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Tracing the Deep Carbon Cycle Using Metal Stable Isotopes: Opportunities and Challenges

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A B S T R A C T

The subduction of marine carbonates and carbonated oceanic crust to the Earth's interior and the return of recycled carbon to the surface via volcanism may play a pivotal role in governing Earth's atmosphere, climate, and biosphere over geologic time. Identifying recycled marine carbonates and evaluating their fluxes in Earth's mantle are essential in order to obtain a complete understanding of the global deep carbon cycle (DCC). Here, we review recent advances in tracing the DCC using stable isotopes of divalent metals such as calcium (Ca), magnesium (Mg), and zinc (Zn). The three isotope systematics show great capability as tracers due to appreciable isotope differences between marine carbonate and the terrestrial mantle. Recent studies have observed anomalies of Ca, Mg, and Zn isotopes in basalts worldwide, which have been interpreted as evidence for the recycling of carbonates into the mantle, even into the mantle transition zone (410–660 km). Nevertheless, considerable challenges in determining the DCC remain because other processes can potentially fractionate isotopes in the same direction as expected for carbonate recycling; these processes include partial melting, recycling of carbonated eclogite, separation of metals and carbon, and diffusion. Discriminating between these effects has become a key issue in the study of the DCC and must be considered when interpreting any isotope anomaly of mantle-derived rocks. An ongoing evaluation on the plausibility of potential mechanisms and possible solutions for these challenges is discussed in detail in this work. Based on a comprehensive evaluation, we conclude that the large-scale Mg and Zn isotope anomalies of the Eastern China basalts were produced by recycling of Mg- and Zn-rich carbonates into their mantle source.

1. Introduction

The fate of marine carbonates during subduction has profound significance for the global carbon cycle, as they represent the major carbon-bearing phases that are recycled into our planet's interior. In the early Earth's mantle, the presence of both high geothermal gradients and mantle convection rates resulted in variable subduction rates that reduced the likelihood of adding crustal carbon into the deep mantle [1]. As Earth's mantle cooled, the mantle environment of subduction zones could permit the influx of crustal carbonates beyond the depth of arc magma generation, resulting in the more efficient addition of crustal carbon to the deep mantle. The transport of Earth's surface carbon into the mantle by subducted slabs and its return to the surface through the degassing of volcanoes constitute the global deep carbon cycle (DCC) [2], which is one of the major factors controlling the distribution of carbon in all terrestrial reservoirs [3,4]. The study of the DCC has invoked a number of scientific issues, including: identification of recycled crustal carbon; the storage, speciation, and fluxes of deep carbon; partial melting of carbonated mantle; and the proportion of subduction-related carbon and primary mantle-derived carbon in the total carbon dioxide (CO_2) released by volcanism. Among these issues, a definite identification of recycled marine carbonates in the Earth's mantle is a first and key step in DCC research.

Carbon isotopes have been widely applied to trace the DCC [2], but strong fractionation induced by magma degassing makes it difficult to elucidate recycled carbonate in volcanic rock sources based on carbon isotopes alone. Although the efficient subduction of organic carbon may play an important role in the rise of Earth's atmospheric oxygen [5], about 95% of subduction-related and primary mantle-derived carbon is inorganic carbon [6], and their carbon isotopic compositions are not significantly different. Thus, it is

also difficult to identify recycled surface carbon in Earth's mantle using carbon isotopes alone. The stable isotopes of divalent metals such as calcium (Ca), magnesium (Mg), and zinc (Zn), which occur as major or trace constituents in carbonate, can be used to identify recycled carbonate in the mantle, primarily due to the limited influence of degassing on isotopic composition of the magmas and the large contrast in isotopic composition between marine carbonates and the terrestrial mantle. In past years, detectable anomalies of Ca, Mg, and Zn isotope compositions (expressed as $\delta^{44/40}Ca = [(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{SRM-915a} - 1] \times 1000$, $\delta^{26}Mg = [(^{26}Mg/^{24}Mg)_{sample}/(^{26}Mg/^{24}Mg)_{DSM-3} - 1] \times 1000$, and $\delta^{66}Zn = [(^{66}Zn/^{64}Zn)_{sample}/(^{66}Zn/^{64}Zn)_{JMC3-0749L} - 1] \times 1000$, respectively) have been widely reported in mantle-derived rocks worldwide, including Hawaii [7], Eastern China including Hainan Island [8–15], the Tibetan Plateau [16–18], the Emeishan large igneous province (ELIP), and Tarim large igneous province (TLIP) [19–21], New Zealand [22], and Vietnam [23]. With the exception of New Zealand, Vietnam, and Hainan Island of China, the studies on most of these locations have speculated that the storage of a large amount of recycling marine carbonates in the mantle is related to subduction of carbonate-bearing oceanic crust.

The application of metal stable isotopes in tracing DCC is innovative and has been rapidly developed in recent years; however, it is critically challenged by the following important facts or potential difficulties: ① Ca, Mg, and Zn isotopes may be fractionated during partial melting of the mantle and the subducted oceanic crust; ② carbonated eclogites in subduction zones also possess extremely light Mg isotope compositions but commonly contain little carbon; ③ isotope anomalies of mantle-derived rocks may be dependent on the species of carbonates being subducted/recycled; ④ carbon and metal cations (Mg, Ca, and Zn) in carbonate may be decoupled during both slab subduction and return of CO_2-bearing magmas into the surface; and ⑤ diffusion-driven kinetic isotope effects may occur in magma sources or when magmas ascend through the overlying lithosphere. In view of potentially causing isotope fractionation in the same direction as expected for carbonate recycling, these processes must be taken into account while applying metal isotopes to DCC research. In this paper, we review the major advances in the application of metal stable isotopes to DCC; more importantly, we provide an ongoing evaluation of the plausibility of potential mechanisms and possible solutions for these difficult challenges.

2. Principle of the use of metal stable isotopes for tracing DCC

To apply the stable isotopes of metals of interest to the study of DCC, three key prerequisites are needed: ① a distinctive isotopic offset must exist between marine carbonates and the terrestrial mantle; ② the isotopic compositions cannot be significantly changed or fractionated during the subduction processes, partial melting, and magmatic differentiation; and ③ the elemental concentration ratios of carbonate to the mantle must be large enough to modify the isotopic composition of the hybridized mantle.

The efficiency of carbon subduction is usually largely controlled by the carbonate contents of the sediment column, and is partly linked to the latitude of the trench. The distribution of carbonate in the surface sediments of oceans is mainly controlled by surface productivity, dissolution, and dilution by noncarbonate biogenic and nonbiogenic sediment [24]. At the Earth's surface, divalent metal carbonates (i.e., Ca, Mg, Sr, Ba, Mn, Fe, Co, Ni, Zn, Cu, Cd, and Pb) constitute the main species of carbonate [25], such as calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), rhodochrosite ($MnCO_3$), smithsonite ($ZnCO_3$), and siderite ($FeCO_3$). Calcium and magnesium are the two most abundant cations in carbonate and constitute the endmember components of Ca-rich and Mg-rich carbonates, respectively. The Mg concentration (C) ratio of

magnesite to the mantle ($C(Mg)_{magnesite}/C(Mg)_{mantle}$) is close to 1, and the Ca concentration of calcite is one order of magnitude higher than that of the fertile mantle (~3.5 wt%, [26]). Thus, the Mg and Ca concentration ratios of carbonate to the mantle could be sufficiently large to significantly alter the Mg–Ca isotope composition of the mantle. Trace Zn^{2+} can replace Mg^{2+} and incorporate into the crystal lattice of carbonate minerals [27]. Although Zn is trace in calcic carbonate (highly variable, but with an average of ~20 μg·g^{-1} [28]), the low Zn concentration of the mantle (~55 μg·g^{-1}; [29]) results in a high $C(Zn)_{carbonate}/C(Zn)_{mantle}$ ratio (~0.4), which is sufficient to modify the Zn isotope composition of the mantle. In particular, dolomite and magnesite in ultrahigh-pressure metamorphic (UHPM) rocks, such as the deeply subducted slab, can have very high Zn concentrations of up to 147 and 449 μg·g^{-1}, respectively [30].

There are significant isotopic offsets between carbonate and the terrestrial mantle for Ca, Mg, and Zn isotopes (Fig. 1) [31–58]. The large isotope differences between marine carbonate and silicate reservoirs primarily reflect isotope fractionation generated during the release of metals into seawater by continental weathering and during carbonate precipitation from seawater. Boron isotopes ($\delta^{11}B$) have also shown potential in tracing recycled crustal materials in sources of carbonatitic melts [59]; however, in this paper, we focus on the stable isotopes of divalent metals (Ca, Mg, and Zn). For Ca and Mg, carbonates are enriched in the lighter isotopes in comparison with the terrestrial mantle (i.e., $\delta^{44/40}Ca_{carbonate} < \delta^{44/40}Ca_{mantle}$ [60]; $\delta^{26}Mg_{carbonate} < \delta^{26}Mg_{mantle}$ [31,61]), although it has been demonstrated that the $\delta^{44/40}Ca$ values of sedimentary carbonates varied with time and some carbonates have higher $\delta^{44/40}Ca$ ratios relative to the mantle [32]. By contrast, carbonates are more enriched in the heavier Zn isotopes in comparison with the mantle ($\delta^{66}Zn_{carbonate} > \delta^{66}Zn_{mantle}$) [10,33], and no evidence has been found to indicate that the $\delta^{66}Zn$ values of sedimentary carbonates varied over geologic time [33,34]. Therefore, negative anomalies of Ca and Mg isotopes (i.e., lower $\delta^{44/40}Ca$ and $\delta^{26}Mg$ relative to those of the mantle) and positive anomalies of Zn isotopes (i.e., higher $\delta^{66}Zn$ relative to that of the mantle) in igneous rocks—if any—may imply the incorporation of recycled sedimentary carbonates in the rock sources.

Due to the distinctive calcium and magnesium contents in Ca-rich and Mg-rich carbonates, the recycling of different species of marine carbonate would impose different Mg–Ca isotopic effects on mantle-derived rocks, such that a combination of Mg and Ca isotopes can quantitatively constrain the speciation of subducted carbonates (see Section 4.3 for details). Since Zn^{2+} (0.74 Å) has a similar ionic radii to Mg^{2+} (0.72 Å) and mainly substitutes for Mg^{2+} in silicates [62], high-temperature processes (e.g., magmatic differentiation and thermal diffusion) are expected to fractionate Mg and Zn isotopes in an identical direction. Therefore, whether light Mg or heavy Zn isotope signatures of igneous rocks reflect recycled carbonates in the sources or isotope fractionation induced by high-temperature processes may be effectively distinguished by combining Mg isotopes with Zn isotopes.

During plate subduction, Mg isotopes are found to be limitedly fractionated [63]. The subducted mafic crust can preserve its primary isotope signature even after deep subduction to the ultrahigh-pressure eclogite facies. Magnesium isotopes are also not significantly fractionated during magmatic differentiation [31,64]. Siliciclastic sediments have heavy Mg isotope composition due to preferential release of light Mg during continental weathering [65], which is in contrast to carbonate sediments; thus, Mg isotopes can be used to discriminate recycled carbonates from siliciclastic sediments. Pons et al. [66] reported progressive decline of Zn isotope ratios during subduction of ultramafic crust (serpentinites), with heavy Zn isotopes preferentially being released into the fluids by incorporating
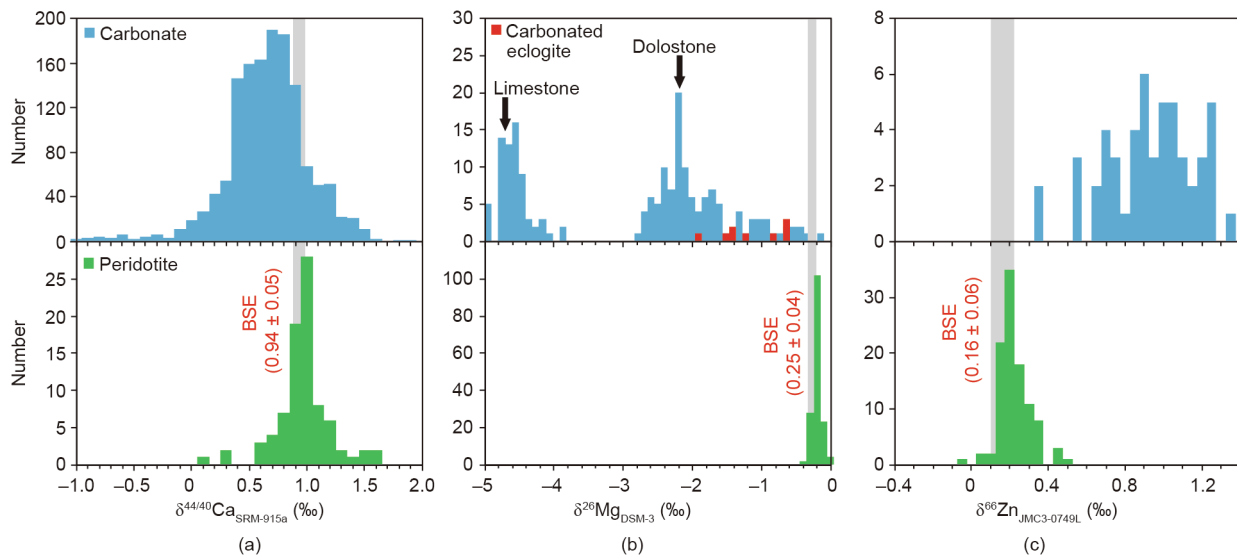
Fig. 1. Data collection for (a) Ca, (b) Mg, and (c) Zn isotopic compositions of sedimentary carbonates, carbonated eclogite, and mantle peridotites. Bulk silicate Earth (BSE) values (represented by the grey band) are from Ref. [38] for $\delta^{44/40}$Ca (relative to SRM-915a), Ref. [31] for δ^{26}Mg (relative to DSM-3), and Ref. [43] for δ^{66}Zn (relative to JMC3-0749L). Data are compiled from the following sources: sedimentary carbonates: $\delta^{44/40}$Ca [32] and references therein, δ^{26}Mg [45–50], δ^{66}Zn [33,34]; carbonated eclogite: δ^{26}Mg [44]; peridotites: $\delta^{44/40}$Ca [36–41], δ^{26}Mg [31,51–57], and δ^{66}Zn [35,42,43,58].

with $ZnCO_3$ and/or $ZnSO_4$. Dehydrated serpentinites have a slightly lighter Zn isotope composition (δ^{66}Zn = 0.16‰ ± 0.06‰) than pre-dehydrated ones (0.32‰ ± 0.08‰). By contrast, during subduction of the mafic oceanic crust, δ^{66}Zn value do not vary across metamorphic facies and the eclogites retain a mid-ocean ridge basalt (MORB)-like isotope composition [67]. Siliciclastic sediments have δ^{66}Zn values similar to or slightly lower than those of the mantle [68], which is also in contrast to the heavy δ^{66}Zn of carbonate; thus, Zn isotopes can be used to discriminate between recycled carbonates and siliciclastic sediments. Magmatic differentiation is found to fractionate Zn isotopes, but the magnitude of fractionation is considerably limited (< 0.1‰) [35,69]. No data is available for Ca isotopes in subduction-related samples, so this clearly needs future investigation. In particular, it is unclear whether selective dissolution of different species of carbonates within the subducted slab causes calcium isotope fractionation, so this topic deserves investigation. Overall, isotope fractionation of Mg and Zn (and possibly of Ca) during subduction-related dehydration is much smaller than the large isotope offset between carbonate and the mantle, making these isotopes powerful tools for tracing the circulation of sedimentary carbonates from the Earth's surface to the mantle.

3. Advances on application of Ca, Mg, and Zn isotopes to DCC

All data available in the literature for basalts with Ca, Mg, and Zn isotope anomalies were compiled, are plotted in Fig. 2 [7–12,14–16,18,19,21–23,31,38,43,70–74], and are briefly summarized below. This dataset is large ($n > 600$) and represents an important step of applying metal stable isotopes to the study of DCC. During the review process of this paper, at least nine papers reporting new data and detectable variations of calcium, magnesium, and zinc isotopes in mantle-derived rocks (peridotites and basaltic rocks) were published [36,37,70–76], highlighting the rapid development of these three isotope systematics in tracing DCC.

3.1. Calcium isotopes

Two studies have reported detectable variations of Ca isotopes in basaltic rocks and linked these variations to recycling of

carbonates. Huang et al. [7] found light Ca isotope signatures in Hawaiian basalts ($\delta^{44/40}$Ca = 0.75‰–1.02‰) relative to the fertile mantle (0.94‰ ± 0.05‰ [38]). They observed decreasing $\delta^{44/40}$Ca with increasing ^{87}Sr/^{86}Sr and Sr/Nb ratios, and attributed the light Ca isotope compositions to recycling of ancient carbonate component ($\sim$4‰) in the Hawaii plume. Recently, Liu et al. [18] reported lower $\delta^{44/40}$Ca values of volcanic rocks from Tengchong in Southwest China (0.67‰–0.80‰) compared with the fertile mantle. A binary mixing model using Mg–Ca isotopes shows that 5%–8% carbonates dominated by dolostone have been recycled into the mantle sources. The recycled carbonates were proposed to have originated from the Indian oceanic crust.

Significant calcium isotope variations have also been found in mantle peridotite xenoliths [36–38,77], but the results and explanations differ considerably. Zhao et al. [77] reported extreme $\delta^{44/40}$Ca variation (−0.08‰ to 0.92‰) in peridotitic xenoliths from the North China Craton, and attributed the coupled light Ca–Fe isotopic signatures in these Fe-rich peridotites to kinetic isotope fractionation during melt-peridotite reaction. No clear role of recycled carbonate was illustrated in that study. Chen et al. [36] reported relatively high $\delta^{44/40}$Ca ratios for clinopyroxene (+0.84‰ to +1.17‰) and orthopyroxene (+0.82‰ to +1.22‰) in peridotite xenoliths from Fanshi area in the North China Craton. The heavy Ca isotope signature in the metasomatic clinopyroxenes, which were formed via metasomatism by both carbonatite melt and carbonate-rich silicate melt, was proposed to reflect a characteristic of evolved sediment-derived hydrous carbonate melts [36]. These authors further predicted that significant Ca isotope fractionation may have occurred during the subduction of carbonate sediments. Recently, Ionov et al. [37] reported calcium isotope data for mantle xenoliths containing metasomatic calcite from the Siberian Craton. These authors found that the $\delta^{44/40}$Ca ratios of the metasomatized peridotites (+0.81‰ to +0.83‰) do not significantly deviate from that of the fertile mantle (< 0.15‰), and the acid-leachates (carbonates) and leaching residues have similar $\delta^{44/40}$Ca values. The authors therefore asserted that Ca isotopes have little use as a tracer of carbonate recycling [37]. Overall, it seems that the calcium isotope data of mantle peridotites is immensely complex, making it difficult to simply relate it to carbonate recycling.
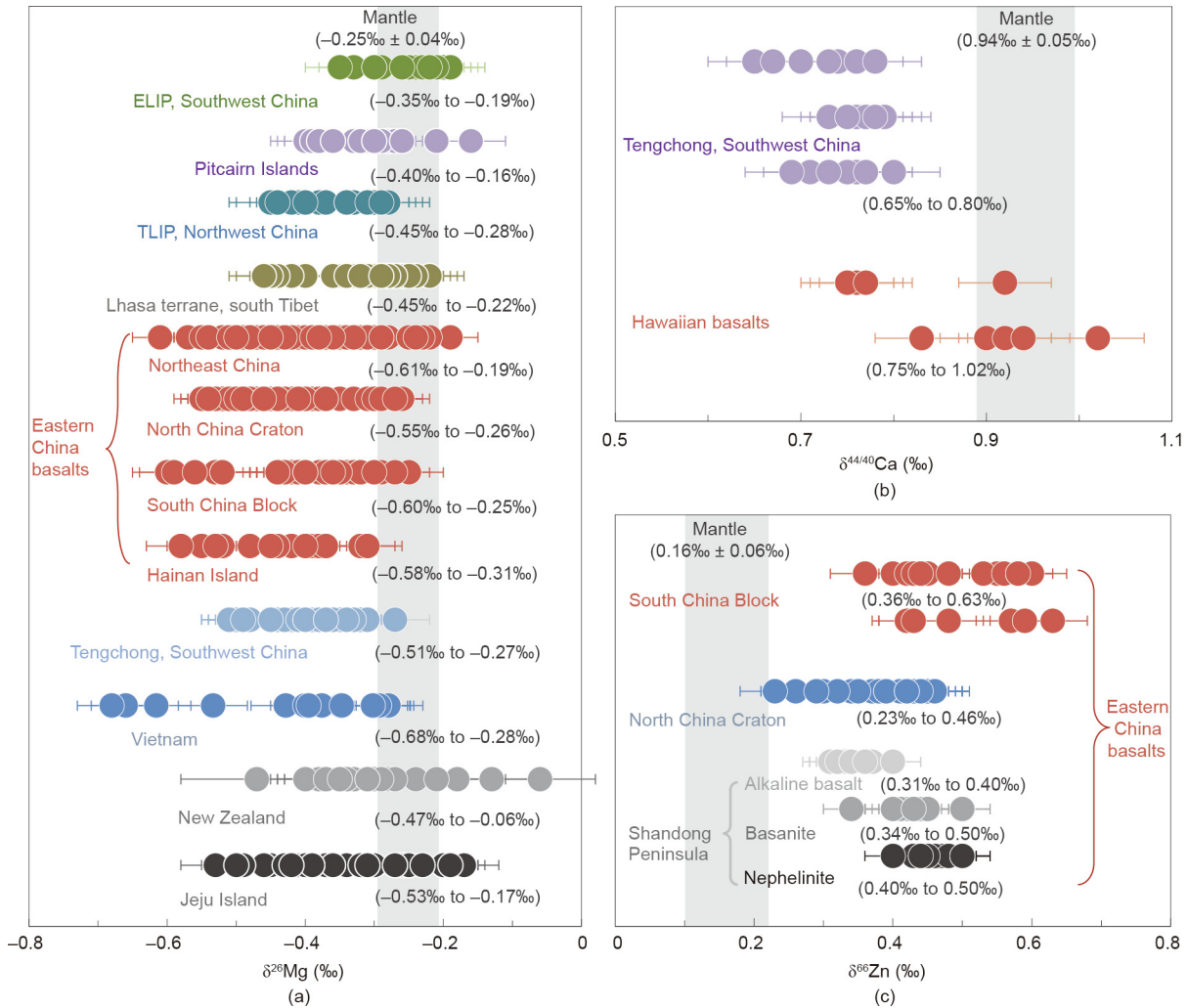
Fig. 2. A data compilation for basalts with isotope anomalies of (a) Mg, (b) Ca, and (c) Zn reported in the literature. Mantle values (represented by the grey band) are from Ref. [38] for $\delta^{44/40}$Ca, Ref. [31] for δ^{26}Mg, and Ref. [43] for δ^{66}Zn. Data are compiled from the following sources: δ^{26}Mg, Northeast China [11,15,70], North China Craton [8,12,14], South China Block [9,12,14], Hainan Island [12], ELIP [19], Pitcairn Islands [74], TLIP [21], Tengchong [18,72], Lhasa terrane [16], Vietnam [23], New Zealand [22], and Jeju Island [71]; $\delta^{44/40}$Ca, Tengchong [18] and Hawaii [7]; δ^{66}Zn, South China Block [10], North China Craton [10], and Shandong Peninsula [73].

3.2. Magnesium isotopes

An important superiority of Mg isotopes relative to other isotope systems (e.g., Ca and Zn) is the huge difference of Mg isotope composition between marine carbonates and the terrestrial mantle (up to 5‰; Fig. 1). In addition, compared with the large contrast in isotope abundances between ^{40}Ca and ^{42}Ca or ^{44}Ca, and the strong interference of ^{40}Ar on ^{40}Ca that represents a significant obstacle to the precise measurement of Ca isotope ratios [78], the analysis of magnesium isotopes is more convenient. These superiorities make Mg isotopes the most commonly applied tracer for the DCC to date. Below, we review the studies that reported Mg isotope anomalies in basalts separately on the basis of regional occurrence of these rocks.

3.2.1. East Asia

Yang et al. [8] reported the first Mg isotope anomaly in alkaline basalts from the north and central North China Craton. They found an abrupt decline of δ^{26}Mg ratios in < 110 Ma basalts relative to > 125 Ma basalts, and attributed this transition to subduction of the West Pacific slab beneath Eastern China in the late Mesozoic. Huang et al. [9] expanded the low-δ^{26}Mg anomaly to Cenozoic

alkaline basalts from South China. Tian et al. [11] and Wang et al. [15] further found low-δ^{26}Mg values in Cenozoic alkaline basalts from Northeast China. Collectively, these studies have expanded the large-scale Mg isotope anomalies of Eastern China basalts to an area of more than 1 000 000 km². Li et al. [12] presented a more comprehensive Mg isotope dataset including arc basalts from the circle-Pacific region, basalts from the western part of the North China Craton, and basalts from the Hainan hot spot. These authors found that low-δ^{26}Mg anomalies only occur in Eastern China and are not present in the western North China Craton; based on Mg–Sr isotope modeling, they proposed that the recycled carbonate is mainly composed of dolomite ± magnesite [12]. High-resolution seismic tomography showed that the Pacific slab is subducting beneath the Japan Islands and becomes stagnant in the mantle transition zone (410–660 km) beneath Eastern China [79]. The low-δ^{26}Mg anomaly of basalts in the mainland of Eastern China coincides with the stagnant Pacific slab in the mantle transition zone beneath Eastern China, suggesting that the large-scale low-δ^{26}Mg anomalies indicate the location of recycled Mg-rich carbonates in the mantle transition zone beneath Eastern China [12]. Su et al. [14] also reported a large Mg isotope dataset on a suite of continental basalts from East Asia, and found a decreasing δ^{26}Mg

trend with increasing distance from the present subduction trench. They attributed these variations to westward subduction of the Pacific oceanic plate beneath East Asia. More recently, Kim et al. [71] extended the low-δ^{26}Mg anomaly in alkaline volcanic rocks to Jeju Island, Korea, and similarly linked it to the stagnant, subducted, carbonate-bearing Pacific slab in the mantle transition zone beneath East Asia.

3.2.2. Tethyan subduction zone

The Tethyan subduction zone is another important area where low-δ^{26}Mg signatures have been widely observed in mantle-derived rocks. Liu et al. [16] found light Mg isotope compositions of Cenozoic ultrapotassic rocks from south Tibet, and attributed the observations to the recycling of carbonated pelites during subduction of the Neo-Tethyan oceanic crust. Ke et al. [17] reported low δ^{26}Mg signatures and negative correlation between δ^{26}Mg and δ^{18}O values for Cenozoic syenites from the Pamir syntaxis, located in the western Himalayan–Tibetan orogen. Modeling on the basis of Mg–O–Sr isotope data indicated that the recycled carbonate is mainly limestone with minor dolostone, suggesting that the metasomatism occurred at depths shallower than 60–120 km. Liu et al. [18] also found low-δ^{26}Mg signatures together with low $\delta^{44/40}$Ca values for the Tengchong volcanic rocks in the southeastern Tibetan Plateau. These studies indicate that recycling of marine carbonate into the mantle may have been widespread during subduction of the Tethyan oceanic crust before and during the Cenozoic. Recently, Tian et al. [72] reported low Mg isotope ratios (−0.51‰ to −0.33‰) in basalts and andesites from Tengchong, and attributed the low-δ^{26}Mg anomalies as well as the extremely high Th/U (6.5–8.3) to dolomite dissolution by slab-derived supercritical liquids in subduction zones.

3.2.3. Large igneous provinces

Cheng et al. [21] reported low-δ^{26}Mg anomalies (−0.45‰ to −0.28‰) in basalts, mafic–ultramafic layered intrusions, diabase dykes, carbonatites, and mantle xenoliths in kimberlitic rocks from the TLIP. These authors proposed two distinct mantle domains as the sources of the TLIP basalts: ① a lithospheric mantle source for basalts and mafic–ultramafic layered intrusions, which was modified by calcite/dolomite and eclogite-derived high-silicon (Si) melts, as evidenced by enriched Sr–Nd, heavy oxygen, and light Mg isotope compositions; and ② a plume source for carbonatite, nephelinite, and kimberlitic rocks, with the involvement of magnesite or periclase/perovskite. Tian et al. [19] reported the mantle-like Mg isotope composition of Permian basalts from the ELIP. They proposed that sedimentary carbonates recycled into the lower mantle beneath the ELIP were very limited (< 2%). Thus, whether or not marine carbonates can be carried into the lower mantle remains open to debate and requires further study.

3.2.4. Low-δ^{26}Mg anomalies proposed to be unrelated to the recycling of carbonate

Five studies have proposed different explanations for low-δ^{26}Mg anomalies observed in basalts from other regions, rather than recycling of marine carbonates. Wang et al. [22] reported Mg isotope data for high-time-integrated $\mu = {}^{238}$U/^{204}Pb mantle (HIMU)-like intraplate basalts from New Zealand (−0.47‰ to −0.06‰). Based on the negative relationship between δ^{26}Mg and (Gd/Yb)$_{normalized}$ these authors attributed the observed low-δ^{26}Mg anomalies to recycling of carbonated oceanic crust (eclogites) in the mantle source. On the basis of high Fe/Mn and Ca/Al, and the absence of negative Hf and Ti anomalies, Li et al. [12] argued that the low-δ^{26}Mg anomalies of basalts from Hainan Island were caused by recycled oceanic eclogites. Sun et al. [70] presented negative correlations between δ^{26}Mg values and TiO$_2$ contents for potassium-rich basalts from Northeast China, and attributed

the low-δ^{26}Mg anomalies to recycling of carbonated eclogites. More recently, Hoang et al. [23] reported Mg isotope data for late Cenozoic intraplate basaltic rocks from Central and Southern Vietnam (−0.62‰ to −0.28‰), and proposed a hybridized source containing peridotite and recycled oceanic crust (carbonated eclogites). Wang et al. [74] found low-δ^{26}Mg anomalies in Pitcairn Island basalts with a typical EM1 affinity. Considering the low Ca/Al ratios, these authors proposed that carbonate–silicate interaction in the subducted sediments exhausted the carbonates but incorporated the isotopically light magnesium of the carbonate into silicates. The latter were subducted into the deep mantle and resulted in the observed low-δ^{26}Mg anomalies.

3.3. Zinc isotopes

Zinc isotopes are a novel tracer for the DCC recently developed by Liu et al. [10]. These authors analyzed Zn isotope data for Mesozoic to Cenozoic basalts from Eastern China that had been previously analyzed for Mg isotopes. The < 110 Ma basalts were shown to have elevated δ^{66}Zn values and display a negative correlation between δ^{66}Zn and δ^{26}Mg, which were interpreted as a result of the recycling of marine carbonates in the mantle source. Given the high Zn concentration of these basalts and the positive relationship between δ^{66}Zn and Zn concentration, Liu et al. [10] argued that the recycled carbonate is Zn-rich and is most likely dominated by magnesite. This argument provides independent evidence for determining the species of recycled carbonate during subduction of the West Pacific slab beneath Eastern China.

Recently, Wang et al. [73] presented a systematic variation of Zn isotopes with Sr–Nd isotopes and incompatible elements (e.g., Nb, Th, and Zn) in nephelinites, basanites, and alkali olivine basalts from the Shandong Peninsula in Eastern China (Fig. 2). Compared with nephelinites and high-alkali basanites that have elevated δ^{66}Zn ratios reflecting carbonate metasomatism of the sources, alkali olivine basalts and low-alkali basanites show a gradual decline of δ^{66}Zn with SiO$_2$, and have Zn–Sr–Nd isotopic and chemical compositions that are shifted toward those of an enriched lithospheric mantle. The authors proposed that infiltration and reaction of silica-undersaturated melts with the lithospheric mantle result in the transition of strongly alkaline melts into weakly alkaline melts, and could be one of the most common causes of compositional diversity in natural alkaline lavas.

4. Challenges and questions

As discussed above, many studies have already reported Ca, Mg, and Zn isotope data for basalts, and have linked the observed isotope anomalies to possible recycling of marine carbonate. However, considerable challenges exist and call into question the unique linkage between the isotope anomalies observed in basalts and carbonate recycling in mantle sources. In particular, several processes can potentially fractionate isotopes in the same direction as expected by carbonate recycling. In this section, particular attention is paid to evaluating the plausibility of these potential mechanisms and providing possible solutions for these challenges—aspects that have been commonly overlooked in earlier work. Our aim is to call attention to the interpretation of isotope data instead of simply linking any isotope anomaly to the carbonate effect without evaluating other possibilities in detail in future studies.

4.1. Partial melting effect

The improved precision of isotope analysis has led to the finding that calcium, magnesium, and zinc isotopes may be fractionated

during mantle melting. Data on mantle minerals show that in equilibrium, olivine and orthopyroxene tend to become enriched in heavy Ca isotopes in comparison to clinopyroxene [39,40]. During partial melting of the mantle, light Ca isotopes preferentially enter into melt because clinopyroxene is consumed first [80,81]. Indeed, the $\delta^{44/40}$Ca of ultramafic rocks is negatively correlated with CaO and positively correlated with MgO [38,40,41], probably reflecting isotope fractionation during the partial melting of mantle peridotites. Kang et al. [38] found that the $\delta^{44/40}$Ca in moderately depleted peridotites (1.07‰ ± 0.04‰) is slightly higher than that in fertile spinel and garnet peridotites (0.94‰ ± 0.05‰), indicating that light Ca isotopes are preferentially partitioned into melt. Ionov et al. [37] also found heavy Ca isotope signatures in refractory, non-metasomatized off-craton peridotites (1.10‰ ± 0.03‰) in comparison to fertile lherzolites due to isotope fractionation during melt extraction. Therefore, partial melting of mantle peridotites may result in light Ca isotope composition in basaltic melts. Since marine carbonates commonly have a lighter $\delta^{44/40}$Ca relative to the fertile mantle, application of Ca isotopes to trace recycled marine carbonates in the source of mantle-derived melts must take this fractionation effect into account.

Magnesium isotopes have generally been suggested to be unfractionated during mantle partial melting [31,82–84], since global peridotite xenoliths and mantle-derived melts (e.g., basalt, komatiite) commonly have identical Mg isotope composition within analytical errors. Recently, Zhong et al. [85] showed that the δ^{26}Mg values of most ocean island basalts (OIBs) are negatively correlated with melting-sensitive trace-element ratios (e.g., Nb/Zr) but uncorrelated with source-sensitive elemental ratios. Modeling calculations suggest that preferential melting of garnet in garnet-bearing sources (e.g., recycled oceanic crust and garnet peridotite) can generate melts with slightly low δ^{26}Mg values (about −0.35‰) at low-degree partial melting [85], since garnet is more enriched in light Mg isotopes in comparison with other coexisting silicate minerals (e.g., clinopyroxene). Zhang et al. [86] evoked a similar mechanism to interpret the low-δ^{26}Mg anomaly observed in the basalts of Eastern China. However, the maximum difference between the δ^{26}Mg values of melts and residue is not greater than 0.1‰ [85], which is unlikely to reconcile with the up to 0.4‰ δ^{26}Mg offset between the Eastern China basalts and the terrestrial mantle [8,9,12].

Recent studies show that zinc isotopes can also be fractionated during mantle melting. A study on peridotites from Siberia and Mongolia found that refractory peridotites have Zn isotope compositions (δ^{66}Zn = +0.14‰ ± 0.05‰) lighter than fertile peridotites (+0.30‰ ± 0.07‰). The authors attributed this difference to pressure-dependent isotope fractionation induced by mantle melting [42]. Based on new data for mantle minerals and oceanic basalts, Wang et al. [35] argued that spinel consumption during mantle melting plays a key role in generating high Zn concentrations and heavy Zn isotope compositions of global basalts. More recently, Sossi et al. [43] suggested that the Zn–O bonding difference between melts and residue may account for the isotope fractionation of Zn during mantle melting. Huang et al. [87] reported that some arc volcanic rocks display a δ^{66}Zn higher than that of the depleted MORB mantle, also suggesting a small Zn isotope fractionation during mantle melting. Although a detailed evaluation of these different hypotheses is beyond the scope of this paper, it is clear that Zn isotope fractionation generated during partial melting of the mantle has a maximum of < 0.1‰, which is unlikely to have resulted in the up to 0.4‰ δ^{66}Zn difference between the Eastern China basalts and the terrestrial mantle [10].

It is very surprising that the isotope effect induced by mantle melting is always in the same direction as the recycling of marine carbonates for all three isotope systematics of Ca, Mg, and Zn. While the magnitude of melting-induced isotope fractionation may be smaller than the isotope offset between carbonate and the mantle, this effect would become outstanding when quantifying the fluxes of recycling carbonate into the mantle. Especially for strongly alkaline basalts, which are commonly generated by extremely low degrees of mantle melting (1%–8%) [88], isotope fractionation produced by partial melting may exert significant influence on the interpretation and quantification of light $\delta^{44/40}$Ca and δ^{26}Mg and heavy δ^{66}Zn values in the mantle sources of basalts. Further research on the application of these isotope systematics to the DCC is required to consider this effect.

4.2. The carbonated eclogite "problem"

As discussed above, five case studies have attributed low-δ^{26}Mg anomalies in basalts from New Zealand, Northeast China, Hainan Island, Vietnam, and Pitcairn Island to recycling of carbonated silicates (eclogites). Distinguishing between carbonated eclogite and marine carbonate in sources of basalts has become a urgent problem, since most carbonated eclogites with extremely low δ^{26}Mg values (e.g., −1.92‰; Fig. 1) contain very little carbon (CO_2 < 0.22 wt%) [44]. The low-δ^{26}Mg signature of carbonated eclogites could have been caused by substantial carbonate-silicate isotopic exchange within the subducted slab [44]. Therefore, if the low-δ^{26}Mg anomalies observed in basalts were produced by the recycling of CO_2-poor carbonated eclogites, their presence would fail to indicate carbon recycling and would only imply the recycling of isotopically light crustal Mg.

Experimental studies have shown that partial melting of typical recycled carbonated oceanic crust (in the form of carbonated eclogite) at a pressure of 3 GPa can produce coexisting silica-rich melt and carbonate-rich melt over a wide temperature range [89]. Metasomatism of the mantle by carbonated eclogite-derived silicate melts will generate pyroxenite, and carbonatitic melts from the melting of recycled carbonate will form carbonated peridotites [90]. Although both metasomatized sources have low δ^{26}Mg values, their diverse roles in the sources of basalts may be distinguished by plotting δ^{26}Mg against major and trace elements that are sensitive to either a peridotitic or pyroxenitic source lithology (e.g., Fe/Mn, Hf/Hf*, Ti/Ti*, CaO/Al$_2$O$_3$, etc.) [12]. For example, high Fe/Mn ratios could be derived from a pyroxenite or eclogite source [91]. Melts from a mantle source hybridized by sedimentary carbonate (i.e., carbonated peridotite) are expected to typically have low Fe/Mn, Hf/Hf*, and Ti/Ti* and high CaO/Al$_2$O$_3$. Li et al. [12] concluded that the nephelinites in Eastern China with the lowest SiO$_2$ and δ^{26}Mg can represent the low δ^{26}Mg component (LMC) in the mantle source, which is characterized by low Fe/Mn, Hf/Hf*, and Ti/Ti* and high CaO/Al$_2$O$_3$ ratios, consistent with the typical features of carbonated peridotite-derived melt. By contrast, a negative relationship of δ^{26}Mg with Fe/Mn ratios and a positive relationship of δ^{26}Mg with CaO/Al$_2$O$_3$ have been observed in Hainan basalts from South China [12]. Compared with partial melts of mantle peridotite, the Hainan basalts have lower Na$_2$O/TiO$_2$, CaO/Al$_2$O$_3$, and Co/Fe, and higher TiO$_2$, Fe/Mn, Zn/Fe, and Zn/Mn [92]. These characteristics were argued to have been caused by a mixing source of recycled oceanic crust (carbonated eclogite) and peridotite [12,92].

There is no available data on Ca and Zn isotopes for carbonated eclogites. Nevertheless, isotopic exchange between sedimentary carbonate and basaltic crust within the subducted slab, which has significantly modified Mg isotopes, should have influenced Ca and Zn isotopes of the recycled oceanic crust as well. The exchange of light Ca and heavy Zn isotopes from carbonate into the basaltic crust is expected to form low-$\delta^{44/40}$Ca and high-δ^{66}Zn carbonated eclogites. Since these components may be carbon-poor but would generate the same isotope effect as the recycling of carbonates, their isotopic compositions need to be

determined in future studies and must be considered when applying Ca and Zn isotopes to trace recycled carbonates in sources of basalts.

4.3. Dependence of isotope anomalies on speciation of recycled carbonates

The great variation of Ca, Mg, and Zn contents in different species of carbonates means that their isotopes are sensitive to the speciation of recycled carbonates in the mantle. For example, Ca-rich carbonate (i.e., calcite) has low Mg and Zn concentrations, such that the recycling of such carbonates will cause a modest change in the Mg and Zn isotope compositions of the carbonated mantle. By contrast, the recycling of Mg-rich carbonate (e.g., magnesite) could result in a remarkable anomaly of Mg and Zn isotopes but limited change in Ca isotope composition due to low Ca concentration. In other words, normal (mantle-like) $\delta^{26}Mg$ or $\delta^{66}Zn$ values of basaltic rocks do not necessarily reflect the absence of recycled carbonates in the rocks' mantle sources, because the recycled carbonate species may be poor in Mg and Zn (e.g., calcite or aragonite). Similarly, normal $\delta^{44/40}Ca$ values of basalts cannot exclude the possibility of a substantial amount of carbonate recycling if the recycled species of carbonate is Ca-poor (e.g., magnesite and siderite). An evaluation of the dependence of Ca, Mg, and Zn isotope anomalies of basalts on the species of recycled carbonate is important, because normal (mantle-like) isotope values may result in an incorrect judgment that there is no recycled crustal carbon in the sources of the studied basalts. The most direct solution to this conundrum may be a combined utilization of all three isotopic systematics.

Theoretical studies based on molecular dynamics [93] have predicted that the solubility of calcite or aragonite is significantly higher than that of dolomite and magnesite at high pressures. This is supported by observations on UHPM rocks from the Alps that showed that while magnesite and dolomite occur as solid inclusions within garnet, the fluid inclusions in garnet and diamond contain only Mg-calcite/calcite daughter crystals [94]. Therefore, the diverse solubility of different carbonate species in dehydrated fluids may play an important role in controlling the Ca, Mg, and Zn isotope compositions of the metasomatized mantle. For example, dehydrated fluids dominated by calcite or aragonite dissolution contain a large amount of Ca but little Mg, which has a limited influence on the Mg isotope composition of the mantle but may cause significant Ca isotope variation. Island arc basalts have a mantle-like or heavier Mg isotope composition in comparison with the mantle, which is best explained by selective dissolution and removal of Ca-rich carbonates from—and leaving Mg-rich carbonates in—the subducting slabs at relatively shallow depths (75–120 km) [12]. By contrast, at depths of > 120 km, Mg-rich carbonates (e.g., dolomite) could be dissolved by the slab-derived supercritical liquid, resulting in significantly low Mg isotope ratios in the mantle and in mantle-derived rocks [72,76].

Although calcite is the major species of carbonate carried by oceanic crust at the initial subduction stage, high-pressure experimentation shows that calcite is unstable at high pressures. When reacting with pyroxene, calcite can be transformed into dolomite at pressures between 23 and 45 kbars (1 bar = 0.1 MPa), or into magnesite under higher pressure [95]. More recent experimental and theoretical studies show that the high-pressure metastable phase of calcite (e.g., $MgCO_3$, $ZnCO_3$, $FeCO_3$) can be stable at pressures greater than 62 GPa, and may play an important role in carbon storage and transport in the deep Earth [96]. As the cationic radius decreases (Ca > Zn > Mg), divalent carbonates can be stable under higher pressure. Thus, the proportion of Mg-rich carbonate retained in the subducted slabs and carried into the deep mantle could be significant. The Mg and Zn isotope systematics have been demonstrated to be effective in tracing the recycling of Mg-rich carbonate [10,12], such as in alkaline basalts from Eastern China, where the recycled carbonates were most likely located in the mantle transition zone (410–660 km). Recently, Cheng et al. [20] reported a low-$\delta^{26}Mg$ anomaly in deeply derived rocks from the TLIP, and attributed it to the recycling of magnesite in the plume source in the lower mantle. By contrast, it could be speculated that calcium isotopes may be more effective in tracing carbon recycling in island arc settings than Mg and Zn isotopes, considering the higher solubility of Ca-rich carbonate (calcite or aragonite) relative to Mg-rich carbonate (e.g., magnesite).

4.4. Decoupling of metals and carbon during the DCC

The most severe challenge for tracing the DCC using metal isotopes is that metals (e.g., Ca, Mg, and Zn) and carbon may be thoroughly separated during the circulation process. This problem has cast doubt on whether or not metal stable isotopes can effectively trace the DCC. "Separation" may happen during slab subduction, mantle melting, magma ascent, and final eruption. During early subduction, the geothermal gradient is high and the decarbonization reaction will release CO_2 but may leave divalent metals in the ongoing subducting plate. This process results in the inefficient deep subduction of carbon, with most carbon being stripped off from the downgoing slab and released back to the exosphere by arc magmatism [1]. Separation of metals and carbon is also reflected in CO_2-poor carbonated eclogites formed via carbonate–silicate interaction within the subducting plate [44]. However, in modern subduction zones, sedimentary carbonates may survive decarbonization, and the downgoing lithologies may experience temperatures cooler than the key decarbonation reactions. The crustal carbon is then expected to avoid the magmatic release in the volcanic arcs and participate in the deeper cycling and mantle processes, as has been observed in East Asia and the TLIP. As discussed in Section 4.3, the recycling of carbonated eclogites and carbonates into mantle sources of basalts can be effectively discriminated by major and trace element indexes.

During melting of the carbonated mantle and the ascent and eruption of magmas, CO_2 and CO_2-rich fluids may escape from magmas even at mantle depths, partition into vapor, and thus separate from metals [97,98]. Therefore, using the metal stable isotopes of the eruptive volcanic rocks to quantify carbon fluxes of the magma sources is questionable and almost impossible. In this case, carbon isotopes serve as the unique tool of the quantification of carbon fluxes in the original magmas and sources [99,100]. As mentioned above, however, strong fractionation induced by magma degassing makes it difficult to use carbon isotopes to identify recycled carbonates in the pre-eruptive magma source of volcanic rocks. Thus, we recommend a combined utilization of carbon and metal isotopes for studying carbon circulation in the surface-mantle-surface system; the metal stable isotopes can be used to trace (and possibly quantify) recycled carbonates into the mantle, and the carbon isotopes can help to quantify the fluxes of the return of recycled carbon to the surface.

4.5. Diffusion effect

A noticeable phenomenon is that almost all of the studied basaltic rocks with Ca, Mg, and Zn isotope anomalies are alkali-rich, such as those in East China [8–15], Southwest China [18], the Tibetan Plateau [16,17], New Zealand [22], Vietnam [23], the TLIP [21], and Pitcairn Island [74]. Most of these alkaline basalts originated from the asthenospheric mantle and had ascended through the sub-continental lithospheric mantle (SCLM) or the oceanic lithospheric mantle before they erupted on the surface. During this process, both thermal and chemical diffusion processes

may happen and potentially cause isotope fractionation. Since the heavier isotopes always concentrate in cold regions and light isotopes concentrate in hot regions during thermal diffusion [101], the ascending of hot (e.g., plume-related) magmas through the SCLM may result in light isotope enrichment of the resultant melts. The diffusion-driven isotope effect thus challenges the interpretation of low-δ^{26}Mg anomalies in basalts as a consequence of carbonate recycling in sources (Fig. 3(a)). Since Zn^{2+} mainly replaces Mg^{2+} in silicate, thermal diffusion between peridotite and silicate melts is expected to fractionate Zn and Mg isotopes in the same direction [102,103]. This expectation is in contrast to the strongly negative relationship between δ^{26}Mg and δ^{66}Zn ratios observed in Cenozoic basalts from Eastern China (Fig. 3(a)). Therefore, we conclude that the large-scale δ^{26}Mg and δ^{66}Zn anomalies of Eastern China basalts are unlikely to have been caused by thermal diffusion.

A potential magnesium (calcium, zinc) concentration difference exists between ascending basaltic melts and surrounding peridotites. Since light isotopes diffuse faster than heavy isotopes [101], a chemical gradient will drive the diffusion of light Mg isotopes from peridotite to melts [104,105], forming low-δ^{26}Mg melts. The diffusion-driven isotope effect, again, challenges the interpretation of low-δ^{26}Mg anomalies in basalts being due to carbonate recycling (Fig. 3(a)). Unlike Mg, Zn is moderately incompatible during mantle melting and basalts have a higher Zn concentration (commonly $> 80\ \mu g \cdot g^{-1}$) than mantle peridotites ($\sim 55\ \mu g \cdot g^{-1}$) [62]. Chemical diffusion may thus result in elevated δ^{66}Zn and a negative relationship between δ^{26}Mg and δ^{66}Zn ratios in basaltic melts. However, the diffusion of zinc from basaltic melts to ambient peridotites is strongly unsupported by the positive relationship between Zn concentration and δ^{66}Zn ratios in Eastern China basalts (Fig. 3(b)) [10]. In other words, the samples with higher δ^{66}Zn ratios are unlikely to have lost more Zn via diffusion because these samples have relatively high Zn concentrations (Fig. 3(b)). Liu et al. [10] has argued that the elevated δ^{66}Zn ratios coupled with the high Zn concentrations of Eastern China basalts were caused by the addition of Zn-rich carbonate (e.g., magnesite) to the mantle sources.

Diffusion may also happen in the source regions of basalts. The recycled carbonate-bearing oceanic crust may partially melt and produce SiO_2-rich melts, which could react with mantle peridotites to form pyroxenite veins. A magnesium concentration gradient will occur between surrounding peridotites and the newly formed pyroxenite veins. The diffusion of light Mg from peridotite to pyroxenite may result in the latter becoming enriched in light Mg isotopes (Fig. 3(a)). Subsequent partial melting of the low-δ^{26}Mg sources may produce low-δ^{26}Mg melts. Again, this model is in conflict with the high Zn concentrations and δ^{66}Zn ratios in Eastern China basalts (Fig. 3), since melts from the pyroxenites with higher δ^{66}Zn ratios, if formed via diffusion, should have relatively lower Zn concentrations in the absence of a significant difference in melting degrees. On the other hand, since diffusion will be very fast at high temperatures [101,106], it is unclear whether the possible diffusion-driven isotope effects of such sources could be preserved at mantle temperatures. Future simulation studies are required in order to quantitatively evaluate whether the predicted, isotopically abnormal sources could be preserved over the interval between pyroxenite formation and subsequent melting to produce basaltic melts.

5. Conclusions

The stable isotopes of divalent metals such as calcium, magnesium, and zinc have been widely applied to research on the DCC in recent years. Most of these studies have linked the observed isotope anomalies to the fingerprint of recycled marine carbonates in the mantle source of basalts, which strengthens the application of Ca, Mg, and Zn isotopes to trace Earth's DCC. Nevertheless, several processes can also fractionate the stable isotopes of Ca, Mg, and Zn to varying extents during the generation of mantle-derived rocks, including isotope fractionation induced by partial melting, the recycling of carbonated eclogite, and thermal/chemical diffusion. These effects create a barrier to the interpretation of low $\delta^{44/40}$Ca and δ^{26}Mg and high δ^{66}Zn values in basalts as the unique consequence of carbonate recycling, and demand consideration when interpreting any isotope anomalies of mantle-derived melts. In addition, isotope anomalies of mantle-derived rocks are dependent on the speciation of recycled carbonates. In this case, multiple isotope systematics must be applied in order to determine the possible speciation of recycled carbonates. Finally, the separation of metals and carbon during slab subduction and magma ascent and eruption must be considered when quantifying the fluxes of carbon during deep carbon cycling.

Based on a comprehensive evaluation of all of these processes, we conclude that the light Mg and heavy Zn isotope compositions
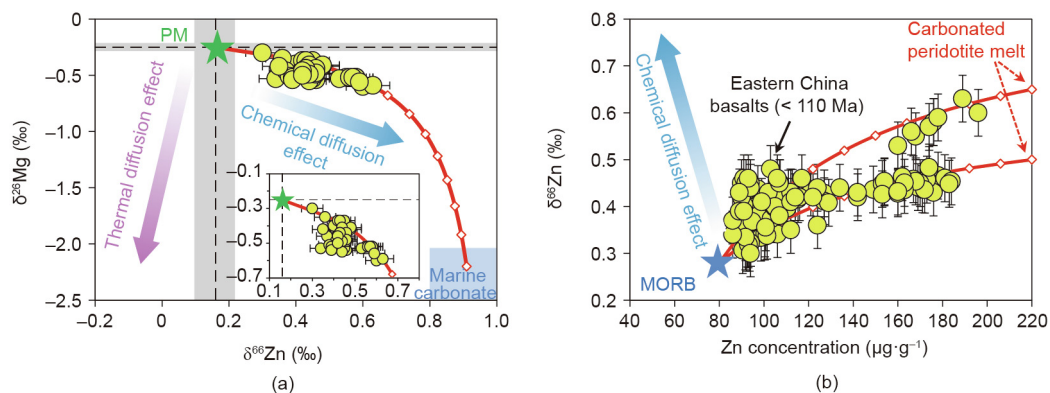

Fig. 3. Plots of (a) δ^{26}Mg versus δ^{66}Zn and (b) δ^{66}Zn versus Zn concentration for < 110 Ma basalts from Eastern China. Recycling of marine carbonate in the mantle source of basalts will produce a negative relationship between δ^{26}Mg and δ^{66}Zn and a positive relationship between δ^{66}Zn and Zn concentration [10]. The modeling curve in (a) refers to the mixing of primitive mantle (C(MgO) = 38 wt%, C(Zn) = 55 $\mu g \cdot g^{-1}$, δ^{26}Mg = −0.25‰, δ^{66}Zn = 0.16‰) with recycled Mg- and Zn-rich carbonate (C(MgO) = 25 wt%, C(Zn) = 280 $\mu g \cdot g^{-1}$, δ^{26}Mg = −0.22‰, δ^{66}Zn = 0.91‰), and the modeling curve in (b) refers to the mixing of MORB (C(Zn) = 80 $\mu g \cdot g^{-1}$, δ^{66}Zn = 0.28‰) with assumed melts derived from carbonated peridotites (C(Zn) = 220 $\mu g \cdot g^{-1}$, δ^{66}Zn = 0.50‰–0.65‰). The increment (diamond symbol) is 10%. The thermal diffusion-driven isotope effect is expected to produce a positive relationship between δ^{26}Mg and δ^{66}Zn. The chemical diffusion-driven isotope effect is expected to produce a negative relationship between δ^{26}Mg and δ^{66}Zn and between δ^{66}Zn and Zn concentration, the latter of which is inconsistent with the observations (see text for details). Data of < 110 Ma basalts from Eastern China are given in Refs. [8–10]. PM: primitive mantle.

of the Eastern China basalts relative to the mantle were caused by the entry of recycled Mg- and Zn-rich carbonates into the mantle transition zone through Western Pacific slab subduction.

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Compliance with ethics guidelines

Sheng-Ao Liu and Shu-Guang Li declare that they have no conflict of interest or financial conflicts to disclose.

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