



# Lithium Isotopic Compositions of Mesozoic and Cenozoic Basalts From South-Eastern China: Implications for Extremely Low $\delta^7\text{Li}$ of Continental-Type Eclogites

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Lithium isotope geochemical studies of oceanic-type eclogites benefited from previous investigation of altered oceanic crust; however, processes of lithium isotope exchange operating on altered protoliths of continental-type eclogites have remained unclear. Here, the Li concentration and isotopic composition of fresh and altered continental basalts from the South China Block were measured to decipher Li and its isotopic fractionation during subaerial alteration processes. The results show that altered South China basalts have higher Li concentration (11.4–117.7 ppm) and lower  $\delta^7\text{Li}$  values (–4.3–+0.5‰) than fresh basalts (Li: 5.0 ppm and  $\delta^7\text{Li}$ : ~3‰). It is found that hydrothermal alteration played an important role in increasing the Li concentration of altered basalts, which is supported by the relation of loss on ignition and Li concentration. Subsequently, continental weathering acted on chlorite-bearing basalts, as evidenced by the occurrence of minor kaolinite and illite and weathering trend of  $\delta^7\text{Li}$  values in these basalts. Detailed petrography and *in situ* geochemical analyses are used to show that chlorite is the chief repository for Li in weathered basalts, supporting that it was responsible for decreasing  $\delta^7\text{Li}$  value by Rayleigh distillation during weathering. Because of the lower  $\delta^7\text{Li}$  values of continental altered basalts than oceanic altered crust, it is concluded that, in addition to the dehydration of subducted slabs and possible Li diffusion, the extremely light Li isotopic values of continental-type eclogites worldwide partly result from isotope fractionation caused by the continental weathering of their protoliths.

**Keywords:** Li isotopes, chlorite, weathering, altered basalts, eclogites

## INTRODUCTION

As a fluid-mobile element, lithium and its isotopes are deemed to represent powerful tracers of different types of fluid–rock reactions, including those operating in subduction zones, hydrothermal alteration, continental weathering, and altered oceanic crusts (AOCs) (Tomascak et al., 2016; Penniston-Dorland et al., 2017). The high- or ultrahigh-pressure (HP/UHP) metamorphic rocks found in subduction zones provide a direct window through which subduction-related fluids may be

investigated (Bebout, 2014; Schmidt and Poli, 2014). Eclogites, as common HP-UHP metamorphic rocks from subduction zones, were found to have higher Li concentrations ([Li]) and lower  $\delta^7\text{Li}$  values than their MORB-type protoliths (Zack et al., 2003; Marschall et al., 2007; Penniston-Dorland et al., 2010; Simons et al., 2010; Halama et al., 2011; Xiao et al., 2011; El Korh et al., 2019; Liu et al., 2019). Because of the limited Li isotopic fractionation occurring during the dehydration of the subducted oceanic crust (Marschall et al., 2007), most models for Li isotopic fractionation have focused on the metasomatism of the AOC and/or the diffusion of Li from country rocks or fluids during exhumation (Marschall et al., 2007; Simons et al., 2010; Halama et al., 2011; Liu et al., 2019) and attempted to explain the increase in [Li] and the decrease in  $\delta^7\text{Li}$  values regardless of whether the eclogites were oceanic or continental. However, the behavior of Li isotopes in fluid-rock interaction differs significantly in ocean floor alteration and continental weathering. First, seawater ( $31.0 \pm 0.1\%$ ; Millot et al., 2004) and submarine hydrothermal fluids ( $+8.0 \pm 1.9\%$ ; Verney-Carron et al., 2015) have relatively constant  $\delta^7\text{Li}$  values, compared to the magmatic, metamorphic, sedimentary, and meteoric fluids present in continental settings and which vary significantly in [Li] and  $\delta^7\text{Li}$  values (12–653 ppm,  $-1.4$ – $41.3\%$ ; Richard et al., 2018). Second, previous studies showed that the  $\delta^7\text{Li}$  values of the AOC generally increase with decreasing fluid temperature and increasing fluid/rock ratios along the ocean drilling profiles (Chan et al., 2002; Gao et al., 2012; Coogan et al., 2017) and the addition of mobile elements (Li, Rb, K, Cs, etc.) in the AOC (Staudigel, 2014). However, most weathered continental basalts show lower  $\delta^7\text{Li}$  values than their fresher equivalents and simultaneously lose mobile elements (Ca, Na, K, and Li) and accumulate immobile elements (Nb and Ti) as evidenced by weathering profiles (Kısakürek et al., 2004; Rudnick et al., 2004; Liu et al., 2013; Tong et al., 2021). Therefore, using the AOC to model continental eclogites is proving to be inadequate, and it is indispensable to investigate the Li isotopic compositions of continental altered basaltic rocks for deciphering variations in [Li] and  $\delta^7\text{Li}$  in continental-type eclogites. Here, detailed investigations of mineralogy, major and trace element concentrations, and Li isotopic compositions were executed on fresh and altered basalts from the South China Block in order to assess the behavior of Li isotopes during hydrothermal alteration and weathering. Our results demonstrate that hydrothermal alteration brought the high [Li] to the altered basalts, while chlorite-bearing altered basalts subsequently underwent weathering, which resulted in a decrease in their  $\delta^7\text{Li}$  values. Different styles of lithium isotopic fractionation were found in altered basalts from continental and oceanic settings, providing a new prospective of protolith on explaining the formation of light Li in continental-type eclogites.

## GEOLOGICAL BACKGROUND AND SAMPLES

The South China Block is composed of the Yangtze Block to the northwest and the Cathaysia Block to the southeast, both of

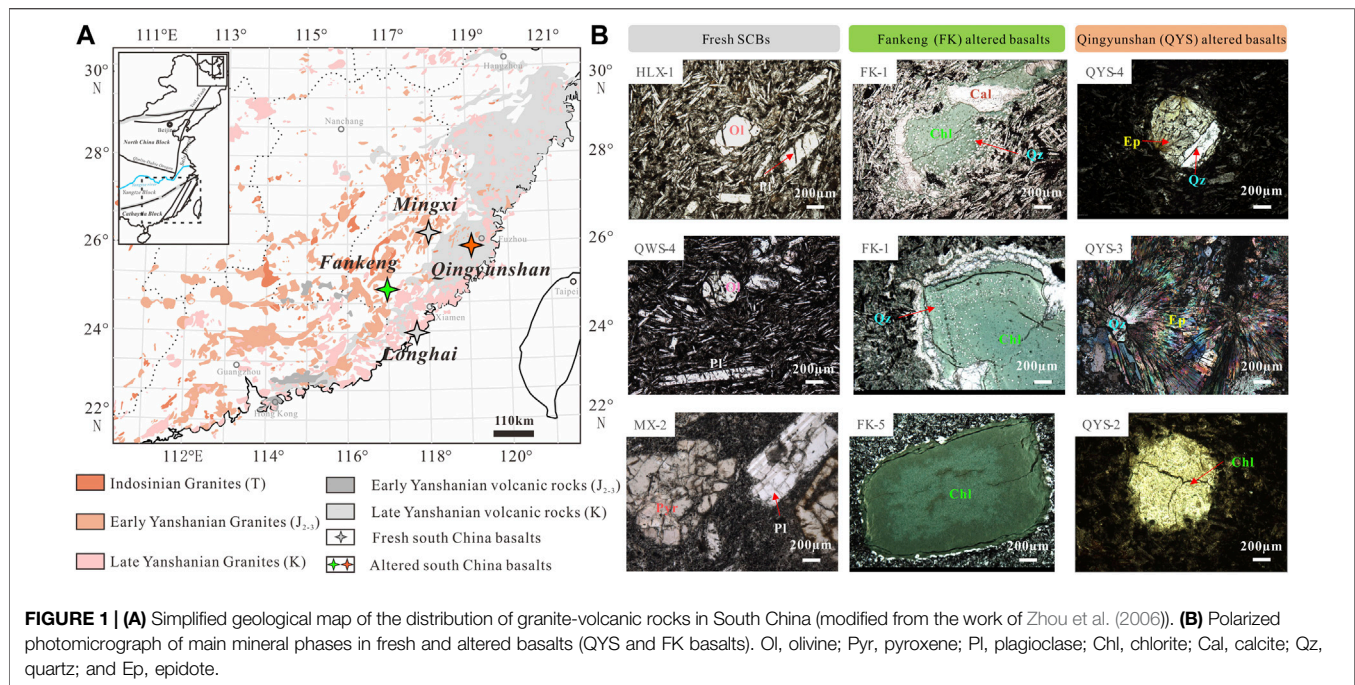
which are separated by the Neoproterozoic Jiangnan orogenic belt (Chen et al., 2008). The widely developed granitoids in the South China Block were coeval with bimodal volcanic suites consisting mostly of felsic rocks with minor amounts of basalts, which are scattered throughout the granitoids (Figure 1A). The Cenozoic and Mesozoic intraplate basalts are sporadically scattered in the Cathaysia Block. These basalts are spatially and temporally associated with the subduction of the Paleo-Pacific Plate and have mixed enriched-mantle II (EM2) and depleted mantle sources (Ho et al., 2003; Chen et al., 2008; Zeng et al., 2016). However, compared to fresh Cenozoic basalts, most Mesozoic basalts underwent varying degrees of chloritization and epidotization (Meng et al., 2012; Cen et al., 2016), thus providing an opportunity to study the Li isotopic behavior during low-temperature alteration processes. Sampling was focused in the Fujian Province (Figure 1A), and samples were divided into fresh South China basalts (fresh SCBs,  $n = 13$ ) and altered South China basalts (altered SCBs,  $n = 13$ ).

The fresh SCBs group includes seven samples from Mingxi and six from Longhai, which erupted at 1.2–2.2 Ma and 14.9–17.1 Ma, respectively (Ho et al., 2003). The basalts include mainly olivine and plagioclase and rarely pyroxene phenocrysts, whereas the groundmass is composed of microcrystalline plagioclase, fine-grained pyroxene, and magnetite (Figure 1B). The altered SCBs group includes seven Qingyunshan (QYS) basalts from the 81–85 Ma bimodal volcanic Yongtai region (Meng et al., 2012) and six Fankeng (FK) basalts from the ~98 Ma bimodal volcanic Fankeng formation (Chen et al., 2008), respectively. The QYS basalts, which were sampled from the fresh outcrop, underwent epidotization and partial chloritization, while FK basalts, which were sampled from the riverbed, underwent variable degrees of chloritization. The QYS basalts with amygdaloidal textures are interspersed with veins consisting of epidote and quartz, whereas the FK basalts have large-grained chlorite occasionally surrounded by quartz and calcite (Figure 1B). Chlorite is the dominant secondary mineral for this study. For comparison with the altered SCBs, the chlorite-bearing hydrothermally altered basalts (HABs) from Hengill, SW Iceland (Verney-Carron et al., 2015), and weathered diabase dyke (WDD) developed on chlorite-bearing diabase from South Carolina, United States (Rudnick et al., 2004), were selected. Both sets of samples were selected because their low-T meteoric alteration is well documented. Within the WDD sample suite, only those located at >6 m depth were considered because they preserved basaltic compositions.

## ANALYTICAL METHODS

### Mineral Identification

Sample mineralogy was determined at the CAS Key laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). Aliquots of the FK basalts were subsequently crushed and



pulverized to <200 mesh for analysis by MapAHF X-ray diffraction (XRD) using a Rigaku Smartlab X-ray diffractometer equipped with a Cu tube, at 2°/min and 0.02° step width, from 3° to 80° 2θ.

### Whole Rock Major and Trace Elements

Rock powders were mixed with Li tetraborate in Pt crucibles with release agents to produce glass discs. The glass discs were analyzed using a Rigaku ZSX Primus II WD X-ray fluorescence spectrometer (XRF) at USTC. Analytical precision for each major element was better than 1%. Loss on ignition (LOI) was measured by gravimetric methods in a muffle furnace. For trace element analysis, sample powders were dissolved in Teflon bombs by heating for 2 days at 200°C in mixed ultra-pure HF, HNO<sub>3</sub> and HClO<sub>4</sub>. After adding Rh as the internal standard, the analyses were performed using an ELAN DRC II quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) at USTC. The samples were carried by 0.85 L/min high-purity argon gas. The analytical uncertainty was better than 5%.

### Analyses of Chlorite

The analyses of major and trace elements in chlorite were conducted at USTC. The major elements were determined on a JEOL JXA-8530 electron microprobe under 15 kV accelerating voltage, 10 nA beam current, and 5 µm beam size. The analytical uncertainty was <1%. The trace element composition of chlorite from the FK basalts was determined using a Coherent ArF excimer UV 193 nm wavelength GeoLas procoupled with an Agilent 7700e quadrupole mass spectrometer (LA-ICP-MS). The sampling spot size was 60 µm. The laser was operated at a frequency of 10 Hz, and ablation times were 40 s. Detailed instrument parameters

and analytical methods are given in the work of Hou et al. (2020).

### Lithium Isotope Analysis

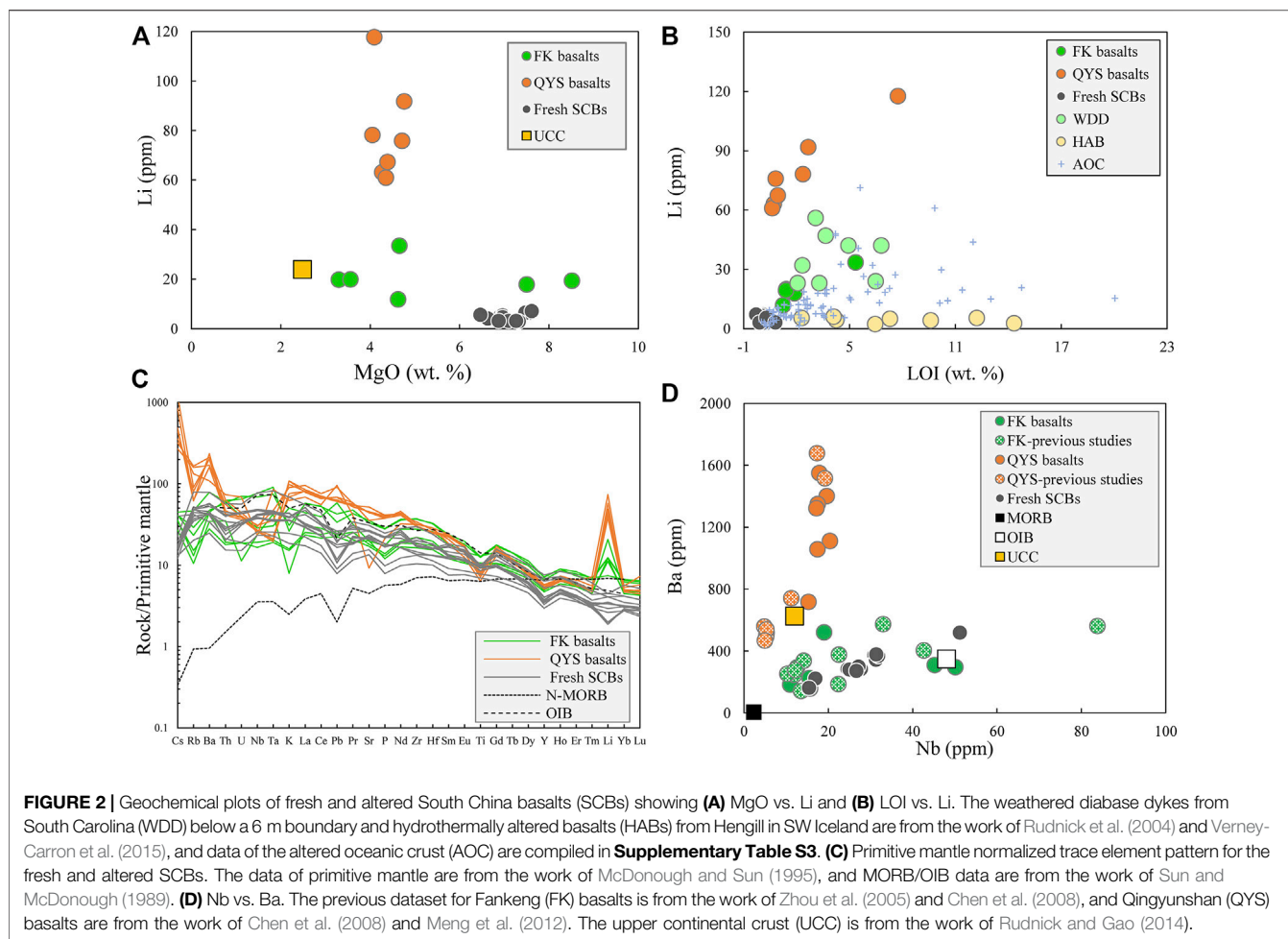
Rock powders were digested in a 1:1 mixture of ultra-pure concentrated HF (24 M) and HNO<sub>3</sub> (16 M) for 24 h at 150°C in Teflon vials, then remobilized in 2 mL 8 M HCl, and refluxed in 3 mL 0.2 M HCl to prepare for cation exchange chromatograph. Detailed liquid chromatography procedures for Li and other ion separation were from the work of Gao and Casey (2012) and Sun et al. (2016). The Li isotopic compositions were measured on a Thermo Scientific Neptune Plus MC-ICP-MS at USTC. The results are expressed as  $\delta^7\text{Li} = \{[(^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{L-SVEC}} - 1] \times 1000\}$ . The long-term external precision of Li isotopic standard L-SVEC and laboratory Li standard solutions (QC) was better than 0.3‰. Repeated determinations of international rock standards (BHVO-2 and BCR-2) showed consistency with previous studies (Supplementary Table S2).

## RESULTS

### Mineral Characteristics

Optical microscope observations from fresh basalts show phenocrysts of olivines, plagioclases, and pyroxenes, while radial epidote, quartz, and minor chlorite are present in the altered QYS basalts (Figure 1B). In the FK basalts, some chlorite pseudomorphs retained the shape of primary ferromagnesian minerals, and tiny blobs of quartz and carbonate are located at crystal edges or are distributed within the matrix (Figure 1B). The different proportion of chlorite and other minerals in the FK basalts was estimated based on the quantitative analysis of





MDI Jade Easy Quant XRD software (**Supplementary Table S1**).

## Major and Trace Element Compositions

The major and trace element composition of basalts is presented in **Supplementary Table S2**. All major elements in altered South China basalts (SCBs) are recalculated to 100% without volatiles. The altered and fresh SCBs are similar in major elements and REE pattern (**Supplementary Figure S3**). The [Li] was not associated with MgO but related with LOI in the altered SCBs (**Figures 2A,B**). Relative to fresh SCBs, the altered SCBs have higher Cs, Pb and Li (**Figure 2C**). Comparing to the QYS basalts, the FK basalts show lower content of U and K and different variation trends of Nb versus Ba (**Figures 2C,D**).

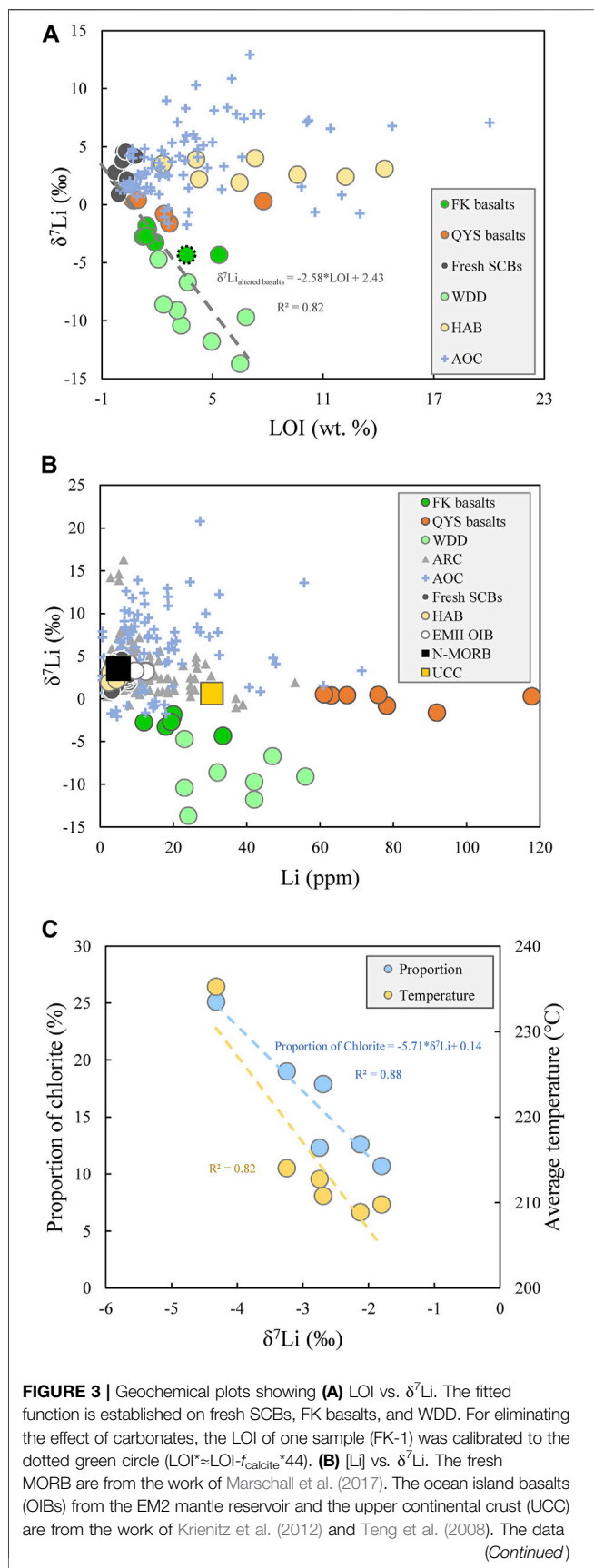
## Chlorite Composition

The major and trace element compositions of chlorite in altered SCBs are integrated in **Supplementary Tables S4, S5**, respectively. The WinCacc program coded by Yavuz et al. (2015) was used for the classification of chlorite. All chlorites from altered SCBs are clinocllore (Mg-chlorite) in discrimination diagrams (**Supplementary Figures S2A,B**).

The whole rock-normalized trace elements in chlorites from the QYS and FK basalts show that clinocllore in altered SCBs have higher [Li] than their corresponding whole rocks (**Supplementary Figure S2C**). According to the chlorite geothermometer in the WinCacc program, the formation temperature of chlorite varies from 156 to 243°C in the FK basalts and 114–253°C in the QYS basalts (**Supplementary Table S6**).

## Lithium Isotope Composition

The  $\delta^7\text{Li}$  values and (Li) of fresh and altered SCBs are provided in **Supplementary Table S2**. The altered SCBs have higher [Li] (11.9–117.7 ppm) and lower  $\delta^7\text{Li}$  values than fresh SCBs (5.0 ppm; +3.0‰) (**Figures 3A,B**). The  $\delta^7\text{Li}$  values of most QYS basalts (+0.4 to +0.5‰) are homogeneous, with two samples having some chlorites (QYS-2 and QYS-3) and lower  $\delta^7\text{Li}$  values (−1.6‰ and −0.8‰). It is worth noting that the FK basalts have higher (Li) and lower  $\delta^7\text{Li}$  values than the altered oceanic crust at any given LOI and [Li] (**Supplementary Table S3**) (**Figures 3A,B**). The FK basalts host more chlorite than most QYS basalts, and the lighter  $\delta^7\text{Li}$  in the FK basalts are associated with greater amounts of chlorite and their formation temperature (**Figure 3C**).



**FIGURE 3 |** sources of the altered oceanic crust (AOC) and arc lavas are summarized in **Supplementary Table S3**. (C) The formation temperature and proportion of chlorite as a function of  $\delta^7\text{Li}$  values for the FK basalts: proportion of chlorite =  $-5.71 \cdot \delta^7\text{Li} + 0.14$ ,  $R^2 = 0.88$ . The higher chlorite formation temperatures are associated with lower  $\delta^7\text{Li}$  values and greater proportions of chlorite.

## DISCUSSION

### Origin of High Li Concentrations in South China Basalts

The altered SCBs, especially the QYS basalts, have higher Li concentration ([Li]) than fresh SCBs and the altered oceanic crust (AOC) (Figures 2A,B). Due to its moderate incompatibility in mafic rocks, the [Li] generally increases with basaltic magma differentiation (Ryan and Kyle, 2004). However, such signature is not found in altered SCBs (Figure 1B). Crustal assimilation occurred in the QYS basalts based on low Nb/La ratios and negative  $\epsilon_{\text{Nd}}(t)$  values (Meng et al., 2012) and negligible crustal assimilation by the FK basalts based on the relation of  $\text{SiO}_2$  and  $\epsilon_{\text{Nd}}(t)$  (Cen et al., 2016). Notwithstanding the low Nb/U ratio and high [Li] of the upper continental crust ( $\text{Nb}/\text{U}_{\text{UCC}} 4.4$  and  $[\text{Li}]_{\text{UCC}} 24 \pm 5$  ppm, Rudnick and Gao 2014), it is impossible to obtain the extremely high [Li] of QYS basalts (on average,  $\text{Nb}/\text{U}_{\text{QYS-10}} 11.0$  and  $[\text{Li}]_{\text{QYS-10}} 117.7$  ppm) by mixing fresh basalt with the upper continental crust (Supplementary Figure S3D).

The dominant secondary mineral is epidote in QYS basalts and chlorite in FK basalts, whereas no secondary minerals are observed in all fresh SCBs (Figure 1B). The chlorites from QYS and FK basalts are classified as Mg-chlorite (Supplementary Figure S2), and most Mg-chlorite and epidote form at temperatures  $>150^\circ\text{C}$  (Beaufort et al., 2015; Bird and Spieler 2004), in agreement with chlorite formation temperatures in our study (Supplementary Table S6). Numerous studies of fluid–rock reactions between fluids and olivine or basalt show the precipitation of chlorite precipitating in the vicinity of carbonates and quartz at  $\geq 150^\circ\text{C}$  (Gysi and Stefánsson 2012; Li et al., 2018), which is akin to the scene observed in altered SCBs (Figure 1B). The correlation between LOI and [Li] suggests that hydrothermal alteration played an important role in increasing [Li] in the QYS and FK basalts (Figure 2B). Chlorite readily incorporates Li from fluid phases (Xiao and Chen 2020). The higher [Li] in chlorite than in whole rocks indicates that chlorite is the primary reservoir for Li in altered SCBs (Supplementary Figure S2C). The partition coefficient of Li between chlorite and fluid ( $D_{\text{Li}}^{\text{chlorite-fluid}}$ ) is related to temperature and is  $1.7 \pm 0.2$  at  $50^\circ\text{C}$ ,  $0.8 \pm 0.1$  at  $150^\circ\text{C}$ , and  $0.35 \pm 0.1$  at  $260^\circ\text{C}$  (Berger et al., 1988). Given the extremely high [Li] in chlorite from the QYS (299.0–545.6 ppm) and FK basalts (83.2–174.5 ppm) (Supplementary Table S5), the hydrothermal fluid would have required extremely high [Li] at  $>150^\circ\text{C}$ . However, the [Li] of most geothermal and submarine fluids summarized from the work of Verney-Carron et al. (2015) does not meet this requirement ([Li] 0.14–9.7 ppm). Silicic magmas generally exsolve fluid-mobile elements (e.g., Li) during late magmatic evolution (Ellis et al., 2018; Neukampf et al., 2020). For example, the [Li] of melt inclusions ( $[\text{Li}]_{\text{avg.}} 244\text{ppm}$ ) was six times greater than that of

groundmass glasses [ $(\text{Li})_{\text{avg}}$ , 43 ppm] in the Mesa Falls Tuff, Yellowstone, suggesting the loss of Li from melt to fluids during the late stage of magma evolution (Neukampf et al., 2019). In addition, quartz-hosted fluid inclusions from the Variscan granite of Southwest England also have remarkably high [Li] (200–363 ppm, Richard et al., 2018). In South China, the upwelling of the asthenospheric mantle facilitated the intrusion of mafic rocks and abundant coeval granitoids (Li and Li, 2007; Li et al., 2014). Because both the QYS and the FK basalts were interspersed by massive amounts of coeval granitoids (Figure 1A), we propose that the granitoid-related fluids metasomatized these basalts.

## Origin of Low $\delta^7\text{Li}$ Values in South China Basalts

The altered SCBs, especially the FK basalts, have lower  $\delta^7\text{Li}$  values than the fresh SCBs, altered oceanic crust (AOC), and MORB (Figures 3A,B). It has been unequivocally demonstrated that Li isotopic fractionation is insignificant at magmatic temperatures (Tomascak et al., 1999; Jeffcoate et al., 2007), except possibly during the latest-, fluid-rich stages of evolution (Ellis et al., 2018; Neukampf et al., 2019, 2020). Additionally, the  $\delta^7\text{Li}$  values of fresh SCBs are similar to those of OIB and MORB, ruling out the possibility that the light  $\delta^7\text{Li}$  values of altered SCBs were derived from the EM2 mantle reservoir (Figure 3B). Assimilation of continental crustal rocks during emplacement of magma would make it impossible to achieve such low  $\delta^7\text{Li}$  values for the altered SCBs, due to their higher content of Li and lower  $\delta^7\text{Li}$  values than UCC (Figure 3B).

Hydrothermally altered basalts (HABs) from Iceland display very little variation in  $\delta^7\text{Li}$  values controlled by chlorite (Figure 3B), suggesting that hydrothermal alteration merely involved with seawater or meteoric water did not induce any significant changes in  $\delta^7\text{Li}$  values of whole rock. Additionally, the higher [Li] and relatively lower  $\delta^7\text{Li}$  values in altered SCBs than HAB suggest that such metasomatic fluid was different from seawater or meteoric water and was capable of increasing the basalts' [Li] and decreasing their  $\delta^7\text{Li}$  values. In combination with the increase in [Li] during alteration, it appears likely that a crustal fluid with a low  $\delta^7\text{Li}$  value, similar to the fluid exsolving from the Variscan granites of Southwest England reported above ( $-1.4\sim+0.9\%$  from Richard et al., 2018), was found, thereby enriching their [Li] and lowering their  $\delta^7\text{Li}$  values. Although both the QYS and the FK basalts underwent hydrothermal alteration (Figure 1B), the FK basalts have lower content of U, Ba, and K than QYS basalts (Figure 2C). In contrast to the  $\delta^7\text{Li}$  values of most QYS basalts (0.3–0.5), the FK basalts have even lower  $\delta^7\text{Li}$  values ( $-4.3\sim-1.8$ ) (Figure 3B). These differences between the QYS and FK basalts suggest that there must have been differences in the low-temperature processes.

The FK basalts were sampled from the riverbed, where the dominant hydrothermal mineral is chlorite and minor weathered clays, such as kaolinite and illite (Supplementary Table S1), were found, suggesting that they underwent both hydrothermal alteration and slight weathering. Additionally, the [Li] and its isotope composition of FK basalts fall between fresh SCBs and weathered diabase dyke (WDD) (Figure 3B), suggesting weathering has occurred in FK basalts. Eliminating the effect of other volatile-

rich minerals on LOI, the fitted function between LOI and  $\delta^7\text{Li}$  of fresh and weathered basalts imply that the clay minerals modified the  $\delta^7\text{Li}$  of weathered rocks (Figure 3A). The good correlation between  $\delta^7\text{Li}$  and the content of chlorite supports that it is chlorite that controlled the Li isotopic composition of the FK basalts (Figure 3C). The lower  $\delta^7\text{Li}$  values in FK basalts than in fresh basalts can, thus, be explained by the preferential incorporation of  $^6\text{Li}$  over  $^7\text{Li}$  in chlorite's octahedral site during weathering, which is corroborated by extremely large Li isotopic fractionation between clays and fluid ( $\Delta^7\text{Li}_{\text{clays-solution}}^{-20^\circ\text{C}}$  up to  $-23\%$ ) found in abundant experimental studies of weathering (Wunder et al., 2006; Millot et al., 2010; Hindshaw et al., 2019; Pogge von Strandmann et al., 2019), calculation model (Fairén et al., 2015), and natural weathered basaltic rocks ( $\delta^7\text{Li}$  as low as  $-20.2\%$ ; Rudnick et al., 2004). The  $\delta^7\text{Li}$  value (0.02‰) of FK basalts before weathering can be estimated by fitted function when the proportion of chlorites is zero, corresponding to an inactivated fractionation effect of chlorite (Figure 3C). At any given [Li], the FK basalts and the WDD have lower  $\delta^7\text{Li}$  values than the AOC (Figures 3A,B), suggesting that continental weathering had a stronger effect in lowering the  $\delta^7\text{Li}$  values of basaltic rocks than low-T alteration on the ocean floor.

## Hydrothermal Alteration and Weathering of the South China Basalts

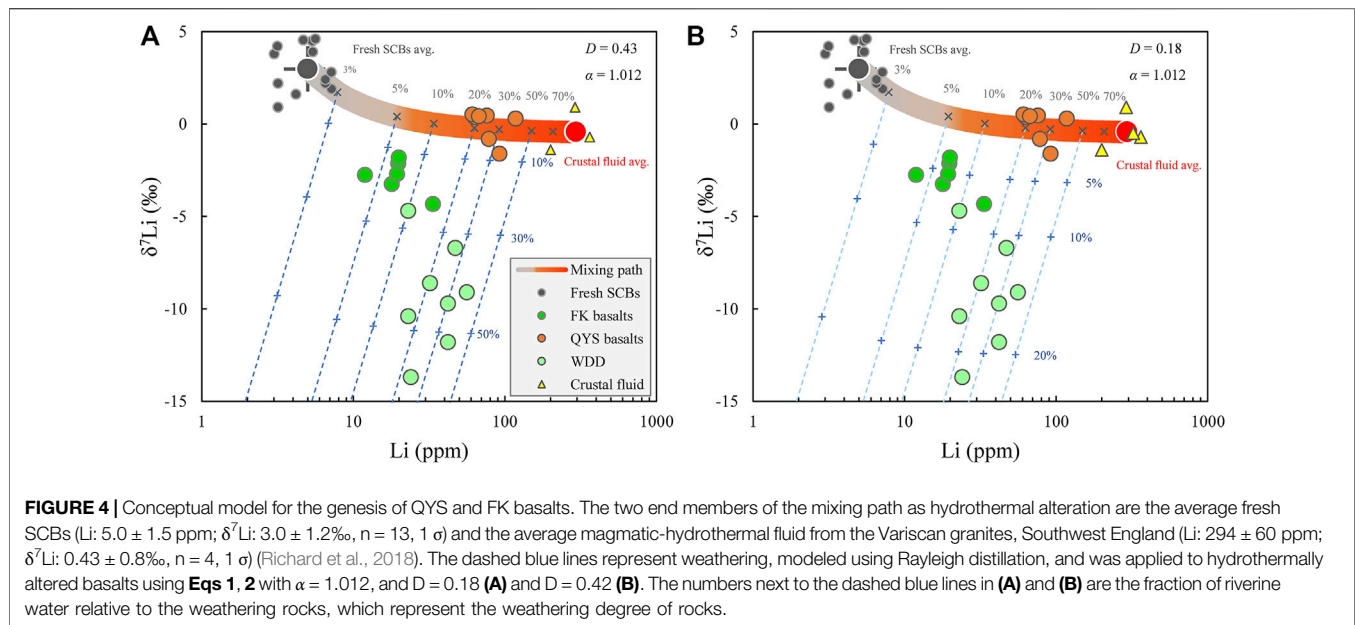
It appears that chlorite served as an “element pool” for imposing restrictions on the mobility of Li during the hydrothermal alteration. Such process set the stage for subsequent weathering to effect even lower  $\delta^7\text{Li}$  values in weathered basalts. In our model, the magmatic fluids from the Variscan granites of Southwest England are selected to represent the hydrothermal fluids which metasomatized the fresh SCBs. The [Li] and  $\delta^7\text{Li}$  values of the QYS basalts were, thus, modeled as mixtures of fresh SCBs and metasomatic fluids which is consistent with the presence of abundant epidote and high LOI in QYS basalts (Figure 3A). According to this model, the QYS basalts correspond to a mixture of fresh SCBs with 20–40% metasomatic fluids, while the FK basalts appear to have experienced lower degrees of metasomatism (4–15%). The overestimated fluid addition of QYS basalts can be attributed to two aspects: 1) crustal contamination increases the [Li] in QYS basalts; 2) the [Li] of real metasomatic fluid is underestimated as evidenced by the high [Li] in chlorite (299.0–545.6 ppm) and low  $D^{\text{chlorite-fluid}}$  ( $\sim 0.8$  at  $150^\circ\text{C}$ ).

The interaction of FK basalts with subaerial water during weathering was modeled by Rayleigh distillation in an open system (Rudnick et al., 2004; Liu et al., 2013) superimposed on previously hydrothermally altered basalts. Using the following equations allows obtaining the [Li] ( $C_{\text{solid}}$ ) and  $\delta^7\text{Li}_{\text{solid}}$  values of weathered rocks:

$$C_{\text{solid}} = C_0 (1 - F)^{\frac{1}{f-1}}, \quad (1)$$

$$\delta^7\text{Li}_{\text{solid}} = [(\delta^7\text{Li})_0 + 1000] f^{(\alpha-1)} - 1000, \quad (2)$$

where  $C_0$  and  $\delta^7\text{Li}_0$  are the [Li] and  $\delta^7\text{Li}$  values of hydrothermally altered basalts,  $F$  is the fraction of riverine water relative to the solid,  $f$  is the fraction of Li remaining in the weathered rocks, and



$D$  and  $\alpha$  are the bulk partition coefficient and fractionation factor. Berger et al. (1988) reported that  $D_{\text{Li}}^{\text{chlorite-fluid}}$  was  $\sim 1.7$  at  $50^\circ\text{C}$ . If the FK basalts are regarded as a binary mixture of “chlorite” and “non-chlorite” parts ( $D_{\text{Li}}^{\text{non-chlorite-fluid}} = 0$ ) and the content of chlorite in FK basalts ranges from 10.7 to 25.1% (Supplementary Table S1),  $D \approx 0.18$  to 0.43, which agrees with the incompatible behavior of Li in rocks during weathering (Kısakürek et al., 2004; Rudnick et al., 2004; Liu et al., 2013). At  $50^\circ\text{C}$ ,  $\alpha^{\text{fluid-rock}}$  is  $\sim 1.012$  according to the work of Marschall et al. (2007), which is close to the value of 1.010 calculated by Vigier et al. (2008), and falls within the range from 1.005 to 1.02 in natural samples reported by Rudnick et al. (2004). As shown in Figure 4, the FK basalts lost a fraction of Li and gained lower  $\delta^7\text{Li}$  values as a result of weathering, and this is supported by the higher proportion of chlorite in the FK basalts resulting in greater Li isotopic fractionation (Figure 3C). In addition, one chlorite-bearing QYS basalt (QYS-2) with low  $\delta^7\text{Li}$  values ( $-1.4\%$ ) also appears to have experienced weathering. Although the present model overlooks other possible sources of Li and any possible kinetic isotopic fractionation (e.g., capillarity-driven diffusion between underground water and the weathered diabase dyke (WDD) above 6 m; Teng et al., 2010), given the similarity of the FK basalts and the WDD and the case made here for weathering having affected these rocks, we speculate that the  $\delta^7\text{Li}$  of weathered SCBs can potentially evolve to WDD during advanced states of weathering (Figure 4). In general, relative to weathering, hydrothermal alteration alone exerts a lesser influence on the Li isotopic fractionation between rocks and fluids (Figure 4).

### Implication for the Origin of Lower $\delta^7\text{Li}$ Values in Continental-Type Eclogites

The weathered basaltic rocks have the trend of higher [Li] and lower  $\delta^7\text{Li}$  values than the fresh basalts and altered oceanic

crust (AOC) (Figure 3B). Coincidentally, such feature agrees with the overarching goal of increasing [Li] and decreasing  $\delta^7\text{Li}$  in orogenic eclogites from previous studies. For example, the light  $\delta^7\text{Li}$  values ( $-12.9 \sim +4.6$ ) of oceanic-type eclogites are generally ascribed to processes operating on the AOC during subduction and exhumation, such as dehydration (Zack et al., 2003), metasomatism (Simons et al., 2010), and diffusion of Li between country rocks/fluids and subducting slabs (Marschall et al., 2007). By contrast, continental-type eclogites have lighter and more scattered  $\delta^7\text{Li}$  values ( $-21.9 \sim +5.4$ ) (Supplementary Figure S4). Most crustal fluids interacting with orogenic eclogites generally have heavy Li isotopic compositions (Simons et al., 2010), while fluid activity in continental collision zones is generally deficient and episodic compared to that in oceanic subduction zones (Zheng and Chen 2016), so crustal fluid metasomatism alone is unlikely to be at the origin of the low  $\delta^7\text{Li}$  values of continental-type eclogites. Although diffusion of Li from surrounding rocks or fluids into eclogites could contribute to the Li isotopic signature of continental eclogites (Marschall et al., 2007), the contribution from weathered protoliths of continental eclogites should not be overlooked. Zhang et al. (2016) found metamorphic zircons in continental-type eclogites from North Qaidam yielding  $\delta^{18}\text{O}$  values higher than those of relict magmatic zircons, which was ascribed to low-T altered protoliths. This low-T process is known to form secondary minerals such as chlorite in continental basalts. Furthermore, chlorite is a common mineral in the subduction zone and an equally important reservoir for Li akin to phengite, possibly keeping Li concentration and isotopic ratios unchanged during prograde metamorphism (Bebout 2014; Barnes et al., 2019). Therefore, weathering must be taken into consideration when trying to understand the origin of extremely low  $\delta^7\text{Li}$  values of continental-type eclogites.



## CONCLUSION

Compared to fresh SCBs, the higher Li concentration in altered SCBs from the Qingyunshan (QYS) and the Fankeng (FK) formations originated from their hydrothermal alteration by magmatic fluids having high [Li]. This magmatic-hydrothermal alteration also recrystallized primary igneous ferromagnesian silicate minerals to chlorite, which is the main repository for Li in the altered SCBs and, thus, controls their Li isotopic compositions. Given that chlorite preferentially incorporates  $^6\text{Li}$  over  $^7\text{Li}$ , this magmatic-hydrothermal alteration lowered the rocks'  $\delta^7\text{Li}$  values. Subsequent weathering of the chlorite-bearing FK basalts further lowered their  $\delta^7\text{Li}$  values, in contrast to the hydrothermally altered QYS basalts. In contrast to previous studies, the weathered basalts, thus, acquired  $\delta^7\text{Li}$  values lower than those of altered oceanic crust, and it becomes clear that continental weathering needs to be considered instead of ocean floor alteration when investigating the origin of low  $\delta^7\text{Li}$  values in continental-type eclogites.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

C-LY: conceptualization, data curation, dormal analysis, funding acquisition, investigation, methodology, visualization, and

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2022.844353/full#supplementary-material>

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