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Continental crust recycling in collisional zones: insights from Li isotope compositions of the syn-exhumation and post-collisional mafic magmatic rocks

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Syn-exhumation and post-collisional mafic magmatism in continental collision orogenic belts may provide insights into the nature of orogenic lithospheric mantle and recycled continental components in continental subduction zones. Lithium and its isotopes have emerged as potentially valuable tools for shedding light on the origin of these magmas, given the contrast Li contents and isotopic compositions between the subducting continental crust and the mantle. Here, we present high-precision Li isotopes data for representative orthogneiss, continental eclogite, syn-exhumation and post-collisional mafic magmatic rocks from the North Qaidam orogen. The syn-exhumation mafic magmatic rocks have relatively higher Li contents (26.5–50.0 ppm) and lower δ^7Li values (–1.01‰–1.48‰) than those of the post-collisional mafic magmatic rocks (Li = 11.1–22.7 ppm, δ^7Li = 1.20‰–3.38‰), which are comparable to those of orthogneiss and continental eclogite, respectively. Dehydration and melting modelling results show that these mafic magmatic rocks have similar Li contents and δ^7Li values to the continental eclogite- and orthogneiss-derived melts but are different from their derived fluids. Monte Carlo simulation for Li-Nd isotopes suggests the syn-exhumation and post-collisional mafic rocks could be derived from an enriched mantle source that contains ~3–8% continental crustal components dominated by the orthogneiss and continental eclogite. The calculated results are consistent with the results from the previous study simulated by trace elements. Therefore, our results highlight Li isotopes as a potential tool to trace the nature of the continental crustal components recycling in continental subduction zones.

KEYWORDS

syn-exhumation mafic magmatic rocks, post-collisional mafic magmatic rocks, Li isotopes, continental crustal components recycling, continental collision zones

1 Introduction

Continental deep subduction orogen is commonly characterized by the presence of ultrahigh-pressure (UHP) metamorphic continent-crust rocks that may have been subducted to mantle depths (Chopin, 2003; Liu et al., 2019). The recognition of granitic melts in UHP metamorphic rocks indicates the significant fluids/melts activity during continental crust exhumation (Auzanneau et al., 2006; Zheng, 2012), which is also realized by the orogenic peridotite exhibiting geochemical compositions similar to continental crust rocks (Bodinier et al., 1990; Hermann et al., 2006; Vrijmoed et al., 2013; Chen et al., 2017). Additionally, arc-like trace element distribution patterns, such as the enrichment of large ion lithophile elements (LILE) and light rare earth elements (LREE) and the depletion of high field strength elements (HFSE) relative to heavy rare earth elements (HREE), are dominated among syn-exhumation and post-collisional mafic magmatic rocks (e.g., Zhao et al., 2015; Zheng et al., 2015; Couzinié et al., 2016). In these regards, the geochemical features of mafic rocks have recorded crust-mantle interactions in continental collisional belts. Though the nature of metasomatic fluids/melts can be diagnosed by the trace elements and O isotopes compositions of minerals in orogenic peridotites directly (Chen et al., 2017), it is still unclear whether these fluids/melts can be recycled into the mantle source of syn-exhumation and post-collisional mafic magmatic rocks and whether the nature of them can be distinguished via the geochemical composition of these rocks.

Lithium, as one of the fluid-mobile elements, exhibits significant mass-dependent fractionation in lower-temperature fluid-participated reactions, such as hydrothermal alteration and dehydration, but only a limited fractionation in high-temperature processes, such as metamorphic dehydration, partial melting, and fractional crystallization (Tomascak et al., 1999; Zack et al., 2003; Tang et al., 2007a; Marschall et al., 2007b; Teng et al., 2007; Simons et al., 2010). The heavy ^{7}Li isotope is preferentially incorporated into the aqueous solution, leading to the complementary remanent enriched in the light ^{6}Li isotope, but remains consistent in melt-mineral separating processes (Marschall et al., 2007a; Halama et al., 2009; Penniston-Dorland et al., 2012; Liu et al., 2019). Consequently, Li isotopes of the arc mafic magmatic rocks have been extensively used to investigate the properties of the recycled crustal materials in oceanic subduction zones, such as altered oceanic crust-derived aqueous fluids and sediments-derived hydrous melts (e.g., Tang et al., 2007b; Penniston-Dorland et al., 2010; Halama et al., 2011; Tang et al., 2014; Tian et al., 2015; Liu et al., 2020). Compared with the oceanic subduction zones, although only a limited amount of fluids is generated during the continental crust subduction stage, a substantial amount of fluids/melts can be generated from the crustal rocks during the exhumation stage (e.g., Auzanneau et al., 2006; Zheng, 2012). Therefore, Li isotopes may also have great potential in tracing the nature of recycled fluids/melts in continental subduction zones.

In this paper, we carried out whole-rock Li isotopes among syn-exhumation and post-collisional mafic magmatic rocks as well as coexisted UHP metamorphic rocks, including continental eclogite and orthogneiss in the North Qaidam UHP metamorphic belt. The North Qaidam orogen was built by the collision between the Qaidam Block and Qilian Block during the Early Paleozoic (Song et al., 2014; Zhang et al., 2017a and reference therein), where partial melting of continental crust at various degrees was recognized. Our results show that Li isotopes of the syn-exhumation and post-collisional mafic magmatic rocks can be explained by incorporating the dehydrated continental eclogite- and orthogneiss-derived melts into the orogenic lithospheric mantle at different proportions. As such, Li isotopes could be a powerful means to decipher the nature of recycled subducted continental crustal components in continental subduction zones.

2 Geological settings and samples

The North Qaidam orogen, located northwest of the Tibetan Plateau, is a typical continental collision orogen. It spans approximately 400 km in an NW-SW direction and is bound by the Qilian Block to the north, the Qaidam Block to the south and the Altyn Tagh fault to the west (e.g., Song et al., 2014; Zhang et al., 2017). Based on rock assemblages and field relationships, four UHP metamorphic terranes were identified, including Dulan, Xitieshan, Lüliangshan, and Yuka terranes (Figure 1). By examining the geochronological and geochemical records of UHP metamorphic rocks and magmatic rocks, it was determined that this belt underwent a complete orogenic cycle from oceanic slab subduction to oceanic/continental collisions, and finally orogen collapse during the Paleozoic (e.g., Wu et al., 2014; Zhu et al., 2015; Chen et al., 2019). Metamorphic rocks in this belt are mainly composed of orthogneiss, paragneiss and their enclosed eclogite as well as garnet peridotites (e.g., Yu et al., 2019). Despite their diversities, they have exhibited a uniform UHP metamorphism at 438–420 Ma. The protolith age of orthogneiss is about 1,000–900 Ma, while that of the eclogite was mainly distributed at about 850 Ma and 516 Ma (Song et al., 2010; Song et al., 2012; Zhang et al., 2016). In combination with their different *in situ* O isotopic compositions for relict zircons, the former group was presumed to be continental eclogite (5.6‰–8.0‰) and the latter group to be oceanic eclogite (2.5‰–5.6‰) (Zhang et al., 2016).

The subducted continental slab was exhumed until about 400 Ma, as indicated by the high amphibole or granulite metamorphism overprinted on the eclogite (Song et al., 2014). The syn-exhumation magmatic rocks emplaced at 420–390 Ma are distributed mainly in the Dulan and Lüliangshang terrane (Wang et al., 2014; Wu et al., 2014; Sun et al., 2020; Yang et al., 2020). The syn-exhumation granitic rocks in the Dulan terrane were mainly formed by partially melting of orthogneiss with a small amount of metasedimentary rocks and continental eclogite, while the trondhjemitic rocks in the Lüliangshang were suggested to be produced by partial melting of continental eclogite during the syn-exhumation stage (Sun et al., 2020; Yang et al., 2020). The syn-exhumation mafic magmatic rocks were suggested to be derived from a lithospheric mantle metasomatized mainly by the orthogneiss-derived felsic melts based on their similar whole-rock Sr-Nd isotopes and zircon *in situ* Hf-O isotopes (Sun et al., 2022).

The post-collisional magmatic rocks with U-Pb ages of 390 to 356 Ma are distributed throughout the belt. The mafic magmatic rocks in this stage generally exhibit arc-like trace

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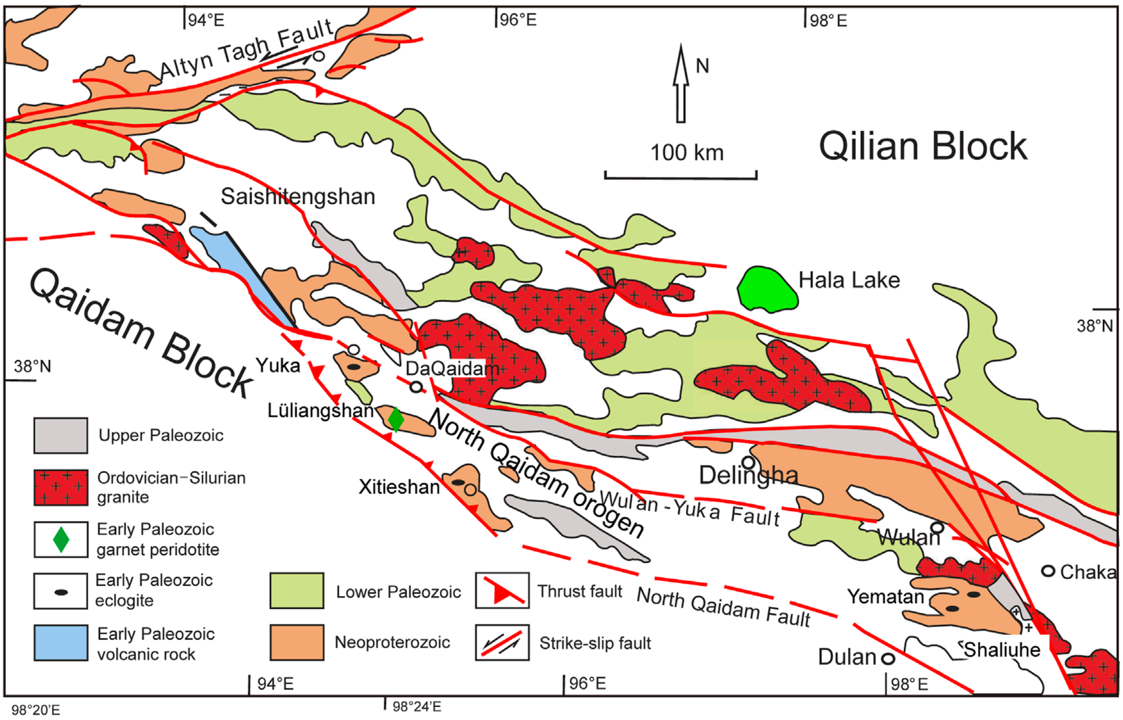

FIGURE 1
Geological sketch map of the North Qaidam orogen (modified from Sun et al., 2022).

element distribution except for three E-MORB (enriched mid-ocean ridge basalt) like rocks in the Dulan area (Zhao et al., 2018; Zhou et al., 2021). Their lithospheric mantle source was suggested to be metasomatized mainly by different agents such as oceanic slab-derived liquid (Zhao et al., 2018), oceanic sediment-derived (Zhou et al., 2021), orthogenesis- and continental eclogite-derived melts (Sun et al., 2022) based on their different trace elements ratios, depleted to enriched whole-rock Sr-Nd isotopes and zircon *in situ* Hf-O isotopes. The post-collisional granites have resulted from partial melting of the upper continental crustal rocks in various proportions with the depleted asthenosphere mantle may also be involved (Wang et al., 2014; Zhao et al., 2018; Sun et al., 2022).

A total of twenty-four samples were selected through the North Qaidam belt, including four syn-exhumation mafic magmatic rocks from the Dulan area in Dulan terrane, six post-collisional mafic magmatic rocks from the Dulan area in Dulan terrane and Aolaoshan area in Yuka terrane, ten continental eclogite samples from Dulan terrane, Xitieshan terrane and Yuka terrane, and four orthogneiss samples from Dulan and Xitieshan terrane. The micrographs of representative rocks are shown in Figure 2. The syn-exhumation (420 ± 8 to 395 ± 2 Ma) and post-collisional (383 ± 5 to 368 ± 3 Ma) mafic magmatic rocks are hornblende gabbro to gabbro-diorite selected from Sun et al. (2022). Though they are generally composed of clinopyroxene, hornblende and plagioclase, the syn-exhumation mafic magmatic rocks (Figure 2A) have more K-feldspar than the post-collisional mafic magmatic rocks (Figure 2B). In addition, some clinopyroxene in post-collisonal mafic magmatic rocks is located inside of hornblende, which may indicates a few rocks may have experienced clinopyroxene fractional crystallization. The representative continental eclogite and orthogneiss are selected from Zhang et al. (2015, 2017). The continental eclogites are fresh and generally composed of garnet, omphacite and rutile, excluding their obvious retrometamorphism during their exhumation (Figure 2C). The orthogneisses are generally composed of biotite, muscovite together with sharply elongated quartz and plagioclase, suggesting they have partial melted at a small degree but without melts lost obviously (Figure 2D).

3 Analysis methods

Whole-rock Li isotopes were analyzed using a Thermo Scientific Neptune Plus multi-collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) at Hefei University of Technology, Hefei. Detailed procedures for sample dissolution, separation, and analysis were carried out at the CAS Key Laboratory of Crust-Mantle Materials and Environments at USTC, Hefei and can be found in Sun et al. (2016). About 50–100 mg of whole-rock powder was weighed and dissolved with ultra-pure $HF+HNO_3$ in a Teflon PFA beaker. After complete dissolution, Li was separated and purified using one column filled with Bio-Rad AG 50WX8 resin (200–400 mesh) and was further purified using another column filled with Bio-Rad AG 50WX-12 resin (200–400 mesh). All separations yielded high Li content and a low Na/Li ratio (<0.5), with a recovery higher than 99.8% and a total procedural blank of less than 30 pg. The long-term external reproducibility, based on repeat runs of pure Li in-house standard solutions, is better than ±0.3‰ (Li-QCUSTC = +8.8 ± 0.3‰, 2SD, n = 161). During Li isotope analysis, the USGS standard BHVO-2 and GSP-2 yielded

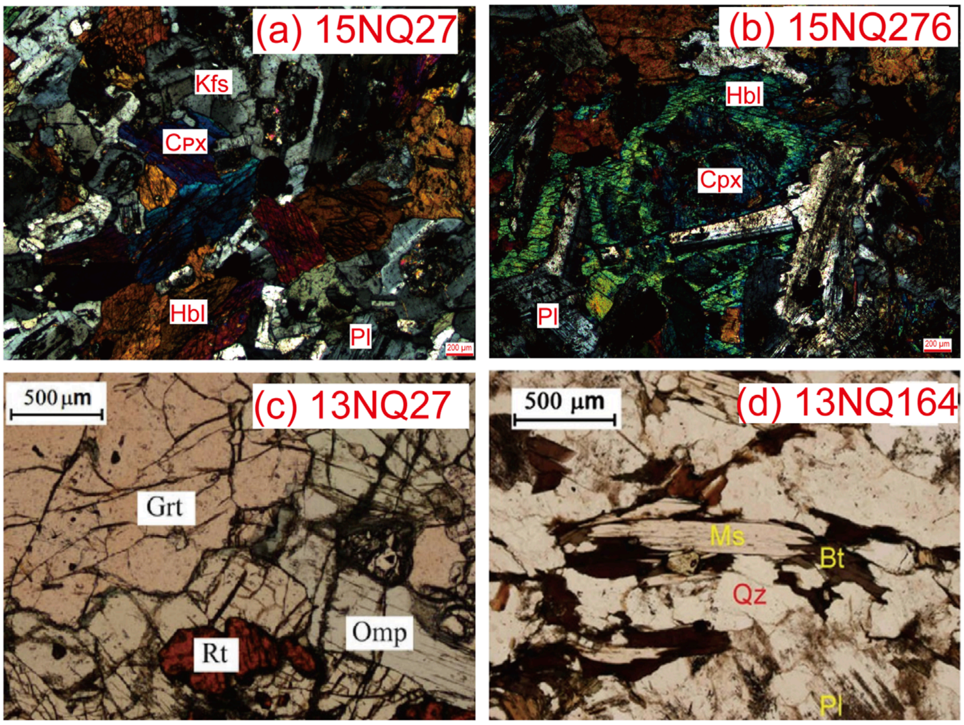

FIGURE 2
Photomicrographs showing representative **(A)** syn-exhumation and **(B)** post-collisional mafic magmatic rocks under cross-polarized light modified from Sun et al. (2022); **(C)** fresh eclogites from the Yematan area from Zhang et al. (2017) and **(D)** orthogneiss from Xitieshan area modified from Zhang et al. (2015) under plane-polarized light in the North Qaidam orogen. Pl: plagioclase, Kfs: K-feldspar, Hbl: hornblende, Cpx: clinopyroxene, Grt: garnet, Rt: rutile, Omp: omphacite, Ms: muscovite, Bt: biotite, Qz: quartz.

δ^7Li values of 5.0 ± 0.1‰ and −0.4 ± 0.1‰, which are consistent with those of previously published results (Gao and Casey, 2012; Sun et al., 2016; Liu et al., 2019).

4 Results

Trace elements data of the syn-exhumation and post-collisional mafic magmatic rocks, continental eclogites, and orthogneiss are cited from previous studies and are presented in Supplementary Table S1. Lithium and other radiogenic isotopic data (Zhang et al., 2016, 2017b; Sun et al., 2022) are presented in Supplementary Table S2.

The syn-exhumation mafic magmatic samples display Li contents of 26.5–50.0 ppm, higher than those of the post-collisional mafic magmatic samples (11.1–22.7 ppm). Notably, these magmatic rocks generally have higher Li contents than fresh MORB (Figure 3, e.g.; Tomascak et al., 2008; Marschall et al., 2017). The continental eclogite contains Li contents of 3.59–19.4 ppm, while the orthogneiss has higher Li contents of 28.2–66.6 ppm.

Most post-collisional mafic magmatic samples have δ^7Li values of 1.20‰–3.38‰ (Figure 3; Supplementary Table S2), lower than those of the fresh N-MORB (3.6‰ ± 2.0‰, Tomascak et al., 2008; Marschall et al., 2017) but higher than those of the syn-exhumation mafic rocks (−1.01‰–1.48‰). The orthogneiss presents relatively consistent δ^7Li values of −0.17‰ to −1.41‰, while the continental eclogites generally have a wider range of δ^7Li values (−9.10‰ to 2.41‰) that can be subdivided into two groups. The first Group has high δ^7Li values of −0.52‰–2.41‰, while the second group has low values of −9.10‰ to −4.54‰.

5 Discussion

5.1 The effect of crustal contamination, fractional crystallization, and alteration

The Li isotopes of basaltic rocks can be affected by crustal contamination and alteration processes (e.g., Chan et al., 2009). Therefore, it is necessary to evaluate the effects of crustal contamination and post-magmatic alteration before using Li isotopes to trace their source features.

The studied samples are fresh, without carbonates and other secondary minerals. As shown in Figure 4A, there is no correlation between the δ^7Li values and LOI (0.33–1.99 wt%) for these samples. Even the sample with the highest δ^7Li value (+3.8‰ ± 0.01‰) still has a relatively low LOI content (1.24 wt%, Figure 4A). In addition, the variable δ^7Li values of the syn-exhumation and post-collisional mafic magmatic rocks show no correlation with their SiO_2 content (Figure 4B) and poor correlation with their Sr-Nd isotope compositions (Figures 5A, B). As the dominant constituent of the North Qaidam continental crust, orthogneiss is among the most important potential contaminants for the mafic magmas. Therefore, the assimilated materials would be expected to display low δ^7Li and $\varepsilon_{Nd}(t)$ values close to those of the orthogneiss. However, such

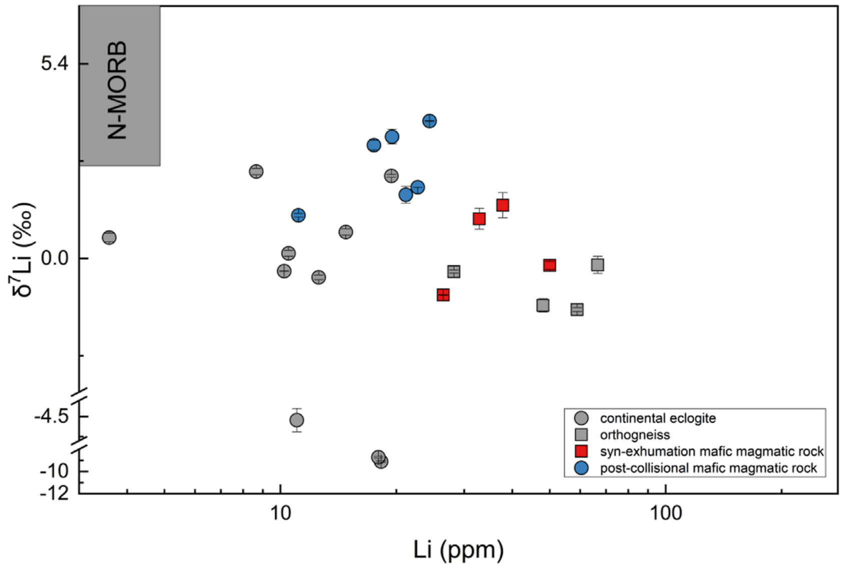

FIGURE 3
Li content *versus* δ^7Li values for continental eclogite, orthogneiss and syn-exhumation and post-collisional mafic magmatic rock in the North Qaidam orogen. The Li contents and δ^7Li values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017).

correlations were not observed among our samples. The individual relationship between syn-exhumation and post-collisional mafic magmatic rocks are different, which indicates the correlation is not caused by crustal contamination, because the crustal contamination would result in similar relationships for these mafic magmatic rocks. In addition, the mafic rocks with the highest SiO_2 content of 56.28% also have MORB-like δ^7Li value (3.6‰ ± 2‰). These observations suggest that crustal contamination did not affect the Li isotopes of the syn-exhumation and post-collisional mafic magmatic rocks significantly. The studied mafic rocks generally exhibit low MgO content and Mg# number, indicating fractional crystallization of mafic minerals during their magma emplacement. Nevertheless, Li isotopes fractionation is limited during high temperatures (~1,200 °C) magma differentiation as certified by previous studies (e.g., Tomascak et al., 1999; Liu et al., 2020).

In summary, the influence of crustal contamination, fractional crystallization, and alteration on the Li isotopes of our samples is negligible. Thus, the whole-rock Li isotopes of our magmatic rocks can be used to trace their mantle source feature and, thus the nature of potentially recycled crustal components therein.

5.2 The origin of the Li isotope variations

The North Qaidam syn-exhumation and post-collisional mafic magmatic rocks display arc-like trace-element patterns, high $(^{87}Sr/^{86}Sr)_i$ ratios and positive to negative $\varepsilon_{Nd}(t)$ values (t = 380 Ma, Figure 5), implying that they were derived from metasomatized lithospheric mantle (Wang et al., 2014; Zhao et al., 2018; Zhou et al., 2021; Sun et al., 2022). A recent investigation on orogenic peridotites in this region revealed variable stages of metasomatism by different metasomatic agents, including low δ^{18}O (<5.6‰) fluids released from the oceanic subduction stage and high δ^{18}O fluids and melts stemmed from the subducted continental crust during the early to late stages of exhumation (Chen et al., 2017). For our samples, they have higher δ^{18}O values for syn-magmatic zircon (Sun et al., 2022) and lower whole-rock δ^7Li values than that of N-MORB, which indicates that the oceanic crust-derived fluids may have less contribution to these mafic magmatic rocks. In this regard, the mantle source of our samples was mainly metasomatized by the continental crust-derived fluids/melts.

Dehydration and partial melting of continental components, such as continental eclogite, orthogneiss and paragneiss, have been recognized during continental crust subduction and exhumation in North Qaidam orogen (Yu et al., 2019 and therein). As the minimal extraction volume of the melts is 7% (Rosenberg and Handy, 2005), we assumed dehydration/melting products with aggressive fraction below 7 wt% are aqueous fluids, while those exceeding 7 wt% are hydrous melts. The reason for selecting such a high fluids content is to encompass the range of Li contents and δ^7Li values of the fluids as much as possible, despite its exceeding minimal water saturation at the solidus for the protolith of the UHP metamorphic rocks in our study. The protolith of the continental eclogite was assumed to be continental flood basalt (CFB) associated with Rodinia broke up during the Neoproterozoic (Song et al., 2012). Therefore, the composition of the fluids/melts released from those crustal materials could be explored by modeling the dehydration or partial melting processes of their protolith and continental eclogite. As the continental crust has experienced UHP metamorphism and subsequent exhumation processes during 438–400 Ma (Song et al., 2014), we modelled the Li contents and δ^7Li values of its released fluids and residues during these two processes. Considering the scarce Li isotopes data for typical CFB currently, the average OIB compositions (Li = 7.4 ppm and δ^7Li = 3.6‰) from Krienitz et al. (2012) were used as the started basalts as they are both mantle plume-related magmatic rocks. The dehydrated process for the model Li contents and δ^7Li values of the OIB-derived fluids and corresponding residues is the same as Simons et al. (2010), and

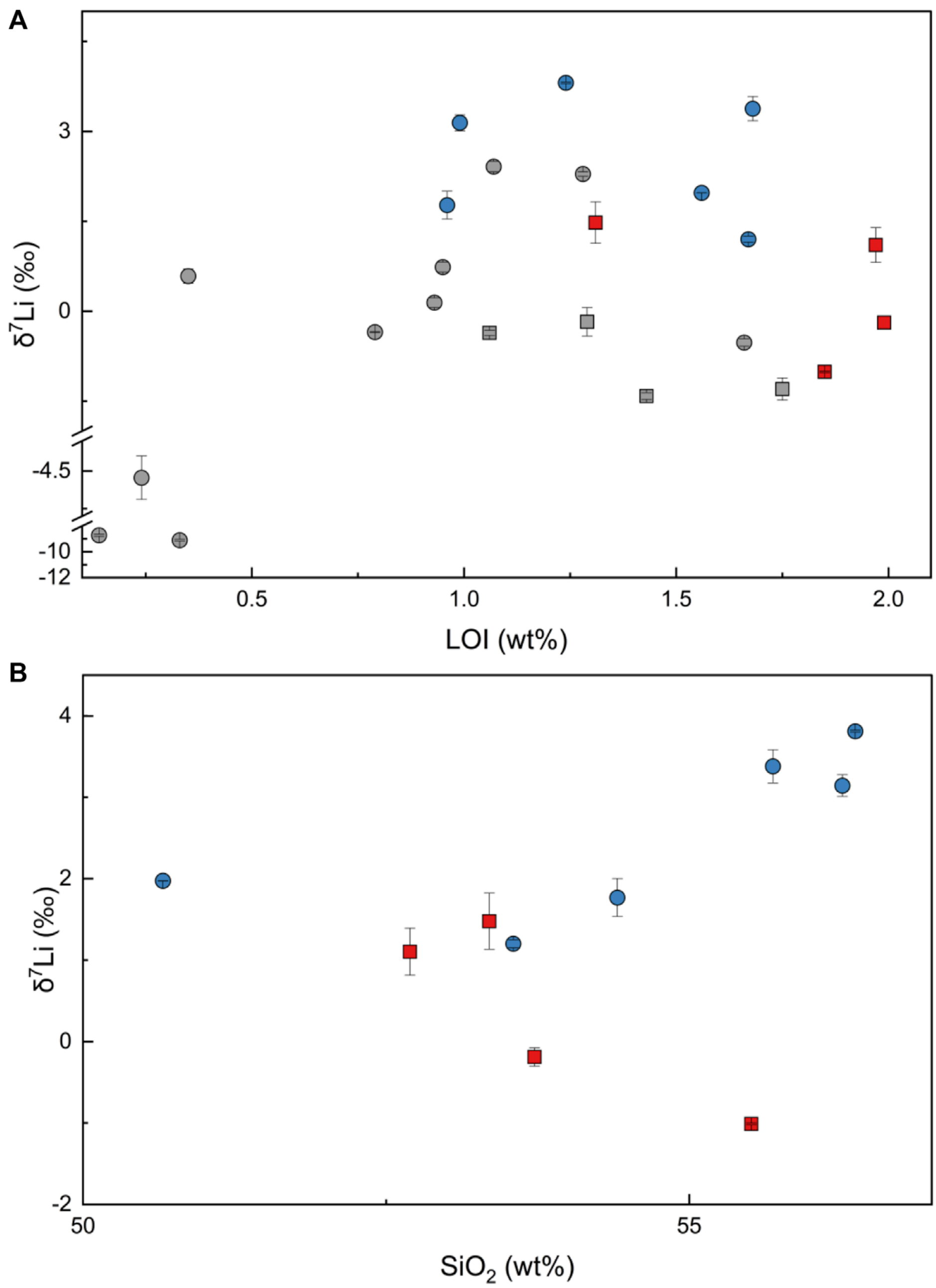

FIGURE 4
(A) LOI (wt%) *versus* δ^7Li values and **(B)** SiO_2 (wt%) *versus* δ^7Li values for continental eclogite, orthogneiss and syn-exhumation and post-collisional mafic magmatic rock in the North Qaidam orogen. The legends are the same as Figure 3.

partial melting process of the continental eclogite was assumed to be Rayleigh fractionation with D = 0.25 and α = 1.004, respectively (Supplementary Table S3).

The modeled results show that the dehydrated residues have systematically lower Li contents and higher δ^7Li values than the continental eclogite when the aggressive fraction of the released fluid is less than 7.1 wt% (Figure 6). The difference of Li content and δ^7Li values between dehydrated residue and continental eclogite suggests some other processes, such as diffusion of Li from surrounding rocks or external fluids (Marschall et al., 2007) may be involved in the generation of continental eclogite except for dehydration. Furthermore, both the modelled fluids and depleted mantle have higher δ^7Li values than our syn-exhumation and post-collisional mafic magmatic rocks suggesting the fluids may not play a key role in their petrogenesis (Figure 6). Instead, the modelled melts with aggressive fraction about 6–24 wt% from the continental eclogite has similar δ^7Li values and Li contents to the post-collisional and most syn-exhumation mafic magmatic rocks (Figure 6), suggesting that these mafic rocks can be formed by partial melting of a mantle source metasomatized by continental eclogite-derived melts. The above inference is also supported by the observation that most of these mafic magmatic rocks exhibit similar whole-rock Sr-Nd isotopes

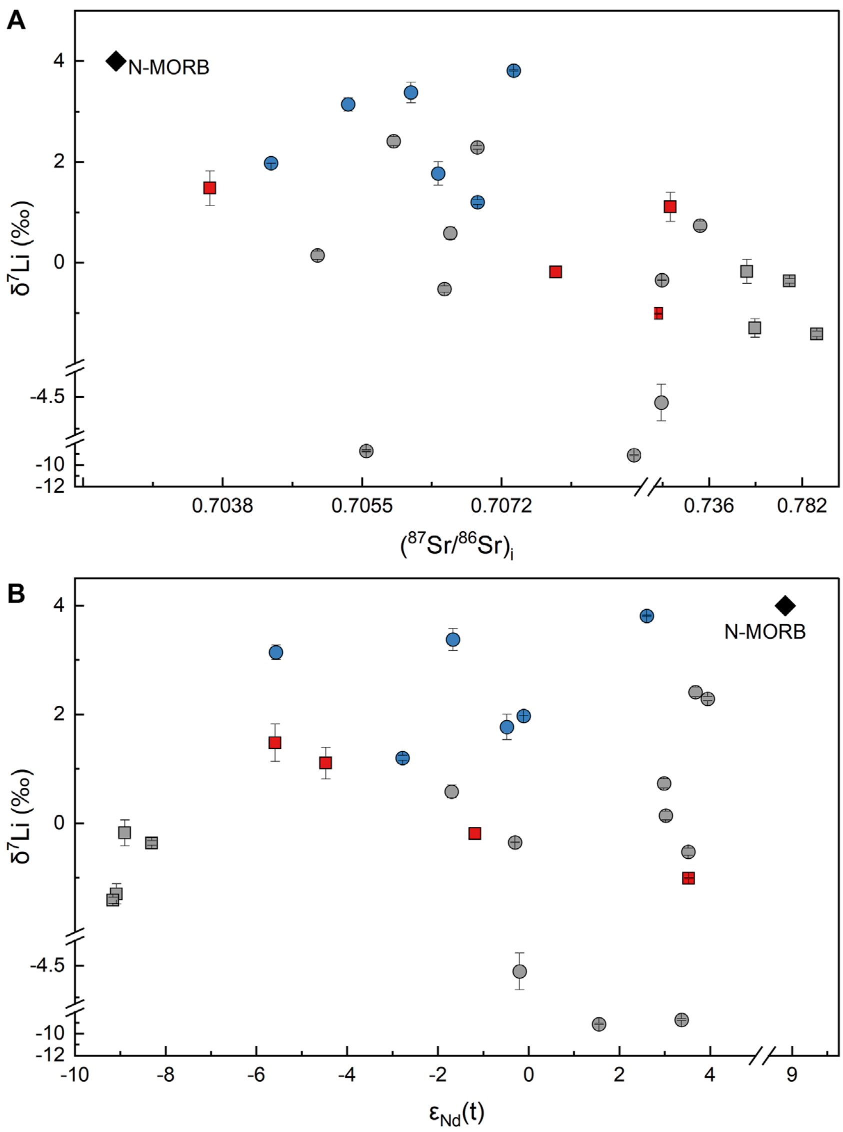

FIGURE 5
(A) $(^{87}Sr/^{86}Sr)_i$ *versus* δ^7Li values and **(B)** $\varepsilon_{Nd}(t)$ *versus* δ^7Li for continental eclogite, orthogneiss and syn-exhumation and post-collisional mafic magmatic rock in the North Qaidam orogen. The δ^7Li value of the MORB is from Tomascak et al. (2008) and $(^{87}Sr/^{86}Sr)_i$ and $\varepsilon_{Nd}(t)$ of the MORB is from Poore et al. (2011). Note: The data is back-calculated to 380 Ma. The legends are the same as Figure 3.

and zircon Hf-O isotopes to the continental eclogites except for a few samples exhibiting more enriched whole-rock Sr-Nd isotopes (Sun et al., 2022).

Considering that the protolith of orthogneiss may be the upper crustal rocks or granites (Fu et al., 2015), the average Li content and δ^7Li value of the upper continental crust (Li = 35 ppm, δ^7Li = 0‰) and granite worldwide (Li = 68 ppm, δ^7Li = 1.4‰) are used as started materials (Sun et al., 2016 and reference therein) for dehydration with modelling parameter same as those in Simons et al. (2010). In terms of the melting processes of the orthogneiss, Rayleigh fractionation with D = 0.25 and α = 1.004 is adopted. As shown in Figure 6, the modelled fluids exhibit higher Li contents and δ^7Li values with an aggressive fraction below 5 wt% than the mafic magmatic rocks, but similar δ^7Li values and higher Li contents with an aggregative fraction from 5 to 7 wt% compared with some mafic magmatic rocks. This indicates that the mantle source of a few mafic magmatic rocks may be metasomatized by orthogneiss-derived fluids with a fraction of about 2 wt%. In terms of the modeled orthogneiss-derived melts, they have similar δ^7Li values and higher Li contents with an aggregative fraction from 6 to 28 wt% compared with the mafic magmatic rocks, suggesting our mafic samples can be derived from enriched lithospheric mantle metasomatized by orthogneiss-derived melts. This inference is also supported by similar whole-rock Sr-Nd isotopes and zircon Hf-O isotopes between the mafic magmatic rocks and the orthogneiss or syn-exhumation granites (Sun et al., 2022).

Although Li isotopes of paragneiss in the North Qaidam orogen were not analyzed in this study, previous study has shown that the δ^7Li values of paragneiss in the Dabie orogen can reach as high as 15‰ (Tan et al., 2020). Hence, it can be inferred that paragneiss-derived fluid/melts would not contribute significantly to our mafic magmatic rocks, which have δ^7Li values lower than 3‰

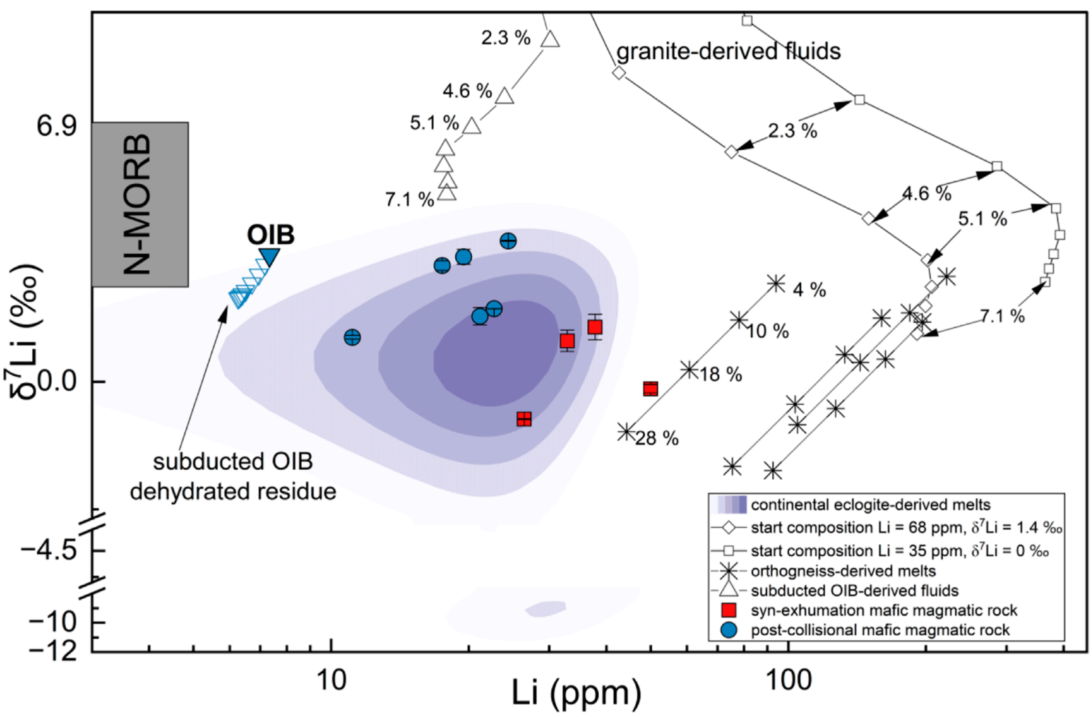

FIGURE 6
Dehydration and melting modelling results of Li contents *versus* δ^7Li values for continental crustal components in the North Qaidam orogen. The OIB data from Genske et al. (2014) is used as the protolith of continental eclogite for dehydration modelling. The upper continental crust and granite data from Sun et al. (2016) is used as the protolith for hydration modelling. The continental eclogite and orthogneiss in this study are used as start materials for melting. The dehydration process is calculated according to the methods of Simons et al. (2010), while the melting process is calculated as Rayleigh fractionation with D = 0.25 and α = 1.004. Due to the limited number of modelled orthogneiss-derived melts compositions, a kernel density plot was only constructed for the continent eclogite-derived melts.

(Figure 6). In addition, the paragneiss in this region shows more enriched whole-rock Sr-Nd isotopes than our samples. Collectively, the Li content and Li isotope compositions indicate that the metasomatic agents for the mantle sources of syn-exhumation and post-collisional mafic magmatic rocks were dominated by continental eclogite- and orthogneiss-derived melts formed during exhumation and a small fraction of orthogneiss-derived fluids may also be involved.

Limited Li isotope fractionation has been diagnosed during high-temperature partial melting processes (e.g., Halama et al., 2009; Liu et al., 2020), which implies that contrasting characteristics of the elements and isotopes from the metasomatic agents can be ultimately recorded by the geochemical compositions of our mafic magmatic rocks. As shown in Figures 7A, B, the syn-exhumation mafic magmatic rocks exhibit relatively low δ^7Li values and high Th/Ce ratios and Rb contents, similar to the orthogneiss. In contrast, post-collisional mafic magmatic rocks exhibit high δ^7Li values and low Th/Ce ratios and Rb contents, comparable to those of the continental eclogite. These differences in trace elements and δ^7Li values signatures suggest that the mantle source of the syn-exhumation mafic magmatic rocks was mainly metasomatized by orthogneiss-derived melts, while that of post-collisional mafic magmatic rocks by continental eclogite-derived melts.

To estimate the proportion of recycled material added to the source of mafic magmatic rocks, as well as the relative contributions of two different crustal metasomatic agents, a Monte Carlo mixing modeling between the depleted mantle (Li = 1.7 ± 0.6 ppm, Jeffcoate et al., 2007; Marschall et al., 2017; δ^7Li = 1.6‰–5.6‰, Tomascak et al., 2008; Nd = 0.71 ppm; Salters et al., 2011; $\varepsilon_{Nd}(t)$ = 8.7, Poore et al., 2011) and the subducted continental crustal components (mainly including orthogneiss and continental eclogite) was executed. The Li contents and isotopes of continental crustal components and continental crust-mantle mixtures can be calculated using the following mass balance equations: $[Li]_{mix} = [Li]_{crust} \times F + [Li]_{mantle} \times (1 - F)$ and $[Li]_{mix} \times [\delta^7Li]_{mix} = [Li]_{crust} \times [\delta^7Li]_{crust} \times F + [Li]_{mantle} \times [\delta^7Li]_{mantle} \times (1 - F)$, where F denotes the mass flux of continental crustal components incorporated into the mantle sources. Meanwhile, the Nd contents and $\varepsilon_{Nd}(t)$ values of the continental crustal components and continental crust-mantle mixtures are also determined. To explore the compositional range of continental crustal components as much as possible, we randomly selected one continental eclogite and one orthogneiss and then mixed them at proportions from 0% to 100% with a step of 5%. The modelled metasomatic agents were mixed with mantle at varying ratios from 1% to 10%, with steps of 1% yielding an unparalleled 48,000 crust-mantle mixtures. The simulation by adding 3%–8% continental crust components to the mantle has nearly replicated the entirety of δ^7Li values observed in syn-exhumation and post-collisional mafic magmatic rocks (Figure 8), except for one post-collisional sample holding slightly elevated δ^7Li values, which may be caused by the different δ^7Li values between the continental crust components and their derived melts as Li is incompatible

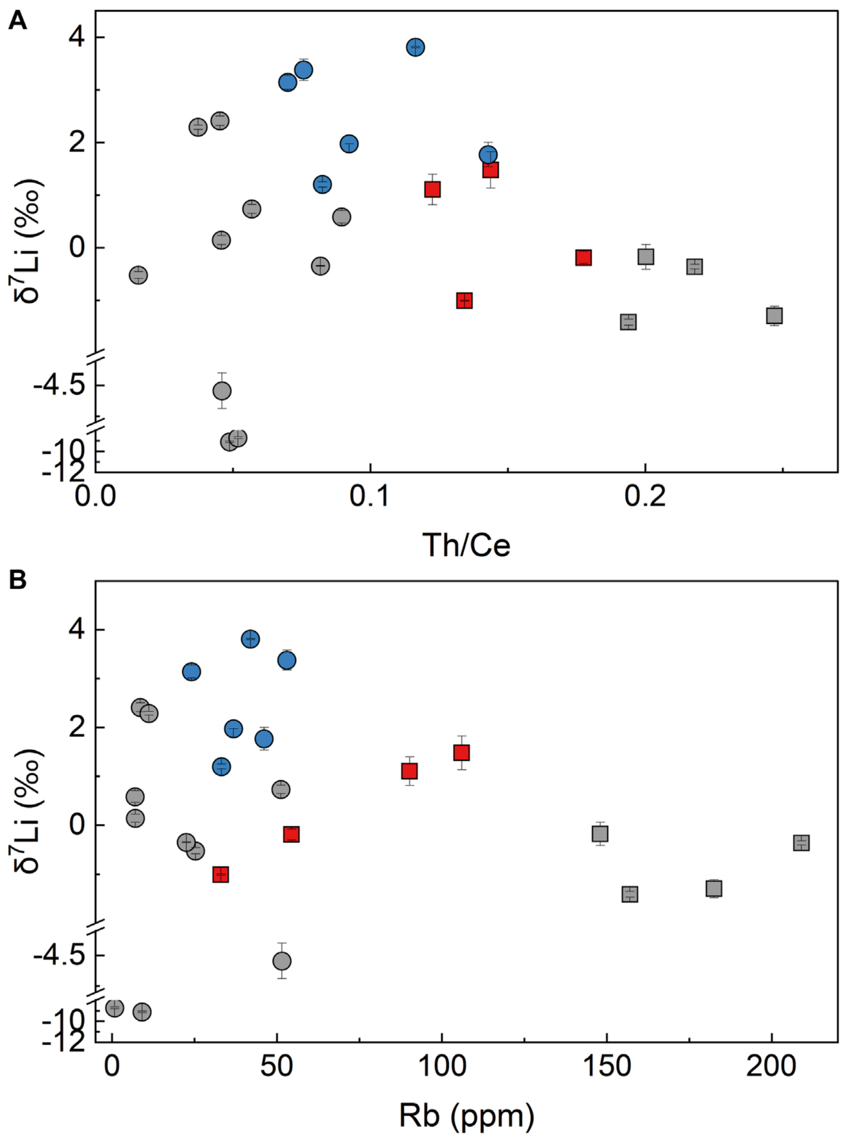

FIGURE 7
(A) Th/Ce ratios *versus* δ^7Li values and **(B)** Rb content *versus* δ^7Li values for continental eclogite, orthogneiss and syn-exhumation and post-collisional mafic magmatic rock in the North Qaidam orogen. The legends are the same as Figure 3.

during partial melting. The relative proportions of continental eclogite to orthogneiss in the mantle sources of the mafic magmatic rocks ranged from 1:10 to 1:1, except sample 15NQ078, which requires an extremely high proportion of eclogite with eclogite to orthogneiss mass ratio up to ~4:1. In addition, our results also show that the proportion of continental eclogite added to the source of syn-exhumation mafic magmatic rocks is lower than that to the source of post-collisional mafic rocks. Furthermore, the Li and Nd isotope modelling results are generally consistent with those of trace elements, where the proportion of the continental crust components was less than 10% and the relative proportions of continental eclogite in the recycled crustal materials were about 16.7%–50.9% in mass. Considering that the continental crust-derived melts have higher incompatible elements (such as Li, Sr, and Nd) contents and δ^7Li values than their sources, the actual amount of continental crust materials added into the mantle may be lower.

The increased proportion of eclogite-derived melts most likely indicates that the melts-peridotite metasomatism tends to generate at shallower depths from syn-exhumation to post-collisonal stages due to the gradual exhumation of the continental crust. In the early exhumation stage, partial melting of orthogneiss is dominant at high pressure, with only a small amount of continental eclogite partial melted (Yu et al., 2019). These resulted melts metasomatize the overlying lithospheric mantle, forming the mantle source for the syn-exhumation mafic magmatic rocks. As continental crust exhumation continues, the decreased pressure and associated increased temperature (Song et al., 2014) favor larger partial melting degrees for both orthogneiss and continental eclogite. However, due to the previous melting event of the orthogneiss which caused the residue orthogneiss more refractory, the relative proportion of continental eclogite-derived melts increased compared to the orthogneiss-deived melts. Therefore, the decreased metasomatic

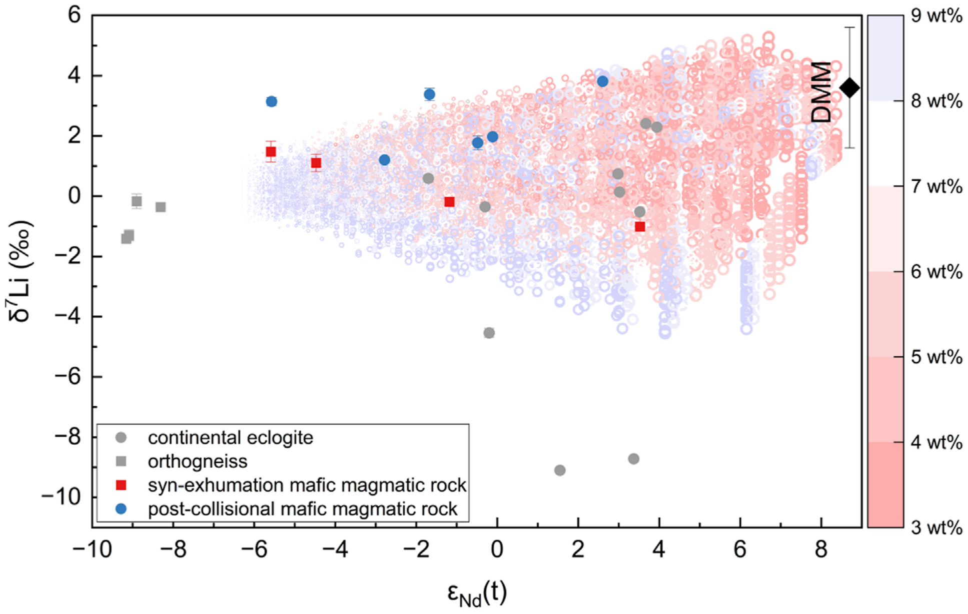

FIGURE 8
Monte Carlo simulation of ε_{Nd}(t) (calculated back to 380Ma) and δ^7Li values. δ^7Li value of 1.6‰–5.6‰ of the DMM is from Tomascak et al. (2008) and ε_{Nd}(t) of the DMM is from Poore et al. (2011). Small circles with different colors represent the random mixing of subducted continental components (continental eclogite + orthogneiss) with the DMM at variable proportions from a Monte Carlo simulation; the diameter of the circles represents the ratios of continental eclogite to orthogneiss in mass using Monte Carlo simulation. CE denotes continental eclogite; OR denotes orthogneiss; DMM denotes depleted mantle.

depths that cause the increased contribution of continental eclogite-derived melts in metasomatic agents to the mantle source of the post-collisional mafic rocks may result in their different Li contents and δ^7Li value from those of syn-exhumation mafic magmatic rocks.

In summary, the incorporation of continental crust components into the mantle at different depths during the continental crust exhumation would result in its heterogeneous geochemical compositions, which was finally manifest by the different Li contents and Li, Sr as well as Nd isotopes in the syn-exhumation and post-collisional mafic magmatic rocks. Therefore, the integration of Li isotopes with other geochemical tracers can be used to effectively trace the recycling of continental crust components in continental collision zones.

6 Li isotope insights on continental crust recycling in continental collision zones

The continental collisional orogeny underwent a series of processes from the early oceanic crust subduction, continent-continent collision, the later exhumation of subducted continental crust, and the final collapse of the orogenic belt (e.g., Song et al., 2015; Zhao et al., 2017; Zheng and Zhao, 2017). During the subduction of oceanic slab, the upper sediments and altered oceanic crust undergo metamorphic dehydration and even partial melting. Since Li is a water-soluble incompatible element, the heavy ^{7}Li isotope will enter the released fluids preferentially at forearc depth, with the later released fluids/melts generally characterized by decreased δ^7Li values as the subduction process proceeds (Moriguti and Nakamura, 1998; Magna et al., 2006). In addition, breakdown of Li-bearing staurolite in metapelite at high P and T can release fluids with isotopically heavier Li than those formed at shallow level (Wunder et al., 2007). In any case, these released aqueous liquids and hydrous melts could metasomatize the overlying lithosphere mantle, subsequently undergoing partial melting to generate the syn-subduction mafic magmatic rocks with variable δ^7Li values (e.g., Bouman et al., 2004; Tang et al., 2012; Tang et al., 2014). For this reason, Li isotope ratios (δ^7Li) and key trace elements ratios (e.g., Li/Y, B/Be, B/Nb, Ce/Pb, Ba/La) of the arc lavas show clear across-arc variations, decreasing with increasing subduction depth, which has been recognized among the island arc volcanic rocks from the Izu arc (Moriguti and Nakamura, 1998). However, most island-arc rocks generally show apparent similar δ^7Li values to those of MORB/mantle, which was assumed to result from indistinguishable δ^7Li values between the MORB and metasomatic agents of subducted oceanic crust (Magna et al., 2006; Tang et al., 2014), or result from buffering the subducted oceanic crust-derived fluids Li signature by the mantle with a MORB-like δ^7Li value (Halama et al., 2009; Liu et al., 2020). Consequently, Li isotopes are frequently used with other whole-rock geochemical indicators to distinguish the nature of subducted recycled material within oceanic subduction zones.

In comparison, the mafic magmatic rocks were scarcely produced during the continental collision but abundant during syn-exhumation and post-collisional stages (Zhao and Zheng, 2009; Dai et al., 2011; Dilek and Altunkaynak, 2007; Eyal et al., 2010; Gülmez et al., 2013; Fang et al., 2020; Moghadam et al., 2022). These mafic magmatic rocks bear evidence of metasomatism of the lithospheric mantle by the continental crust-derived fluids/melts during the continental crust subduction and exhumation stages (e.g., Zhao et al., 2012; Sun et al., 2022). In the North Qaidam orogen, partial melting of the continental crust during exhumation was recognized based on the comparable whole-rock Sr-Nd and zircon Hf-O isotopes compositions between the syn-exhumation granites and the continental crust components (Wang et al., 2014; Sun et al., 2020; Yang et al., 2020). Reaction of such continental crust-derived melts with mantle peridotite could form fertile and enriched mantle sources for the syn-exhumation and post-collisional mafic magmatic rocks. Apart from that, continental crust-derived fluids-peridotites interaction during the early stage of the subducted continental crust exhumation has also been recorded by the trace element compositions of clinopyroxene from the orogenic peridotites in this belt (e.g., Song et al., 2007; Xiong et al., 2015; Chen et al., 2017). However, this type of metasomatism was not revealed by the Li isotope compositions of the mafic magmatic rocks in our study, which consistently have lower δ^7Li values than fresh MORB and the modeled continental crust-derived fluids. The different responses to continental crust-derived fluids between minerals in orogenic peridotite and the mafic magmatic rocks may suggest that mantle buffering plays an important role in the redistribution of Li isotopes, especially when a limited amount of fluid is produced in the early stage of continental crust exhumation.

Instead, the melts-involved metasomatism in the later exhumation stage has been realized by the Li isotopes of the syn-exhumation and post-collisional mafic magmatic rocks. Notably, the syn-exhumation mafic magmatic rocks have high Li contents and low δ^7Li values similar to the orthogneiss throughout the entire belt. In contrast, the post-collisional mafic magmatic rocks have low Li contents and high δ^7Li values similar to the continental eclogite. The differing geochemical compositions of metasomatic agents result in distinct lithium contents and isotopic compositions in syn-subduction and post-collisional mafic rocks. Therefore, our study clearly shows that the distinct Li isotopes compositions of continental crust-derived melts could be preserved in the syn-exhumation and post-collisional mafic magmatic rocks from the North Qaidam orogen. In this regard, Li isotopes can be used as a potentially powerful tool to trace the nature of different recycled continental materials.

7 Conclusion

The syn-exhumation mafic magmatic rocks in the North Qaidam orogen have higher Li content and lower δ^7Li values comparable to the orthogneiss, while the post-collisional mafic magmatic rocks have lower Li content and higher δ^7Li values comparable to the continental eclogite. Monte Carlo two-endmember mixing simulation suggests that up to 3%–8% recycling of orthogneiss and continental eclogite into the depleted mantle, along with the proportional mixture of continental eclogite and orthogneiss about 16.7%–50.9%, can account for the large Li-Nd isotopic range observed in these mafic magmatic rocks. Therefore, we suggest the syn-exhumation and post-collisional mafic magmatic rocks in the North Qaidam orogen were derived from a heterogeneous lithospheric mantle source metasomatized by the dehydrated continental crust-derived melts during the exhumation stage. These findings illustrate the potential utility of Li isotopes, in conjunction with other geochemical indicators, in tracing the origin of various recycled continental crustal components in the orogenic lithospheric mantle.

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

G-CS: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Writing–original draft, Writing–review and editing. Z-FZ: Conceptualization, Investigation, Writing–original draft, Writing–review and editing. L-QD: Conceptualization, Formal Analysis, Writing–original draft, Writing–review and editing. R-XC: Investigation, Methodology, Writing–original draft, Writing–review and editing. LC: Data curation, Investigation, Writing–original draft, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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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.2024.1400885/full#supplementary-material

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