of river water. Therefore, when using lithium isotopes to reappear the chemical weathering process of continental silicates, it is necessary to comprehensively consider the impact of various environmental factors and take other geochemical means such as carbon and magnesium isotopes into use.

4. **The use of lithium isotopes in tracing slab subduction Process**

Slab subduction is an important way for the surface material of the earth to enter the deep underground, and it is one of the most important mechanisms of crust-mantle material circulation. The new oceanic crust produced by the mid-ocean ridge is pushed by the expansion of the mid-ocean ridge and dragged by the subducting slab, as a result, it continuously migrates to far end and collides with the continental/oceanic slab at the edge of the slab. Due to oceanic crust is denser than continental crust, when the collision happens, it tends to subducts under the continental crust. The geochemical composition of oceanic sediments, water-bearing oceanic crust and lithospheric mantle has changed significantly due to the influence of seawater/hydrothermal alteration and changes in the subduction environment. Generally, due to the influence of seawater and hydrothermal fluids, oceanic sediments and altered oceanic crust have high $\delta^7\text{Li}$ values. As the subduction proceeding, pressure and temperature increase, the subducting slabs are dehydrated, forming a dehydrated fluid with the heavy lithium isotopes characteristics and residual subduction slabs with light lithium isotopes characteristics. The dehydrated fluid migrates upward to replace the overlying mantle wedge, and the water-bearing mantle wedge melts to form island arc magma.
Fig. 2 Schematic illustration of Li isotope geochemical behaviors

Tomascak et al. (2000) studied global island arc magma (Kurile, Aleutian and Sunda island arcs) and showed that island arc magma in most parts of the world has a relatively uniform lithium isotopic composition ($\delta^7\text{Li}=+2.1$ to $+5.1\%$), but in some areas, island arc rocks with large changes in lithium isotopes have been discovered. For example, the results of lithium isotopic studies on Western Anatolia ultra-potassium and calc-alkaline volcanic rocks show that the $\delta^7\text{Li}$ can be as low as $-6\%$ (Agostini et al. 2008), and calc-alkaline island arc lava with $\delta^7\text{Li}$ values as high as $+12\%$ was found in Panama (Tomascak et al., 2000). In addition, Moriguti and Nakamura (1998) studies on mantle wedge rocks in the Izu area show that the lithium isotopes of the subduction zone in this area also have a certain degree of heterogeneity, and their $\delta^7\text{Li}$ values show a decreasing tendency as the depth increase.

The gradual decrease of the $\delta^7\text{Li}$ value of the dehydrated slab fluid and the difference in the physical properties of the subduction zone (the thermal structure of the subducting slab, the subduction angle, etc.) are the main causes for the changes in the lithium isotopic composition of the mantle wedge and island arc rocks. Agostini et al. (2008) believed the subduction is approaching to the end, the subduction slow down, the subducted slab lost lots of lithium at a relatively shallow depth and form the low $\delta^7\text{Li}$ character in residual slabs. When the slab is subducted to the deep, the released high-temperature, lithium-rich fluid will inherit the low $\delta^7\text{Li}$ characteristics of the slab, and substitute the mantle wedge to produce island arc magma with low $\delta^7\text{Li}$ characteristics. Studies have shown that in high-angle subduction zones, the overlying mantle wedge is thicker, and the dehydrated fluid with high $\delta^7\text{Li}$ characteristics is buffered by the overlying mantle rock before reaching the partial melting zone. Hence, the island arc magma formed by melting lost the dehydrated fluid character. On the contrary, it shows the lithium isotopic characteristics that similar to MORB. In very slow low-angle subduction zones (such as Western Anatolia), the overlying mantle wedge is thinner and has a weaker effect on the release of fluids from the subduction zone. The heavy lithium isotopic characteristics in the fluid are preserved, and act with the mantle wedge to generate the island arc rock with high $\delta^7\text{Li}$ characteristic.

Only a few subduction slabs can reach the mantle, and form eclogite by advanced metamorphism. The lithium content of eclogite varies greatly ($1\times10^{-6}$ to $50\times10^{-6}$, average $16.3\pm4.6\times10^{-6}$) (Marschall et al., 2007b), and the lithium isotopic composition of eclogite varies widely. And most eclogites have a lower $\delta^7\text{Li}$ value ($-35$ to $+8\%$) than MORB. At present, the genetic models of eclogite with extremely light $\delta^7\text{Li}$ values, mainly include metamorphic dehydration fractionation and diffusion fractionation.

Zack et al. (2003) used Rayleigh fractionation to calculate and analyze ($\alpha=1.007, D=0.02$), the result shows that in an environment where temperature reach to 300$^\circ$C, as long as 30% of the chlorite lost 4% water, it can cause a 14% decrease in subducted rocks. So, it is proposed that the dehydration fractionation can form the extremely low $\delta^7\text{Li}$ value in the eclogite. However, the strong fractionation caused by slab dehydration is limited to low temperature and shallow environment. When subducting to a certain depth, due to the influence of temperature and pressure, the degree of fractionation of lithium isotopes gradually decreases (Marschall et al., 2006). Marschall et al. (2007a) modified the Rayleigh distillation model based on the changes in temperature and pressure during the metamorphic process of the subduction zone. By using the general alteration of the oceanic crust (Li content is
7.6×10^{-6}, δ_{7}Li=+10‰) and highly altered oceanic crust (Li content 33.1‰, δ_{7}Li=+11.8‰) as an example, it is found that from the initial subduction to the formation of eclogite, the δ_{7}Li value of the slab does not change more than 3‰, indicating dehydration only cannot form eclogite with extremely low δ_{7}Li value. Since ^{6}Li is more likely to enter the solid phase than ^{7}Li, the difference in the diffusion rate between these two isotopes will cause more light lithium get into the rock, especially in the deep high temperature environment, the effect of diffusion and fractionation will be more significant. Therefore, many scholars have proposed that the extremely negative lithium isotope characteristics of eclogite may be due to diffusion and fractionation. These two fractionation models both have certain limitations. In the actual subduction process, the mineral-fluid isotopic fractionation is very complicated, and the dehydration fractionation model rely too much on the selection of fractionation coefficient. Whether the diffusion kinetics model is valid should be tested by the lithium isotope diffusion and fractionation profile in the actual geological environment.

5. Conclusions
(1) The characteristics of the lithium content and isotopic composition of various reservoirs in nature are basically clear: the lithium isotope composition of the upper mantle is generally uniform (average δ_{7}Li=+4‰), and affected by factors such as the addition of deep subduction slabs, there are some inhomogeneity to some extent. There are obvious differences in the composition of lithium isotope between oceanic and continental crusts, and the lithosphere composition of oceanic crust of different oceanic types varies, and the lithium isotope composition is affected by the composition of the oceanic crust lithosphere. From the bottom to the top of the continental crust, the lithium content gradually increases. The lithium isotopes of the upper crust and the lower crust vary greatly. The heterogeneity of the upper crust is mainly caused by the difference in the degree of weathering of the continental crust, while, the cause of the heterogeneity in the lower crust has not been known.
(2) The dissolution of silicate minerals and the formation of secondary clay minerals are important processes in the process of continental chemical weathering, which control the geochemical characteristics of lithium in the weathering crust and river systems. However, the Ph value of the river water, the geographical location of the basin and the climatic conditions also affect the lithium isotopic composition of the river water. Therefore, using lithium isotopes to reappear the chemical weathering of continental silicates requires comprehensive consideration of various environmental factors and a combination of multiple geochemical methods.
(3) Oceanic slabs subducted and dehydrated, forming a dehydrated fluid with heavy lithium isotopes and residual plates with the light lithium isotopes. The dehydrated fluid act with the overlying mantle wedge to form island arc magma. Whether the island arc magma can retain the heavy lithium isotope characteristics of the dehydrated fluid depend on the structure of the subduction zone. Generally, low-angle subduction has a weak buffering effect on dehydrated fluid due to the thin thickness of the overlying mantle wedge, and the characteristics of heavy lithium isotopes are easily retained. The remaining slabs continue to subduct, part of them can reach the crust-mantle boundary, lead to the mantle heterogeneity, and together with the normal mantle become the source of OIB. The extremely low δ_{7}Li value of eclogite is the result of the combined effect of lithium isotope dehydration fractionation under low temperature environment and kinetic diffusion fractionation under high temperature environment.

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