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# High-temperature inter-mineral magnesium isotope fractionation in mantle xenoliths from the North China craton

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## ABSTRACT

To investigate the magnitude and mechanism of inter-mineral Mg isotope fractionation at mantle temperatures, we measured Mg isotopic compositions of coexisting olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), phlogopite (Phl) and spinel (Spl) from harzburgite, lherzolite and clinopyroxenite xenoliths in the North China craton. These xenoliths are well-characterized and formed over a wide temperature range from ~800 to 1150 °C. The coexisting Opx and Ol have constant and indistinguishable Mg isotopic compositions, with $\delta^{26}$Mg ranging from −0.29 to −0.22‰ in Ol and from −0.28 to −0.22‰ in Opx ($\Delta^{26}Mg_{Opx-Ol} = \delta^{26}Mg_{Opx} - \delta^{26}Mg_{Ol} = -0.04$ to +0.04‰; n = 11). By contrast, Mg isotopic compositions of Cpx and Phl are variable and slightly heavier than coexisting Ol ($\Delta^{26}Mg_{Cpx-Ol} = 0$ to +0.13‰, n = 13; $\Delta^{26}Mg_{Phl\text{-}Ol} = +0.11$ to +0.20‰, n = 3). Isotope fractionations between coexisting Cpx and Ol are correlated with temperatures, implying equilibrium isotope fractionation. The degree and direction of isotope fractionations among these mantle silicates agree with theoretical predictions, suggesting that inter-mineral Mg isotope fractionation is primarily controlled by the Mg–O bond strength, with stronger bonds favoring heavier Mg isotopes. Cpx and Phl have shorter and thus stronger Mg–O bonds, and hence are isotopically heavier than coexisting Ol. Compared with coexisting silicates, $\delta^{26}$Mg values of spinels are more variable and much heavier, ranging from +0.03 to +0.28‰. The $\Delta^{26}Mg_{Spl-Ol}$ values vary significantly from +0.25 to +0.55‰ (n = 10) and show an excellent, positive, linear correlation with $10^6/T^2$(K) [$\Delta^{26}Mg_{Spl-Ol} = 0.63(\pm 0.12) \times 10^6/T^2(K) - 0.03(\pm 0.08)$], indicating equilibrium Spl–Ol isotope fractionation. The absence of intra-mineral isotopic variation and quantitative diffusion calculations further confirm isotope exchange equilibrium between coexisting Spl and Ol. Our results demonstrate the existence of measurable Mg isotope fractionation between mantle minerals and suggest that the large high-temperature equilibrium Spl–Ol Mg isotope fractionation in peridotite xenoliths can potentially be used as a geothermometer in mantle geochemistry.

## 1. Introduction

Whether there is detectable high-temperature inter-mineral Mg isotope fractionation between coexisting mantle minerals and whether the isotope fractionation reflects equilibrium partitioning or open-system behavior, are highly debated. Several studies reveal limited (i.e., ≤0.2‰) Mg isotope fractionation between coexisting pyroxene and olivine in fifteen mantle peridotite xenoliths (Handler et al., 2009; Wiechert and Halliday, 2007; Yang et al., 2009). By contrast, two studies, each based on two samples, reported significant (up to ~0.4‰) Mg isotope fractionation between coexisting pyroxene and olivine (Chakrabarti and Jacobsen, 2010; Young et al., 2009). Specifically, Young et al. (2009) reported up to 0.8‰ Mg isotope fractionation between coexisting spinels and olivines in two peridotite xenoliths and interpreted the large isotope fractionation as a result of equilibrium isotope partitioning.

The direct way to solve the above debates is to experimentally calibrate Mg isotope fractionation factors in mantle minerals and melts. However, to date, such studies are still not available. Alternatively, equilibrium isotope fractionation is temperature-dependent, with the magnitude of isotope fractionation decreasing with increasing temperature. Therefore, inter-mineral Mg isotope fractionations between coexisting minerals in a suite of natural samples that formed over a large range of temperature, if any, should show temperature-dependent variation. None of those earlier studies mentioned above, however, have taken into account the temperature effects.

Here, we measured coexisting olivine, orthopyroxene, clinopyroxene, phlogopite, and spinel from thirteen mantle xenoliths in the North

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China craton that formed over a wide (>300 °C) temperature range. Our results demonstrate that there are detectable equilibrium Mg isotope fractionations between coexisting spinel/clinopyroxene/phlogopite and olivine, and undetectable fractionation between coexisting orthopyroxene and olivine in mantle xenoliths; the large spinel–olivine Mg isotope fractionation can potentially be used as a geothermometer in mantle geochemistry; and the Earth, as represented by these mantle xenoliths, has a chondritic Mg isotopic composition.

## 2. Samples

Samples studied here include olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), spinel (Spl) and phlogopite (Phl) from thirteen peridotite and clinopyroxenite xenoliths hosted by three Cenozoic volcanoes in the North China craton (NCC). All samples represent residues after the extraction of partial melts in the spinel stability field, and are well-characterized, with petrology, mineralogy, chemical and isotopic compositions presented in previous studies (Wu et al., 2006; Zhao et al., 2007).

### *2.1. Kuandian peridotite xenoliths*

The Kuandian peridotite xenoliths were collected from the Huangyishan alkaline basalts in the NCC (Wu et al., 2006). They range from refractory harzburgite to relatively fertile lherzolite, and show a complex distribution in the rare earth element (REE) patterns, with depletion to remarkable enrichment of light REEs relative to heavy REEs, suggesting various degrees of metasomatism. Based upon the two-pyroxene Ca thermometry of Brey and Köhler (1990), the Kuandian peridotites formed over a large range of equilibrium temperature from 807 to 1150 °C, with the amphibole-bearing lherzolite (HY2-06) having the lowest temperature of 807 °C (Wu et al., 2006). Uncertainties of the estimated equilibrium temperatures are ±15 °C ($1\sigma$) that are independent of compositional parameters (Brey and Köhler, 1990).

The mineral modes of Kuandian peridotites are: 52–75% Ol, 23–31% Opx, 3–16% Cpx, and 1–3% Spl, with sample HY2-06 containing ~2% amphibole (Wu et al., 2006). The olivine separates have Fo contents [$=$ molar $100\times\mathrm{Mg}/(\mathrm{Mg}+\mathrm{Fe}^{2+})$] ranging from 90.2 to 91.8, and represent residues after the extraction of various extents of partial melts in the spinel stability field (Wu et al., 2006). Clinopyroxene separates have trace element patterns similar to bulk peridotites, indicative of various degrees of enrichment due to secondary metasomatism. The spinels exhibit relatively uniform contents of MgO (19.4 to 22.3 wt.%) and FeO (10.4 to 12.1 wt.%), but large variations in $Al_2O_3$ (43.3 to 56.8 wt.%), $Cr_2O_3$ (8.7 to 25.7 wt.%), and Cr# [$=$ molar $100\times\mathrm{Cr}/(\mathrm{Cr}+\mathrm{Al})$, from 9.0 to 28.5] (Wu et al., 2006).

Olivine, Opx, Cpx and Spl from ten Kuandian peridotite xenoliths were chosen for Mg isotopic analysis. Magnesium isotopic compositions of these bulk peridotites were reported in Teng et al. (2010a).

### *2.2. Hannuoba olivine–clinopyroxenite xenolith*

The Hannuoba phlogopite-bearing olivine–clinopyroxenite (DMP06-50) was collected from the Cenozoic Hannuoba volcano in the NCC. This sample is composed of 20% Ol, 2% Opx, 60% Cpx, 5% Spl, and 13% phlogopite, with a two-pyroxene Ca equilibrium temperature of 965 °C (Zhao et al., 2007). As shown by the high modes of phlogopite and clinopyroxene as well as chemical compositions of clinopyroxene, this clinopyroxenite sample was subject to strong metasomatism. The clinopyroxene separates display a strong LREE-enriched pattern with $(\mathrm{La/Yb})_N=12$ (Zhao et al., 2007) and the phlogopite is enriched in alkaline elements, Ti, Cr, and radiogenic Sr isotopes, suggesting strongly secondary metasomatism by $H_2O$-rich fluids and formation through interactions of melts with lherzolites (Zhao et al., 2007). Here, Ol, Opx, Cpx, and Phl from this olivine–clinopyroxenite sample were separated for Mg isotopic analysis.

### *2.3. Sanyitang peridotite xenoliths*

The Sanyitang peridotite xenoliths were collected from Cenozoic basalts from the Sanyitang volcano in Jining area of the NCC. Two peridotite samples (SYT06-41 and SYT06-42) were chosen for Mg isotopic analysis in this study. Both are phlogopite-bearing spinel lherzolites and have similar two-pyroxene Ca equilibrium temperatures (941 and 945 °C) (Zhao et al., 2007). The mineral mode is 60% Ol, 15% Opx, 13% Cpx, and 10% phlogopite in sample SYT06-41, and 58% Ol, 17% Opx, 10% Cpx, and 13% phlogopite in sample SYT06-42. Significant metasomatism also occurred for these two samples, as indicated by their high phlogopite modes.

Magnesium isotopic compositions of Ol, Opx and Cpx from these two peridotites were analyzed by Yang et al. (2009). Here we analyzed the phlogopite separates and re-analyzed Ol and Cpx from these two spinel lherzolite samples.

## 3. Analytical methods

Dissolution of silicate minerals, column chemistry and instrumental analysis followed procedures reported in previous studies (Li et al., 2010, 2011; Liu et al., 2010; Teng et al., 2007, 2010a,b; Yang et al., 2009). Only a brief description is given below.

Approximately 1–3 mg Ol, Opx, Cpx and Phl were dissolved in a mixture of Optima-grade $\mathrm{HF}+\mathrm{HNO_3}+\mathrm{HCl}$ at 160 °C. Spinel separates were crushed to 40–60 mesh size and handpicked under a binocular microscope. Six to eight unaltered grains (weighted 1–2 mg) of each spinel sample were then pulverized in an agate mortar with an agate pestle, and cleaned with Milli-Q water (18.2 MΩ cm) three times. For some peridotite samples, different batches of spinel separates from the same sample were analyzed to evaluate possible intra-mineral Mg isotopic variation. The crushed spinel powder was completely dissolved in 1:1 $\mathrm{HCl}+\mathrm{HF}$ in high-pressure bombs in a muffle furnace at 220 °C for about 30 h. In preparation for column chemistry, all sample solutions were dried down, refluxed with concentrated Optima $HNO_3$ at 160 °C, and finally dissolved in 1 N $HNO_3$.

Magnesium was purified by cation exchange chromatography using Bio-Rad AG50W-X8 (200–400 mesh) resin. Each sample was processed through column chemistry twice in order to obtain a pure Mg solution with concentration ratios of other cations to Mg less than 0.05. Some spinel samples were processed through column chemistry four times to further evaluate the efficiency of our procedure on separation of matrix elements (e.g., Cr) from Mg. The final solutions were heated to dryness in a vented laminar-flow hood and dissolved in 3% $HNO_3$ for mass spectrometry.

Magnesium isotopic ratios were measured by the sample-standard bracketing method using a *Nu Plasma* multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the Isotope Laboratory of the University of Arkansas. At least one well-characterized standard was run during each batch of sample analysis. Magnesium isotope data are reported in the δ-notation relative to Mg isotope standard DSM3: $\delta^{x}\mathrm{Mg}=[(^{x}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{x}\mathrm{Mg}/^{24}\mathrm{Mg}_{\mathrm{DSM3}})-1]\times 10^3$, where x refers to 25 or 26.

The long-term external reproducibility on $^{26}\mathrm{Mg}/^{24}\mathrm{Mg}$ ratio measurement is better than ±0.07‰ (2 SD), based on replicate analyses of natural and synthetic standard solutions (Teng et al., 2010a). An in-house olivine standard from Kilbourne Hole (KH) and seawater were analyzed multiple times for accuracy check during the course of this study. Multiple analyses of KH yielded an average $\delta^{26}\mathrm{Mg}$ value of $-0.27\pm0.04$ (n = 13; 2 SD, Table 1), identical to that ($\delta^{26}\mathrm{Mg}=-0.27\pm0.07$; 2 SD) reported by Teng et al. (2010a) and Liu et al. (2010). Seawater analyzed in this study yielded $\delta^{26}\mathrm{Mg}$ of $-0.86\pm0.05$ (2 SD), in agreement with previously reported values of $-0.85\pm0.05$ (2 SD) (Li