Metasomatism-induced mantle magnesium isotopic heterogeneity: Evidence from pyroxenites

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Abstract

High-precision Mg isotopic measurements on diverse mantle pyroxenite xenoliths collected from Hannuoba, North China Craton, revealed multi-stage **interaction** between the lithospheric mantle with melts of different origins. The garnet-bearing pyroxenites yield variable $\delta^{26}\text{Mg}$ values from -0.48 to -0.10‰, consistent with their origin as reaction products between mantle peridotites and melts from subducted oceanic slab with highly heterogeneous $\delta^{26}\text{Mg}$. Most of their constituent olivine, clinopyroxene, and orthopyroxene have indistinguishable $\delta^{26}\text{Mg}$ ratios around the normal mantle range **(-0.25 ± 0.07‰, Teng et al., 2010)**. **The lack of fractionation among these three phases agrees with their similar bonding environments for Mg (6-fold), and hence indicates a general isotopic equilibrium among them.** By contrast, garnets have variably lighter $\delta^{26}\text{Mg}$ values (-0.75 to -0.37‰, n = 15), **consistent with their higher coordination number for Mg (8-fold), and thus weaker Mg-O bonds.** The magnitude of fractionation between garnet and olivine/pyroxene, however, is not correlated with equilibrium temperature, and therefore reflects disequilibrium Mg partitioning. Considering the metasomatic origin of these garnets, the disequilibrium isotopic fractionation is most likely the result of rapid and incomplete metasomatic reaction during which garnets were formed at the expense of isotopically heavier co-existing minerals, particularly spinels. The two garnet-free clinopyroxenites, which display highly enriched light rare earth element (LREE) patterns and very low Ti/Eu ratios, are characterized by extremely light $\delta^{26}\text{Mg}$ (as low as -1.51‰). Their formation possibly indicates an episode of carbonatite **infiltration**. In comparison, the Cr and Al websterites, as well as an orthopyroxenite, all have mantle-like whole-rock and mineral $\delta^{26}\text{Mg}$ ratios, **with equilibrated clinopyroxene-orthopyroxene pairs.** Their presence thus implies different episodes of **asthenosphere-derived** silicate **melt injection** into the mantle. Collectively, these observations suggest that mantle metasomatism plays an important role in producing inter-mineral Mg isotopic disequilibrium and local Mg isotopic variation in the lithospheric mantle. Therefore, Mg isotopes can be used to trace metasomatic activities in the mantle.

Keywords: Magnesium isotopes, pyroxenite xenoliths, mantle metasomatism, disequilibrium fractionation, equilibrium fractionation

1. Introduction

Magnesium is a major rock-forming element with three stable isotopes (mass 24, 25, and 26). The fractionation of Mg isotopes during partial melting and magma differentiation is limited in the mantle ($\leq 0.07\text{‰}$ for $\delta^{26}\text{Mg}$, Teng et al., 2007, 2010). By contrast, over 7‰ fractionation in $^{26}\text{Mg}/^{24}\text{Mg}$ has been found at Earth's surface through continental weathering and carbonate precipitation (Wombacher et al., 2011; Liu et al., 2014). The highly variable $\delta^{26}\text{Mg}$ values found in crustal materials compared with the uniform $\delta^{26}\text{Mg}$ ratios characterizing mantle-related rocks and minerals thus highlights the potential of using Mg isotopes to trace crustal recycling (e.g., Yang et al., 2012).

A well-constrained mantle $\delta^{26}\text{Mg}$ value is a prerequisite for resolving crustal signal unambiguously from that of the mantle. Previous analyses on lherzolite-harzburgite-dunite series peridotites worldwide yielded largely consistent $\delta^{26}\text{Mg}$ values, and hence suggest a homogeneous mantle ($\delta^{26}\text{Mg} = -0.25 \pm 0.07\text{‰}$, Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Teng et al., 2010; Huang et al., 2011; Liu et al., 2011). However, more recent studies on strongly metasomatized peridotites, particularly wehrlites, found $\delta^{26}\text{Mg}$ values deviated from the mantle range (Yang et al., 2009; Pogge von Strandmann et al., 2011; Xiao et al., 2013) with evidence for disequilibrium inter-mineral fractionation (Young et al., 2009; Xiao et al., 2013). Meanwhile, continental basalts are also frequently found to be distinctively depleted in heavy Mg isotopes (Yang et al., 2012; Huang et al., 2015) when compared to the homogeneous oceanic basalts with mantle-like $\delta^{26}\text{Mg}$ (Bourdon et al., 2010; Teng et al., 2010). With the general recognition of a compositionally heterogeneous mantle where magmatic refertilization is widespread (Kelemen et al., 1998), it thus needs further investigation on the scale, distribution, and extent of Mg isotopic heterogeneity caused by open-system isotopic exchanges between mantle rocks and migrating metasomatic melts.

Pyroxenites that form veins cross-cutting the mantle are more direct samples than metasomatized peridotites for this purpose as their occurrence marks zones of higher melt/rock ratios in the mantle (Garrido and Bodinier, 1999). They have been variously interpreted as high-pressure cumulates from migrating asthenosphere-derived magmas (Frey, 1980; Irving, 1980), reaction products of metasomatic melts with mantle peridotite wall rocks (Garrido and Bodinier, 1999), in-situ melts of the host peridotites (Chen et al.,

2001), or remnants of subducted oceanic crust (Allègre and Turcotte, 1986) (See Downes, 2007 for a review). Due to their more fusible nature than the ambient peridotites (Anderson, 2005), pyroxenites have been regarded as an important lithologic heterogeneity in the mantle, and are often invoked to explain the chemical and isotopic variations observed in oceanic and continental basalts (Sobolev et al., 2005, 2007). Yet, whether their presence will also cause Mg isotopic heterogeneity in the mantle and related volcanic rocks is still unknown, due to the lack of Mg isotopic data on mantle pyroxenites.

Here, we present the first systematic Mg isotopic analyses on a variety of mantle pyroxenite xenoliths, along with major and trace element data for the whole rocks and constituent minerals. The xenoliths were collected from the Hannuoba basaltic plateau (27 to 14 Ma, Zhu, 1998) distributed along the north margin of the North China Craton (NCC), where the entire section of the ancient lithospheric mantle has been modified by intense and multi-stage melt-rock interactions (Tang et al., 2008). These xenoliths were taken as physical evidence for different episodes of melt injection events (Chen et al., 2001; Xu, 2002; Fan et al., 2005; Liu et al., 2005, 2010c). Therefore, they are ideal samples for studying the influence of mantle metasomatism on generating Mg isotopic variation in the mantle. The variable Mg isotopic composition of the pyroxenites and their disequilibrium inter-mineral fractionations indicate a heterogeneous distribution of Mg isotopes in the mantle induced by mantle metasomatism.

2. Sample petrology

Twenty five pyroxenite and two lherzolite xenoliths were selected for Mg isotopic measurements to cover the wide range of texture, modal and compositional mineralogy of a larger sample collection. They are generally very large and fresh (Fig. 1A), and can be broadly divided into garnet-bearing and garnet-free groups. The garnet-bearing group contains two lherzolites, 15 websterites and three clinopyroxenites, in order of increasingly darker appearance. Some garnet pyroxenites form veins infiltrating the host spinel lherzolites, while other discrete samples (without peridotite hosts) with a similar mineralogy could be fragments from wider garnet pyroxenite veins. These xenoliths consist mainly of olivine, garnet, clinopyroxene, orthopyroxene with accessory spinel

(Fig. 1B; Table S1). The most prominent petrographic features of these xenoliths are the secondary nature of the constituent garnet and its close association with spinel. Garnets commonly form rims on spinels, giving rise to the typical spinel-cored garnets (Fig. 1C). The observation that garnet gradually replaces spinel suggests garnet was formed at a later stage, at the expense of spinel (Fig. 1D-G). Notably, the relic spinel cores display embayed and amoeboidal grain boundaries (Fig. 1C), suggesting that garnets have grown in the presence of melts (Keshav et al., 2007). Garnets also formed from the triple-junctions of co-existing minerals and gradually occupy their grain boundaries, as well as engulf adjacent olivine or pyroxene grains (Fig. 1H-J), until growing into noticeably large grains that are much coarser than other co-existing mineral phases or typical garnets seen in garnet peridotites (Fig. 1G). Moreover, different garnet grains are often connected to each other, forming veins in the olivine-pyroxene matrix, and showing elongation along the vein direction (Fig. 1A).

While garnet is usually in reacting relationship to olivine and pyroxene, olivine and pyroxene grains frequently show triple-junction contact, implying textural equilibrium (Fig. 1K and M). Olivines are typically subhedral granular or elongated under deformation. Some olivine grains also occur as anhedral relic phase in garnets or as elongated crystals that gradually taper out between garnets and pyroxenes, suggesting their possible role as a reactant in the garnet-forming reaction. Pyroxenes are generally the dominant phase and occur as large tabular or polygonal grains (Fig. H and K). Both olivine and orthopyroxene are often strained and exhibit multiple kink bands (Fig. 1K). Undulatory extinction is occasionally observed in orthopyroxene as well. These deformation features are consistent with plastic deformation at high temperature and suggestive of a non-cumulative origin for these xenoliths (e.g. Ionov et al., 2005). Trapped melt/fluid inclusions are commonly found in pyroxenes (Fig. 1L) and some clinopyroxene grains have sieved rims with irregular glass films. In addition to these common mineral phases, glass veins with sparse tiny metasomatic phlogopite and apatite are observed (Fig. 1N - P).

The garnet-free group includes three green Cr websterites (ranging from clinopyroxene-rich to orthopyroxene-rich in composition), one dark Al websterite, two grayish green Cr clinopyroxenites, and one dark brown orthopyroxenite. Following the

classification proposed by Wilshire and Shervais (1975), the Cr websterites are characterized by the presence of emerald green Cr-diopside, while diopsides in the Al websterite are more enriched in Al. The two types of pyroxenes have a similar grain size in two Cr websterites while clinopyroxene is much smaller and less abundant in the orthopyroxene-rich Cr websterite and in the orthopyroxenite.

In addition to these xenoliths, two Hannuoba basalts were also analyzed to help identify the presence of subducted crustal material in the Hannuoba mantle, as eastern China basalts that carrying a light $\delta^{26}\text{Mg}$ signal were generally thought to have had their mantle source been modified by carbonatitic melts released from subducted oceanic crust (Yang et al., 2012; Huang et al., 2015). Although metamorphosed oceanic crust (i.e., eclogites) have shown highly heterogeneous, and generally light, Mg isotopic composition (Wang et al., 2012), it still needs to be tested to what extent carbonatite metasomatism can shift the Mg isotopic composition of mantle rocks as previous measurements on carbonate-metasomatized peridotites did not show noticeable deviation from mantle value (Handler et al., 2009; Teng et al., 2010). Due to the lack of strongly carbonatite-metasomatized sample in our sample collection from Hannuoba, a carbonatite-metasomatized garnet lherzolite from western Qinling, China, was analyzed. It has carbonatite-like trace element patterns and Sr-Pb isotopic composition and displays positive Sr and Ba anomalies, attesting to the influence of carbonatite metasomatism, while their high Nb and Ta concentrations suggest the influence of subducted components (Su et al., 2012b).

3. Methods for Mg isotopic analysis

Chemical separation of Mg and subsequent isotopic analyses were performed at the University of Arkansas, Fayetteville, following the method developed in Teng et al. (2007). All chemical procedures were performed in a metal-free clean laboratory. Pre-cleaned Savillex Teflon® screw-top beakers were used exclusively during chemical separation and instrumental analyses.

The whole-rock powders used for major and trace elemental analyses were used here for Mg isotopic measurements. In addition, optically clean mineral fragments were handpicked under a binocular microscope to > 99% purity and triple cleaned with Milli-

Q® water in an ultra-sonic bath (≥ 10 minutes per wash). The mineral and whole-rock samples were attacked sequentially with Optima-grade concentrated HF-HNO₃, HNO₃-HCl and HNO₃, following the method detailed in Yang et al. (2009). An ultrasonic bath was used to accelerate dissolution by disrupting sample size and hence increasing the solid-acid interface. All samples were finally taken up in 1 N HNO₃ and loaded onto pre-cleaned Bio-Rad cation-exchange resin (AG50W-X8, 200-400 mesh). Matrix elements were eluted away in the first 16 mL of 1 N HNO₃, and Mg was collected in the following 19 mL of the same acid. This purification procedure was repeated twice to ensure maximum elimination of the matrix. The total procedural blank was < 10 ng, representing $< 0.1\%$ of Mg loaded onto the column (Teng et al., 2010).

Magnesium isotopic ratios were measured on a *Nu Plasma* MC-ICPMS. Sample solutions were introduced into the ion source with “wet” plasma condition, which has been demonstrated to be more resistant to matrix effects and concentration mismatch than the “dry” plasma introduction for Mg isotopic analysis (Teng and Yang, 2014). Matching in acid molarity and Mg concentration among all analyzed solutions are crucial for accurate Mg isotopic analyses (Teng and Yang, 2014). Therefore, all the sample and standard solutions were prepared at the day of measurement using the same batch of 3% Optima-grade HNO₃. Also, the standard solutions were prepared in the same numbers, container type, and liquid volume to those of sample solutions, to minimize the effect of evaporation during a batch run. The intensity matching between samples and standards were kept within 95% to avoid instrumental bias in Mg isotopic measurement (Teng and Yang, 2014). At a typical Mg concentration of 300 ppb, ²⁴Mg background is negligible ($< 10^{-4}$ V) compared to sample signals (3 to 4 V). The instrumental fractionation was corrected by sample-standard bracketing technique assuming a linear mass fractionation drift during a batch run. All Mg isotope data are reported in delta (δ) notation on DSM-3 scale (Galy et al., 2003). The $\delta^X\text{Mg}$ values reported represent parts per thousand (‰) deviations of a ratio relative to the average of the two standard ratios measured before and after:

$$\delta^X\text{Mg} = 10^3 \times \left\{ \frac{(^X\text{Mg} / ^{24}\text{Mg})_{\text{sample}}}{(^X\text{Mg} / ^{24}\text{Mg})_{\text{DSM3}}} - 1 \right\},$$

where X refers to mass 25 or 26.

The accuracy of Mg isotopic analysis was assessed in two ways. First, five international rock standards (DTS-1, PCC-1, BHVO, MAG-1, and Murchison meteorite) were processed through the same procedure as all the unknown samples. They yielded $\delta^{26}\text{Mg}$ values comparable to previously published data (Table 1), and thus provide warranty for our entire analytical procedure, including sample digestion, chemical separation and mass spectrometry. Then, two in-house standards (e.g., Kilbourne Hole olivine and Hawaiian seawater) were processed through column chemistry and analyzed along with unknown samples during each batch run. The results of these in-house standards also agree with literature values (Table 1).

The analytical reproducibility is also critical, particularly in that some data obtained in this study deviate significantly from previously published values for the same type of minerals or rocks, and there is no literature reference for mantle pyroxenites and pyroxenitic garnets. Analytical results from repeat analyses of the same sample, from dissolution or column chromatography to isotopic measurement, were reproduced within $\pm 0.05\text{‰}$ (2SD) for $\delta^{26}\text{Mg}$ (Tables 2). Therefore, the reproducibility during the analytical period of this study is consistent with the conservative long-term (four-year) external precision for Mg isotopic data reported from this laboratory ($< \pm 0.07\text{‰}$ for $\delta^{26}\text{Mg}$, Teng et al., 2015).

4. Results

Major and trace element data for the bulk Hannuoba xenoliths are reported in Tables S2 and S3, respectively. Their average mineral compositions are presented in Tables S4-8. The temperature and pressure estimates based on different geothermobarometers are provided in Table 3. Relevant analytical methods are also provided in the supplementary materials.

4.1. Whole-rock major and trace element compositions

The Hannuoba pyroxenites and garnet-bearing lherzolites display much wider compositional variations compared with spinel-facies peridotites and wehrlites (Fig. 2), reflecting their more varied mineralogy (Fig. 2C). While they are more enriched in fusible components than peridotites by having higher Al_2O_3 (5.41-14.4 wt.%) and CaO

(1.35-21.6 wt.%) (Fig. 2A and B), their Mg# and Ni contents are much higher than those of basalts (Fig. 2D). In particular, the garnet-bearing group extends from that close to the peridotite field to Si- and Al-rich field approaching the Jiaohe pyroxenites (Fig. 2C), which were interpreted as remnants of subducted oceanic crust (Yu et al., 2010). The two Hannuoba basalts analyzed here fall within the range of published basalt data (Fig. 2). One of them belongs to the tholeiitic group while the other with slightly higher alkali content and lower SiO₂ belongs to the alkali group based on the TAS diagram (Total Alkalies vs. SiO₂, Le Bas et al., 1986, not shown).

Most of the xenoliths have higher rare earth element (REE) contents than the spinel peridotite residuals reported in the literature, except the orthopyroxenite that falls within the spinel peridotite field (Fig. 3A and C). The REE patterns of garnet-bearing lherzolites and pyroxenites are characterized by flat heavy REE and variable light REE (LREE), ranging from LREE-enriched to LREE-depleted to others having flat patterns. The two garnet-bearing lherzolites and a Cr websterite display U-shaped REE patterns (Fig. 3A and C) that are also typical for spinel lherzolites (e.g. Rudnick et al., 2004), which is generally interpreted as the result of re-introduction of highly incompatible elements by metasomatic melts after partial melting (Coltorti and Grégoire, 2008). These garnet-bearing xenoliths are also distinctive in their enrichment in fluid-mobile large ion lithophile element (LILE) concentrations with significant peaks at Pb (0.2 to 0.9 ppm) and Sr (41 to 368 ppm) in the primitive mantle-normalized trace element diagrams with no obvious Eu anomaly presented (Fig. 3B and D). The two garnet-free Cr clinopyroxenites contain the highest Σ REE (65.2 and 105 ppm) among all the samples and show convex-upwards REE patterns (Fig. 3C), which is commonly observed for cumulative pyroxenites (Frey and Prinz, 1978). The Al websterite exhibits a similar REE pattern with the apex shifts from Ce to Nd (Fig. 3C).

4.2. Mineral chemistry

Except spinel, all the other constituent minerals exhibit a compositional affinity to non-cratonic peridotites, and are significantly different from those of pyroxenite cumulates worldwide (Fig. 4A and B). In addition, only olivine in the garnet-bearing xenoliths displays clear compositional zoning (Fig. 1M), with a Mg-rich core (Mg# =

86.3 to 91.0) and a Fe-rich rim ($Mg\# = 82.1$ to 90.8). Up to $\sim 500\ \mu m$ wide zoning has been observed in back-scattered electron images, and the intra-grain differences in $Mg\#$ can be as large as 6.5, attesting to the major element disequilibrium within individual grains.

All the garnets in samples studied here were replaced by kelyphite consisting of fine-grain intergrowths of spinel and plagioclase (Liu et al., 2005), although fresh relic garnets have rarely been reported (Chen et al, 2001; Liu et al., 2005). These kelyphites still possess an almost identical bulk chemical composition to garnets, with only few analyses yielding higher contents of Na_2O , suggesting alkali ingress from metasomatic melts (Liu et al., 2010c). Garnets are rich in pyrope end-member ($Pyr_{69.0-74.9}$, $Alm_{11.8-18.7}$, $Gro_{10.1-16.8}$), consistent with their relatively high $Mg\#$ (78.8 to 85.8) and mantle origin. Their CaO and Cr_2O_3 contents fall within the websteritic field (Sobolev et al., 1973) (Fig. 4C).

Pyroxenes show limited compositional variation in the Wo-En-Fs quadrilateral (Fig. 5). Clinopyroxenes have an average composition of $Wo_{45.6}En_{48.9}Fs_{5.52}$, and concentrated on the boundary between diopside and augite while orthopyroxenes range in composition from enstatite to bronzite ($En_{85.6}$ to $En_{90.2}$). In contrast to the Cr-rich spinels commonly found in mantle xenoliths, spinels from the xenoliths analyzed here are Cr-poor and Al-rich, with moderate $Mg\#$ (70.8 to 80.3). Their $Cr\#$ values (1.46 to 15.6) are close to the low $Cr\#$ end of non-cratonic peridotitic spinels and spinels found in the reaction zone between a lherzolite and its host basalt, suggesting late-stage modification (Zhang et al., 2007a) (Fig. 4D).

Garnet-free pyroxenites consist mainly of pyroxene with minor spinel. Clinopyroxenes are all diopside with slightly different compositions (Fig. 5). Those from the Cr websterites are Cr-rich ($Wo_{45.0-49.1}En_{42.6-49.8}Fs_{5.16-9.12}$, with Cr_2O_3 up to 1.1 wt.%), while those from the Al websterite are more Al-, Fe-, and Na-rich ($Wo_{48.0}En_{41.2}Fs_{10.8}$), and those from the clinopyroxenites are Ca-rich ($Wo_{50.7}En_{43.0}Fs_{6.3}$). Orthopyroxenes range from enstatite to bronzite, with those from the Cr websterites being more Mg-rich ($Fs = 9.48-20.1$) and those from the Al websterite being more Fe-rich ($Fs = 24.3$). In addition, clinopyroxenes from the clinopyroxene-rich Cr websterites fall within the peridotite compositional field, whereas those from the Al websterite, the orthopyroxenite,

and the orthopyroxene-rich Cr websterite falls along the metasomatic trend defined by Iran pyroxenites that formed via interaction between lithospheric mantle and slab melts (Fig. 3B) (Su et al., 2014). Spinels from the Cr websterites have higher Cr# (26.8 and 10.3) and Mg# (72 and 59.6) than those from the Al websterites (Cr# = 1.02, Mg# = 56.4).

4.3. Temperature and pressure estimates

Equilibrium partitioning of Mg-Fe among clinopyroxene, orthopyroxene and olivine, as indicated by the 1:1 linear correlations between the Mg# of these three minerals (Fig. 6A and B) (Keshav and Sen, 2004), and their general straight and smooth grain boundaries, permits temperature estimates for the Hannuoba xenoliths. Temperatures estimated from five different thermometers agree within 50°C (Table 3). This consistency in turn reflects equilibrium distribution of relevant elements among the co-existing minerals. The calculated temperatures and pressures for most garnet-bearing xenoliths fall within the ranges of 900 to 1040°C, and 1.5 to 2.0 GPa, respectively (Table 3), consistent with previous estimates (e.g. Chen et al., 2001; Xu, 2002; Liu et al., 2003, 2005, 2010; Fan et al., 2005) and overlap with the range for Hannuoba spinel peridotites (839 to 1072°C, Chen et al., 2001, Rudnick et al., 2004), while are higher than the Hannuoba garnet-bearing mafic granulites (768-835°C, Liu et al., 2010b). Garnet-free pyroxenites generally yield lower equilibrium temperatures (844-868°C), except the Cr-rich websterite that has an equilibrium temperature (1039°C) similar to the peridotites. These estimates also agree with the estimates reported by Xu (2002) and Chen et al. (2001).

4.4. Magnesium isotopic compositions

Magnesium isotopic compositions of the garnet-bearing xenoliths are reported in Table 4 for both whole rocks and mineral separates. Calculated inter-mineral fractionations are given in Table 5 along with mineral equilibration temperature derived from Wells (1977) geothermometer, as this thermometer is commonly used for pyroxenites (e.g., Ying et al., 2013, Su et al., 2014) and yields temperature estimates that are in good agreement with other calibrations. Mg isotopic compositions of the garnet-

free xenolith group and the two Hannuoba basalts, as well as the carbonatite-metasomatized garnet peridotite from Qinling are presented in Table 6, along with their inter-mineral fractionation and equilibrium temperatures, if applicable. All our samples (including reference materials) fall on a mass-dependent isotope fractionation line, with $\delta^{25}\text{Mg}$ being 0.516 times $\delta^{26}\text{Mg}$ ($R^2 = 0.99$); therefore, only $\delta^{26}\text{Mg}$ values are used in the following and discussion sessions.

4.4.1. Whole-rocks

The xenoliths and basalts analyzed in this study have shown a more scattered isotopic distribution than the normally homogeneous mantle peridotites and oceanic basalts, with most samples shifting to the lighter-than-mantle side (Fig. 7A). The two Hannuoba garnet-bearing lherzolites and the one from western Qinling have similar $\delta^{26}\text{Mg}$ values of -0.33‰ to -0.39‰, slightly lighter than the three literature data (-0.21 to -0.23‰, Teng et al., 2010; Pogge von Strandmann et al., 2011). The $\delta^{26}\text{Mg}$ values of 12 garnet websterites range from -0.43 to -0.10‰ and those of the three garnet clinopyroxenites vary from -0.48 to -0.18‰.

In contrast to the large variation displayed by the garnet-bearing xenoliths, both the Cr and Al websterite, and the orthopyroxenite have mantle-like $\delta^{26}\text{Mg}$ values (-0.17 to -0.32‰). The two garnet-free clinopyroxenites yield $\delta^{26}\text{Mg}$ values of -1.26‰ and -1.51‰, which are the lightest $\delta^{26}\text{Mg}$ values found in this study and reported in the literature for mantle rocks. The two Hannuoba basalts yield $\delta^{26}\text{Mg}$ of -0.35‰ and -0.50‰, falling into the range reported for the nearby Taihang basalts (-0.30 to -0.54‰, Yang et al., 2012).

4.4.2. Mineral separates (olivine, Cpx, Opx, and garnet)

The 69 mineral separates in the garnet-bearing xenoliths span a total $\delta^{26}\text{Mg}$ range of 0.80‰, from -0.75‰ in garnet to +0.05‰ in olivine. Among all the mineral phases, garnets show the widest variation, from -0.37 to -0.75‰, and are systematically lighter than co-existing olivine and pyroxene, which have $\delta^{26}\text{Mg}$ values concentrated in the mantle range (Fig. 7B). The $\delta^{26}\text{Mg}$ values of olivine vary from -0.40 to +0.05‰, while

those of clinopyroxene and orthopyroxene exhibit a similar range of -0.46 to +0.02‰ and -0.37 to 0‰, respectively, comparable to published data (e.g., [Handler et al., 2009](#); [Yang et al., 2009](#); [Young et al., 2009](#); [Huang et al., 2011](#); [Liu et al., 2011](#); [Xiao et al., 2013](#)). The average mineral $\delta^{26}\text{Mg}$ values based on all analyses is -0.22 ± 0.24 (n = 20, 2SD) for olivine, -0.21 ± 0.20 (n = 19, 2SD) for clinopyroxene, and -0.21 ± 0.21 (n = 15, 2SD) for orthopyroxene.

The four clinopyroxene and orthopyroxene pairs from the garnet-free websterites and the orthopyroxene from the orthopyroxenite have mantle-like $\delta^{26}\text{Mg}$ values, with $\delta^{26}\text{Mg}$ varying from -0.24 to -0.33‰ in clinopyroxene and -0.21 to -0.28‰ in orthopyroxene. Clinopyroxenes from the two clinopyroxenites are much lighter than the normal mantle clinopyroxene range (-1.34‰ and -1.47‰), whereas are consistent with their extremely light whole-rock $\delta^{26}\text{Mg}$ values.

5. Discussion

Our data show that the pyroxenite xenoliths have variable Mg isotopic compositions, which might be genetically linked to different episodes of melt activity in the Hannuoba lithospheric mantle. The broad zircon age spectrum and large elemental and isotopic variation in Sr-Nd-Pb-Li-Fe for peridotitic and pyroxenitic xenoliths revealed that the mantle beneath this region has been subjected to multi-stage modification by both crustal- and mantle-derived melts ([Song and Frey, 1989](#); [Tatsumoto et al., 1992](#); [Liu et al., 2004, 2005, 2010c](#); [Rudnick et al., 2004](#); [Tang et al., 2007](#); [Choi et al., 2008](#); [Zhang, 2009](#); [Zheng et al., 2009](#); [Zhao et al., 2010](#)). In this section, we first explore the genetic connection between the Mg isotopic composition of each pyroxenite group and their corresponding origin. Then, we evaluate whether inter-mineral Mg isotope partitioning within each xenolith group has reached equilibrium or not by comparison with theoretical calculations and empirical data. When disequilibrium inter-mineral fractionations are observed, their possible driving forces are examined. Finally, we discuss the implications of $\delta^{26}\text{Mg}$ variation in mantle pyroxenites on mantle Mg isotopic heterogeneity.

5.1 Garnet-bearing lherzolites and pyroxenites

5.1.1 Origin of garnet-bearing xenoliths

The occurrence of garnet pyroxenite veins infiltrating the host peridotites establishes their formation at mantle depths, which is consistent with the temperatures and pressure estimates of ~1000°C and 1.5-2.0 Ga based on their mineral compositions. The bulk rocks do not share a common composition with MORB (Fig. 2) and lack the positive Eu anomalies (Fig. 3A) that are typical for oceanic gabbros (e.g., Stracke et al., 2003). These characteristics rule out their origin as recycled oceanic lithosphere. Their major element compositions also plot off the extension trends between the Hannuoba peridotites and calculated equilibrium melts (Fig. 2A and B), and their $\delta^{26}\text{Mg}$ range is much wider than that of the normal mantle, arguing against their origin as in situ melting of the host peridotites suggested by Chen et al. (2001). Their major constituent minerals show a strong mantle-affinity while are significantly different from those in pyroxenite cumulates worldwide (Fig. 4A and B). The lack of convex-upward REE patterns that are typical for cumulative pyroxenites (Frey and Prinz, 1978) and the presence of deformation features are also inconsistent with a cumulate origin (Ionov et al., 2005).

Liu et al. (2005) alternatively proposed a replacive origin for these garnet-bearing pyroxenites. In their model, peridotites are converted to garnet pyroxenites by reaction with melts from ancient subducted oceanic slab, which results in formation of pyroxene and garnet at the expense of olivine (Yaxley and Green, 1998; Rapp et al., 1999). This metasomatic origin explains the decoupled major-trace elemental features which show that while the whole rocks are enriched in highly incompatible elements (e.g., Rb, Ba Sr and Pb) (Fig. 3B) with some showing relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ for their ϵ_{Nd} (Xu et al., 2002), their major mineral phases still preserve peridotite affinities (Fig. 4A and B). Later experimental studies (Wang et al., 2010; Zhang et al., 2012) have successfully reproduced similar garnet pyroxenites by reacting a Hannuoba spinel lherzolite with a quartz eclogite from central China. Subsequent finding of 315 Ma igneous zircons together with the record of coeval subduction-related magmatism (Zhang et al., 2009) provided further support to this explanation.

5.1.2 Whole-rock Mg isotopic variation

Building on previous discussions, the new Mg isotopic data obtained here further substantiate the replacive origin for these garnet-bearing xenoliths and the critical role of recycled oceanic crust in forming them. In view that the majority of olivine and pyroxene still preserve their mantle-like $\delta^{26}\text{Mg}$, the formation of secondary isotopically light garnet thus requires addition of light Mg into the bulk rocks from an external source. The isotopically light alkali basalts that host the xenoliths might be a possible candidate. However, lighter Mg isotopes diffuse faster than their heavy counterparts and they preferentially diffuse toward the hot end along a thermal gradient (Richter et al., 2009 and references therein). Therefore, diffusion of Mg from the xenoliths into their host magmas during magma ascent will result in depletion of light isotopes in these xenoliths, which is opposite to our observation here. In addition, given a typical ascent rate for xenolith-bearing alkali basalts of about 0.1 to 10 m/s (Spera, 1984), and an entrained depth of approximately 60 km for the xenoliths in this study, the magma should have reached the surface in hours or days. Likewise, basaltic flows commonly cool on the order of weeks (Flynn et al., 1994). The rapid eruption and cooling of alkali basalts thus precludes extensive interaction between the xenoliths and the host magma. Therefore, the garnets and their host xenoliths must have acquired their Mg isotopic characteristics before entrainment by the host magma.

The isotopically light Hannuoba alkali basalts may alternatively imply the presence of subducted slab in their mantle source, which is a common explanation for the isotopically light basalts found on eastern China (Fig. 7B) (e.g. Yang et al., 2012; Huang et al., 2015). This argument is mainly based on the finding of cratonic eclogites that are generally depleted in heavy Mg isotopes (Wang et al., 2012), which were taken as evidence for incorporation of sedimentary carbonates during low-temperature alteration of oceanic crust. The light Mg in carbonates can be incorporated into silicates by metamorphic de-carbonation or fluid-mediated isotopic exchange (Wang et al., 2014a). The major element compositions of these garnet-bearing xenoliths lie on the binary mixing trends between mantle peridotites and recycled oceanic crustal pyroxenites (Fig. 2). Their Mg isotopic compositions can also be explained by the triangle defined by mixing between oceanic crust, as represented by the cratonic eclogites (Wang et al., 2012)

and NCC peridotites (Teng et al., 2010) (Fig. 8). The presence of altered subducted slab and sediments in the mantle beneath the Hannuoba region may also contribute to the low $\delta^7\text{Li}$ signature that characterize Hannuoba peridotites (Tang et al., 2007), and the formation of Al-rich sapphirine in Hannuoba mantle clinopyroxenites (Su et al., 2012a).

5.1.3 Inter-mineral Mg isotope fractionation

Mantle minerals are generally found to be in isotopic equilibrium since high temperature promotes isotope diffusion (Urey, 1947). To reach equilibrium, heavy isotopes are preferentially concentrated in minerals with stronger chemical bonds due to their higher vibrational frequency and therefore greater energy reduction upon isotope exchange (Bigeleisen, 1965). Since Mg only occurs with one oxidation state (+2) in common minerals, the key factor determining Mg-O bond strength is the coordination number of Mg in different minerals. Within a mineral class (e.g., silicates, carbonates, oxides), mineral with higher coordination sites for Mg^{2+} allows a larger Mg^{2+} effective ionic radii, therefore longer and weaker Mg-O bonds, which favors lighter Mg isotopes (see Young et al., 2015 for a thorough discussion).

Each Mg^{2+} is bonded to six neighboring oxygen anions in the predominant upper mantle minerals (olivine, clinopyroxene, and orthopyroxene) with a similar bond strength. Therefore, only limited fractionation occur between them, which is thought to result from the subordinate, but stronger, $\text{Mg}^{\text{III}}\text{O}$ bonds in pyroxene than the $\text{Mg}^{\text{IV}}\text{O}$ bonds in olivine (Young et al. 2009, 2015; Liu et al., 2010a, 2011). The Mg isotope fractionation between most co-existing pyroxene and olivine in this study is barely analytically resolvable, with $\Delta^{26}\text{Mg}_{\text{Cpx-Ol}} = \delta^{26}\text{Mg}_{\text{Cpx}} - \delta^{26}\text{Mg}_{\text{Ol}} = -0.06$ to $+0.08\text{‰}$ ($n = 17$), $\Delta^{26}\text{Mg}_{\text{Opx-Ol}} = \delta^{26}\text{Mg}_{\text{Opx}} - \delta^{26}\text{Mg}_{\text{Ol}} = -0.02$ to $+0.09\text{‰}$ ($n = 14$), and $\Delta^{26}\text{Mg}_{\text{Cpx-Opx}} = \delta^{26}\text{Mg}_{\text{Cpx}} - \delta^{26}\text{Mg}_{\text{Opx}} = -0.08$ to $+0.05\text{‰}$ ($n = 14$). The magnitude of this fractionation agrees with published Mg isotope data on equilibrated peridotitic pyroxene and olivine (Handler et al., 2009; Yang et al., 2009; Chakrabarti and Jacobsen, 2010; Huang et al., 2011; Liu et al., 2011; Pogge von Strandmann et al., 2011; Xiao et al., 2013), and falls within the ranges of DFPT calculation (Schauble, 2011; Huang et al., 2013), as well as the ranges defined by empirical measurements (Liu et al., 2011a) (Fig. 10A and B). Therefore, these

observations suggest a broad equilibrium Mg isotope fractionation between pyroxene and olivine in these samples.

Compared to the 6-fold coordinated Mg in olivine and pyroxene, Mg is 8-fold coordinated in garnet and 4-fold coordinated in spinel, respectively. Therefore, garnets are enriched in light Mg isotopes while spinels have a greater affinity for heavy Mg isotopes. In addition, cation substitution has been suggested to exert a secondary control on the Mg isotopic composition of spinel (Liu et al., 2011; Shauble, 2011; Xiao et al., 2013), as it has both tetrahedral and octahedral sites available for Mg, with $[YO_6]$ octahedrons sharing edge with each other. By contrast, Mg isotopic composition of garnet should be much less sensitive to cation substitution since its $[YO_6]$ octahedrons are well separated from each other by $[SiO_4]^{4-}$ (Huang et al., 2013).

The isotopically lighter garnets found in the present study are thus consistent with expectations from DFPT calculations (Huang et al., 2013) and measurements on equilibrated eclogitic garnet and pyroxene (Li et al., 2011; Wang et al., 2012, 2014b). Nonetheless, these garnets appear to be out of Mg isotopic equilibrium with co-existing olivines and pyroxenes, as most of the observed fractionation factors are smaller than the expected values at equilibrium (Fig. 10C). Based on the calculated clinopyroxene-orthopyroxene mineral equilibrium temperature of $\sim 1000^\circ\text{C}$, the empirical equilibrium fractionation line would predict a clinopyroxene-garnet fractionation of $\sim 0.52\%$ (Li et al., 2011; Wang et al., 2012), while seven out of the 14 clinopyroxene-garnet pairs only have fractionation between 0.36 and 0.42%. If these values are taken as equilibrium fractionations, then they would require the equilibrium temperatures to be higher than 1380°C (Fig. 10D and E). Such high temperatures seem implausible for the Hannuoba area, as both peridotites and pyroxenites have equilibrium temperatures around 1000°C . Additionally, over a limited temperature range, the fractionation between garnet and olivine/pyroxene is highly variable, opposed to relatively constant fractionation as would be expected for isotopic equilibrium (Fig. 10C). Therefore, we interpret that these garnets have not yet reached isotopic equilibrium with the co-existing olivine and pyroxene.

5.1.4. Mechanism of disequilibrium garnet-olivine/pyroxene fractionation

The deviation of garnet-olivine/pyroxene fractionation from the equilibrium values implies superimposition of kinetic processes on temperature-dependent Mg isotope partitioning among these minerals. Since garnet accounts for a smaller modal abundance than the predominant olivine and pyroxene, both of which have mantle-like $\delta^{26}\text{Mg}$ and high Mg concentration, the kinetic effects should be more obviously seen in garnets. Considering that $\delta^{26}\text{Mg}$ in olivine and pyroxene are relatively invariant around the normal mantle value, the reduced $\Delta^{26}\text{Mg}_{\text{Grt-Ol/Cpx/OpX}}$ values are therefore mainly caused by variably higher-than-equilibrium $\delta^{26}\text{Mg}$ in garnets. Although there is no published $\delta^{26}\text{Mg}$ value on peridotitic garnet for comparison, The Mg isotopic composition of garnets in the Hannuoba lherzolites and pyroxenites are much heavier than garnets from cratonic eclogites formed at similar temperatures (-0.61 to -0.72‰ in Wang et al., 2012). For example, garnet as heavy as -0.37‰ ($\delta^{26}\text{Mg}$) has been found in this study.

Based on discussion in previous sections, the most relevant process accounting for the disequilibrium inter-mineral fractionation is incomplete melt-rock interaction that produced these garnets. The highly variable grain size (even within one hand specimen) and modal abundance of garnet, together with their anhedral shape, are significantly different from the relatively euhedral garnets commonly found in garnet peridotites and eclogites. Petrographic observations of garnet replacing spinel (Fig. 1C-G) also suggest a clear metasomatic origin for the garnets, instead of being the primary refractory phase present in peridotites. Therefore, the later-formed garnets could partly inherit the heavy Mg isotope composition from its embedded isotopically heavy spinels, olivine, or pyroxene grains, and therefore shifted their $\delta^{26}\text{Mg}$ signals in the heavier direction. For example, using the $\Delta^{26}\text{Mg}_{\text{Spl-Ol}}$ vs. temperature calibration of Liu et al. (2011), spinel equilibrated with the co-existing olivine in these garnet pyroxenites should be as heavy as +0.11‰. The broad negative correlation between MgO content in spinel and $\delta^{26}\text{Mg}$ of garnet supports this explanation (Fig. 10F). With progressively Mg lose from spinel to the surrounding garnet, garnet exhibits an increasingly heavier $\delta^{26}\text{Mg}$. Deviation from this trend may suggest additional Mg input to garnet from olivine or pyroxene (Fig. 1H-J). Similar incomplete isotopic exchange processes during rock-melt interaction have also been invoked for the inter-mineral Mg-Fe-Li isotope disequilibrium found in peridotites

from this craton (Tang et al., 2007, 2011; Yang et al., 2009; Zhang et al., 2010; Zhao et al., 2010; Xiao et al., 2013).

Among the generally equilibrated olivine-pyroxene mineral pairs, samples D 01, D 09 and D 7S seem to have an anomalous, larger fractionation, suggesting additional influence of small-scale diffusional processes associated with the different Mg diffusivity in these minerals. Sample D 7S has the lightest olivine (-0.40‰), clinopyroxene (-0.46‰), and orthopyroxene (-0.37‰), reflecting isotopic exchange with the inferred isotopically light metasomatic melt, and the consequent reduced fractionation of garnet relative to these minerals (e.g., $\Delta^{26}\text{Mg}_{\text{Cpx-Grt}} = 0.11\text{‰}$). On the other hand, sample D 01 and D 09 documents the largest garnet-olivine/pyroxene fractionations in this study (e.g., $\Delta^{26}\text{Mg}_{\text{Ol-Grt}} = -0.80\text{‰}$), and their clinopyroxene-garnet fractionations are consistent with equilibrium fractionation values. Therefore, the anomalously heavy $\delta^{26}\text{Mg}$ in olivines ($\delta^{26}\text{Mg} = +0.05$ and 0.00‰) may result from diffusional loss of light Mg isotopes to garnet during re-equilibration with isotopically light garnet ($\delta^{26}\text{Mg} = -0.75\text{‰}$ and -0.76‰). This explanation is consistent with the faster diffusion of Mg in olivine than in pyroxene (Chakraborty, 2010; Cherniak and Dimanov, 2010).

The Mg isotopic disequilibrium in the garnet-bearing pyroxenites suggests that the melt-rock interaction that gave rise to these xenoliths probably occurred shortly before their entrainment into the host basalts, especially considering the rapid diffusion rate at mantle temperatures. For example, the self-diffusion coefficient of Mg in garnet ($\sim 1.6 \times 10^{-15} \text{ cm}^2/\text{s}$ at 1000°C , Ganguly, 2010) predicts that Mg isotopic disequilibrium may persist for ~ 1.25 Ma over 2.5 mm in width. Further constraints on the timing of metasomatism may be provided by the olivine Mg-Fe zoning present in some samples. Taking the self-diffusion coefficient of Mg in olivine ($\sim 3.2 \times 10^{-15} \text{ cm}^2/\text{s}$ at 1000°C , Chakraborty, 2010), the widest observed elemental zoning ($\sim 500 \text{ }\mu\text{m}$) would be obliterated after 25 kyr. Therefore, these samples have probably been entrained by host magma and transported to the surface not long after the garnets started to form, and thus there was not sufficient time for the metasomatic garnets to reach isotopic equilibrium with the primary olivine and pyroxenes.

5.2 Garnet-free websterites and orthopyroxenite

Both Cr and Al pyroxenites are commonly found in alkali basalts along with peridotites at Hannuoba and worldwide, either as composite xenoliths along with wall rock peridotites or as discrete xenoliths. They are generally interpreted as crystallization products of high-pressure basaltic melts as they pass through the lithospheric mantle (Frey and Prinz, 1978; Irving, 1980; Xu, 2002). The Cr websterites and Al websterites, as well as the orthopyroxenite analyzed here have mantle-like $\delta^{26}\text{Mg}$ for both whole rocks (-0.18 to -0.32‰) and minerals (-0.21 to -0.33‰). In comparison, Hannuoba alkali basalts have lighter $\delta^{26}\text{Mg}$ values, and are markedly different in Sr-Nd-Pb isotopic composition from the pyroxenites (Xu et al., 2002; Choi et al., 2008). Therefore, these xenoliths are not co-genetic with their host basalts.

Lithium isotopic characteristics of the Hannuoba peridotites suggested modification of the lithospheric mantle by asthenospheric melts (Tang et al., 2007), which should have $\delta^{26}\text{Mg}$ values identical to mantle peridotites, as sampled by global oceanic basalts (Teng et al., 2010). Therefore, the Cr and Al websterites and the orthopyroxenite analyzed here may represent different episodes of silicate melt injection from the asthenosphere. Xu (2002) further suggested the involvement of recycled continental crust in their parental magmas based on Sr-Nd isotopic evidence. However, limited contributions from continental crust are difficult to manifest themselves in Mg isotopic compositions since crustal materials from continents have much lower Mg concentration than the mantle and major Mg-bearing minerals in crustal rocks, including biotite, hornblende and pyroxene, have a broadly mantle-like $\delta^{26}\text{Mg}$ (Liu et al., 2010a).

5.3 Garnet-free clinopyroxenites

The two garnet-free clinopyroxenites analyzed here yield consistent light $\delta^{26}\text{Mg}$ values for both whole rocks and clinopyroxene fragments, which are also the lightest values reported for mantle rocks so far. These extremely light Mg isotopic compositions imply that their origin may be closely related to migration of carbonatitic melts in the mantle, which are considered to be a major source of light Mg isotopes (Young and Galy, 2004). The two clinopyroxenites show the strongest enrichment in LREE among all the pyroxenites studied here (Fig. 3C), with La/Yb_(N) of 16.4 and 17.1. Their elevated Zr/Hf ratios (40.0 and 43.6) than the primitive mantle (36.2) (Fig. 3D) also suggest influence

from carbonatites, which typically have high Zr/Hf ratios (e.g., Rudnick et al., 1993). More importantly, their low Ti/Eu ratios (Fig. 9) are consistent with their origin from carbonatites (Rudnick et al., 1993; Coltorti et al., 1999). Clinopyroxenes with similar composition have also been found in a few Hannuoba peridotite xenoliths (Yu et al., 2006).

The presence of 48-64 Ma igneous zircons with pronounced enrichments in REE, U, and Th in garnet pyroxenites (Liu et al., 2010c) and the discovery of carbonatite veins cutting through host peridotites in the Hannuoba locality (Fan et al., 2010; Liu et al., 2010c) also support carbonatitic melt activity. Using the average Ti/Eu ratio of carbonatite reported in Fan et al. (2010), the Mg isotopic composition of these clinopyroxenites can be explained by binary mixing between mantle peridotites and recycled carbonates with $\delta^{26}\text{Mg}$ values of -3.00 to -5.00‰ (Fig 11), which is the typical $\delta^{26}\text{Mg}$ range of carbonate minerals (Young and Galy, 2004; Saenger and Wang, 2014). In addition, the estimated compositions of hypothetical melts in equilibrium with the two garnet-free clinopyroxenite xenoliths are similar to those of carbonatites from the North China Craton (Ying et al., 2004). Therefore, we interpret these clinopyroxenites to be formed by de-carbonation of migrating carbonatite melts, during which the isotopically light Mg together with Ca from the carbonates will be incorporated into Cpx with the release of CO_2 (Yaxley et al., 1991, 1998; Rudnick et al., 1993; Knoche et al., 1999).

The carbonatitic melts gave rise to these light clinopyroxenites are more likely sourced from recycled carbonate instead of asthenosphere, as experimental study of Macris et al. (2013) has shown no analytically resolvable fractionation between magnesite and olivine at $> 800^\circ\text{C}$, while the fractionation increases significantly at lower temperature (e.g., 0.44‰ at 600°C). This is consistent with the extremely light $\delta^{26}\text{Mg}$ values found in sedimentary carbonates (e.g., -5.54‰, Wombacher et al., 2011). Considering the geographical contiguity of the Hannuoba basaltic plateau to the Taihang mountains and the similarity between the $\delta^{26}\text{Mg}$ feature of the Hannuoba basalts to that of the Taihang basalts, it is reasonable to infer that the Hannuoba lithospheric mantle has likely been affected by the same carbonatitic metasomatic event. Moreover, the isotopically light ($\delta^{26}\text{Mg} = -0.39\text{‰}$) garnet lherzolite from western Qinling, which has

subjected to strong carbonatite metasomatism, further confirms that the $\delta^{26}\text{Mg}$ value of mantle xenoliths can be lowered by reaction with carbonatite melts.

5.4. Implications on mantle $\delta^{26}\text{Mg}$ heterogeneity

Previous Mg isotopic measurements on global peridotite xenoliths and oceanic basalts have suggested a homogeneous mantle with respect to Mg isotope distribution (Teng et al., 2010). However, there is now accumulating evidence for the existence of local mantle domains with variable $\delta^{26}\text{Mg}$ values that are thought to be the result of interaction of normal $\delta^{26}\text{Mg}$ mantle with migrating mantle melts/fluids (e.g., Yang et al., 2012; Xiao et al., 2013; Huang et al., 2015). For example, the formation of different types of Hannuoba mantle pyroxenites have been related to injection of melts with diverse compositions into the subcontinental lithospheric mantle (SCLM), which register these pyroxenites with different $\delta^{26}\text{Mg}$ characteristics. Likewise, basalts erupted on continents have frequently been found to be isotopically light (Yang et al., 2012; Huang et al., 2015; and this study), in contrast to the homogeneous oceanic basalts (Teng et al., 2010). Since partial melting and subsequent magma differentiation do not fractionate Mg isotopes (Teng et al., 2007; 2010), the distinct $\delta^{26}\text{Mg}$ signals carried by these continental basalts should largely reflect their source heterogeneity. Soughing out the cause of these mantle anomalies is thus critical for us to better understand the overall Mg isotopic composition of the bulk silicate Earth.

The main feature distinguishes basalts generated at continental settings from those at oceanic setting is the existence of a thick layer of SCLM on top of the asthenosphere, which continuously digesting deep fluids/melts rising upward, replenishing the SCLM with elements that were depleted due to earlier melting events. As a result, the SCLM becomes a compositionally and lithologically heterogeneous reservoir (e.g., Brooks et al., 1976; Foley, 2008), contributing to continental magmatism by itself or together with contributions from asthenospheric melts (e.g. McDonough et al., 1990 and reference therein).

Recycled oceanic crusts have been considered as a primary contributor in the origin of mantle anomalies as they can presumably carry the surface fractionation signals imparted by seafloor alteration into the deep mantle (Yang et al., 2012). The recycled

carbonated oceanic crust (-0.80 to -0.14‰, Wang et al., 2012) and the overlying sediments (-5.31 to -1.09‰, Young and Galy, 2004; Tipper et al., 2006a and b; Brenot et al., 2008; Pogge von Strandmann, 2008; Hippler et al., 2009; Higgins and Schrag, 2010) will thus become an anomalous Mg isotopic reservoir in the mantle. When partial melting occurs, their heterogeneous Mg isotopic features may propagate into the ambient mantle via a variety of metasomatic melts (e.g., carbonatite, carbonated silicate, and silicate melts), which percolate and infiltrate the mantle wall-rock. The reaction products, as represented by the diverse pyroxenites studied here, do exhibit a larger variation in $\delta^{26}\text{Mg}$ than peridotites, with $\delta^{26}\text{Mg}$ values as low as -1.51‰ having been found. Due to their relatively lower solidus temperatures, pyroxenites will melt preferentially with a higher melt-producing efficiency relative to the ambient peridotites. Therefore, when contributed to continental magmatism, these heterogeneous pyroxenites will further modify the Mg isotopic composition of mantle-derived volcanic rocks.

Subducted slabs have also been suggested in the source region of oceanic island basalts (OIB). The absence of isotopically distinct OIB (Teng et al., 2010) may partially due to the relatively cold and conductive nature of the SCLM, which keeps the isotopically distinct domains last longer than those in the warmer sub-oceanic mantle, where large-scale convection and continuous melting at the mid-ocean ridge tend to eliminate all heterogeneities. In contrast, the long-term stability of the SCLM makes it an increasingly heterogeneous reservoir through time. During eruption gaps of continental magmatism, the SCLM can receive frequent melt modifications and consequently give rise to new anomalous $\delta^{26}\text{Mg}$ domains. In addition, oceanic-continental subduction is a more frequent phenomenon than oceanic-oceanic subduction. Therefore, there might be more relic slabs sitting beneath the continents. Frequent subduction from circum plates around continents also makes the SCLM a relatively closed system, preventing the isotopically heterogeneous domains from incorporating into the global mantle convection.

6. Conclusions

This study presents the first systematic dataset for high-precision Mg isotopic analyses on mantle pyroxenites, coupled with their whole rock and mineral chemical compositions. It highlights the potential of using Mg isotopes along with the traditional

Sr-Nd-Pb isotopic systematics to trace melt activities in the mantle and the origin of different types of mantle pyroxenites. The following conclusions can be drawn:

- (1) The garnet-bearing lherzolites and pyroxenites, which represent reaction products between peridotites and slab-derived melts, have variable $\delta^{26}\text{Mg}$ ranging from -0.48 to -0.10‰ (n=17). There is a broad isotopic equilibrium among co-existing olivine, clinopyroxene, and orthopyroxene. However, garnet that is formed in a reacting relationship with spinel, olivine, and pyroxene has not yet reached $\delta^{26}\text{Mg}$ equilibrium with these minerals. Contributions of heavy Mg isotopes from the enclosed spinel drove the $\delta^{26}\text{Mg}$ of garnet to variably heavier values of 0.76 to -0.37‰ (n = 15).
- (2) Both garnet-free websterites and orthopyroxenite have $\delta^{26}\text{Mg}$ values (-0.17 to -0.32‰) comparable to that of the mantle range ($-0.25 \pm 0.07\text{‰}$, Teng et al., 2010). They may thus represent different episodes of asthenospheric melts injection into the subcontinental lithospheric mantle.
- (3) The extremely light $\delta^{26}\text{Mg}$ values exhibited by the two garnet-free clinopyroxenites imply an episode of carbonatitic melt activity. The carbonatitic melts are likely to have been involved in the mantle source of Hannuoba alkali basalt, which also exhibits a light Mg isotopic composition.

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Figure captions

Fig. 1. Petrological and petrographic characteristics of garnet-bearing xenoliths. (A): A hand specimen of garnet websterite with garnet-rich veins. (B): A scanned thin section image of a garnet websterite showing the typical mineral assemblage of Ol-Cpx-Opx-Grt-Spl. (C): A photomicrograph of a typical spinel-cored garnet. (D) – (G): Photomicrographs showing gradual replacement of spinel by garnet. (H) – (J): A photomicrograph showing garnet engulfs and consumes pyroxene and olivine grains. (K) A photomicrograph showing the triple junction and kink bands in Opx. (L) A photomicrograph showing the fluid/melt inclusions in pyroxene. (M) A Back-scattered electron (BSE) image showing texturally equilibrated but compositionally zoned olivine grains. (N) A BSE image showing the rare metasomatic Ap and Phl in a glass vein. (O) and (P) BSE images showing a glass vein in the xenolith, with chemically zoned olivine. (P) is a close-up of (O) to show the intergrowth texture of kelyphitic garnet. All the garnets in our sample collection have been decomposed to kelyphites. Ol = olivine; Cpx = clinopyroxene; Opx = orthopyroxene; Grt = garnet; Spl = spinel; Ap = apatite; Phl = phlogopite; Gls = glass; Pl = plagioclase.

Fig. 2. Major (A-C) and trace (D) element variations of Hannuoba mantle xenoliths studied here in relation to their MgO (wt.%). Data for Hannuoba peridotites (Song and Frey, 1989; Chen et al., 2001; Rudnick et al., 2004; Fan et al., 2005; Choi et al., 2008) and Beiyuan wehrlites (Xiao and Zhang, 2011; Xiao et al., 2013) are plotted for comparison. The star denotes the composition of primitive mantle from McDonough and Sun (1995). The dash grey lines represent the compositional fields of typical cratonic peridotites defined by Tanzanian xenoliths (Lee and Rudnick, 1999). The orange solid lines represent extension between the residual Hannuoba peridotites and calculated equilibrium melts taken from Xu (2002). The data for Jiaohe oceanic crustal pyroxenites field are from Yu et al. (2010). The data for Hannuoba basalts are from Zhi et al. (1990), Basu et al. (1991), Fan et al. (1991), Liu et al. (1994), Qian et al. (2015) and this study (open square). The fields of MORB in (A) and (B) are from Downes (2007) with data from Melson et al. (1976), Schilling et al. (1983), Korenaga and Kelemen (2000), in (C)

is from Bodinier and Godard (2014) with data from the PetDB database, and in (D) is from Yu et al. (2010) with data from Jacob (2004). Major element data are from Table S2. Mineral compositional data for Ol, Cpx, Opx, Grt in (C) are from Table S4-8. Lherz = Lherzolite, Webst = Websterite, Cpxnt = Clinopyroxenite, Opxnt = Orthopyroxenite.

Fig. 3. Trace element features for Hannuoba mantle xenoliths. (A) and (C) are chondrite-normalized REE patterns for garnet-bearing and garnet-free xenoliths, respectively; (B) and (D) are primitive mantle-normalized trace element patterns for garnet-bearing and garnet-free xenoliths, respectively. Chondrite values are from Anders and Grevesse (1989); Primitive mantle and N-MORB values are from McDonough and Sun (1995). Light blue fields represent data of Hannuoba spinel lherzolites from Rudnick et al. (2004) and Song and Frey (1990). Trace element data are from Table S3.

Fig. 4. Mineral chemical composition plots for Hannuoba mantle xenoliths. (A) Mg# vs. NiO wt.% in olivine. (B) Mg# vs. Al₂O₃ wt.% in clinopyroxene. (C) Mg# vs. Cr# in spinel. In (A) and (B), fields of cratonic and non-cratonic mantle peridotites, and pyroxenite cumulates worldwide are from Walter (2003). Data for mantle peridotitic xenoliths from the Tanlu Fault Zone regions are from Fan et al. (2000), Gao and Zhang (1994), Rudnick et al. (2004), Wang et al. (1987), Xu et al. (1998), Yan et al. (2003), Zhang et al. (2007b), and Zheng et al. (1998). Metasomatism trend in (B) is from Su et al. (2014). Data for spinels from the peridotite-basalt reaction zone are from Zhang (2007a). (A) - (C) are modified from Zhang et al (2007a). (D) Garnet composition in terms of CaO wt.% vs. Cr₂O₃ wt.%, modified after Sobolev et al. (1973). Mineral chemical data are from Tables S4-8.

Fig. 5. Wo-En-Fs classification quadrilateral of pyroxenes from Hannuoba mantle xenoliths.

Fig. 6. Mg# correlations between co-existing Cpx-Ol (A) and Opx-Ol (B). Mg# = 100 × molar Mg/(Mg + Fe). The best-fit lines are obtained by setting the intercepts to zero. Data are from Table S6-8.

Fig. 7. Compilation of $\delta^{26}\text{Mg}$ (‰) for mantle-related rocks (A) and mineral separates (B). Mantle range is defined as $\delta^{26}\text{Mg} = -0.25 \pm 0.07\text{‰}$ (Teng et al., 2010). Global seawater range is defined as $\delta^{26}\text{Mg} = -0.83 \pm 0.09\text{‰}$ (Ling et al., 2011). Data for Hannuoba mantle xenoliths are from Table 4 and 6. Literature data are shown as grey open symbols while colorful symbols are data from this study. Data sources: Spl: Young et al. (2009), Liu et al. (2011), Xiao et al. (2013); Ol, Cpx and Opx: Young et al. (2009), Handler et al. (2009), Yang et al. (2009), Liu et al. (2011), Huang et al. (2011), Xiao et al. (2013); Cratonic eclogite, eclogitic Cpx and Grt: Wang et al. (2012); Pyroxenite: Liu et al. (2011); Oceanic basalts: Bourdon et al. (2010), Teng et al. (2010); Continental basalts: Yang et al. (2012), Huang et al. (2015); Peridotites: Young et al. (2009), Yang et al. (2009), Bourdon et al. (2010), Teng et al. (2010), Huang et al. (2011), Liu et al. (2011), Pogge von Strandmann et al. (2011), Xiao et al. (2013); Wehrlites: Yang et al. (2009), Teng et al. (2010), Pogge von Strandmann et al. (2011), Xiao et al. (2013).

Fig. 8. $\delta^{26}\text{Mg}$ (‰) of the Hannuoba garnet-bearing xenoliths in relation to their MgO (wt.%). The two grey lines represent mixing lines between peridotites from the North China Craton (Teng et al. 2010) and cratonic eclogites from South African (Wang et al., 2012). End-member compositions: The lightest eclogites has a $\delta^{26}\text{Mg}$ value of -0.798‰ and MgO content of 7.37 wt.%, while the heaviest eclogite has a $\delta^{26}\text{Mg}$ value of -0.139‰ and MgO content of 17.05 wt.%. The $\delta^{26}\text{Mg}$ values for NCC peridotites range from -0.27‰ to -0.21‰ .

Fig. 9. Ti/Eu vs. $(\text{La/Yb})_{\text{N}}$ plot for distinguishing between carbonatite metasomatism and silicate metasomatism (Coltorti et al., 1999).

Fig. 10. (A) and (B): Correlations of inter-mineral fractionation between Cpx-Ol and Opx-Ol with $10^6/T^2$ (T in K). $\Delta^{26}\text{Mg}_{\text{X-Y}} = \delta^{26}\text{Mg}_{\text{X}} - \delta^{26}\text{Mg}_{\text{Y}}$, where X and Y represent different mineral phases. The theoretically calculated lines of Schauble (2011) [black solid lines], and Cpx-Ol equilibrium fractionation line established by natural samples (Liu et al., 2011) [dashed line] are plotted for comparison. Data are from Table 4. (C)

Variation of $10^3 \ln \alpha_{\text{Cpx-Grt}}$ with $10^6/T^2$ (T in K) based on density functional theory calculation in [Huang et al. \(2013\)](#). Theoretical equilibrium fractionation lines between co-existing garnet and clinopyroxene at 0 GPa (green solid line) and 2 GPa (blue solid line), and that established by empirical measurements on equilibrated eclogitic Grt-Cpx pairs (orange dash line) are shown for reference. (D) and (E) Correlation of $\delta^{26}\text{Mg}_{\text{Grt}}$ vs. $\delta^{26}\text{Mg}_{\text{Cpx}}$ and $\delta^{26}\text{Mg}_{\text{Ol}}$ vs. $\delta^{26}\text{Mg}_{\text{Grt}}$ at different equilibrium temperatures. (F) Negative correlation between $\delta^{26}\text{Mg}$ of Grt and MgO content of Spl. The calculated equilibrium Mg isotope fractionation lines are from [Huang et al. \(2013\)](#) by assuming the equilibrium pressure of 1.5 GPa throughout. Data for cratonic eclogites ([Wang et al., 2012](#)) and orogenic eclogites ([Li et al., 2011](#); [Wang et al., 2014b](#)) are shown for comparison, with estimated peak metamorphic pressure of 5 GPa and 3 GPa, respectively. Data are from [Tables 4 and 5](#).

Fig. 11. (A) $\delta^{26}\text{Mg}$ (‰) versus Ti/Eu ratio for the two Hannuoba garnet-free clinopyroxenites can be modeled by binary mixing between peridotites from the North China Craton ([Teng et al. 2010](#)) and carbonatites that have $\delta^{26}\text{Mg}$ of -3.00 to -5.00‰. Ti/Eu ratios of the carbonatites are based on the average composition of Hannuoba carbonatites reported by [Fan et al. \(2010\)](#). Error bars for $\delta^{26}\text{Mg}$ are smaller than the sample symbols. (B) Calculated equilibrated melts with these clinopyroxenites by using the Cpx-carbonatite partition coefficients provided in [Adam and Green \(2001\)](#). Compositions of carbonatites from the North China Craton ([Ying et al., 2004](#)) and Hannuoba basalts ([Qian et al., 2015](#)) are shown for comparison.

Table 1

Magnesium isotopic compositions (‰) of standards analyzed during the course of this study, and comparison with literature data

Standard	Description	n	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	Standard	Description	n	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD							
Hawaii Seawater (in-house)	HI		-0.92	0.07	-0.48	0.05	KH Olivine (in-house)	Kilbourne Hole, NM		-0.29	0.07	-0.18	0.06							
			-0.84	0.07	-0.45	0.05				-0.30	0.08	-0.15	0.07							
			-0.89	0.07	-0.48	0.06				-0.29	0.07	-0.13	0.05							
			-0.79	0.06	-0.40	0.06				-0.22	0.07	-0.13	0.04							
			-0.82	0.06	-0.41	0.05			Average	This study	16	-0.27	0.05	-0.14	0.05					
			-0.83	0.06	-0.43	0.05	Teng et al. (2010)	16								-0.27	0.07	-0.14	0.04	
			-0.83	0.06	-0.40	0.04	Teng et al. (2007)	24								-0.31	0.09	-0.14	0.08	
			-0.85	0.07	-0.44	0.07	DTS-1 (USGS)	Dunite, Twin Sisters mountain, WA									-0.31	0.08	-0.14	0.07
			-0.83	0.08	-0.42	0.07				-0.30	0.06	-0.15	0.06							
			-0.87	0.07	-0.44	0.07	Average	This study	2	-0.30	0.05	-0.14	0.04							
			-0.82	0.07	-0.44	0.05								Recommended	-0.302	0.027	-0.132	0.031		
			-0.84	0.07	-0.44	0.05	PCC-1 (USGS)	Peridotite, Cazadero, CA		-0.20	0.07	-0.10	0.05							
			-0.84	0.06	-0.43	0.06			Recommended	-0.229	0.041	-0.101	0.028							
		Average	This study	13	-0.84	0.07	-0.43	0.05	BHVO (USGS)	Basalt, Hawaiian Volcanic Observatory		-0.22	0.06	-0.14	0.05					
	-0.20										0.07	-0.08	0.03							
Average	This study								2	-0.21	0.05	-0.10	0.38							
														Recommended	-0.207	0.039	-0.123	0.027		
														W-1 (USGS)	Diabase, Centreville, VA		-0.15	0.06	-0.08	0.05
																Recommended	-0.164	0.030	-0.079	0.024
KH Olivine (in-house)	Kilbourne Hole, NM		-0.25	0.08	-0.13	0.06	MAG-1 (USGS)	Marine mud, Gulf of Maine		-0.24	0.06	-0.07	0.06							
			-0.26	0.06	-0.13	0.04			Recommended	-0.252	0.045	-0.113	0.036							
			-0.26	0.05	-0.17	0.05	Murchison chondrite	Carbonaceous (CM2), VIC, Australia		-0.29	0.06	-0.14	0.06							
			-0.25	0.06	-0.11	0.05				-0.28	0.07	-0.15	0.05							
		Average	This study	2	-0.29	0.04	-0.15	0.04												
									Pogge von Strandmann et al. (2011)	1	-0.23	0.02	-0.13	0.01						
									Teng et al. (2010)	4	-0.31	0.07	-0.17	0.03						
									Teng et al. (2007)	4	-0.41	0.05	-0.21	0.05						
			Yang et al. (2009)	4	-0.31	0.06	-0.17	0.06												
			Wiechert & Halliday (2007)	13	-0.26	0.25	-0.14	0.14												
			Wombacher et al. (2009)	17	-0.26	0.09	-0.13	0.07												
			Bourdon et al. (2010)	2	-0.19	0.08	-0.11	0.02												
					-0.25	0.08	-0.09	0.07												
					-0.25	0.05	-0.10	0.04												
			-0.25	0.05	-0.13	0.04														
			-0.29	0.07	-0.12	0.06														
			-0.29	0.06	-0.14	0.05														

n indicates number of analyses. Recommended values are from [Teng et al. \(2015\)](#).

Table 2

Reproducibility check of Mg isotopic measurements (‰) relative to standard DSM3

Sample	Ol				Sample	Cpx			
	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD		$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD
D 01	0.06	0.06	0.04	0.04	D 06	0.02	0.05	-0.01	0.04
D 01 rc	0.04	0.07	0.02	0.07	D 06 rc	0.00	0.07	0.00	0.06
Average	0.05	0.05	0.03	0.03	Average	0.02	0.04	-0.01	0.03
D 06	-0.03	0.08	-0.02	0.06	D 07	-0.12	0.05	-0.07	0.04
D 06 rd	0.01	0.06	0.01	0.04	D 07 rc	-0.09	0.07	-0.06	0.06
Average	0.00	0.05	0.00	0.03	Average	-0.11	0.04	-0.06	0.03
D 09	-0.01	0.07	0.00	0.05	D 09	-0.11	0.05	-0.06	0.04
D 09 rd	0.01	0.06	0.04	0.04	D 09 rd	-0.12	0.07	-0.08	0.06
Average	0.00	0.05	0.03	0.03	Average	-0.11	0.04	-0.07	0.03
D 22	-0.29	0.07	-0.14	0.07	D 7S	-0.45	0.05	-0.20	0.04
D 22 rr	-0.28	0.06	-0.13	0.06	D 7S rc	-0.47	0.07	-0.24	0.06
D 22 rc	-0.26	0.07	-0.14	0.03	Average	-0.46	0.04	-0.21	0.03
Average	-0.28	0.04	-0.13	0.03	D 2S	-0.11	0.07	-0.08	0.06
D 7S	-0.39	0.06	-0.19	0.04	D 2S rr	-0.11	0.06	-0.05	0.06
D 7S rc	-0.41	0.07	-0.23	0.07	D 2S rc1	-0.14	0.06	-0.07	0.06
Average	-0.40	0.05	-0.20	0.03	D 2S rc2	-0.11	0.07	-0.04	0.03
D 2S	-0.12	0.07	-0.08	0.05	Average	-0.12	0.03	-0.05	0.02
D 2S rc	-0.16	0.07	-0.09	0.07					
Average	-0.14	0.05	-0.08	0.04					
Sample	Grt				Sample	Opx			
	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD		$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD
D 6S	-0.53	0.05	-0.23	0.05	D 06	-0.02	0.06	0.01	0.05
D 6S rr	-0.53	0.07	-0.28	0.03	D 06 rc	0.01	0.07	0.00	0.06
D 6S rc	-0.49	0.07	-0.27	0.03	Average	-0.01	0.05	0.00	0.04
Average	-0.52	0.03	-0.27	0.02	D 07	-0.09	0.06	-0.04	0.05
D 01	-0.74	0.07	-0.38	0.05	D 07 rc	-0.10	0.07	-0.04	0.05
D 01 rr	-0.76	0.08	-0.40	0.06	Average	-0.10	0.05	-0.04	0.03
Average	-0.75	0.05	-0.39	0.04	D 09	0.00	0.06	0.04	0.04
D 06	-0.39	0.08	-0.18	0.07	D 09 rd	0.00	0.07	0.00	0.05
D 06 rr	-0.38	0.06	-0.19	0.06	Average	0.00	0.04	0.02	0.03
D 06 rc1	-0.36	0.06	-0.20	0.05	D 7S	-0.37	0.06	-0.17	0.05
D 06 rc1rr	-0.34	0.06	-0.18	0.06	D 7S rc	-0.38	0.07	-0.19	0.05
D 06 rc2	-0.37	0.06	-0.20	0.06	Average	-0.37	0.05	-0.18	0.03
Average	-0.37	0.03	-0.19	0.03					
D 07	-0.47	0.05	-0.27	0.05					
D 07 rc	-0.51	0.06	-0.25	0.05					
Average	-0.48	0.04	-0.26	0.04					
D 4S	-0.48	0.08	-0.22	0.07					
D 4S rc	-0.50	0.07	-0.26	0.07					
D 4S rcrr	-0.45	0.07	-0.23	0.05					
Average	-0.47	0.04	-0.23	0.04					
D 3S	-0.72	0.06	-0.37	0.06					
D 3S rc1	-0.75	0.07	-0.37	0.07					
D 3S rc1rr	-0.72	0.07	-0.38	0.05					
D 3S rc2	-0.75	0.07	-0.40	0.03					
Average	-0.73	0.03	-0.39	0.02					
Sample	Whole rock				Sample	Whole rock			
	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD		$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD
D 06	-0.10	0.07	-0.05	0.05	D 06	-0.10	0.07	-0.05	0.05
D 06 rc	-0.10	0.07	-0.05	0.05	D 06 rc	-0.10	0.07	-0.05	0.05
Average	-0.10	0.05	-0.05	0.03	Average	-0.10	0.05	-0.05	0.03
D 3S	-0.48	0.07	-0.24	0.07	D 3S	-0.48	0.07	-0.24	0.07
D 3S rr	-0.50	0.06	-0.26	0.06	D 3S rr	-0.50	0.06	-0.26	0.06
D 3S rc1	-0.48	0.06	-0.23	0.06	D 3S rc1	-0.48	0.06	-0.23	0.06
D 3S rc2	-0.48	0.07	-0.27	0.03	D 3S rc2	-0.48	0.07	-0.27	0.03
Average	-0.48	0.03	-0.25	0.02	Average	-0.48	0.03	-0.25	0.02

rr = repeat instrumental analysis on the same Mg-cut solutions;

rc = repeat column chemistry from another aliquot of dissolved sample solutions;

rd = full chemical replicates, including sample dissolution, column chemistry and instrumental analysis.

The weighted averages are calculated based on inverse-variance weighted model using Isoplot 3.75-4.15.

Table 3

Temperature (°C) and pressure (GPa) estimates for Hannuoba garnet-bearing xenoliths

Sample	<i>T (W)</i>	T (B&K1)	T (B&K2)	T (L&D)	T (N&T)	Mg isotope thermometry			P (N&G)	P (B&K1)	P (B&K2)	P (H&G)
	<i>Cpx-Opx</i>	Ca in Opx	Opx-Grt-Cpx	CaO in Opx	Cpx	Ol-Grt	Cpx-Grt	Opx-Grt	Opx-Grt	Ca in Opx	Opx-Grt-Cpx	Grt-Opx
D 02 L	<i>1028</i>	1057	1052	1071	1019	1622	1795	1625	1.87	2.06	1.79	1.66
D 6S L	<i>1020</i>	1057	1019	1069	1023	1376	1597	1472	1.87	2.02	1.43	1.63
D 01 W	<i>974</i>	997	1022	1028	944	776	1113	1170	1.60	1.86	1.73	1.45
D 04 W	<i>1032</i>	1061	1036	1077	1020	1404	1421	1381	1.86	1.99	1.69	1.64
D 06 W	<i>973</i>	1010	1033	1039	946	1264	1375	1396	1.56	1.84	1.64	1.40
D 07 W	<i>991</i>	990	1039	1033	946	1436	1397	1334	1.57	1.63	1.69	1.39
D 09 W	<i>975</i>	985	1011	1027	943	804	1006	879	1.55	1.61	1.64	1.42
D 12 W	<i>1021</i>	1063	1028	1072	1010				1.90	2.14	1.78	1.68
D 22 W	<i>991</i>	1060	1002	1066	978				1.77	2.19	1.54	1.53
D 4S W	<i>989</i>	1028	1011	1056	969	1631	1904	1896	1.66	1.77	1.27	1.43
D 5S W	<i>985</i>	997	1065	1030	948	1551	1599	1601	1.60	1.75	1.91	1.48
D 7S W	<i>951</i>	959	1007	1016	882	2000	2817	2003	1.42	1.38	1.35	1.24
J 13 W	<i>997</i>	1024	1080	1046	978	1202	1355	1365	1.66	1.96	1.87	1.50
J 15 W	<i>970</i>	997	1033	1032	915	1184			1.54	1.73	1.62	1.40
D802 W	<i>997</i>	1030	1030	1049	974				1.74	1.93	1.71	1.55
J 805 W	<i>975</i>	996	1044	1037	934				1.48	1.62	1.55	1.32
J 613 W	<i>1040</i>	1059	1084	1083	1021				1.74	1.80	1.70	1.51
J 07 C					1029	1294	1297	1357				
D 2S C					895	1199	1300					
D 3S C					877	1039	1130					

Italics indicate values used for Fig. 10.

T (W): Cpx-Opx thermometer of Wells (1977).

T (B&K1) and P (B&K1): Ca in Opx thermobarometer of Brey and Köhler (1990).

T (B&K2) and P (B&K2): Cpx-Opx thermobarometer of Brey and Köhler (1990).

T (L&D): Wo in Opx thermometer of Lindsley and Dixon (1976).

T (N&T): Single Cpx thermobarometer of Nimis and Taylor (2000).

P (N&G): Grt-Opx geobarometer of Nickel and Green (1985), using the temperature calculated by thermometer of Wells (1977).

P (H&G): Grt-Opx geobarometer of Harley and Green (1985), using the temperature calculated by thermometer of Wells (1977).

Mg isotope thermometry using parameters provided in Huang et al. (2013).

Table 4

Magnesium isotopic compositions (‰) relative to standard DSM3 of mineral separates and whole rock powders from Hannuoba mantle xenoliths

Sample	Ol (n = 20)				Grt (n = 15)				Cpx (n = 19)				Opx (n = 15)				Whole rock (n = 17)			
	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD
D 02 L	-0.30	0.07	-0.15	0.05	-0.53	0.07	-0.26	0.06	-0.29	0.05	-0.17	0.04	-0.26	0.06	-0.14	0.05	-0.36	0.06	-0.18	0.06
D 6S L	-0.21	0.06	-0.16	0.04	-0.52	0.03	-0.27	0.02	-0.22	0.05	-0.13	0.04	-0.19	0.06	-0.10	0.05	-0.33	0.07	-0.17	0.07
D 01 W	0.05	0.05	0.03	0.03	-0.75	0.05	-0.39	0.04	-0.20	0.05	-0.11	0.04	-0.27	0.06	-0.12	0.04	-0.32	0.07	-0.12	0.05
D 04 W	-0.33	0.07	-0.16	0.05	-0.63	0.07	-0.31	0.06	-0.27	0.05	-0.15	0.04	-0.27	0.06	-0.14	0.05	-0.43	0.07	-0.21	0.05
D 06 W	0.00	0.05	0.00	0.03	-0.37	0.03	-0.19	0.03	0.02	0.04	-0.01	0.03	-0.01	0.05	0.00	0.04	-0.10	0.05	-0.05	0.03
D 07 W	-0.19	0.07	-0.08	0.05	-0.48	0.04	-0.26	0.04	-0.11	0.04	-0.06	0.03	-0.10	0.05	-0.04	0.03	-0.24	0.07	-0.15	0.05
D 09 W	0.00	0.05	0.03	0.03	-0.76	0.05	-0.39	0.05	-0.11	0.04	-0.07	0.03	0.00	0.04	0.02	0.03	-0.20	0.07	-0.09	0.07
D 12 W	-0.28	0.07	-0.14	0.05					-0.27	0.07	-0.12	0.06	-0.26	0.07	-0.12	0.05	-0.34	0.06	-0.18	0.06
D 22 W	-0.28	0.04	-0.13	0.03					-0.25	0.06	-0.15	0.05	-0.28	0.06	-0.17	0.04	-0.26	0.07	-0.11	0.07
D 4S W	-0.24	0.06	-0.12	0.04	-0.47	0.04	-0.23	0.04	-0.25	0.05	-0.14	0.04	-0.26	0.06	-0.13	0.05	-0.27	0.07	-0.12	0.07
D 5S W	-0.23	0.06	-0.11	0.04	-0.48	0.05	-0.24	0.05	-0.18	0.07	-0.11	0.06	-0.20	0.06	-0.12	0.04	-0.26	0.07	-0.10	0.07
D 7S W	-0.40	0.05	-0.20	0.03	-0.56	0.05	-0.28	0.04	-0.46	0.04	-0.21	0.03	-0.37	0.05	-0.18	0.03	-0.35	0.07	-0.18	0.05
J 13 W	-0.18	0.06	-0.12	0.04	-0.58	0.05	-0.29	0.05	-0.18	0.05	-0.06	0.04	-0.21	0.06	-0.10	0.05	-0.21	0.07	-0.09	0.07
J 15 W	-0.29	0.05	-0.15	0.04	-0.70	0.05	-0.33	0.05									-0.36	0.07	-0.19	0.05
D802 W	-0.27	0.06	-0.12	0.05					-0.24	0.07	-0.12	0.06								
J 805 W	-0.31	0.06	-0.15	0.05					-0.23	0.07	-0.10	0.06	-0.26	0.06	-0.13	0.05				
J 613 W	-0.33	0.07	-0.19	0.05					-0.31	0.07	-0.16	0.05								
J 07 C	-0.26	0.07	-0.12	0.05	-0.61	0.05	-0.30	0.05	-0.19	0.07	-0.09	0.06	-0.24	0.06	-0.13	0.04	-0.34	0.06	-0.22	0.06
D 2S C	-0.14	0.05	-0.08	0.04	-0.54	0.07	-0.30	0.06	-0.12	0.03	-0.05	0.02					-0.18	0.07	-0.12	0.07
D 3S C	-0.23	0.06	-0.12	0.04	-0.73	0.03	-0.39	0.02	-0.20	0.05	-0.09	0.04					-0.48	0.03	-0.25	0.02
<i>Average</i>	-0.22	0.24	-0.11	0.13	-0.58	0.23	-0.29	0.12	-0.21	0.20	-0.11	0.10	-0.21	0.21	-0.11	0.12	-0.30	0.19	-0.15	0.11

L = Lherzolite; W = Websterite; C = Clinopyroxenite; n indicates sample numbers for each mineral phase.

2SD = 2 times the standard deviation of the population of n repeated measurements of the standards during an analytical session.

For samples that have been analyzed more than once, the weighted averages (in bold) are reported. Detailed measurement data are reported in [Table 2](#).

Average values in the last line are arithmetic mean values.

Table 5

Inter-mineral Mg isotope fractionations in Hannuoba garnet-bearing xenoliths

Sample	Temp. (°C)	$\Delta^{26}\text{Mg}_{\text{Ol-Grt}}$ (n = 15)	2SD	$\Delta^{26}\text{Mg}_{\text{Cpx-Grt}}$ (n = 14)	2SD	$\Delta^{26}\text{Mg}_{\text{Opx-Grt}}$ (n = 12)	2SD	$\Delta^{26}\text{Mg}_{\text{Cpx-Ol}}$ (n = 19)	2SD	$\Delta^{26}\text{Mg}_{\text{Opx-Ol}}$ (n = 15)	2SD	$\Delta^{26}\text{Mg}_{\text{Cpx-Opx}}$ (n = 15)	2SD
D 02 L	1028	0.24	0.10	0.24	0.09	0.28	0.10	0.01	0.08	0.04	0.09	-0.03	0.08
D 6S L	1020	0.31	0.07	0.30	0.06	0.33	0.07	-0.02	0.08	0.01	0.09	-0.03	0.08
D 01 W	974	0.80	0.07	0.55	0.07	0.48	0.08	-0.25	0.07	-0.32	0.08	0.07	0.08
D 04 W	1032	0.30	0.10	0.36	0.09	0.37	0.10	0.06	0.08	0.06	0.09	0.00	0.08
D 06 W	973	0.36	0.06	0.38	0.05	0.36	0.06	0.02	0.07	0.00	0.07	0.03	0.06
D 07 W	991	0.29	0.08	0.38	0.06	0.39	0.06	0.08	0.08	0.09	0.08	-0.01	0.06
D 09 W	975	0.76	0.07	0.65	0.07	0.76	0.07	-0.11	0.06	0.00	0.07	-0.11	0.06
D 12 W	1021							0.01	0.10	0.02	0.10	-0.01	0.10
D 22 W	991							0.03	0.07	-0.01	0.07	0.04	0.08
D 4S W	989	0.24	0.08	0.22	0.06	0.21	0.07	-0.02	0.08	-0.02	0.09	0.01	0.08
D 5S W	985	0.26	0.08	0.30	0.09	0.28	0.08	0.04	0.09	0.03	0.09	0.01	0.09
D 7S W	951	0.16	0.07	0.11	0.06	0.19	0.06	-0.06	0.06	0.03	0.07	-0.08	0.06
J 13 W	997	0.40	0.08	0.39	0.07	0.37	0.08	0.00	0.08	-0.02	0.09	0.02	0.08
J 15 W	970	0.41	0.07										
D802 W	997							0.03	0.09				
J 805 W	975							0.07	0.09	0.04	0.09	0.03	0.09
J 613 W	1040							0.02	0.10				
J 07 C	1029	0.35	0.09	0.42	0.09	0.38	0.08	0.08	0.10	0.03	0.09	0.05	0.09
D 2S C	895	0.40	0.09	0.42	0.08			0.03	0.06				
D 3S C	877	0.50	0.07	0.53	0.06			0.03	0.08				
Average		0.39	0.36	0.38	0.28	0.37	0.29	0.00	0.15	0.00	0.19	0.00	0.10

Temp. = Temperature

Table 6

Magnesium isotopic compositions (‰) of mineral separates and whole rock powders from Hannuoba garnet-free pyroxenite xenoliths, basalts, and a Qinling garnet peridotite xenolith

Sample	Rock type	Cpx				Opx				Whole rock				T	$\Delta^{26}\text{Mg}_{\text{Cpx-Opx}}$	2SD
		$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD			
D 11	Cr Webst	-0.33	0.06	-0.11	0.05	-0.28	0.06	-0.16	0.05	-0.32	0.06	-0.156	0.06	1039	-0.04	0.09
D 17	Cr Webst	-0.25	0.06	-0.11	0.05	-0.23	0.06	-0.13	0.04					844	-0.02	0.08
D 18	Cr Webst	-0.24	0.07	-0.13	0.06	-0.28	0.06	-0.15	0.05					849	0.04	0.09
D 19	Al Webst	-0.29	0.07	-0.12	0.06	-0.21	0.06	-0.11	0.04	-0.26	0.06	-0.13	0.06	868	-0.08	0.09
D 23	Cpxnt	-1.34	0.06	-0.69	0.05					-1.26	0.06	-0.67	0.06			
J 53	Cpxnt	-1.47	0.07	-0.76	0.06					-1.51	0.07	-0.80	0.05			
J 53rr	Cpxnt	-1.38	0.07	-0.68	0.05					-1.40	0.06	-0.77	0.06			
J 53rr2	Cpxnt	-1.39	0.07	-0.73	0.05											
J 52	Opxnt					-0.21	0.07	-0.12	0.05	-0.17	0.06	-0.09	0.06	873		
DA 0605	Alkali Basalt									-0.50	0.08	-0.28	0.07			
DA 0605rr	Alkali Basalt									-0.51	0.07	-0.26	0.05			
DA 0608	Tholeiitic Basalt									-0.35	0.06	-0.18	0.05			
QL 08-1	Grt Peridotite									-0.39	0.08	-0.21	0.07			

Webst = websterite; Cpxnt = Clinopyroxenite; Opxnt = Orthopyroxenite; Grt = garnet.

Figure

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11