



First-principles calculations of equilibrium Mg isotope fractionations between garnet, clinopyroxene, orthopyroxene, and olivine: Implications for Mg isotope thermometry



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ABSTRACT

Equilibrium fractionation factors of Mg isotopes at high temperature and pressure are investigated for pyrope, majorite, clinopyroxene, orthopyroxene, and olivine using density functional theory. The calculated equilibrium fractionation factors are in good agreement with previous study (Schauble, 2011), suggesting that our calculations are reliable and accurate. The results reveal significant inter-mineral Mg isotope fractionations due to different coordination environment of Mg in minerals. Specifically, pyrope, where Mg is in eight-fold coordination, is more enriched in light Mg isotopes than olivine and pyroxene where Mg is in six-fold coordination. The calculated isotope fractionation for Mg isotopes between clinopyroxene and pyrope is consistent with observations from natural eclogites (Li et al., 2011; Wang et al., 2012). Our calculation also reveals substantial pressure effect on Mg isotope fractionations among garnet, pyroxene, and olivine.

Equilibrium fractionation of Mg isotopes between pyrope and pyroxene (and olivine) could be used as a novel and independent thermometry with precision much better than the traditional garnet–clinopyroxene Fe–Mg exchange thermometry because such fractionation is significantly greater than the current uncertainties of Mg isotope analyses ($\sim 0.05\%$ amu⁻¹). These Mg isotope thermometries could have wide applications in high-temperature mafic igneous and metamorphic rocks where garnet co-exists with pyroxene or olivine. Equations for equilibrium Mg isotope fractionation factors between garnet (pyrope and majorite) and pyroxene and between garnet and olivine as a function of temperature and pressure are also presented in this study.

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1. Introduction

Magnesium is one of the most important major elements in the crust and mantle. Because the difference of relative mass in Mg isotopes (²⁴Mg, ²⁵Mg, and ²⁶Mg) is up to 8%, Mg isotopes can be significantly fractionated in numerous geological processes. Recent advances in Mg isotope analytical methods using multi-collector ICP-MS have revealed large fractionations in natural samples (e.g., Bourdon et al., 2010; Galy et al., 2003; Li et al., 2011; Wang et al., 2012; Young and Galy, 2004). This makes Mg isotope geochemistry as a promising geochemical tool in the studies of a variety of geological processes from low temperature chemical weathering to high temperature magmatism (e.g., Black et al., 2006;

Huang et al., 2009a; Li et al., 2011; Liu et al., 2011b; Schauble, 2011; Strandmann et al., 2008, 2011; Teng et al., 2007, 2010; Tipper et al., 2008a, 2008b; Young et al., 2009).

Although it was believed that equilibrium fractionation of stable isotopes may be small at high temperature (Urey, 1947), recent measurements of mafic minerals and theoretical calculations demonstrated that inter-mineral Mg isotope fractionation is measurable on the basis of current precision ($< 0.1\%$, 2SD) due to different coordination environment of Mg cations in minerals (e.g., Huang et al., 2011; Li et al., 2011; Liu et al., 2011b; Wang et al., 2012; Young et al., 2009). Mg isotope data are reported in δ notation as defined by

$$\delta^{26}\text{Mg} = \left[\frac{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{sample}}}{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{DSM3}}} - 1 \right] \times 1000. \quad (1)$$

Li et al. (2011) observed that equilibrium Mg isotope fractionation between coexisting clinopyroxene and garnet ($\delta^{26}\text{Mg}_{\text{cpx}} - \delta^{26}\text{Mg}_{\text{garnet}} = \Delta^{26}\text{Mg}_{\text{cpx-garnet}}$) is $1.14 \pm 0.04\%$ at ~ 600 °C, reflecting different coordination numbers of Mg in these two minerals

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(six in clinopyroxene vs. eight in garnet). Because such inter-mineral fractionation is more than 10 times that of analytical errors, Mg isotope fractionation between garnet and clinopyroxene could potentially provide a novel geo-thermometry with good precision and wide applications (Li et al., 2011).

The main obstacle for establishing the Mg isotope geothermometry and understanding mechanisms for Mg isotope fractionation is the lack of quantitative information about inter-mineral equilibrium fractionations as a function of temperature. Experimental studies demonstrate that Mg isotopes in silicate melts can be kinetically fractionated by chemical and thermal diffusion due to temperature and chemical activity gradients (Huang et al., 2009b, 2010; Richter et al., 2009). It is thus difficult to achieve isotopic equilibrium in silicate melt in high temperature–pressure apparatuses, and it is more so in minerals because of much slower diffusion in solid. Therefore, only a few experimental studies on Fe, Si, and Ni isotopic equilibrium between minerals at high pressure conditions have been reported (e.g., Lazar et al., 2012; Shahar et al., 2008, 2011). Because experimental calibration of equilibrium Mg isotope fractionation factors is not yet available, the equilibrium temperature cannot be derived from inter-mineral Mg isotope fractionation. This significantly limits the application of Mg isotope thermometry in igneous and metamorphic rocks.

Advances in computational chemistry involving first-principles calculations and nuclear resonance vibration techniques provide an excellent opportunity to investigate equilibrium isotopic fractionations (e.g., Dauphas et al., 2012; Liu et al., 2011a; Rustad and Yin, 2009; Schauble, 2011; Young et al., 2009). Specifically, equilibrium fractionation factors of Mg isotopes between olivine, spinel, and pyroxene have been calculated in Young et al. (2009) and Schauble (2011). However, equilibrium fractionation of Mg isotopes between garnet and other mafic minerals have not been theoretically studied. Furthermore, the pressure effect on Mg isotope fractionation is unclear either, which may cause substantial uncertainty in the applications of Mg isotope geothermometry.

Here, we use first-principles calculations based on density functional theory to estimate equilibrium Mg isotope fractionations between the common mafic minerals with different coordination numbers of Mg, including pyrope (${}^{\text{VIII}}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), majorite (${}^{\text{VIII}}\text{Mg}_3{}^{\text{VI}}[\text{MgSi}]\text{Si}_3\text{O}_{12}$), olivine (${}^{\text{VI}}\text{Mg}_2\text{SiO}_4$), clinopyroxene ($\text{Ca}{}^{\text{VI}}\text{MgSi}_2\text{O}_6$), and orthopyroxene (${}^{\text{VI}}\text{MgSiO}_3$). We focus on systematic variations of isotope fractionation factors as a function of temperature and pressure. This study sheds important light on understanding Mg isotope fractionation in nature systems and provides theoretical work for garnet–pyroxene and garnet–olivine Mg isotope thermometries. Future experimental measurements will be helpful for fully establishing such a new thermometry.

2. Calculation methods

The equilibrium isotope fractionation is mass-dependent and arises from changes in vibrational (phonon) frequencies by isotopic substitution (Bigeleisen and Mayer, 1947; Kieffer, 1982; Urey, 1947). The isotope fractionation factor of the element X between the material A and B (α_{A-B}) is defined as the ratio of their isotope ratios. Since the isotope fractionation factor between the phase A and a perfect gas of X atoms is the reduced partition function ratio β_A of the element X (Richet et al., 1977), α_{A-B} can be rewritten as: $\alpha_{A-B} = \beta_A / \beta_B$.

The reduced partition function ratio β is defined in the harmonic approximation as:

$$\beta_A = \left(\frac{Q_h}{Q_l} \right) = \prod_i^{3N} \frac{u_{ih} e^{-(1/2)u_{ih}} (1 - e^{-u_{ih}})}{u_{il} (1 - e^{-u_{il}}) e^{-(1/2)u_{il}}}, \quad (2)$$

where Q is the vibrational partition function, h and l refer to the heavy and light isotope, respectively, $u_{ih,l} = h\omega_{ih,l}$, is vibrational (phonon) frequency of mode i , k_B is Boltzmann constant, T is the temperature, and N is the number of atoms in the unit cell. The product runs over all $3N$ phonon modes. The isotope fractionation factor is usually reported in per mil and is expressed as $1000\ln\alpha_{A-B} = 1000(\ln\beta_A - \ln\beta_B)$. A positive $1000\ln\alpha_{A-B}$ means that material A is enriched in the heavy isotopes relative to the material B.

We need to know the effects of isotopic substitution on the phonon density of state for both materials to calculate the fractionation factor. It is hard to obtain the phonon density of state and its mass-dependence from experimental studies. First-principles calculations based on density functional theory can precisely predict the phonon density of state of many materials without introducing any adjustable parameters (e.g., Baroni et al., 2001; Wentzcovitch et al., 2010). The reliable and predictive isotopic fractionation factors have been obtained by many recent first principles calculations studies (e.g., Blanchard et al., 2009; Javoy et al., 2012; Li et al., 2009; Li and Liu, 2011; Méheut et al., 2007, 2009; Rustad and Dixon, 2009; Schauble, 2004, 2011).

Electronic structures and phonon frequencies of minerals are calculated using Quantum espresso, a package based on density functional theory, plane wave, and pseudopotential (Giannozzi et al., 2009). The calculation details for some of minerals discussed in this study are very similar to previous studies (Karki et al., 2000; Li et al., 2007; Tsuchiya et al., 2004; Wu et al., 2008; Wu and Wentzcovitch, 2007; Yu et al., 2008, 2010, 2011; Yu and Wentzcovitch, 2006). These studies focused on the phonon properties and thermodynamics properties of minerals. The strong agreement in thermodynamics properties and high temperature equation of states between these studies and experiments indicated that local density approximation (LDA) (Perdew and Zunger, 1981) for exchange correlation functional works well for calculating structures and vibrational properties of minerals. Therefore LDA is adopted in this study.

The pseudopotential for aluminum and calcium were generated by Vanderbilt method (Vanderbilt, 1990) with valence configuration $3s^23p^1$ and cutoff radii 1.77 Bohr for aluminum and configuration $3s^23p^64s^1$ and cutoff radii 1.85 Bohr for calcium. The pseudopotential for magnesium was generated by the method of von Barth and Car with cutoff radii 2.5 Bohr for all channels using five configurations, $3s^23p^0$, $3s^13p^1$, $3s^13p^{0.5}3d^{0.5}$, $3s^13p^{0.5}$, and $3s^13d^1$ with decreasing weights 1.5, 0.6, 0.3, 0.3, and 0.2, respectively. Those for oxygen and silicon were generated by the method in Troullier and Martins (1991). The cutoff radii are 1.45 Bohr for oxygen with configuration $2s^22p^4$ and 1.47 Bohr for silicon with the configuration $3s^23p^43d^0$. The plane-wave cutoff energy is 70 Ry. Brillouin zone summations over electronic states were performed over $N_1 \times N_2 \times N_3$ k mesh with N_i dependence on the materials (see Table S1). The structures were well optimized using variable cell shape molecular dynamics (Wentzcovitch, 1991). Dynamical matrices were computed on regular q mesh using density-functional perturbation theory (DFPT) (Baroni et al., 2001) and then interpolated in a dense q mesh to obtain the vibrational density of state of minerals. The sizes of the regular and dense q mesh also depend on materials (Table S1).

β in Eq. (2) is volume-dependent since phonon frequencies from first-principles calculations are a function of volume. It is more practical to express β as a function of pressure (P) and temperature (T). The transform requires the equation of state, $P(V, T)$, which can be derived from Helmholtz free energy. The Helmholtz free energy in the quasi-harmonic approximation is given by

$$F(V, T) = U(V) + \sum_{qj} \frac{\hbar\omega_{qj}(V)}{2} + k_B T \sum_{qj} \ln \left(1 - \exp \left[\frac{\hbar\omega_{qj}(V)}{k_B T} \right] \right), \quad (3)$$

where q is a wave vector in the first Brillouin zone, j is an index of phonon mode with frequency ω_{qj} , V and T are the volume and temperature of the system, and K_B and h are the Boltzmann and Planck constants, respectively. The first, second, and third terms in Eq. (3) are the static internal, zero-point, and vibrational energy contributions, respectively. The calculated Helmholtz free energy versus volume is fitted by the third-order Birch–Murnaghan finite strain equation of states.

3. Results

3.1. Crystalline structure

The crystal structures of pyrope, majorite, clinopyroxene, orthopyroxene, and olivine are shown in Fig. 1 with emphasis on Mg–O polyhedrons. Mg is six-fold coordinated in olivine and pyroxene, but eight-fold coordinated in pyrope. Three Mg cations in majorite ($^{VIII}Mg_3^{VI}[MgSi]Si_3O_{12}$) are eight-fold coordinated, and one Mg cation is six-fold coordinated. Calculated crystal structure parameters are presented in Table S2 with comparisons with experimental data. The corresponding atom positions based on lattice parameters in Table S2 are listed in Table S3. The LDA static calculation usually slightly underestimates the equilibrium volume. After taking account of the vibrational effect, which can increase the equilibrium volume, LDA can well predict the crystal structure at ambient conditions (see Ref. Wentzcovitch et al. (2010) and Table S2). The errors are less than 0.5% for all of lattice parameters of five minerals in Table S2 except the volume

of pyrope. This suggests that LDA should be a good exchange correlation for vibrational frequencies because frequencies are sensitive to the lattice parameters.

The calculated frequencies of pyroxene, garnets, and olivine are shown in Fig. S1 and Table S4, agreeing well with the measured values. The calculated vibration properties of forsterite and majorite in this study are almost identical with the previous works (Li et al., 2007; Yu et al., 2011) since all works use the same pseudopotential and similar calculation details. Other LDA study (e.g., McKeown et al. (2010) for forsterite) also shows similar result. Generally, frequencies of these minerals in this study are slightly higher than those in Schauble (2011), which are based on general gradient approximation (GGA) exchange correlation. This is because LDA predicts a smaller volume than GGA, but this does not affect the value of $1000\ln\alpha$ because the systematic offsets of $1000\ln\beta$ are canceled out (see the results in the following section). Therefore, LDA is a good exchange correlation for the structures and β of the minerals in this study.

3.2. Calculated Mg isotope fractionation data

Polynomial fitting of reduced partition function ratios of $^{26}Mg/^{24}Mg$ ($10^3\ln\beta_{26-24}$) at zero pressure are shown in Table 1 and Fig. 2. More data are available in Supplementary Materials. $10^3\ln\beta_{26-24}$ of all minerals decrease dramatically with increasing temperature. Our calculations show that the order of heavy isotope enrichment is clinopyroxene > orthopyroxene > olivine although fractionation between pyroxene and olivine is small at high temperature (Fig. 2b). Such order is consistent with observations

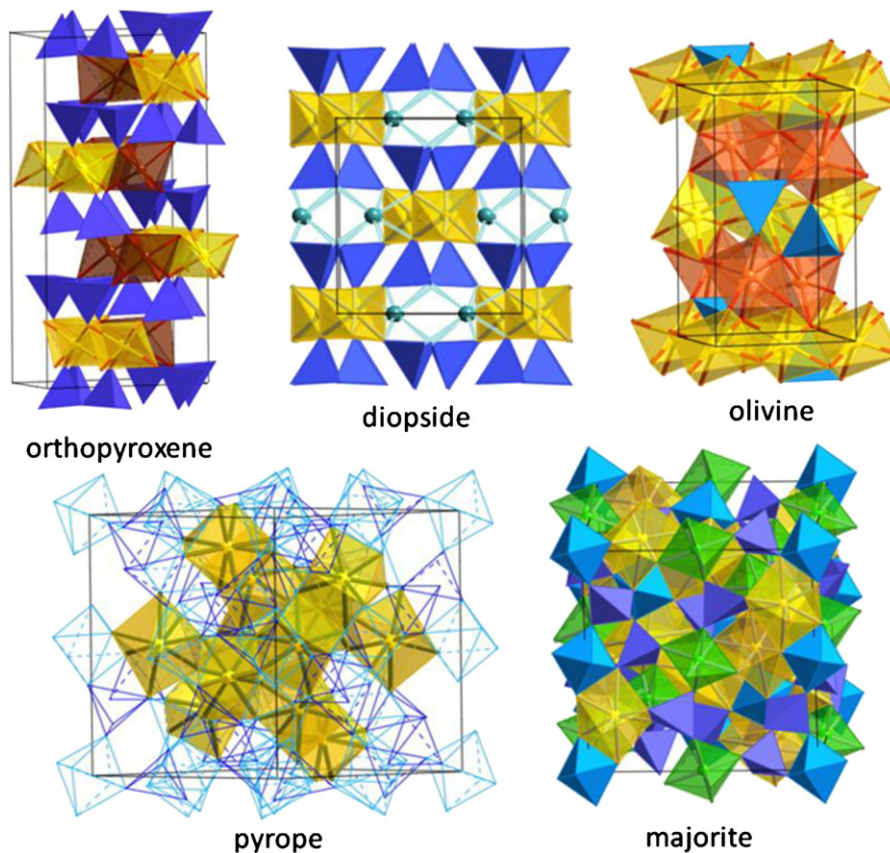


Fig. 1. The mineral structures of orthopyroxene ($^{VI}MgSiO_3$), clinopyroxene ($Ca^{VI}MgSi_2O_6$), olivine ($^{VI}Mg_2SiO_4$), pyrope ($^{VIII}Mg_3Al_2Si_3O_{12}$), and majorite ($^{VIII}Mg_3^{VI}[MgSi]Si_3O_{12}$). Translucent Mg–O polyhedrons (yellow, red, or green) with Mg–O bonds are highlighted to show the difference of coordination environment of Mg. Symmetry equivalent Mg–O polyhedrons are shown in the same color. Tetrahedrons are SiO_4 with blue in olivine and purple in other minerals. Blue octahedrons in majorite are SiO_6 . Tetrahedrons (SiO_4) and octahedrons (AlO_6) are shown in frame to make Mg–O polyhedrons clearer for pyrope. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in peridotite xenoliths and theoretical work in previous studies (Huang et al., 2011; Liu et al., 2011b; Schauble, 2011; Yang et al., 2009; Young et al., 2009). Our results also predict that pyroxene and olivine are significantly enriched in heavy Mg isotopes relative to garnet (pyrope and majorite). For instance, at 1000 °C and 0 GPa, $\Delta^{26}\text{Mg}_{\text{cpx-pyrope}}=0.60\%$, more than six times that of current analytical precision ($\sim 0.1\%$, 2σ). The reason for such large fractionation is the different coordination environment of Mg in minerals (Fig. 1 and Table 1). Based on the equilibrium isotope fractionation theory, if two phases are in thermodynamic equilibrium, the phase with smaller coordination number generally has shorter and stronger bond with higher vibrational energy than the one with larger coordination number, and thus it is more enriched in heavy isotopes. Our calculations are fully consistent with this theoretical prediction.

Comparisons of our results with literature values are plotted in Fig. 3. Schauble (2011) estimates $10^3\ln\beta$ of Mg-bearing minerals at volume corresponding to zero pressure of static first-principles calculation. Fig. 3a shows that $10^3\ln\beta$ of periclase (MgO), clinopyroxene, orthopyroxene, and olivine in this study is systematically higher than the values reported in Schauble (2011), which is due to the different approximation of exchange correlation functional. This study used LDA, while Schauble (2011) used general gradient approximation (GGA). Despite of the differences

Table 1

Calculated reduced partition function ratios of $^{26}\text{Mg}/^{24}\text{Mg}$ ($1000\ln\beta$) for olivine, clinopyroxene, orthopyroxene, pyrope, and majorite at 0 GPa and 400–2000 K.

	Formula	a	b	c
Olivine	$^{\text{VI}}\text{Mg}_2\text{SiO}_4$	2.0748	0.1052	-0.0119
Clinopyroxene	$\text{Ca}^{\text{VI}}\text{MgSi}_2\text{O}_6$	2.2442	0.1028	-0.0117
Orthopyroxene	$^{\text{VI}}\text{Mg}_2\text{Si}_2\text{O}_6$	2.2501	0.0665	-0.0081
Pyrope	$^{\text{VIII}}\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1.3022	0.0492	-0.0055
Majorite	$^{\text{VIII}}\text{Mg}_3^{\text{VI}}[\text{MgSi}]\text{Si}_3\text{O}_{12}$	1.8072	0.0507	-0.0061

$1000\ln\beta = ax + bx^2 + cx^3$, where $x = 10^6/T^2$. T is temperature in Kelvin.

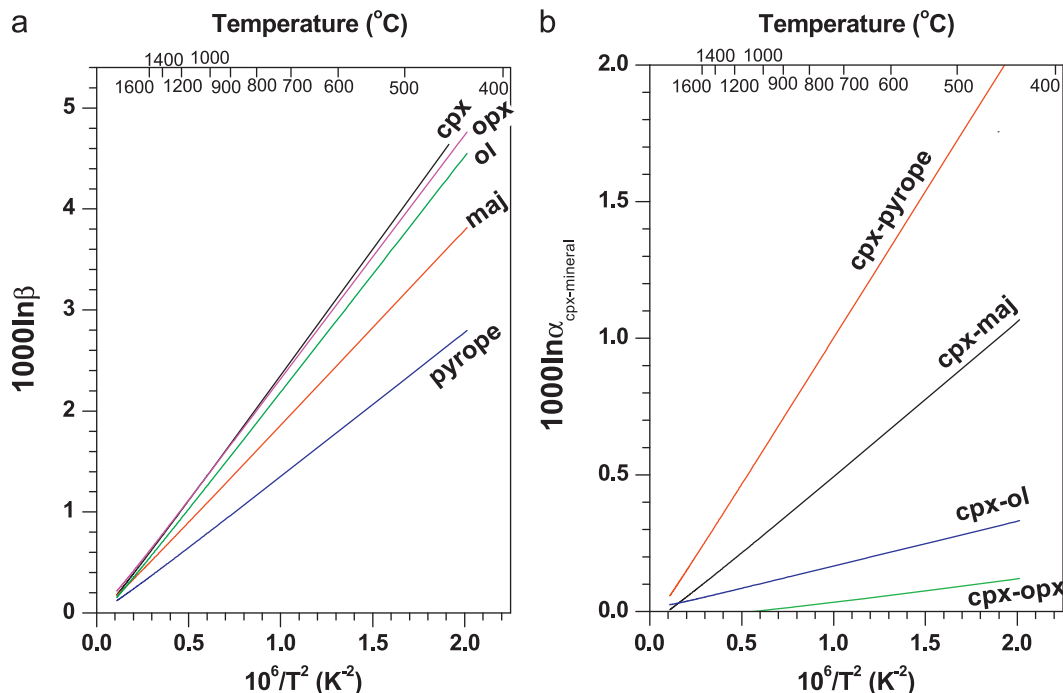


Fig. 2. (a) Calculated reduced partition function ratios ($10^3\ln\beta_{26/24}$) for clinopyroxene (cpx), orthopyroxene (opx), olivine (ol), majorite (maj), and pyrope at zero pressure. (b) Equilibrium fractionation factors of $1000\ln\alpha_{\text{cpx-mineral}}$ at zero pressure. It is clearly shown that cpx is significantly enriched in heavy Mg isotopes than pyrope and majorite, while equilibrium fractionation between pyroxene and olivine at high temperature (> 1000 °C) is indistinguishable with current analytical precision.

in $10^3\ln\beta$, $10^3\ln\alpha_{\text{A-B}}$ values in two studies are in good agreement, right on the line with slope of 1:1 (Fig. 3b). For instance, at 1000 °C and 0 GPa, $10^3\ln\alpha_{\text{cpx-ol}}=0.08$ (this study), well consistent with the value in Schauble (2011) ($10^3\ln\alpha_{\text{cpx-ol}}=0.1$). Taking a normal temperature for spinel lherzolite of ~ 1000 °C, these calculated fractionation factors are also identical to the Mg isotopic offsets between pyroxene and olivine measured from mantle peridotite xenoliths (Chakrabarti and Jacobsen, 2010; Huang et al., 2011; Liu et al., 2011b; Yang et al., 2009; Young et al., 2009). For example, $10^3\ln\alpha_{\text{cpx-ol}}$ range from 0‰ to 0.13‰ in Liu et al. (2011b); the average $10^3\ln\alpha_{\text{cpx-ol}}$ in Huang et al. (2011) is $0.1 \pm 0.15\%$ (2σ , $n=18$).

We also calculated oxygen isotope fractionation factors between mantle minerals for comparisons with previous studies to demonstrate the consistency of first-principles calculation (Table 2). Fig. 4 shows that $10^3\ln\alpha$ of oxygen isotopes between orthopyroxene and olivine calculated in this study agrees well with the results in Méheut et al. (2009) in both direct and magnitude of fractionation, and our calculated $10^3\ln\alpha_{\text{cpx-ol}}$ is consistent with the values in Schauble (2011). The agreements in both O and Mg isotope fractionations suggest that our calculation is reliable and accurate. Because experimental studies on calibrating Mg isotope fractionation factors between minerals at high temperature are not yet available, first-principles theory can undoubtedly provide important insights into inter-mineral Mg isotope fractionations.

3.3. Temperature and pressure effects on Mg isotope fractionation

It is well accepted that the effect of temperature dominates isotope fractionation between phases in thermodynamic equilibrium (Clayton et al., 1975; Valley, 2001), but the pressure effect is also important for better understanding isotope fractionation at high pressure (Polyakov and Kharlashina, 1994). Therefore, in order to obtain accurate Mg isotope thermometry which will be applied to natural samples subjected to high pressure conditions, it is

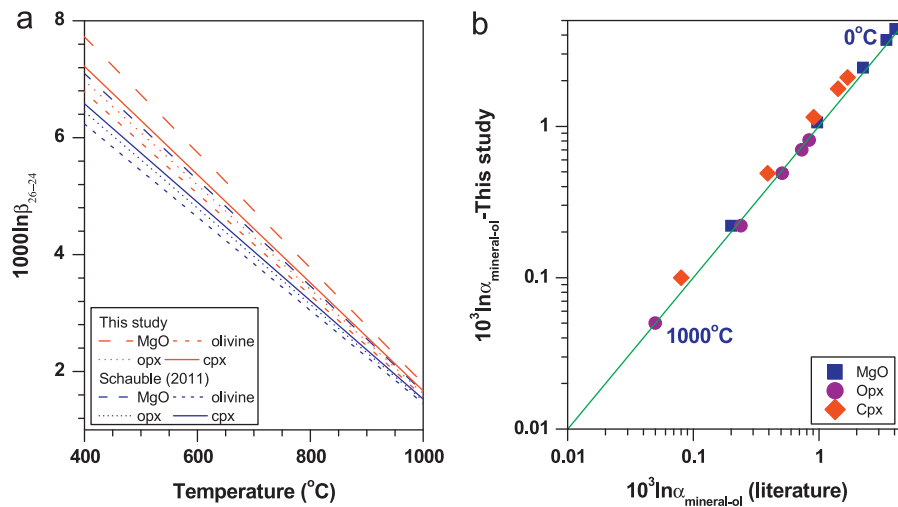


Fig. 3. Comparison of the calculated $^{26}\text{Mg}/^{24}\text{Mg}$ fractionation factors (red lines) with literature values (blue lines). Due to the difference of approximation (LDA in this study and GGA in Schauble (2011)), $1000\ln\beta$ in this study is systematically higher than the values in Schauble (2011), but the $1000\ln\alpha_{\text{mineral-olivine}}$ ($1000\ln\beta_{\text{mineral-olivine}}$) are in excellent agreement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

The formula for oxygen isotope fractionation factors between pyroxene and olivine and comparison with literature data.

	Formula	Data source
$10^3\ln\alpha_{\text{opx-olivine}}$	$0.0591 + 1.1867x - 0.077x^2 + 0.0044x^3$	This study
	$0.08 + 1.027x - 0.0389x^2 + 0.00081x^3$	Méheut et al. (2009)
$10^3\ln\alpha_{\text{cpx-olivine}}$	$0.7129x + 0.0099x^2$	This study
	$0.7257x - 0.04352x^2$	Schauble (2011)

$x = 10^6/T^2$, where T is temperature in Kelvin. The data are fitted with temperature range from 400–1500 °C.

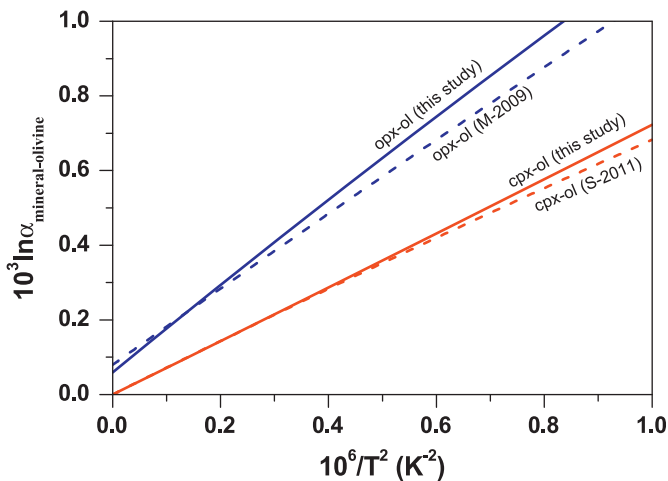


Fig. 4. Comparison of calculated $10^3\ln\alpha_{\text{cpx-ol}}$ and $10^3\ln\alpha_{\text{opx-ol}}$ of $^{18}\text{O}/^{16}\text{O}$ in this study with literature values. The opx-ol data (M-2009) are from Méheut et al. (2009) and cpx-ol data (S-2011) are from Schauble (2011).

important to examine the pressure effect on isotope fractionation. The method adopted in this study has successfully predicted the pressure effect on the volume (namely equation of states) for many minerals including forsterite and majorite (e.g., Li et al., 2007; Wentzcovitch et al., 2010; Yu et al., 2011). The calculated equations of states for pyrope, diopside, and orthoenstatite also agree well with the experimental data (see Fig. S2). Generally, increasing pressure will decrease the minerals volume, and thus increase strength and stiffness of Mg–O bonds, which will further increase $10^3\ln\beta_{26/24}$ of

minerals. As clearly shown in Fig. 5, at the same temperature, $10^3\ln\beta_{26/24}$ of clinopyroxene and pyrope increase dramatically with pressure increasing from 0 GPa to 10 GPa. If $10^3\ln\beta_{26/24}$ of phases in thermodynamic equilibrium are enhanced by the exactly same magnitude with increasing pressure, isotope fractionation factor between two minerals will not be affected by pressure. Otherwise, pressure will inevitably affect inter-mineral isotope fractionation.

Table 3 summarizes polynomial fitting of equilibrium fractionation factors as a function of temperature and pressure. Our calculation shows that, at 1200 K, increasing pressure from 0 GPa to 5 GPa changes $10^3\ln\alpha_{\text{cpx-olivine}}$ from 0.117‰ to 0.159‰, which is indeed negligible at current analytical precision. However, our results also reveal measurable pressure effect on equilibrium isotope fractionation factors between minerals with Mg coordination number of eight (pyrope and majorite) and those with Mg coordination number of six (such as pyroxene and olivine) (Fig. 6). For instance, keeping temperature constant at 1200 K, $10^3\ln\alpha_{\text{cpx-pyrope}}$ increases from 0.673‰ at 0 GPa to 0.785‰ at 3 GPa, and to 1‰ at 10 GPa. Therefore, the pressure effect also plays an important role in changing inter-mineral Mg isotope fractionation at the high temperature and pressure conditions in the deep Earth.

4. Implications for Mg isotope thermometry

4.1. Criteria for an ideal Mg isotope thermometry

Geothermometries provide essential information for the thermal history of rocks and tectonic units. Because large inter-mineral Mg isotope fractionations have been observed in recent literature, such fractionations can be used as a new type of Mg isotope thermometry (e.g., Li et al., 2011; Liu et al., 2011b). There are a few criteria for an ideal Mg isotopic thermometry. First, the thermometry should be based on large isotope fractionation between common rock-forming minerals relative to analytical precision. Second, Mg content in the minerals of interest should be high enough so that measurement of Mg isotopes is relatively easy. And third, inter-mineral isotope fractionation should mainly be a function of temperature, not sensitive to other physical or chemical parameters.

Spinel-olivine Mg isotope thermometry has been suggested in Young et al. (2009) and Schauble (2011) on the basis of isotope fractionation between Mg with coordination number of four

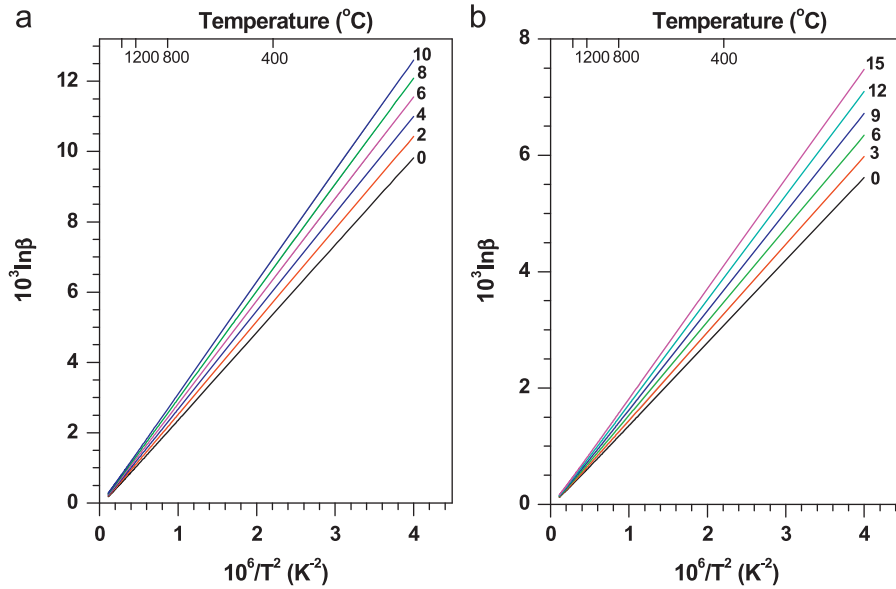


Fig. 5. Pressure effect on $10^3 \ln \beta$ of clinopyroxene and pyrope. Increasing pressure can dramatically increase $10^3 \ln \beta$. Numbers near the solid lines denote pressure with unit of GPa.

Table 3

Equilibrium fractionation factors for olivine, clinopyroxene, orthopyroxene, pyrope, and majorite as a function of temperature and pressure.

	$f_1(P)$	$10^3 f_2(P)$	$10^6 f_3(P)$
$10^3 \ln \alpha_{\text{ol-pyrope}}$	$0.7757 + 0.0436P - 0.0006P^2$	$55.532 - 4.504P + 0.081P^2$	$-6360.30 + 409.18P - 8.29P^2$
$10^3 \ln \alpha_{\text{opx-pyrope}}$	$0.9427 + 0.03582P - 0.0003P^2$	$18.867 - 1.756P - 0.016P^2$	$-2688.10 + 118.57P + 2.02P^2$
$10^3 \ln \alpha_{\text{cpx-pyrope}}$	$0.9462 + 0.0569P - 0.0008P^2$	$53.168 - 4.786P + 0.083P^2$	$-6129.2 + 418.77P - 8.29P^2$
$10^3 \ln \alpha_{\text{cpx-majorite}}$	$0.4411 + 0.0504P - 0.0007P^2$	$51.533 - 4.020P + 0.071P^2$	$-5562.4 + 356.15P - 7.19P^2$

$10^3 \ln \alpha_{A-B} = f_1(P)(10^6/T^2) + f_2(P)(10^6/T^2)^2 + f_3(P)(10^6/T^2)^3$, where T is temperature in Kelvin and P is pressure in GPa. The temperature range for the equations is from 400 K to 2000 K. The equations were fitted based on least squares method.

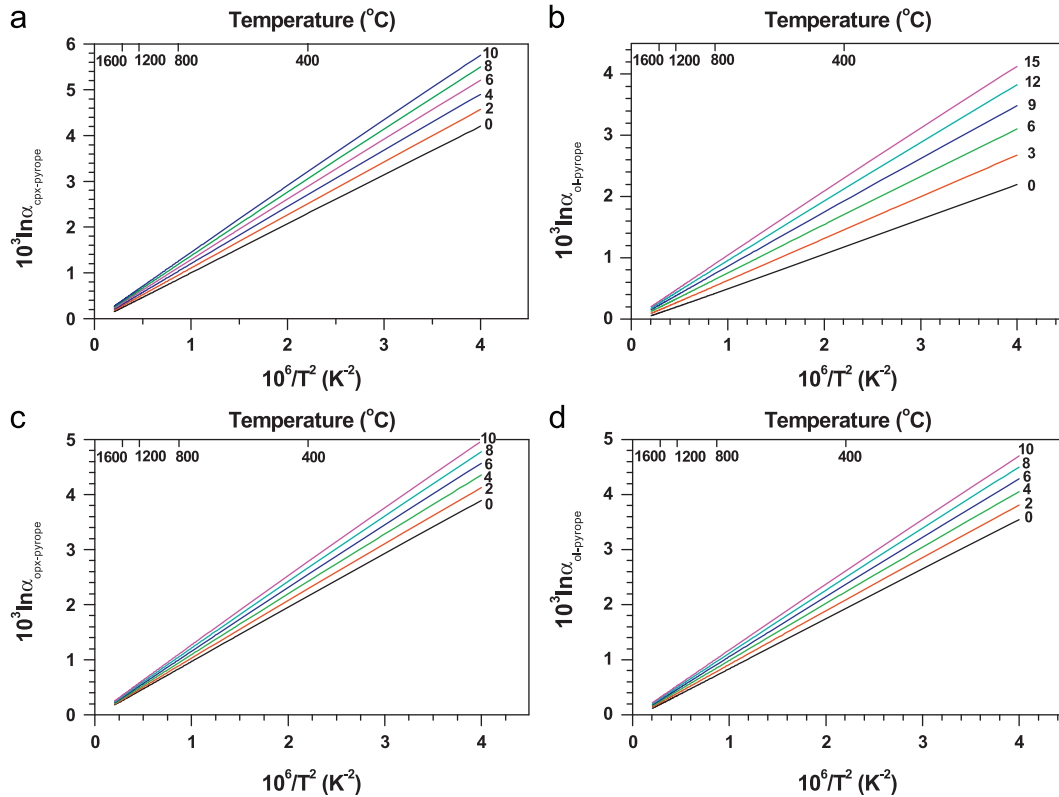


Fig. 6. The pressure effect on $10^3 \ln \alpha_{\text{cpx-pyrope}}$, $10^3 \ln \alpha_{\text{cpx-majorite}}$, $10^3 \ln \alpha_{\text{opx-pyrope}}$, and $10^3 \ln \alpha_{\text{ol-pyrope}}$. Although increasing temperature dramatically decreases magnitude of isotope fractionations, increasing pressure can substantially enhance $10^3 \ln \alpha$. Numbers near the solid lines are pressure in GPa.

(spinel) and six (olivine). However, as pointed out in Liu et al. (2011b), because Mg cations can occupy two positions in natural spinel (tetrahedral and octahedral sites) and their relative proportion is difficult to be quantified, $\Delta^{26}\text{Mg}_{\text{spinel-olivine}}$ is not only a function of temperature but also the chemical composition of spinel. Furthermore, as the theoretical calculations show, substitution of Al^{3+} , Cr^{3+} , and Fe^{3+} in the octahedral site of the spinel can cause significant variations of $1000\ln\beta_{26-24}$ even at temperature up to 1000 K (Schauble, 2011). Therefore, although $\Delta^{26}\text{Mg}_{\text{spinel-olivine}}$ is large (0.25–0.78‰, from Young et al. (2009) and Liu et al. (2011b)) relative to the current precision, fractionation of Mg isotopes between spinel and olivine is not an ideal thermometry.

On the contrary, equilibrium Mg isotope fractionations between garnet, pyroxene, and olivine satisfy all criteria for the ideal thermometry and they have the potential to accurately indicate the temperatures of igneous and metamorphic rocks. The magnitude of Mg isotope fractionation between garnet and minerals with Mg coordination number of six is significantly larger than the current analytical precision ($< 0.05\text{‰ amu}^{-1}$) (Li et al., 2011; Liu et al., 2011b; Wang et al., 2012; Young et al., 2009). Furthermore, YO_6 octahedrons of garnet are well separated with each other by $[\text{SiO}_4]^{4-}$ tetrahedrons unlike the case of spinel where YO_6 octahedrons are shared with edge each other. That Cr^{3+} and Fe^{3+} substitutes Al^{3+} in the Y site will change to a less extent on Mg–O bond length in garnet than the case in spinel. Consequently, $\Delta^{26}\text{Mg}_{\text{garnet-olivine}}$ and $\Delta^{26}\text{Mg}_{\text{garnet-pyroxene}}$ should be much less sensitive to substitution of cations than $\Delta^{26}\text{Mg}_{\text{spinel-olivine}}$. Mg–O bond lengths should be insensitive to the substitution of Ca or Fe on the nearest Mg site since Mg^{2+} cations are also well separated with each other. Therefore, Mg isotope fractionations among garnet, pyroxene, and olivine provide a robust geothermometry.

4.2. Comparison with garnet–clinopyroxene elemental thermometry

Because garnet and clinopyroxene are two of the most common minerals in mafic and ultramafic rocks in the crust and the upper mantle (e.g., Jagoutz et al., 2006; Stixrude and Lithgow-Bertelloni, 2007), thermometries based on major element exchange between garnet and clinopyroxene have been widely used in estimating temperature of mafic and ultramafic metamorphic and igneous rocks (e.g., Brey et al., 1986; Ravna, 2000a; Ravna, 2000b; Simakov and Taylor, 2000; Putirka, 2008). The garnet–clinopyroxene Fe–Mg thermometry with correction of non-ideality of Ca in mineral solid solution was proposed to have uncertainty of 30–50 °C (Ravna and Paquin, 2003). However, these thermometries are all subjected to the uncertainty of estimating the proportions of Fe^{3+} and Fe^{2+} in clinopyroxene due to uncertainty of major element contents measured by electron microprobe and unknown redox conditions of original experiments which were used to calibrate the thermometries. The uncertainty is at least ± 100 °C and it could be larger if the clinopyroxene is iron-poor (Carswell and Zhang, 1999).

Another type of garnet–clinopyroxene thermometry is based on Ca–Tschermack solubility in clinopyroxene coexisting with garnet and its uncertainty of temperature estimates is about 19% with an applicable temperature range from 650 °C to 1700 °C (Simakov and Taylor, 2000). Because major element data were normally reported with uncertainties of one standard deviation, the uncertainty of garnet–clinopyroxene major element thermometry could be greater than 200 °C if the level of confidence is similar to Mg isotope data (2SD). Such large errors of major element thermometry significantly compromise the reliability of applying mineral temperatures to constraining a number of fundamental geological processes such as exhumation

of metamorphic rocks, evolution of the upper mantle, and formation of igneous rocks (e.g., Brey et al., 1986; Carswell and Zhang, 1999; Li et al., 2011; Putirka, 2008; Ravna, 2000a, 2000b; Simakov and Taylor, 2000; Wang et al., 2012; Williams et al., 2009).

Because the precision of Mg isotope data is better than 0.05‰ amu^{-1} (2SD), Mg isotope thermometry can tremendously improve precision of temperature estimate. However, unlike oxygen isotope thermometries not showing measurable pressure effect on isotope fractionations at high temperature (e.g., Valley, 2001), the pressure effect on Mg isotope fractionation between garnet and clinopyroxene should be considered in order to obtain accurate temperature estimate (Table 3). For instance, taking a $\Delta^{26}\text{Mg}_{\text{cpx-pyrope}}$ of 1‰, this value translates into equilibrium temperature of 1025 K at 1 GPa, 1075 K at 3 GPa, and 1130 K at 6 GPa. That is, increasing pressure by 5 GPa increases the estimated temperature by 105 °C. However, if the mineral equilibrium pressure is determined by other methods, the error of temperature estimate mainly comes from uncertainty of Mg isotope analysis. Taking 0.05‰ as the precision of $\delta^{26}\text{Mg}$ data (1σ), the error of Mg isotope thermometry is $\sim \pm 30$ °C, much better than the garnet–clinopyroxene Mg–Fe exchange thermometry.

It is also important to compare the range of applicable temperatures of these two thermometries. Because isotopic diffusion occurs faster than chemical diffusion in a chemically disturbed system (e.g., Leshner, 1990; van der Laan et al., 1994), it takes shorter time to diffuse enough materials to regain inter-mineral isotopic equilibrium than elemental equilibrium. Therefore, the closure temperature for Mg isotope thermometry (below which there is no any significant diffusion of Mg isotopes to change isotopic composition of minerals) should be lower than that of the Fe–Mg exchange thermometry. It thus suggests that the applicable temperature range Mg of isotope thermometry may be larger than the garnet–clinopyroxene elemental thermometry.

Finally, we emphasize that both isotopic and elemental thermometries can only be used to systems in thermodynamic equilibrium. The estimated temperature could be erroneous if the rocks are retrograded or not fresh unless additional evidences show that garnet and clinopyroxene is still in chemical equilibrium.

4.3. Applications of Mg isotope thermometries

Because garnet, clinopyroxene, orthopyroxene, and olivine widely occur in mafic rocks, garnet–pyroxene and garnet–olivine Mg isotope thermometries can be applied to a variety of rocks, including skarns, granulites, garnet–pyroxenites, eclogites, and garnet-bearing peridotites. As an example, we apply garnet–clinopyroxene Mg isotope thermometry to investigate the equilibrium temperature of well-studied eclogites from Bixiling in the Dabie Orogen, Central-Eastern China (Xiao et al., 2000; Zhang et al., 1995) and those from Kaalvallei and Bellsbank kimberlite in South Africa (Wang et al., 2012; Williams et al., 2009).

Garnets, omphacites, and whole rock powder of five fresh Bixiling eclogites were measured for Mg isotope composition in Li et al. (2011). Although retrograde minerals such as amphibole and plagioclase are observed as symplectites in the eclogites, the analyzed minerals are fresh and the peak metamorphic pressure of the eclogites is > 2.7 GPa (Li et al., 2011; Zhang et al., 1995). Taking that the equilibrium pressure of garnet and omphacite is 3 GPa and $\Delta^{26}\text{Mg}_{\text{omphacite-garnet}} = 1.14 \pm 0.04\text{‰}$ (Li et al., 2011), the temperature estimated by clinopyroxene–garnet Mg isotope thermometry is 732 (+20/–15) °C (Fig. 7). This value is slightly higher than the temperature range estimated from garnet–clinopyroxene Fe^{2+} –Mg thermometry (541–724 °C) (Li et al., 2011; Zhang et al., 1995), but well consistent with the results of fresh eclogites reported in Xiao et al. (2000) (718–757 °C).

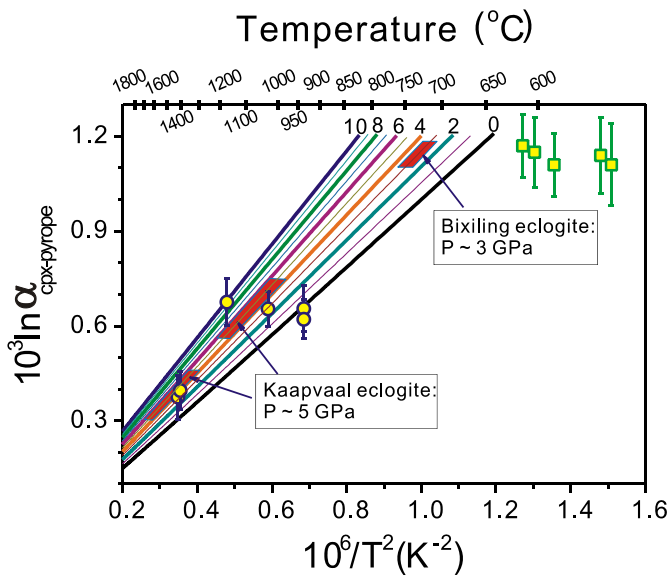


Fig. 7. Application of clinopyroxene–garnet Mg isotope thermometry to estimating equilibrium temperature of eclogites. The green squares are Bixiling eclogites from the Dabie orogen, Central-Eastern China. Mg isotope data and temperature estimated by clinopyroxene–garnet Fe–Mg exchange thermometry are from Li et al. (2011). Assuming that the equilibrium pressure is 3 GPa and $10^3 \ln \alpha_{\text{cpx-pyroxene}}$ is $1.14 \pm 0.04\%$, the estimated temperature is $732 (+20/-15)^\circ\text{C}$. The yellow circles are data of Kaalvaal eclogites from Kaalvallei and Bellsbank kimberlites, South Africa (Wang et al., 2012). The pressure for Kaalvaal eclogites was estimated around 5 GPa (Helen Williams, Personal Communication), and the temperatures estimated using Mg isotope thermometry are well consistent with the values based on garnet–clinopyroxene Fe–Mg exchange thermometry (Williams et al., 2009). Numbers near the solid lines are pressure in GPa. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Application of the Mg isotope thermometry to eclogites observed in Kaalvallei and Bellsbank kimberlites in South Africa also gives consistent temperature data with the values estimated by garnet–clinopyroxene Fe–Mg exchange thermometry (Williams et al., 2009). For instance, temperatures of sample Kaalvallei-A and 382 using Mg isotope thermometry are 1440°C and 1087°C , respectively, close to the values (1401°C and 1030°C) obtained by garnet–clinopyroxene elemental thermometry in Williams et al. (2009). The agreement of temperatures obtained by independent methods demonstrates that the Mg isotope thermometry could provide a reliable and independent tool in estimating temperatures in garnet-bearing mafic rocks.

We should mention that the large fractionation of Mg isotopes between garnet and phengite was also observed in the Bixiling eclogites (Li et al., 2011). Therefore, fractionation of Mg isotopes between garnet and other common mafic minerals with Mg coordination number of six (such as amphibole and biotite) could provide more useful thermometries with wider applications. Clearly, more theoretical and experimental work is warranted to fully establish such promising thermometries in the future.

5. Conclusions

Although high precision Mg isotope data of igneous and metamorphic rocks are increasingly published in literature, theoretical and experimental studies for Mg isotope fractionation mechanism are still rare. This study investigates equilibrium fractionation of Mg isotopes between minerals with different coordination numbers of Mg (i.e., eight in pyrope and six in pyroxene and olivine). We also estimate Mg isotope equilibrium fractionation factors of majorite, where $1/4$ of Mg is six-fold

coordinated and $3/4$ is eight-fold. Although the reduced partition function ratios of $^{26}\text{Mg}/^{24}\text{Mg}$ in this study are systematically different than the values in previous study (Schauble, 2011) due to different approximation in the first-principles calculation, the equilibrium fractionation factors ($\Delta^{26}\text{Mg}_{\text{cpx-ol}}$ and $\Delta^{26}\text{Mg}_{\text{opx-ol}}$) are in good agreement, demonstrating that our results are reliable and consistent.

Our calculation predicts significant Mg isotope fractionation among garnet, pyroxene, and olivine with different coordination numbers, consistent with the observed fractionation between clinopyroxene and garnet in natural fresh eclogites. Mg isotope fractionation between garnet and pyroxene (and olivine) could be used a novel geothermometry in the study of high-temperature garnet-bearing mafic rocks. Furthermore, this study shows that, although Mg isotope fractionation is dominantly controlled by temperature, pressure may also play an important role in changing inter-mineral fractionations. If the mineral equilibrium pressure can be obtained by other methods, clinopyroxene–garnet Mg isotope thermometry could provide independent temperature estimates with precision much better than the traditional garnet–clinopyroxene elemental thermometry on the basis of major element exchange. Equations of garnet–orthopyroxene and garnet–olivine Mg isotope thermometries are also presented in this study.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.epsl.2013.02.025>.

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