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High-temperature inter-mineral magnesium isotope fractionation in eclogite from the Dabie orogen, China

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ABSTRACT

To investigate the magnitude and mechanism of inter-mineral Mg isotope fractionation at high temperatures, we report high-precision analyses of Mg isotopes for 10 whole rocks and 13 mineral separates for a set of eclogites from Bixiling in the Dabie orogen, China. Magnesium isotopic compositions of whole rocks (δ^{26}Mg of −0.44 to −0.26‰) are similar to the estimated δ^{26}Mg values of the mantle, suggesting Mg isotopic inheritance from a gabbroic protolith with limited Mg isotope fractionation during eclogite-facies metamorphism. By contrast, mineral separates are highly heterogeneous, with δ^{26}Mg values ranging from +0.30 to +0.60‰ in phengite, from +0.16 to +0.40‰ in omphacite and from −0.95 to −0.74‰ in garnet. Phengite and omphacite are >1‰ heavier in δ^{26}Mg than coexisting garnet, indicating large high-temperature inter-mineral Mg isotope fractionations. The constant $\Delta^{26}Mg_{omphacite-garnet}$ ($=\delta^{26}Mg_{omphacite}-\delta^{26}Mg_{garnet}$) value (1.14±0.04‰), together with homogeneous mineral chemistry and equilibrium oxygen isotopic partitioning between omphacite and garnet, suggests an equilibrium Mg isotope fractionation, controlled by the difference in coordination number of Mg between omphacite (six) and garnet (eight). The 1.14‰ fractionation is the largest high-temperature equilibrium inter-mineral Mg isotope fractionation observed so far and makes the omphacite-garnet Mg isotope fractionation a potential geothermometer. By contrast, Mg isotope fractionations between phengite and garnet and between phengite and omphacite vary from 1.25 to 1.47‰ and from 0.14 to 0.32‰, respectively. This implies Mg isotopic disequilibria between phengite and garnet/omphacite, which might result from the Mg isotopic variation in phengites due to Mg isotope exchange between phengites and retrograde fluids in Bixiling eclogites.

1. Introduction

Magnesium is a major element in the mantle, crust and hydrosphere with >8% relative mass difference between ^{26}Mg and ^{24}Mg, making it potentially an excellent isotopic tracer of geological processes. Knowledge on behaviors of Mg isotopes during different geological processes is the prerequisite for applying Mg isotopes as tracers. In particular, studying the magnitude and mechanism of high-temperature inter-mineral Mg isotope fractionation is crucial for applying Mg isotopic systematics in magmatic and metamorphic systems.

Previous studies have found small Mg isotope fractionation between coexisting olivines and pyroxenes in mantle xenoliths (Handler et al., 2009; Yang et al., 2009) and between coexisting hornblendes and biotites in granitoids (Liu et al., 2010). Such limited inter-mineral Mg isotope fractionations are consistent with theoretical studies as all of these major Mg-rich minerals have the same Mg coordination (i.e., six; Deer et al., 1992), which doesn't favor large inter-mineral Mg isotope fractionation at high temperatures (Liu et al., 2010). By contrast, Mg coordination is different among major Mg-rich minerals in eclogites, with coordination number of Mg being eight in garnet and six in omphacite and phengite (Deer et al., 1992). Hence, large Mg isotope fractionation is expected to occur between garnet and coexisting omphacite and phengite in eclogites, with garnet isotopically lighter than omphacite and phengite. However, to our knowledge, no single Mg isotopic datum has been published for eclogites.

In order to investigate the magnitude and mechanism of high-temperature Mg isotope fractionation between coexisting garnet, omphacite and phengite, we carried out high-precision Mg isotopic analyses on whole rocks and mineral separates from Bixiling eclogites in the Dabie orogen, China. Our results demonstrate that Bixiling eclogites have mantle-like Mg isotopic composition, suggesting limited Mg isotope fractionation during eclogite-facies metamorphism of mafic rocks. By contrast, large Mg isotope fractionation occurs between garnet and coexisting omphacite and phengite. Whereas phengite may be in Mg isotopic disequilibrium with garnet and omphacite, the omphacite–garnet is in equilibrium, with garnet 1.14‰ lighter than omphacite. The largest so far recognized high-

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temperature equilibrium Mg isotope fractionation between omphacite and garnet makes it a potential geothermometer.

2. Geological setting and samples

The Dabie–Sulu orogenic belt in east-central China is a continental collision zone between the North China Block and South China Block (Fig. 1a), which formed in the Triassic (e.g., Ames et al., 1993; Li et al., 1993; Zheng, 2008). The Dabie orogen in the western part and the Sulu orogen in the eastern part were linked in the Triassic, but subsequently offset by the Tancheng–Lujiang fault by >500 km (Xu et al., 1987). Rocks occurring in this orogenic belt include gneisses, schists, eclogites, amphibolites, marbles, migmatites and minor ultramafic rocks, with metamorphic grade ranging from greenschist facies to ultrahigh-pressure (UHP) eclogite facies (e.g., Cong, 1996; Liou et al., 1996; Zheng et al., 2005). The occurrence of inclusions of micro-diamond and coesite in minerals from eclogites and gneisses indicates that the continental crust had been subducted to mantle depths (e.g., Okay et al., 1989; Wang et al., 1989; Xu et al., 1992). Studies of stable isotopes and cooling history of UHP metamorphic rocks further indicate rapid subduction, short mantle residence and rapid initial exhumation processes during the continental collision (Li et al., 2000; Zheng et al., 2003, 2009).

This study is focused on UHP eclogites at Bixiling in the Dabie orogen, where the UHP meta-mafic and ultramafic complex occurs as a tectonic block within foliated UHP quartzofeldspathic gneisses (Fig. 1b). It mainly consists of banded eclogites with many elongated lenses of meta-ultramafic rocks (Zhang et al., 1995). Petrological and geochemical studies suggest that Bixiling eclogites have an igneous protolith with the gabbroic texture of cumulates (Chavagnac and Jahn, 1996; Zhang et al., 1995).

Fresh eclogite samples were collected along a north–south road section across the Bixiling complex (Fig. 1b). These eclogites are composed of garnet, omphacite, quartz and minor phengite, rutile and symplectites (amphibole + plagioclase), with MgO contents ranging from 5.05 to 10.47% (Table 1). Ten eclogites and thirteen Mg-rich minerals (omphacite, garnet and phengite) separated from five samples were used for Mg isotopic analyses. The estimated Fe–Mg exchange temperatures for these five eclogites range from 541 to 614 °C (Table 1), within the previously estimated temperature range of 540 to 725 °C for Bixiling eclogites (Zhang et al., 1995).

Table 1
Whole-rock and mineralogical characteristics of Bixiling eclogites in the Dabie orogen.

Sample ID	MgO (wt%)	Estimated modes for minerals[a]						T (°C)[b]
		Omp	Grt	Phg	Qtz	Rt	Sym	
bxl-1[c]	10.47	33	54	1	10	2	–	586
bxl-2		33	55	–	–	8	4	
bxl-3		36	60	1	–	3	–	
bxl-4	5.18	34	52	2	2	4	6	549
bxl-5	5.05	13	52	3	13	5	14	603
bxl-6	5.15	30	60	4	–	4	2	541
bxl-8	5.79	33	37	–	22	2	6	614
bxl-12	7.88	44	45	2	3	3	3	
bxl-13	6.65	38	55	–	–	5	2	
bxl-14[d]	8.09	37	45	–	14	4	–	

[a] Omp = omphacite; Grt = garnet; Phg = phengite; Qtz = quartz; Rt = rutile; Sym = Symplectite.
[b] Temperatures estimated by using the clinopyroxene–garnet Fe^{2+}–Mg geothermometer (see Table S2 for details).
[c] GPS coordinates for sample bxl-1 are 30°43.93′ N and 116°17.13′ E.
[d] GPS coordinates for sample bxl-14 are 30°43.76′ N and 116°16.99′ E.

3. Analytical methods

3.1. Mineral chemistry

Chemical compositions of garnet, omphacite and phengite in Bixiling eclogites were determined by electron microprobe (EMP) using a JXA-8100 Jeol Superprobe equipped with wavelength dispersive spectrometers (WDS) and energy dispersive spectrometer (EDS) combined micro-analyzer at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current and 1 μm probe diameter. Detailed analytical procedures were described in Liu and Ye (2004), and both natural and synthetic minerals were used for standard calibration. Analyzed errors with 1σ are 0.04% for Si, 0.05% for Al and Mg, 0.08% for Ca, Na and K, and 0.12% for Cr, Fe and Mn, respectively.

3.2. Magnesium isotope

Magnesium isotopic analyses were performed at the Isotope Laboratory of the University of Arkansas, Fayetteville, following the

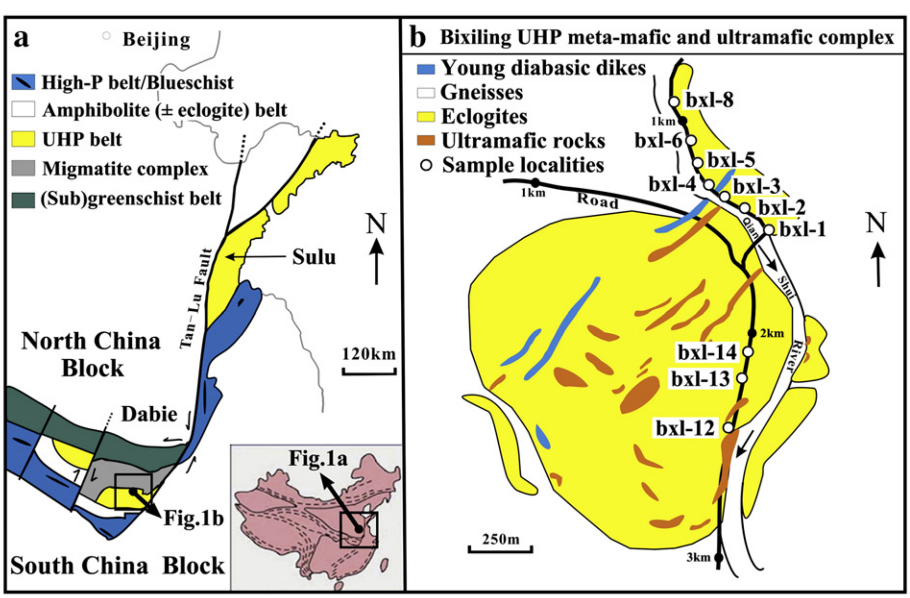

Fig. 1. (a) Simplified tectonic map of the Dabie–Sulu ultrahigh-pressure (UHP) metamorphic zone in east-central China. (b) Sketch map of the Bixiling UHP meta-mafic and ultramafic complex with sample localities.
Maps are modified after Zhang et al. (1995).

Table 2
Magnesium isotopic compositions of whole rocks and mineral separates in Bixiling eclogites and reference materials.

Sample ID	Whole rock or minerals[a]	Column times[b]	δ^{26}Mg (‰)	2SD[c]	δ^{25}Mg (‰)	2SD
bxl-2	WR	2	−0.37	0.07	−0.20	0.05
bxl-3	WR	2	−0.29	0.07	−0.13	0.05
bxl-12	WR	2	−0.34	0.06	−0.18	0.05
bxl-13	WR	2	−0.26	0.06	−0.12	0.05
bxl-14	WR	2	−0.28	0.06	−0.14	0.05
bxl-1	WR	2	−0.29	0.07	−0.16	0.05
	Omp	2	+0.39	0.09	+0.23	0.05
		4	+0.40	0.05	+0.22	0.05
	Grt	2	−0.71	0.09	−0.35	0.05
		4	−0.77	0.09	−0.38	0.05
bxl-4	WR	2	−0.32	0.06	−0.15	0.05
	Omp	2	+0.22	0.09	+0.08	0.05
		4	+0.21	0.05	+0.11	0.05
	Grt	2	−0.90	0.09	−0.46	0.05
		4	−0.91	0.09	−0.45	0.05
		Replicate	−0.94	0.09	−0.50	0.05
	Phg	2	+0.47	0.09	+0.25	0.05
		4	+0.51	0.05	+0.29	0.05
bxl-5	WR	2	−0.39	0.07	−0.20	0.05
		Replicate	−0.37	0.09	−0.24	0.06
	Omp	2	+0.25	0.09	+0.12	0.05
		4	+0.30	0.05	+0.17	0.05
	Grt	2	−0.87	0.09	−0.48	0.05
		4	−0.87	0.09	−0.46	0.05
	Phg	2	+0.59	0.09	+0.32	0.05
		4	+0.60	0.05	+0.32	0.05
bxl-6	WR	2	−0.44	0.07	−0.22	0.05
		Replicate	−0.43	0.09	−0.22	0.06
	Omp	2	+0.16	0.07	+0.09	0.07
		4	+0.16	0.09	+0.06	0.05
	Grt	2	−0.94	0.08	−0.51	0.05
		4	−0.96	0.09	−0.47	0.05
	Phg	2	+0.30	0.09	+0.14	0.08
		4	+0.29	0.05	+0.16	0.05
bxl-8	WR	2	−0.30	0.09	−0.16	0.06
	Omp	2	+0.25	0.09	+0.18	0.08
		4	+0.25	0.05	+0.13	0.05
	Grt	2	−0.93	0.07	−0.46	0.07
		4	−0.91	0.05	−0.46	0.05
Reference materials		Data source	δ^{26}Mg (‰)	2SD	δ^{25}Mg (‰)	2SD
IL-Mg-1[d]		This study	−0.08	0.06	−0.05	0.06
		Replicate	−0.03	0.06	−0.02	0.06
		Replicate	−0.04	0.08	−0.02	0.05
		Replicate	−0.06	0.09	−0.02	0.05
		Replicate	−0.06	0.05	−0.02	0.05
		Replicate	−0.02	0.09	−0.01	0.06
		Average	−0.05	0.04	−0.02	0.03
		Yang et al. (2009)	+0.03	0.04	+0.02	0.04
		Teng et al. (2010a)	−0.01	0.06	−0.01	0.07
		Teng et al. (2010b)	+0.01	0.06	+0.01	0.07
KH olivine[e]		This study	−0.35	0.08	−0.18	0.05
		Replicate	−0.33	0.06	−0.18	0.06
		Replicate	−0.31	0.07	−0.17	0.05
		Replicate	−0.27	0.09	−0.14	0.05
		Replicate	−0.27	0.06	−0.14	0.05
		Replicate	−0.30	0.09	−0.13	0.06
		Average	−0.31	0.06	−0.16	0.05
		Yang et al. (2009)	−0.32	0.10	−0.19	0.05
		Liu et al. (2010)	−0.27	0.04	−0.12	0.05
		Teng et al. (2010a)	−0.27	0.07	−0.14	0.04
		Teng et al. (2010b)	−0.28	0.04	−0.16	0.04
Allende chondrite		This study	−0.31	0.08	−0.17	0.05
		Replicate	−0.36	0.09	−0.16	0.05
		Replicate	−0.34	0.07	−0.20	0.07
		Average	−0.34	0.05	−0.18	0.04
		Galy et al. (2003)	−0.30	0.07	−0.16	0.03
		Baker et al. (2005)	−0.36		−0.18	0.03
		Teng et al. (2007)	−0.37	0.06	−0.19	0.07
		Yang et al. (2009)	−0.28	0.10	−0.17	0.07
		Young et al. (2009)	−0.39	0.04	−0.21	0.01
		Teng et al. (2010a)	−0.30	0.05	−0.15	0.04
		Teng et al. (2010b)	−0.30	0.06	−0.16	0.03

Notes to Table 2:
[a] WR = whole rock; Omp = omphacite; Grt = garnet; Phg = phengite.
[b] 2 = processed through column two times; 4 = processed through column four times. Replicate = repeated column chemistry and measurement of different aliquots of a stock solution.
[c] 2SD = 2 times the standard deviation of the population of n repeat measurements of a simple solution.
[d] IL-Mg-1 is a synthetic solution with concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1.
[e] KH olivine is an in-house reference solution made from Kilbourne Hole olivine.

established procedures (Li et al., 2010; Teng et al., 2010a,b; Yang et al., 2009). A brief description is given below.

Fresh mineral grains were handpicked under a binocular microscope before dissolution. Both whole-rock powders and handpicked mineral grains were dissolved in Savillex screw-top beakers in a combination of HF–HCl–HNO_3. Chemical separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50W-X8 resin in 1N HNO_3 media. The same column procedure was performed twice or four times (for mineral separates) in order to obtain a pure Mg solution for mass spectrometry and to check the efficiency of our column to separate Mg from interference cations. At least two reference materials were processed through column chemistry with each batch of unknown samples.

Magnesium isotopic compositions were analyzed by the standard bracketing method using a Nu Plasma MC-ICP–MS at low resolution mode. The precision on the measured $^{26}Mg/^{24}Mg$ ratio, based on ≥4 repeat runs of the same sample solution during analytical sessions of this study, is ≤±0.09‰ (2SD, Table 2). The results are reported in the conventional δ notation that is defined as $\delta^{26}Mg = [(^{26}Mg/^{24}Mg)_{sample}/(^{26}Mg/^{24}Mg)_{DSM3} - 1] \times 1000$. Magnesium isotope fractionation between mineral phases are denoted by $\Delta^{26}Mg_{X-Y} = \delta^{26}Mg_X - \delta^{26}Mg_Y$, where X and Y represent different mineral phases.

When the equivalent 2SD uncertainties are considered, Mg isotopic compositions of solution, mineral and rock reference materials analyzed during the course of this study agree with previously published values (Baker et al., 2005; Galy et al., 2003; Liu et al., 2010; Teng et al., 2007, 2010a,b; Yang et al., 2009; Young et al., 2009), confirming that our data are accurate (Table 2). Mineral separates that were processed through columns twice and four times yielded identical δ^{26}Mg values (Table 2). This indicates that interference cations can be efficiently removed after two times of the column procedure and further assuring the precision of our data.

4. Results

Whole rock and mineralogical characteristics of Bixiling eclogites are reported in Table 1. Magnesium isotopic compositions of whole rocks and mineral separates, together with reference materials, are reported in Table 2. Average Mg isotopic compositions of garnet, omphacite and phengite and corresponding inter-mineral Mg isotope fractionations in individual samples are reported in Table 3. All samples analyzed in this study fall on a single isotopic mass-dependent fractionation line with a slope of 0.522 (not shown).

In contrast to their variable MgO contents (from 5.05 to 10.47%, Table 1), δ^{26}Mg values of Bixiling eclogites display a limited variation, from −0.44 to −0.26‰, and are similar to the estimated δ^{26}Mg values of the mantle (Fig. 2). By contrast, δ^{26}Mg values of mineral separates are highly variable (>1.5‰), with δ^{26}Mg ranging from −0.95 to −0.74‰ for garnet, from +0.16 to +0.40‰ for omphacite and from +0.30 to +0.60‰ for phengite (Fig. 2).

Overall, significant inter-mineral Mg isotope fractionations occur between garnet, omphacite and phengite (Fig. 2). $\Delta^{26}Mg_{omphacite-garnet}$ values are almost constant, ranging from 1.11 to 1.17‰ with an average

Table 3
Inter-mineral Mg isotope fractionations in Bixiling eclogites.

Sample ID	$\delta^{26}Mg_{Omp}$ (‰)[a]	$\delta^{26}Mg_{Grt}$ (‰)[a]	$\delta^{26}Mg_{Phg}$ (‰)[a]	$\Delta^{26}Mg_{Omp-Grt}$ (‰)[b]	$\Delta^{26}Mg_{Phg-Grt}$ (‰)[b]	$\Delta^{26}Mg_{Phg-Omp}$ (‰)[b]
bxl-1	+0.40	−0.74		1.11		
bxl-4	+0.22	−0.92	+0.49	1.14	1.41	0.27
bxl-5	+0.28	−0.87	+0.60	1.15	1.47	0.32
bxl-6	+0.16	−0.95	+0.30	1.11	1.25	0.14
bxl-8	+0.25	−0.92		1.17		

[a] Average values of multiple measurements (listed in Table 2) of that particular mineral. Omp = omphacite; Grt = garnet; Phg = phengite.
[b] $\Delta^{26}Mg_{Omp-Grt} = \delta^{26}Mg_{omphacite} - \delta^{26}Mg_{garnet}$; $\Delta^{26}Mg_{Phg-Grt} = \delta^{26}Mg_{phengite} - \delta^{26}Mg_{garnet}$; $\Delta^{26}Mg_{Phg-Omp} = \delta^{26}Mg_{phengite} - \delta^{26}Mg_{omphacite}$.

value of 1.14 ± 0.04‰ (2SD, Fig. 3). By contrast, $\Delta^{26}Mg_{phengite-garnet}$ and $\Delta^{26}Mg_{phengite-omphacite}$ values are variable, ranging from 1.25 to 1.47‰ and from 0.14 to 0.32‰, respectively (Table 3).

5. Discussion

Protoliths of Bixiling eclogites are gabbro cumulates that formed from differentiation of mantle-derived basaltic magma (Chavagnac and Jahn, 1996; Zhang et al., 1995). As basaltic differentiation causes no detectable Mg isotope fractionation at current precision (Teng et al., 2007, 2010a), these gabbros should have mantle-like Mg isotopic composition. The mantle-like Mg isotopic compositions of Bixiling eclogites (Fig. 2) hence suggest the inheritance of Mg isotopic signatures from their mantle source and limited Mg isotope fractionation during eclogite-facies metamorphism of mafic rocks.

In contrast to the limited Mg isotopic variation in whole rocks, there are large Mg isotope fractionation among garnet, omphacite and phengite in eclogites (Fig. 2). Such fractionations may result from kinetic (F. Huang et al., 2010; Richter et al., 2008, 2009a,b) or equilibrium (Young et al., 2009) isotope fractionation. Below, we first discuss the mechanism of inter-mineral Mg isotope fractionations between garnet, omphacite and phengite and then explore the application of the large high-temperature equilibrium inter-mineral Mg isotope fractionation as a potential geothermometer.

5.1. Equilibrium Mg isotope fractionation between omphacite and garnet

Although both equilibrium and kinetic Mg isotope fractionations can occur at high temperatures, several lines of evidence indicate that the large Mg isotope fractionation between omphacite and garnet in eclogites represents equilibrium isotope fractionation.

Recent experimental studies document large Mg isotope fractionation during chemical diffusion and thermal diffusion, with light isotopes diffusing faster than heavy ones during chemical diffusion and diffusing preferentially toward the hot end during thermal diffusion (F. Huang et al., 2010; Richter et al., 2008, 2009a,b). In both cases, large and systematic mineral-scale variations in MgO contents should occur. However, MgO contents do not display significant variations within single omphacite or garnet (Fig. 4), nor among different omphacite grains or garnet grains in individual samples (Table S1). These observations thus rule out the chemical diffusion-driven kinetic Mg isotope fractionation as a possible cause for the observed omphacite–garnet Mg isotope fractionation.

Furthermore, the observed $\Delta^{26}Mg_{omphacite-garnet}$ values for the five samples are almost constant (Fig. 3), regardless of the variations in chemical compositions of omphacite and garnet (Table S1). This further rules out the chemical diffusion-driven kinetic fractionation as the cause for the omphacite–garnet Mg isotope fractionation, as a much larger variation in $\Delta^{26}Mg_{omphacite-garnet}$ value would be expected during the inter-mineral diffusion.

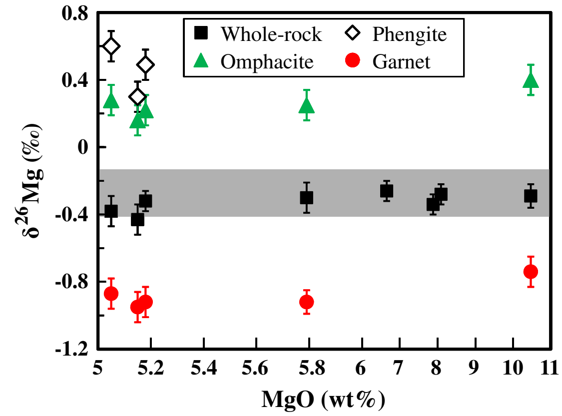

Fig. 2. $\delta^{26}Mg$ vs. MgO (wt%) for Bixiling eclogites and phengite, omphacite and garnet separates. Using whole-rock MgO contents for relevant mineral separates. Note the different scale on x-axis between 5–6 and 6–11. The gray band represents the estimated $\delta^{26}Mg$ values of the mantle (i.e., from −0.41 to −0.13‰, Bourdon et al., 2010; Dauphas et al., 2010; Handler et al., 2009; Teng et al., 2007, 2010a; Yang et al., 2009). Error bars represent 2SD uncertainties. Data are from Tables 1 and 2.

Finally, previous studies suggest that equilibrium O isotope partitioning is generally achieved between coexisting omphacite and garnet in eclogites (Xiao et al., 2000; Zheng et al., 1999, 2003). Since Mg diffuses faster than O in both clinopyroxene and garnet (Fig. 5), the attainment of O isotope equilibrium between omphacite and garnet in eclogites can be used as an indicative of the Mg isotope equilibrium. The same principle has been applied to the equilibrium assumption for mineral Sm–Nd and Rb–Sr isochron dating of eclogite-facies metamorphic rocks (Xie et al., 2004; Zhao et al., 2006; Zheng et al., 2002).

In general, equilibrium inter-mineral isotope fractionation is controlled by the difference in the bonding environment of the cation of interest between coexisting minerals, with heavier isotopes being

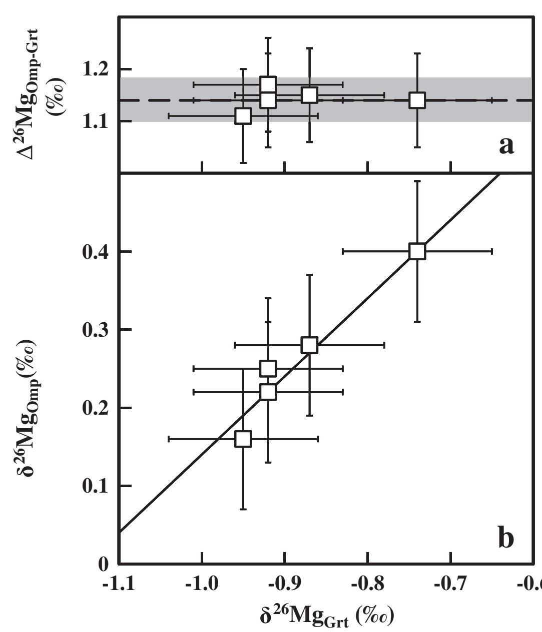

Fig. 3. (a) $\Delta^{26}Mg_{Omp-Grt}$ vs. $\delta^{26}Mg_{Grt}$ and (b) $\delta^{26}Mg_{Omp}$ vs. $\delta^{26}Mg_{Grt}$ for Bixiling eclogites. Grt = garnet; Omp = omphacite; $\Delta^{26}Mg_{Omp-Grt} = \delta^{26}Mg_{omphacite} - \delta^{26}Mg_{garnet}$. The horizontal dash line and grey band in (a) represent the average value of $\Delta^{26}Mg_{Omp-Grt}$ and 2SD, i.e., 1.14 ± 0.04‰ (2SD). The solid line in (b) represents a function of $\delta^{26}Mg_{Omp} = \delta^{26}Mg_{Grt} + 1.14$. Error bars are set as ± 0.09‰, i.e., the external precision on $\delta^{26}Mg$ during analytical sessions of this study. Data are from Table 3.

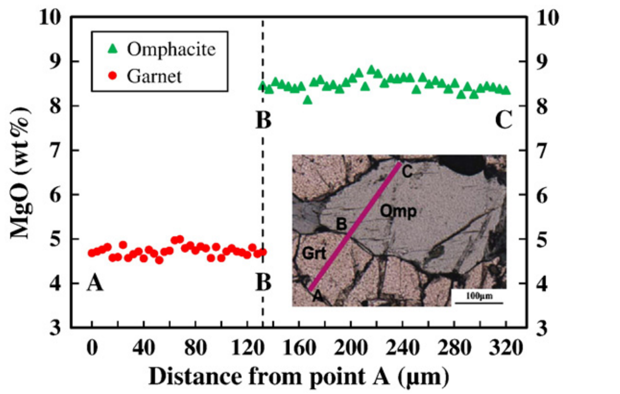

Fig. 4. The variations of MgO content along a profile through coexisting garnet and omphacite grains (the inserted photo) in sample bxl-4. The analytical spots (1 μm in diameter) are smaller than the symbols in the figure.

preferentially enriched in minerals with a lattice site that has stronger bonds (e.g., Bigeleisen and Mayer, 1947; Urey 1947). Minerals with lower Mg coordination generally have shorter (i.e., stronger) Mg—O bonds, hence favoring heavier Mg isotopes (Liu et al., 2010; Young et al., 2009). Magnesium coordination is six in omphacite whereas it is eight in garnet (Deer et al., 1992). Hence heavy Mg isotopes are expected to be enriched in omphacite, which is consistent with our observation (Fig. 3). As Mg and Fe^{2+} cations occupy the same lattice sites in both omphacite and garnet, omphacite is also expected to have heavier Fe isotopes than coexisting garnet. This is consistent with previous studies showing that omphacite is ~0.3 to 0.4‰ heavier in δ^{56}Fe than coexisting garnet in eclogites (Beard and Johnson, 2004; Williams et al., 2009).

5.2. Disequilibrium Mg isotope fractionation between phengite and garnet/omphacite

Similar to the direction of Mg isotope fractionation between omphacite and garnet, phengite also has heavier Mg isotopic composition than coexisting garnet (Fig. 2). This observation, in the first order, agrees with the expectation of equilibrium inter-mineral Mg isotope fractionation as phengite has lower Mg coordination than garnet (six vs. eight; Deer et al., 1992). However, the $\Delta^{26}Mg_{phengite-garnet}$ and $\Delta^{26}Mg_{phengite-omphacite}$ values are variable and do not display any correlation with temperatures (Table 3), suggesting that Mg isotope fractionation between phengite and garnet/omphacite in these samples may be out of thermodynamic equilibrium.

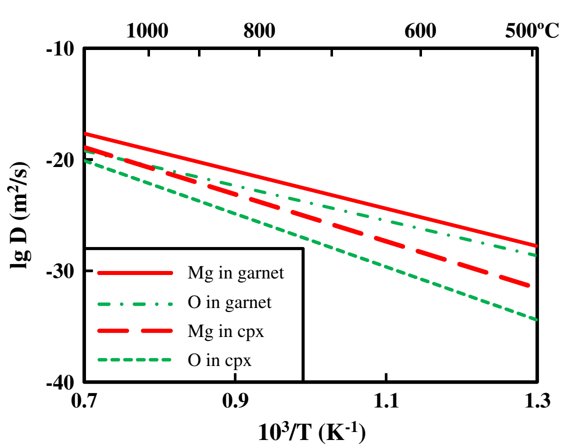

Fig. 5. Comparison of diffusion rates of Mg and O in garnet and clinopyroxene (cpx). Data sources: Mg in garnet (Perchuk et al., 2009), O in garnet (Coghlan, 1990), Mg in cpx (Dimanov and Sautter, 2000), O in cpx (Ryerson and McKeegan, 1994).

Mineral chemistry analyses demonstrate that the Mg content is variable and positively correlated with the Si content among phengite grains in Bixiling eclogites (Fig. 6 and Table S3). The Si content of phengite generally decreases with decreasing pressure (e.g., Ferraris et al., 2005; Massonne and Schreyer, 1987; Velde, 1967). Hence the variable Si content indicates that phengites in these eclogites formed at different metamorphic stages. The O isotope geothermometer yielded lower temperatures for quartz–phengite pairs than those for quartz–garnet and quartz–omphacite pairs in Bixiling eclogites, suggesting that phengites probably experienced retrograde O isotope exchange with fluids whereas garnet and omphacite are more resistant (Xiao et al., 2000; Zheng et al., 1999). Possible equilibrium or diffusive Mg isotope exchange between phengites and retrograde fluids could modify the Mg isotopic compositions of phengite grains that formed at different stages, leading to the disequilibrium fractionation between phengite and garnet/omphacite in Bixiling eclogites. Nonetheless, more systematic studies are needed to understand the mechanisms of Mg isotope fractionation between phengite and garnet/omphacite in eclogites.

5.3. Implications for large equilibrium omphacite–garnet Mg isotope fractionation

Large equilibrium inter-mineral isotope fractionation can be used as a geothermometer (e.g., Hoefs, 2009). The 1.14‰ omphacite–garnet Mg isotope fractionation is more than 10 times larger than the current analytical uncertainty of Mg isotopes (i.e., ±0.09‰ on δ^{26}Mg). In this sense, the fractionation of Mg isotopes between omphacite and garnet observed in this study is the largest so far recognized high-temperature equilibrium inter-mineral isotope fractionation among non-traditional stable isotopes [e.g. Li (Jeffcoate et al., 2007), Mg (Handler et al., 2009; Liu et al., 2010; Yang et al., 2009; Young et al., 2009), Ca (S. Huang et al., 2010) and Fe (Beard and Johnson, 2004; Shahar et al., 2008; Williams et al., 2009)]. This makes omphacite–garnet Mg isotope fractionation a potential geothermometer.

Assuming the linear correlation between equilibrium fractionation factor ($10^3\ln\alpha_{X-Y} = \Delta^{26}Mg_{X-Y}$) and $1/T^2$ (T is the temperature in Kelvin) at high temperatures, only one pair of $\Delta^{26}Mg_{X-Y}$ and T data is needed to determine the parameter “A” in the fractionation equation $10^3\ln\alpha_{X-Y} = A/T^2$. The constant $\Delta^{26}Mg_{omphacite-garnet}$ value of 1.14‰ for the five eclogite samples (Fig. 3) corresponds to the equilibrium temperature of Mg isotope exchange between omphacite and garnet, i.e., 852 K, estimated by using the clinopyroxene–garnet Fe–Mg exchange geothermometer (Table S2). According to this pair of $\Delta^{26}Mg_{omphacite-garnet}$ and T data, a possible equilibrium fractionation factor between omphacite and garnet as a function of temperature is obtained with $10^3\ln\alpha_{omphacite-garnet} = 0.83 \times 10^6/T^2$ (Fig. 7).

When compared to the recently proposed spinel–olivine Mg isotope geothermometer (Young et al., 2009), the potential clinopyroxene

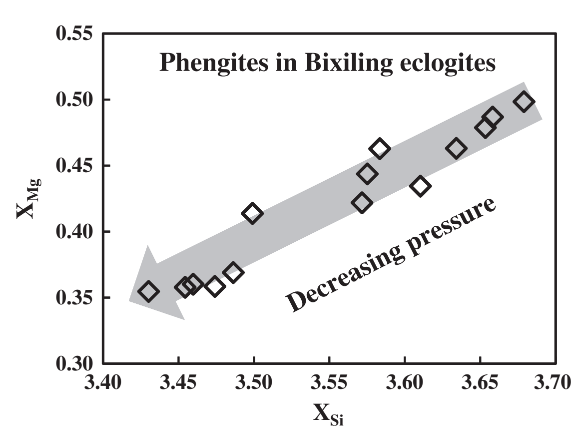

Fig. 6. X_{Mg} vs. X_{Si} (apfu) for phengite grains in Bixiling eclogites. Data are from Table S3.

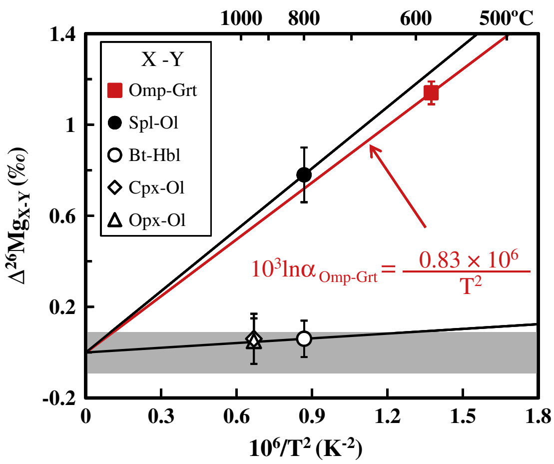

Fig. 7. Equilibrium high-temperature inter-mineral Mg isotope fractionations. $\Delta^{26}Mg_{X-Y} = \delta^{26}Mg_X - \delta^{26}Mg_Y$, where X and Y represent different mineral phases. Omp = omphacite; Grt = garnet; Spl = spinel; Ol = olivine; Bt = biotite; Hbl = hornblende; Cpx = clinopyroxene; Opx = orthopyroxene. The horizontal grey band represents undetectable inter-mineral Mg isotope fractionation i.e., $\Delta^{26}Mg_{X-Y} = 0 \pm 0.09$‰ (2SD). The red solid line represents the equilibrium equation of omphacite–garnet Mg isotope fractionation calibrated with the Bixiling eclogites in this study, i.e., $10^3\ln\alpha_{Omp-Grt} = 0.83 \times 10^6/T^2$. Error bars represent 2SD uncertainties.
Data sources: Omp–Grt (this study), Spl–Ol (Young et al., 2009), Bt–Hbl (Liu et al., 2010), Cpx–Ol and Opx–Ol (Handler et al., 2009; Yang et al., 2009).

(omphacite)–garnet Mg isotope geothermometer suggested here may have two advantages. First, in contrast to the spinel–olivine Mg isotope geothermometer, which can only be used in spinel peridotite, the clinopyroxene–garnet Mg isotope geothermometer can be widely used in garnet peridotite, garnet pyroxenite and eclogite. Second, the clinopyroxene–garnet Mg isotope geothermometer can be precisely calibrated by the well-established clinopyroxene–garnet Fe–Mg exchange geothermometer (e.g., Ellis and Green, 1979; Krogh, 1988; Powell, 1985; Ravna, 2000). This is difficult for the spinel–olivine Mg isotope geothermometer due to limitations of the spinel–olivine Fe–Mg exchange geothermometer (e.g., Coogan et al., 2007; Engi and Evans, 1980; Kessel et al., 2007). This is more important because no experimental data are available for high-temperature inter-mineral Mg isotope fractionation yet. Nonetheless, further studies on laboratory and well-characterized natural samples are needed in order to calibrate and apply the potential spinel–olivine and clinopyroxene–garnet Mg isotope geothermometers in natural systems.

6. Conclusions

The main conclusions from this study are:

(1) The $\delta^{26}Mg$ values of Bixiling eclogites range from −0.44 to −0.26‰, similar to those of their protolith, i.e., gabbro cumulates that formed through differentiation of mantle-derived basaltic magma. This suggests the inheritance of the Mg isotopic signature of eclogites from their gabbroic protolith and thus a limited Mg isotope fractionation during eclogite-facies metamorphism of mafic intrusive rocks.

(2) Magnesium isotopic compositions of coexisting garnet, omphacite and phengite in eclogites are highly variable, with $\delta^{26}Mg$ values ranging from −0.95 to −0.74‰ in garnet, from +0.16 to +0.40‰ in omphacite and from +0.30 to +0.60‰ in phengite. Phengite and omphacite are >1‰ heavier in $\delta^{26}Mg$ than coexisting garnet, indicating large inter-mineral Mg isotope fractionations.

(3) The constant $\Delta^{26}Mg_{omphacite-garnet}$ value (1.14 ± 0.04‰), together with homogeneous mineral chemistry and equilibrium oxygen isotopic partitioning between omphacite and garnet, suggests equilibrium Mg isotope fractionation between omphacite and garnet in Bixiling eclogites, produced by the difference in coordination number of Mg between omphacite (six) and garnet (eight).

(4) The variable $\Delta^{26}Mg_{phengite-garnet}$ and $\Delta^{26}Mg_{phengite-omphacite}$ values imply Mg isotopic disequilibria between phengite and garnet/omphacite. Such disequilibria might result from the Mg isotopic variation in phengites, which resulted from Mg isotope exchange between phengites and retrograde fluids.

(5) The large equilibrium isotope fractionation makes omphacite-garnet Mg isotope fractionation a potential geothermometer, with $10^3\ln\alpha_{omphacite-garnet} = 0.83 \times 10^6/T^2$.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.01.035.

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