Light Mg Isotopic Composition in the Mantle Beyond the Big Mantle Wedge Beneath eastern Asia

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Abstract

Low-δ26Mg basalts are commonly interpreted to represent melts derived from carbonated mantle sources. The mantle domain feeding low-δ26Mg Cenozoic basalts in eastern China overlaps the so-called Big Mantle Wedge (BMW) above the stagnant Pacific slab in the mantle transition zone, which indicates that the BMW is an important carbon reservoir generated by the slab. However, Mg isotopic composition in the nearby mantle beyond the BMW and, thus, the spatial extent of carbonated components in the mantle beneath eastern Asia have not yet been extensively characterized. Therefore, it remains largely unconstrained if additional or alternative carbon reservoirs exist. Here we carried out a geochemical study on Cenozoic Huihe nephelinites, which crop out ~500 km west of the present-day BMW. These rocks are characterized by negative K, Zr, Hf, and Ti anomalies, high Zr/Hf, Ca/Al ratios, and low δ26Mg values, which suggest that they are derived from a carbonated mantle source. The composition of the nephelinites demonstrates that low δ26Mg mantle components exist at significant distances from the present-day BMW, which highlights that in addition to the stagnant Pacific slab, other oceanic slab(s) also contribute(s) carbonate-bearing crustal materials to the mantle sources of Cenozoic volcanism in eastern Asia.

1. Introduction

Cenozoic basalts (sensu lato, including any mantle-derived volcanic rocks, e.g., basalts, basanites, and nephelinites) are widespread in eastern China, forming an important part of the West Pacific volcanic zone (e.g., Fan & Hooper, 1991; Liu, 1992; Zhou & Armstrong, 1982). These volcanic rocks are generally interpreted to represent melts generated in the asthenosphere because they have ocean island basalt-type elemental signatures, for example, they show enrichment in Nb and Ta and depletion in K and Pb relative to light rare earth elements (LREEs; e.g., Liu, 1992; Zhou & Armstrong, 1982; Zou et al., 2000; Chen et al., 2009; Zeng et al., 2011). Low Ca and high Ni contents of their olivine phenocrysts (e.g., Hong et al., 2013; Li, Xu et al., 2016; Liu, Ren et al., 2015; Qian et al., 2015; Wang et al., 2011; Xu et al., 2012), high whole-rock FC3MS values (here FC3MS = FeO/CaO – 3 * MgO/SiO2; >0.65; Yang & Zhou, 2013; Yang et al., 2016), and high Fe/Mn (>60) and high 10,000 * Zn/Fe (>14) ratios (Liu et al., 2008; Xu et al., 2018; Zhang et al., 2009) suggest that these basalts (sensu lato) have pyroxenitic/eclogitic mantle sources. The distinct δ18O values of phenocrysts relative to typical mantle indicate that such pyroxenitic/eclogitic components may derive from subducted oceanic crusts and sediments (e.g., Liu, Xia, Deloule et al., 2015; Liu, Xia, Ingrin et al., 2015; Liu, Wang et al., 2017; Xu et al., 2012). Heavy δ66Zn signatures (δ66Zn = 0.30‰ to 0.63‰; Liu et al., 2016) of the basalts, compared to peridotite mantle values (δ66Zn = 0.16 ± 0.06‰; Sossi et al., 2018), reflect contributions from isotopically heavy subducted carbonated material (average δ66Zn = 0.91 ± 0.47‰; Pichat et al., 2003). Highly variable but consistently light Mg isotopic compositions of these rocks (δ26Mg = −0.60‰ to −0.25‰; Huang, Li, et al., 2015; Tian et al., 2016; Wang et al., 2017; Yang et al., 2012; Li et al., 2017; Yu et al., 2019) are also usually attributed to recycled sedimentary carbonates (with extremely light Mg isotopic compositions; δ26Mg = −5.57‰ to −0.38‰; Huang, Ke, et al., 2015; Wombacher et al., 2011; Young & Galy, 2004) in the mantle sources.

All elemental and stable isotopic compositions of the Cenozoic basalts (sensu lato) in eastern China thus highlight the importance of carbonated crustal material in their mantle sources, which is typically...
interpreted to derive from the subducted Pacific slab (e.g., Li, Ma, et al., 2016; Liu, Xia, Deloule, et al., 2015, Liu, Xia, Ingrin, et al., 2015; Liu, Wang, et al., 2017; Liu, Xia, et al., 2016; Sakuyama et al., 2013; Xu et al., 2012, 2017; Xu et al., 2018; Yu et al., 2019). The present‐day subducted Pacific slab has been seismically detected in the mantle transition zone beneath eastern Asia, with its western edge extending to about 120°E longitude, where it roughly coincides with the eastern margin of the Daxing’ anling‐Taihang Gravity Lineament (DTGL; Figure 1; Huang & Zhao, 2006; Wei et al., 2012). The region above this stagnant slab has been termed the “Big Mantle Wedge” (BMW; Zhao et al., 2009), which extends to over 1,000 km from the trench, where the BMW and the crustal section above are considered as an intraplate setting (Xu et al., 2018). Cenozoic basalts occurring to the east of the DTGL in eastern China have consistently light Mg isotopic compositions and define a large low δ²⁶Mg anomaly within the BMW (δ²⁶Mg = −0.60‰ to −0.34‰; Huang, Li, et al., 2015; Tian et al., 2016; Wang et al., 2017; Yang et al., 2012; Sun, Teng, et al., 2017; Su et al., 2017; Li et al., 2017). Basalts erupted at Chaihe in the nearby DTGL area (Figure 1a), in contrast, show terrestrial, mantle‐like Mg isotopic composition (δ²⁶Mg = −0.34‰ to −0.19‰; Li et al., 2017; Sun, Teng, et al., 2017), which may suggest a spatial relationship between the large‐scale Mg isotopic anomaly and the stagnant Pacific slab or the BMW beneath eastern Asia (Li et al., 2017). However, additional data on the Mg isotopic composition of basalts generated beyond the BMW beneath eastern Asia are not yet available. Adding to the database is thus crucially important for further constraining the geodynamic evolution, the complexity of mantle sources beneath eastern Asia, and the longevity of Earth’s carbon cycle.

To further our understanding, we have targeted Cenozoic volcanic rocks erupted west of the DTGL in the Huihe volcanic field (Figure 1), for which we report whole‐rock Mg, Sr, Nd, Pb, and Hf isotopic data, as well as major- and trace-element compositions. For comparison, we compiled geochemical data for the Cenozoic Chaihe basalts (Chen et al., 2017; Ho et al., 2013; Li et al., 2017; Sun, Teng, et al., 2017; Xue et al., 2019; Zhao & Fan, 2012) and for Cenozoic basalts (sensu lato) from areas above the BMW, including data for Shandong nephelinites that have erupted in the eastern part of the North China Craton (Figure 1a).

Figure 1. (a) Distribution of Cenozoic volcanic centers in northeast China. The red dashed line represents the surface expression of the western edge of the stagnant Pacific slab in the mantle transition zone beneath eastern Asia (Huang & Zhao, 2006). The gray belt shows the northern segment of the DTGL modified from Xu (2007). The boundaries between the major blocks are shown as brown bold lines. (b) Late Cenozoic basalts and sample locations of the Huihe volcanic field. DTGL = Daxing’anling-Taihang Gravity Lineament; XMOB = Xing’an Mongolia Orogenic Belt.
2. Geological Setting and Samples

The Huihe volcanic field is located within the Xing’an-Mongolia Orogenic Belt (XMOB) in Northeast China (Figure 1a). The XMOB forms the eastern part of the Paleozoic Central Asian Orogenic Belt, which is bound by the North China Craton to the south and by the Siberian Craton to the north (Figure 1a; Jahn et al., 2000; Xiao et al., 2015). During the late Mesozoic, the tectonic regime beneath the XMOB changed from compression to extension during continued subduction of the paleo-Pacific plate. This change in tectonic regime resulted in asthenospheric upwelling, extensive magmatism, and the formation of rift basins (Meng, 2003; Wu et al., 2002; Zorin, 1999). In the Cenozoic, in contrast, the XMOB experienced only small-scale intraplate magmatism on both sides of the DTGL (Figure 1a). The DTGL trends ~NEE. It is oriented subparallel to the Tanlu fault zone, which is a crustal-scale strike-slip fault zone in eastern China. Across the DTGL, the Bouguer gravity anomaly decreases rapidly from ~0.1 to ~0.04 cm/s² from west to east (Ma, 1989; Xu, 2007). Crustal elevation, morphology, and crustal and lithospheric thickness also change considerably across this lineament (Li & Mooney, 1998; Ma, 1989; Menzies, 1998; Tao et al., 2014; Ye et al., 1987; Zhang et al., 2014). The Huihe volcanic field is located to the west of the DTGL and about 500 km west of the vertical projection line of the front edge of the stagnant Pacific slab in the mantle transition zone (Figure 1b). It is also located ~150 km further west, and thus further beyond the BMW, than the Chaihe basaltic field.

The Huihe volcanic field with Late Neogene age consists of six monogenic volcanoes with diameters of less than 10 km (Figure 1b), which crop out along the Huihe River. Jurassic igneous rocks and Quaternary sediments dominate the rest of the outcrops.

The Huihe volcanic rocks are porphyritic with olivine (15%) and clinopyroxene (<5%) phenocrysts and a groundmass of volcanic glass, olivine, plagioclase, and clinopyroxene. Some olivine phenocrysts are partially altered to iddingsite, while the rocks are largely unaltered away from exposed surfaces and fractures. Any effects of alteration have been considered and are later discussed in detail.

3. Whole-Rock Compositions of the Huihe Nephelinites

Thirteen samples from the Huihe volcanoes were selected for whole-rock major- and trace-element and Sr, Nd, Pb, and Hf isotopic analysis. Nine of the Huihe samples, plus seven samples from the Chaihe volcanic field, were further selected for whole-rock Mg isotopic analysis. Measurements of whole-rock major elements were made using a Thermo Scientific ARL 9900 X-ray fluorescence spectrometer at the State Key Laboratory for Mineral Deposits Research, Nanjing University. Trace-element compositions were determined using an ELAN 6100DRC Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Department of Geology, Northwest University, Xi’an. Sr, Nd, Pb, and Hf isotopic compositions were measured at the State Key Laboratory for Mineral Deposits Research, Nanjing University. Sr isotopic analyses were performed using a Finnigan MAT Triton Tl thermal ionization mass spectrometry, while Nd, Pb, and Hf isotopic compositions were obtained using a Thermo Scientific Neptune Plus multicollector ICP-MS. Mg isotopic analysis was performed using the sample-standard bracketing method on a Thermo Scientific Neptune multicollector ICP-MS under “wet” plasma conditions in a medium-resolution mode at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, and the Key Laboratory of Crust‐Mantle Materials and Environments, Chinese Academy of Sciences in the University of Science and Technology of China, Hefei, following the procedures established and described by An et al. (2014). Accuracy and reproducibility of data can be found in supporting information Tables S2–S4. The analytical results are given in Tables S1 and S2, which are consistent with those of previous studies (An et al., 2014; An & Huang, 2014; Bizzarro et al., 2005; Bourdon et al., 2010; Bouvier et al., 2008; Galy et al., 2003; Huang et al., 2012; Huang, Ke, et al., 2015; Huang, Li, et al., 2015; Jochum et al., 2016; Lai et al., 2015; McDonough & Sun, 1995; Teng, 2017; Teng et al., 2015; Von Pogge Strandmann, 2008; Von Pogge Strandmann et al., 2011; Wimpenny et al., 2014; Wombacher et al., 2011; Young & Galy, 2004; Zhong et al., 2017). Petrography and elemental and Sr, Nd, Pb, and Hf isotopic compositions of the Chaihe basalts have been reported elsewhere (Xue et al., 2019). Further details of the analytical methods are given in Supporting Information S1 (following An et al., 2014; White et al., 2000).

According to the nomenclature of Le Bas et al. (1986), samples from the Huihe volcanic field are mainly nephelinites, while one of our samples is classified as basanite (Figure 2; yet hereafter we refer to all
Huihe rocks as nephelinites for reasons of simplicity). These strongly
alkaline rocks have low SiO₂ (37.68–41.28 wt.%), medium to high MgO (7.51–10.95 wt.%), high CaO (10.57–13.06 wt.%), TiO₂ (3.50–3.72 wt.%), alkalis (Na₂O + K₂O = 4.82–6.27 wt.%), and high Ca/Al ratios (1.2–1.7). No correlation is observed between their MgO content and the concentration of other oxides (Figure S3). In a chondrite-normalized REE diagram (Figure 3), the alkaline Huihe rocks show a pattern of strong LREE enrichment (La/Yb = 29.6–55.2) with no Eu and Ce anomalies. In a primitive-mantle normalized multi-element diagram (Figure 3), the Huihe nephelinites resemble ocean island basalts in terms of their enrichment in Nb and Ta and their depletion in K and Pb relative to the LREEs. It is noteworthy that the patterns of the Huihe nephelinites resemble those of the Shandong nephelinites as they all show negative Zr, Hf, and Ti anomalies (Hf/Hf* = 0.58–0.69, Ti/Ti* = 0.62–0.83 for Huihe nephelinites; Hf/Hf* = 0.50–0.69, Ti/Ti* = 0.40–0.52 for Shandong nephelinites; Zeng et al., 2010; Figure 3). Besides, all Huihe nephelinites also have superchondritic Zr/Hf ratios (43.5–46.6; Zr/Hf = 44.4–50.8; Zeng et al., 2010). The trace-element concentrations of the Chaihe basalts are lower than those of the Huihe and Shandong nephelinites, and their patterns show less pronounced Zr, Hf, and Ti anomalies (Hf/Hf* = 0.74–0.85, Ti/Ti* = 0.87–1.56; Ho et al., 2013; Li et al., 2017).

Variation in the Sr, Nd, Pb, and Hf isotopic compositions of the Huihe nephelinites is limited (Figure 4). The rocks show less depleted Sr-Nd isotopic compositions (⁸⁷Sr/⁸⁶Sr = 0.7037–0.7043, εNd = 3.5–5.7) than the Chaihe basalts (⁸⁷Sr/⁸⁶Sr = 0.7035–0.7037, εNd = 4.9–6.7; Ho et al., 2013; Li et al., 2017; Zhao & Fan, 2012; Figures 4a and 5), while their Pb isotopes are more radiogenic (²⁰⁶Pb/²⁰⁴Pb = 18.442–18.831, ²⁰⁷Pb/²⁰⁴Pb = 15.527–15.559, and ²⁰⁸Pb/²⁰⁴Pb = 38.522–39.003) than those of the Chaihe basalts (Figure 4c). On a plot of εNd versus εHf, all samples plot near or below the terrestrial reference line (Vervoort et al., 2011).

The Huihe nephelinites have δ²⁶Mg values ranging from −0.47‰ to −0.35‰, while the Chaihe basalts have δ²⁶Mg values ranging from −0.32‰ to −0.24‰. In a plot of δ²⁵Mg′ versus δ²⁶Mg′ (Figure S1), all our samples and the analyzed United States Geological Survey (USGS) geological reference materials fall along the mass-dependent fractionation line for Mg isotopes (Young & Galy, 2004). The δ²⁵Mg values of the Huihe nephelinites are significantly lower than those of
the terrestrial mantle (average $\delta^{26}\text{Mg} = -0.25 \pm 0.04 \text{‰}$; Teng, 2017; or $\delta^{26}\text{Mg} = -0.23 \pm 0.04 \text{‰}$; Lai et al., 2015) and the Chaihe basalts ($\delta^{26}\text{Mg} = -0.32 \text{‰}$ to $-0.19 \text{‰}$; Li et al., 2017; Sun, Teng, et al., 2017), while they are comparable to those of other Cenozoic sodic basalts in eastern China ($\delta^{26}\text{Mg} = -0.60 \text{‰}$ to $-0.30 \text{‰}$; Li et al., 2017; Sun et al., 2017; Sun et al., 2014; Wang et al., 2017; Yan & Zhao, 2008; Yan et al., 2007; Zhang et al., 2016; Zhang et al., 1995; Zhao et al., 2014; Zou et al., 2008; Zou et al., 2003. North China: Basu et al., 1991; Chen et al., 2009; Choi et al., 2008; Guo et al., 2016; Han et al., 1999; Ho et al., 2011; Li, Ma, et al., 2016; Wang et al., 2011; Xu et al., 2012; Yu et al., 2015; Zeng et al., 2013; Zhang et al., 2012; Zou et al., 2000. South China: Li, Xu, et al., 2016; Yu et al., 2017; Ho et al., 2003; Huang et al., 2013; Sun et al., 2017; Zeng et al., 2013; Zou et al., 2000), including data for the Chaihe basalts (big gray dots; Ho et al., 2013; Li, Ma, et al., 2016; Zhao & Fan, 2012; Xue et al., 2019). Data for EM1-type (Pitcairn Islands), EM2-type (Samoa Islands) oceanic basalts, and Pacific, Indian MORB (mid-ocean ridge basalt) are from Stracke (2012). Data for DMM are from Workman and Hart (2005). NHRL = Northern Hemisphere Reference Line; DMM = depleted MORB mantle.

**Figure 4.** Variation in the Sr, Nd, Pb, and Hf isotopic composition of the Huihe nephelinites. Data for Cenozoic basalts in Eastern China are shown for comparison (NE China: Basu et al., 1991; Chu et al., 2013; Kuritani et al., 2009; Liu, Chen, et al., 2017; Rasskazov et al., 2011; Sun, Teng, et al., 2017; Sun et al., 2014; Wang et al., 2017; Yan & Zhao, 2008; Yan et al., 2007; Zhang et al., 2016; Zhang et al., 1995; Zhao et al., 2014; Zou et al., 2008; Zou et al., 2003. North China: Basu et al., 1991; Chen et al., 2009; Choi et al., 2008; Guo et al., 2016; Han et al., 1999; Ho et al., 2011; Li, Ma, et al., 2016; Wang et al., 2011; Xu et al., 2012; Yu et al., 2015; Zeng et al., 2013; Zhang et al., 2012; Zou et al., 2000. South China: Li, Xu, et al., 2016; Yu et al., 2017; Ho et al., 2003; Huang et al., 2013; Sun et al., 2017; Zeng et al., 2013; Zou et al., 2000), including data for the Chaihe basalts (big gray dots; Ho et al., 2013; Li, Ma, et al., 2016; Zhao & Fan, 2012; Xue et al., 2019). Data for EM1-type (Pitcairn Islands), EM2-type (Samoa Islands) oceanic basalts, and Pacific, Indian MORB (mid-ocean ridge basalt) are from Stracke (2012). Data for DMM are from Workman and Hart (2005). NHRL = Northern Hemisphere Reference Line; DMM = depleted MORB mantle.

4. Origin of the Light Mg Isotopic Composition of the Huihe Nephelinites

Loss on ignition values of the analyzed Huihe nephelinites vary from 0.97 to 2.34 wt.%. Together with the partial alteration of some olivine phenocrysts to iddingsite, this suggests that our selected samples have experienced minor alteration. However, good correlations between Nb and other fluid-mobile elements such as La, Sr, Th, and U (Figure S2) imply that the chemical effect of low-temperature alteration is limited. More importantly, there is no correlation between loss on ignition and $\delta^{26}\text{Mg}$ (Figure S3), and we thus rule out that low-temperature alteration had a measurable effect on the Mg isotopic compositions of the Huihe nephelinites.

Fractional crystallization and crustal contamination also have the potential to affect Mg isotopic compositions. Crustal contamination may be particularly important in the evolution of continental intraplate
basalts (compared to oceanic intraplate basalts) as they traverse thick, fusible crust. The Huihe nephelinites, however, have depleted Sr-Nd-Hf isotopic compositions ($^{87}$Sr/$^{86}$Sr = 0.7037–0.7043, $\varepsilon_{Nd} = 3.5$–5.7, and $\varepsilon_{Hf} = 4.8$–6.9; Figures 4a and 4b), indicating that crustal contamination had limited influence on their isotopic compositions. Their Ce/Pb (22.5–42.1) and Nb/U ratios (46.1–68.8) are moreover close to those of oceanic basalts (Nb/U = 47 ± 10, Ce/Pb = 25 ± 5; Hofmann et al., 1986) and much higher than those of continental crust (Nb/U = 3.9, Ce/Pb = 6.1; Rudnick & Gao, 2003). In combination, the elemental and isotopic compositions thus suggest that crustal contamination has had a negligible effect on the chemical composition of the Huihe nephelinites.

The relatively low Mg# (51.3–62.5) and low Ni (120–216 ppm) character of the Huihe nephelinites indicates that they have experienced fractionation of olivine, supported by the presence of olivine phenocrysts. There is no significant correlation between MgO and any of the other whole-rock major oxides, precluding significant fractionation of clinopyroxene or Ti-Fe oxides (Figure S4). The absence of whole-rock Eu anomalies (Figure 3) also highlights that fractionation of plagioclase did not play a role. Since previous studies have shown that basalt differentiation through olivine fractionation does not significantly fractionate Mg isotopes (Teng et al., 2007), the low $\delta^{26}$Mg values of the Huihe nephelinites are taken to be characteristic for the primary magmas.

Variable degrees of partial melting of a peridotitic/pyroxenitic source can affect Mg isotopic composition of primary melts, but the effect is limited (<0.1‰; Stracke et al., 2018; Zhong et al., 2017). As illustrated in Figure 6c, the $\delta^{26}$Mg values of pyroxenite/peridotite-derived melts decrease with their melting degrees, but they are still higher than those of the Huihe nephelinites investigated here. Thus, low-degree partial melting of peridotite or pyroxenite alone also cannot account for the low $\delta^{26}$Mg values of the Huihe nephelinites.

The low $\delta^{26}$Mg values (as low as $-0.47$‰) of the Huihe nephelinites thus cannot be explained by crustal contamination, crystal fractionation, or low-degree partial melting but require an isotopically light mantle source component.

5. Nature of the Light Mg Isotope Mantle Component

Sedimentary carbonates have extremely light Mg isotopic compositions ($\delta^{26}$Mg = -5.57‰ to -0.38‰; Huang, Ke, et al., 2015; Wombacher et al., 2011; Young & Galy, 2004). Light Mg isotopic signatures of basalts have therefore been widely interpreted to reflect contributions from this isotopically light component in the form of recycled carbonates in their mantle sources (e.g., Huang, Li, et al., 2015; Li et al., 2017; Wang et al., 2017; Yang et al., 2012). Melts with light Mg isotopic signature, but low or moderately low CaO contents, however, cannot be produced by direct partial melting of carbonate-bearing source rocks (Wang et al., 2018). Wang et al. (2018) proposed that during subduction, reaction between carbonate and silicate minerals in subducted sediments may exhaust source carbonate, producing pyroxenitic components with isotopically light magnesium.

High-pressure melting experiments have shown that melts from carbonate-bearing peridotite/pyroxenite are characterized by negative K, Zr, Hf, and Ti anomalies, low SiO$_2$, high CaO, and high Ca/Al ratios, which are distinct from those of melts derived from carbonate-free peridotite/pyroxenite (Dasgupta et al., 2006; Dasgupta et al., 2007; Dasgupta et al., 2009). Among Cenozoic volcanic rocks in eastern China, such elemental signatures have first been observed for the Cenozoic Shandong nephelinites, which suggested a carbonated mantle source (Zeng et al., 2010). The Huihe nephelinites are also characterized by low SiO$_2$ (37.68–41.28 wt.%), high CaO (10.57–13.06 wt.%), and high Zr/Hf and high Ca/Al ratios (Zr/Hf = 43.5–

Figure 5. Variation in La/Sm versus (a) $^{87}$Sr/$^{86}$Sr and (b) $^{143}$Nd/$^{144}$Nd for the Huihe nephelinites compared to the Chaihe basalts (data from Ho et al., 2013; Li et al., 2017; Zhao & Fan, 2012; Xue et al., 2019). Black and white dots represent samples collected from Tuofengling and Delehe in the Chaihe volcanic field, respectively. Other Chaihe basalts are shown by gray dots.
46.6, Ca/Al = 1.19–1.72), as well as negative K, Zr, Hf, and Ti anomalies (low Ti/Ti* and Hf/Hf*; Hf/Hf* = 0.58–0.69, Ti/Ti* = 0.62–0.83; Figure 3). We take these so-called “carbonatitic fingerprints,” together with their light Mg isotopic compositions, to infer that the Huihe nephelinites had a carbonated mantle source. The Huihe nephelinites thus have major- and trace-element and isotopic compositions that are characteristic for melts derived from carbonated mantle sources. The question is thus, from which type of carbonated mantle component the Huihe magmas derived. We first discuss possible types of recycled carbonates and their fate during subduction, and then evaluate how sources and melts with isotopically light Mg yet unradiogenic Sr isotopic character can be generated.

Carbonate minerals transferred into the mantle by subduction are mainly calcite and dolomite (Morlidge et al., 2006). The proportion of magnesite in sedimentary carbonates is very low, and the contribution of sedimentary magnesite in mantle sources can therefore be ignored. Calcite incorporates only minor amounts of MgO and thus has no major effect on Mg isotopic compositions of MgO-rich peridotitic mantle. Dolomite is therefore the only primary carbonate mineral which has the potential to significantly modify the Mg isotopic compositions of the peridotitic mantle. However, because of its high Sr content, mixing of dolomite into the peridotitic mantle modifies not only its Mg isotopic compositions but also its Sr isotopic compositions toward high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which contrasts with the low (unradiogenic) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7037–0.7043) of the Huihe nephelinites (Figure 7). We therefore further examine if light Mg isotopic and unradiogenic Sr isotopic source compositions can be derived from dolomite-rich components that have undergone reaction during subduction.

Figure 6. Plots of $\delta^{26}\text{Mg}$ versus selected element ratios for the Huihe nephelinites. Cenozoic Low $\delta^{26}\text{Mg}$ sodic basalts from eastern China (gray diamonds) and Chaihe basalts are shown for comparison (Huang, Li, et al., 2015; Huang & Xiao, 2016; Li et al., 2017; Qian et al., 2015; Su et al., 2017; Sun, Teng, et al., 2017; Tang et al., 2006; Wei, 2014; Xue et al., 2019; Yang et al., 2011; Yang et al., 2012). Yellow dots represent new measured $\delta^{26}\text{Mg}$ values of Chaihe samples in this study. The horizontal gray bar ($\delta^{26}\text{Mg} = -0.23 \pm 0.04$‰) and diagonally striped bar ($\delta^{26}\text{Mg} = -0.25 \pm 0.04$‰), respectively, mark the $\delta^{26}\text{Mg}$ values of the terrestrial mantle according to Lai et al. (2015) and Teng (2017). Modeled pyroxenite melting and peridotite melting trends are modified from Zhong et al. (2017) with newly calculated La/Sm. Initial element concentrations for pyroxenite and peridotite are from Gale et al. (2013) and McDonough and Sun (1995), whereas partition coefficients are from Pertermann et al. (2004), Davis et al. (2011), and Salters and Stracke (2004). Details of the calculations are given in Table S6.

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The isotopic compositions and element concentrations of endmembers are given in Table S7 (with data from Aizawa et al., 1999; Delavault et al., 2016; Hauff et al., 2003; Ho et al., 2013; Huang & Xiao, 2016; Huang, Shen, et al., 2015; Huang et al., 2018; Johnson & Plank, 1999; Kessel et al., 2005; Li et al., 2017; Liu, Zhao, et al., 2015; Salters & Stracke, 2004; Teng, 2017; Xue et al., 2019; Zhao & Fan, 2012). Symbols are equivalent to those in Figure 6. AOC = Altered Oceanic Crust.

High-pressure experiments have revealed that dolomite is unstable at high pressure, where it decomposes into magnesite and aragonite (Morlidge et al., 2006; Sato & Katsura, 2001). Experimental work has moreover shown that the majority of slab geotherms intersects the melting curve of carbonate-bearing oceanic crust at depths of ~300–700 km, where the subducted crust will experience low-degree partial melting, releasing calcic carbonatitic melts (Thomson et al., 2016). Therefore, when carbonate is subducted into the lower upper mantle or the mantle transition zone, dolomite [CaMg(CO₃)₂] decomposes, releasing calcic carbonatitic melt (CaCO₃), while secondary magnesite (MgCO₃) forms the main residue. Calcic carbonatitic liquids will segregate close to the site of their formation, locally metasomatizing the mantle. However, such Ca-rich metasomatized mantle is not a suitable source candidate for the Huihe nephelinites, given that calcic carbonatitic liquids do not significantly affect the Mg isotopic compositions of the mantle yet. Mantle domains rich in secondary magnesite, derived from the deep upper mantle/mantle transition zone, in contrast, have the potential to generate mantle sources with light Mg isotopic signature for the Huihe nephelinites.

To further explore the effects of carbonate recycling on Mg isotopic composition of the mantle, we construct a source mixing model using Mg and Sr isotopes (Figure 7). In this model, we assume that the mantle source of the Huihe nephelinites is a mechanical mixture consisting of recycled carbonate and ambient mantle peridotite, to quantitatively estimate the proportion of recycled carbonate. For the peridotite, we chose a δ⁵²Mg value of −0.25‰ (i.e., the estimated average for peridotite; Teng, 2017). For the Sr isotopic composition of the ambient mantle peridotite, we have used the average ⁸⁷Sr/⁸⁶Sr composition of the Chaihe basalts (0.7036), (1) because the Cenozoic Chaihe basalts have erupted in close spatial association to the Huihe nephelinites (Figure 1a), (2) because the Chaihe basalts have homogeneous and depleted Sr-Nd-Hf isotopic compositions (Figures 4a and 4b), and (3) because the Chaihe basalts have a peridotitic source (Xue et al., 2019). We further assume in our model that the residual, secondary magnesite has a Mg, Sr isotopic composition equivalent to that of recycled dolomite (i.e., we use the average Mg-Sr isotopic compositions of global dolomite, δ⁵²Mg = −1.89‰, ⁸⁷Sr/⁸⁶Sr = 0.7090; Huang & Xiao, 2016). A summary of the isotopic compositions and element concentrations of the modeled endmembers is given in Table S7. It can be assumed that most Sr partitioned into the segregated calcic carbonatitic liquid and that the residual magnesite has higher Mg and lower Sr contents than the ambient mantle peridotite. If we further consider minor Mg isotopic fractionation induced by low-degree partial melting (Stracke et al., 2018; Zhong et al., 2017), then our model predicts that ≤5–10% residual magnesite contributed to the mantle source of the Huihe nephelinites (Figure 7).

6. Relationship Between Huihe Nephelinites and Chaihe Basalts

Both Huihe nephelinites and Chaihe basalts occur west of the present-day stagnant Pacific slab and thus beyond the BMW. Because of their close spatial and temporal relationship (Figure 1a) and their similar Sr-Nd-Pb isotopic compositions (Figure 4), it is reasonable to discuss their possible genetic relationship. When the compositions of the Huihe and Chaihe rocks are plotted together, good correlations can be observed for δ⁵²Mg values and selected elemental ratios. As illustrated in Figure 6, δ⁵²Mg is positively correlated with Ti/Ti⁺ yet negatively correlated with Ca/Al, La/Sm, and La/Yb. The roughly similar Sr, Nd, and Pb isotopic compositions of the nephelinites and basalts (Figure 4) and the variable enrichment of incompatible elements (Figure 3) suggest that magmas at the two eruptive centers may have been generated by different-degree melting of similar mantle sources.

If this is correct, then the question arises how the similar sources have generated melts with significantly different Mg isotopic composition (average δ⁵²Mg = −0.41 ± 0.03‰ for Huihe nephelinites, average δ⁵²Mg = −0.28 ± 0.03‰ for Chaihe basalts in this study, and average δ⁵²Mg = −0.29 ± 0.04‰ for Chaihe...
basalts in previous studies; Li et al., 2017; Sun, Teng, et al., 2017). As carbonation lowers the solidus of mantle peridotite/eclogite (Dasgupta et al., 2005; Dasgupta et al., 2007; Dasgupta & Hirschmann, 2007), the carbonated part in a heterogeneous mantle melts first, thus contributing a higher proportion to melts at low-degree melting. With increasing melting degrees, contributions from carbonated material decrease as other lithologies (such as carbonate-free peridotite or eclogite/pyroxenite) also start to melt. Previous experimental studies have shown that near-solidus melts of carbonated peridotite/pyroxenite are carbonatitic, while carbonated silicate melts form with increasing degree of melting (Dasgupta et al., 2006, 2007). Thus, at higher degrees of melting, the so-called carbonatitic fingerprints are diluted (Huang, Li, et al., 2015; Zeng et al., 2010). Therefore, we suggest that the large difference in the Mg isotopic compositions of the Huihe nephelinites and the Chaihe basalts can be explained by variable degrees of melting of enriched, carbonated components. As illustrated in Figures 5 and 6, we posit that the Huihe nephelinites, which have higher La/Sm ratios than the Chaihe basalts, were produced by lower-degree partial melting. The lower δ²⁶Mg values and lower Ti/Ti* and higher Ca/Al ratios record higher contributions from carbonated components. The higher δ²⁶Mg values and higher Ti/Ti* and lower Ca/Al ratios of the Chaihe basalts, in contrast, record higher contributions from mantle silicates. In addition, the heavier Mg isotopic compositions of individual Chaihe basalt samples are most likely derived from recycled gabbroic lower oceanic crust. We suggest this (1) because the two Chaihe samples with the highest δ²⁶Mg values have positive Eu anomalies (Figure 3) and relatively low δ¹⁸O values (δ¹⁸O = 5.92‰; Chen et al., 2017), which indicates the contribution of recycled lower oceanic crust, and (2) because the gabbroic lower oceanic crust has mantle-like or slightly heavier Mg isotopic compositions (Huang, Ke, et al., 2015).

7. Implications for Carbon Recycling Beneath Eastern Asia

Yang et al. (2012) first suggested that the light Mg isotopic signature of continental basalts and other volcanic rocks from the North China Craton erupted after 110 Ma is linked to the subduction of the Pacific slab during the Mesozoic-Cenozoic. Huang, Li, et al. (2015) found that the <110-Ma-old basalts from the South China block also have light Mg isotopic compositions, which support the interpretation that recycled carbonated material in the mantle beneath eastern China was derived from the subducted Pacific slab, because only the Pacific slab has an influence on both the North and the South China blocks. Su et al. (2017) found that δ²⁶Mg values of Cenozoic basalts in eastern China decrease with increasing distance from the present-day subduction trench, suggesting that this trend is related to the westward subduction of the Pacific slab. As the main low δ²⁶Mg anomaly of the erupted volcanic rocks spatially overlaps the stagnant Pacific slab in the mantle transition zone beneath eastern China, Li et al. (2017) also suggested a genetic relationship between the large-scale Mg isotopic anomaly and the stagnant Pacific slab or the BMW beneath eastern Asia. The light Mg isotope composition of the Huihe nephelinites demonstrates that recycled carbonate also exists in the mantle at least ~500 km west beyond the present-day BMW region. This could indicate that the front edge of the subducted Pacific slab has retreated since the early Mesozoic, if the light Mg isotopic components are indeed related to the Mesozoic-Cenozoic Pacific plate subduction and the BMW. The other possibility is that the recycled carbonates in the mantle beyond the BMW are not derived from the subducted Pacific slab. Paleo-subduction beneath eastern Asia may have also transported carbonated material into the mantle, for example, the southwestern subduction of the Paleo-Asian oceanic slab, which commenced in the Ordovician and ceased in the Permo-Triassic (Xiao et al., 2003).

Furthermore, even within the BMW beneath eastern Asia, carbonated material which is not derived from the subducted Pacific slab also exists. Potassic basalts from Wudalianchi and Nuominhe (NE China) also have low δ²⁶Mg values (δ²⁶Mg = −0.61‰ to −0.31‰; Wang et al., 2017; Tian et al., 2016; Sun, Teng, et al., 2017), but their extraordinarily unradiogenic Pb isotopic compositions (206Pb/204Pb = 16.5–17.4; Liu, Chen, et al., 2017; Wang et al., 2017) cannot be derived from partial melting of young (Mesozoic-Cenozoic) carbonated components of the Pacific plate. Using a three-stage Pb growth model, Wang et al. (2017) suggested that the carbonated components were subducted into the mantle ~2.2 Ga ago and that they were isolated from nearby mantle since then.

Thus, prior to the subduction of the Pacific plate, carbonated materials supplied by other oceanic slabs have already existed both in and beyond the mantle of the BMW beneath eastern Asia, which have generated the light Mg isotopic signatures of at least some of the Cenozoic intraplate volcanics in eastern
Asia. This implies that the resident time of carbon in the mantle beneath eastern Asia is significantly longer than the ~60 ×10⁶ years estimated by Li et al. (2017). It further implies that a genetic relationship between the Cenozoic basalts erupted in eastern Asia and the stagnant Pacific slab should continue to be evaluated.

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