



Investigation of magnesium isotope fractionation during granite differentiation: Implication for Mg isotopic composition of the continental crust

Sheng-Ao Liu ^{a,b,*}, Fang-Zhen Teng ^{b,*}, Yongsheng He ^a, Shan Ke ^{b,c}, Shuguang Li ^a

^a CAS Key Laboratory of Crust–Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

^b Isotope Laboratory, Department of Geosciences and Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701, USA

^c State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Science and Mineral Resources, China University of Geosciences, Beijing 100083, China

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ABSTRACT

High-precision Mg isotopic analysis was performed on a suite of well-characterized I-type granitoids and associated hornblende and biotite minerals from the Dabie Orogen in central China, to address the behavior of Mg isotopes during granite differentiation. Although these granitoids formed through different degrees of partial melting and fractional crystallization, with large variations in elemental and mineral compositions, their $\delta^{26}\text{Mg}$ values vary from -0.26 to -0.14 and are indistinguishable within our analytical precision ($\pm 0.07\%$; 2 SD). Coexisting hornblendes and biotites in these granitoids display similar Mg isotopic composition, with $\delta^{26}\text{Mg}$ ranging from -0.31 to -0.14 in hornblendes and -0.23 to -0.12 in biotites. The inter-mineral fractionation factors ($\Delta^{26}\text{Mg}_{\text{Hbl-Bt}} = \delta^{26}\text{Mg}_{\text{Hbl}} - \delta^{26}\text{Mg}_{\text{Bt}}$) vary from -0.10 to -0.02 , with an average $= -0.06 \pm 0.08$ (2 SD). The limited inter-mineral fractionation agrees with the theoretic prediction that Mg cations in both hornblende and biotite are octahedrally coordinated with oxygen, which restricts the magnitude of equilibrium isotope fractionation. Overall, data from both bulk granitoids and associated mineral separates suggest that Mg isotope fractionation during I-type granite differentiation is limited. Collectively, granitoids studied here have Mg isotopic composition similar to that of terrestrial basalts and peridotites ($\delta^{26}\text{Mg} = -0.21 \pm 0.07$ vs. -0.25 ± 0.07 ; 2 SD), confirming that magmatic processes do not significantly fractionate Mg isotopes. The continental crust in the Dabie Orogen, as sampled by these I-type granitoids, has a mantle-like Mg isotopic composition. Given that significant Mg isotope fractionation occurs during chemical weathering processes, Mg isotopes may potentially be used for tracing granite genesis, in particular, if sedimentary materials are involved in granite sources.

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1. Introduction

Recent developments of analytical techniques and observations from both natural and experimental studies have greatly improved our understanding of the behaviors of Mg isotopes during a variety of geological processes. For example, Mg isotopes have been documented to largely fractionate during weathering (Tipper et al., 2006, 2008; Brenot et al., 2008; Pogge von Strandmann et al., 2008; Hippler et al., 2009), evaporation (Davis et al., 1990; Richter et al., 2007), and chemical and thermal diffusion (Richter et al., 2008; Huang et al., 2009). These large variations are far beyond currently achievable analytical precision ($>5\%$ vs. 0.07%) and make Mg isotopes a potentially useful tracer for these processes. By contrast, little Mg isotope fractionation is inferred to occur during crystal–melt differentiation of basaltic magmas (Teng et al., 2007, 2010), which confirms that equilibrium isotope fractionation

during high-temperature processes is small (Bigeleisen and Mayer, 1947; Urey, 1947).

Compared to studies of Mg isotopes in basalts, Mg isotopic systematics of continental rocks, especially granitoid rocks, remain poorly constrained. This partially results from the relatively low Mg concentrations of granitoids, which makes it difficult to precisely measure their Mg isotopic compositions. To date, only one study has reported Mg isotopic data for biotites in granitoids and found $\sim 0.8\%$ variation, with biotites in more evolved granites having heavier Mg isotopic compositions (Shen et al., 2009). This large isotopic variation was interpreted as the source effect that the granitoids had assimilated various amounts of recycled surface-weathered materials (Shen et al., 2009), by assuming that magmatic differentiation does not fractionate Mg isotopes significantly, as shown in studies of basaltic lavas from Kilauea Iki lava lake (Teng et al., 2007). However, it remains uncertain whether Mg isotopes are fractionated during fractional crystallization of granitic magmas or not, which occurs at lower temperatures than basaltic magmas.

In order to investigate the behaviors of Mg isotopes during granite differentiation and constrain Mg isotopic composition of the continental

* Corresponding authors.

E-mail addresses: lsa@mail.ustc.edu.cn (S.-A. Liu), fteng@uark.edu (F.-Z. Teng).

crust, we carried out high-precision Mg isotopic analysis on a suite of I-type granitoids and associated hornblende and biotite minerals from the Dabie Orogen in central China. Compared to A-type and S-type granites, I-type granites are the most common type and represent the end-products of extreme fractional crystallization of primitive basaltic magmas or remelting (s) of pre-existing crust (Kemp et al., 2007). Our results indicate that Mg isotope fractionation during granite differentiation is limited, and hence Mg isotopic composition of granites can be used to trace that of their sources. The continental crust in the Dabie Orogen, based on I-type granitoids, has a mantle-like Mg isotopic signature. This is in sharp contrast to biotites from I-type granitoids in southern California (Shen et al., 2009), suggesting overall a heterogeneous Mg isotopic composition of the continental crust.

2. Geological background and samples

The Dabie Orogen in central China is the largest ultrahigh pressure metamorphic (UHPM) belt on the Earth and was formed by northward subduction of the Yangtze Block to the North China Block in Triassic (see reviews of Li et al., 1993, 2000). The exposed UHPM rocks are composed mainly of granitic gneisses, with minor proportions of other rock types (e.g., eclogite, jadeite quartzite, marble and metapelite) enclosed as layers within the regional granitic gneisses (e.g., Liou et al., 2000). The exhumed UHPM rocks were later intruded by voluminous post-collisional granitoids and minor mafic-ultramafic plutons during the early Cretaceous (e.g., Li et al., 1998a,b, 1999; Ma et al., 1998; Jahn et al., 1999). These post-collisional granitoids have been widely investigated in previous studies (Chen et al., 2002; Wang et al., 2007; Xu et al., 2007; Zhao et al., 2007; Huang et al., 2008), suggesting that the granitoid rocks were derived from high-pressure partial melting of the mafic lower continental crust of the mountain root during ~143 to 130 Ma (Wang et al., 2007; Xu et al., 2007).

Eleven samples including eight granites and three granodiorites were selected for Mg isotopic analysis. They are classified as I-type granitoids in terms of the metaluminous affinity (e.g., A/CNK = 0.82 to 0.96; Table 1), and belong to high-K calc-alkaline rock series with total $K_2O + Na_2O$ contents ranging from 7.7 to 9.3 wt.% (Table 1). The eight granites are coarse-grained and consist of K-feldspar (35–45%), plagioclase (25–35%), quartz (20–35%), biotite (0.5–15%), and hornblende (0.5–8%) (Fig. 1). Compared to the granites, the granodiorites have higher modal proportions of hornblende (8–12%), with plagioclase (40–60%), K-feldspar (20–25%), quartz (10–15%), and biotite (5–8%). Both granites and granodiorites contain small amount of accessory minerals of zircon and sphene (Fig. 1). Hornblende and biotite occur as the dominant magnesian silicate

phases in these granitoids (Fig. 1) with modal abundance ratios between hornblende and biotite ranging from ~0.1 to 10 (Fig. 2a). These large mineralogical variations correspond to significant variations in bulk granitoid chemical compositions, e.g., SiO_2 (65.4 to 70.3 wt.%) and MgO (0.66 to 3.31 wt.%) (Fig. 2b).

3. Analytical methods and accuracy check

Hornblende and biotite grains were first separated within the grain-size fraction of 180–300 μm by using a Frantz® magnetic separator, and then handpicked under a binocular microscope. All mineral grains are unaltered and approximately 100% pure after twice handpickings. Biotite grains are brown to black in color and translucent to opaque; hornblende mineral grains generally occur as brown or black, stubby, prismatic crystals.

Major element concentrations of granitoids were determined by a PANalytical AXIOS advanced sequential X-ray spectrometer at University of Göttingen. The long-term analytical precision is better than 1% (Hartmann, 1994). Magnesium isotopic analyses were performed at the Isotope Laboratory of the University of Arkansas, Fayetteville. Procedures for sample dissolution, column chemistry and instrumental analysis are similar to those reported in previous studies (Teng et al., 2007, 2010; Yang et al., 2009). A brief description is given below.

Approximately 2–30 mg of samples was dissolved, based on their Mg concentrations, in order to obtain ~10 μg Mg for high-precision isotopic analysis. Samples were first dissolved in a 3:1 (v/v) mixture of Optima-grade HF and HNO_3 acids in a Savillex screw-top beaker, followed by heating at a temperature of 160 °C on a hotplate in an exhaust hood. The sample solutions were then dried at 120 °C. The dried residues were refluxed with a 1:3 (v/v) mixture of Optima-grade HNO_3 and HCl acids, followed by heating at 160 °C and then evaporating to dryness. The samples were refluxed with concentrated HNO_3 at 160 °C until complete dissolution was achieved, and subsequently evaporated to dryness at 80 °C. This dried residue was finally dissolved in 1 N HNO_3 , in preparation for ion exchange column chemistry.

Magnesium was purified by cation exchange chromatography using Bio-Rad 200–400 mesh AG50W-X8 cation exchange resin. The Bio-Rad 200–400 mesh AG50W-X8 resin was washed by using 6 N HCl, 18.2 M Ω cm Milli-Q® water, 0.5 N HF, and 1 N HNO_3 multiple times. Before processing samples, well-characterized standard solutions including pure Mg standard, synthetic standard and olivine standard were first processed through the column chemistry to test the new set of resin. The same column procedure was then processed 2 times for all sample solutions in order to obtain a pure Mg solution.

Table 1

Whole-rock geochemical characteristics and modal abundance of biotite and hornblende in the granitoids from the Dabie Orogen.

Sample no.	Modal abundance (%)		SiO_2	MgO	Na_2O	K_2O	CaO	Al_2O_3	A/CNK	CIA
	Biotite	Hornblende								
<i>Granite</i>										
07LD-1	0.5–1	5–8	69.2	1.08	4.73	3.84	2.38	15.9	0.94	48.5
07LD-2	1–2	5–8	68.5	1.32	4.75	3.74	2.49	15.8	0.93	48.3
07ZB-1	3–5	0.5–1	68.6	0.91	5.10	3.96	2.14	16.3	0.95	48.7
07ZB-6	5–10	3–5	65.6	1.29	5.31	4.02	2.70	17.1	0.92	47.8
07FJ-2	3–5	0.5–1	70.3	0.66	4.59	4.37	1.86	15.5	0.96	48.9
07FJ-6	5–10	1–2	68.1	1.46	4.12	3.54	3.06	15.1	0.89	47.5
07DT-3	5–15	0.5–2	67.3	1.39	4.22	4.36	2.36	15.5	0.94	48.4
YFD-8	5–10	0.5–1	68.7	1.25	4.43	3.62	2.42	15.8	0.94	47.9
<i>Granodiorite</i>										
07MC-1	3–5	10	65.9	3.20	4.09	3.72	3.49	14.7	0.83	45.5
07MC-3	5–8	10–12	65.4	3.31	4.21	3.60	3.63	14.8	0.82	45.2
07MC-6	3–5	8–10	66.8	2.92	4.21	3.76	3.27	14.6	0.84	45.6

Major element data are normalized to 100% on a volatile-free basis. Data for sample YFD-8 are from Wang et al. (2007). A/CNK is the molar ratio of $Al_2O_3/(CaO + Na_2O + K_2O)$. CIA, the chemical index of alteration, is the molar ratio of $100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$ as defined by Nesbitt and Young (1982).

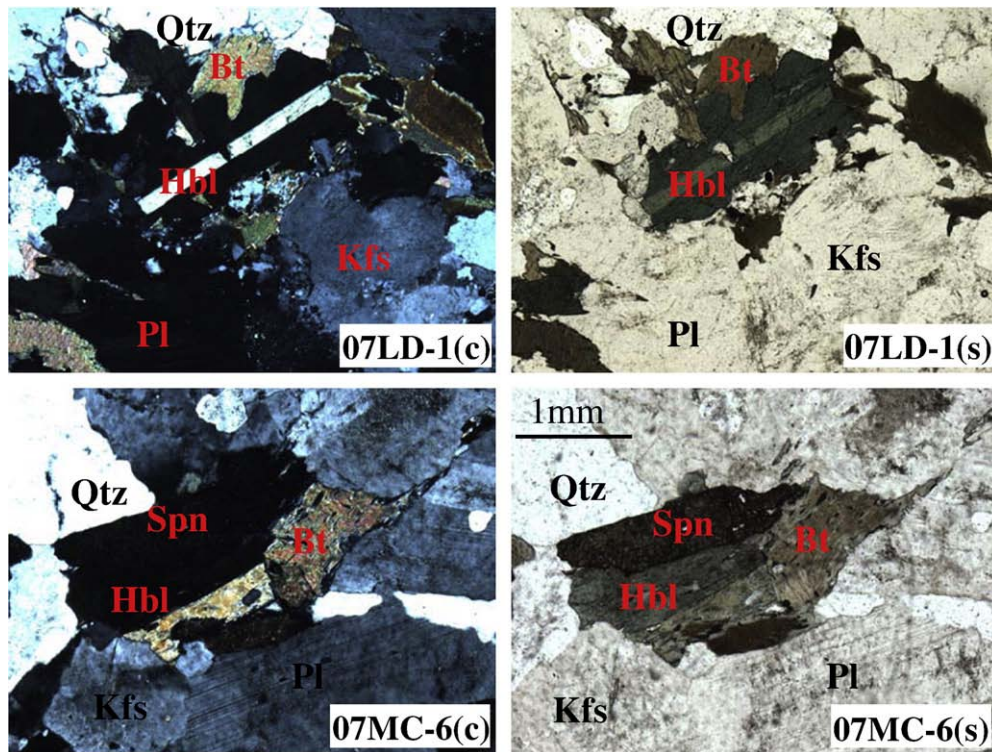


Fig. 1. Photomicrographs for representative granite sample (07LD-1) and granodiorite sample (07MC-6) from the Dabie Orogen. “(c)” means under cross polarizer; “(s)” means under single polarizer; Hbl = hornblende; Bt = biotite; Pl = plagioclase; Kfs = K-feldspar; Qtz = quartz; Spn = sphene.

For some hornblende and biotite samples, an additional anion exchange chromatography with Bio-Rad 200–400 mesh AG1-X8 pre-cleaned resin in 1 N HCl–0.5 N HF that aims to separate Mg from Ti was applied. The final solutions were heated to dryness in a vented laminar-flow hood and subsequently dissolved in 3% HNO₃ for mass spectrometry.

Magnesium isotopic compositions were determined by the sample-standard bracketing method using a *Nu Plasma* high-resolution multicollector – inductively coupled plasma – mass spectrometer (MC–ICP–MS). Isotopic analysis was conducted at a low-resolution mode, with ²⁶Mg, ²⁵Mg and ²⁴Mg measured simultaneously in separate Faraday cups (H5, Ax and L4, respectively). Each sample solution was repeated 4 times on ratio measurements within a session. Magnesium isotope data are reported in standard δ -notation in per mil relative to DSM-3 (Galy et al., 2003):

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

where *X* refers to 25 or 26.

The long-term external reproducibility on ²⁶Mg/²⁴Mg ratio is ± 0.07 (2 SD), based on replicate analysis of natural and synthetic standard samples (Teng et al., 2010). Two Mg isotope standard solutions, including an in-house Kilbourne Hole olivine standard (KH-1) and a synthetic granite standard solution (IL-granite) with element concentration ratio of Mg:Al:Fe:Ca:K:Na:Ti:Ni = 1:30:5:5:20:10:0.1:0.1, were analyzed for accuracy check during the analysis of samples. The olivine KH-1 yielded a $\delta^{26}\text{Mg}$ value of -0.27 ± 0.04 (2 SD), which is in agreement with that reported by Teng et al. (2010) ($\delta^{26}\text{Mg} = -0.27 \pm 0.07$; 2 SD, $n = 16$). The synthetic granite standard (IL-granite), with one processed through main Mg column only and two processed through both main Mg column and Ti column, yielded a $\delta^{26}\text{Mg}$ value of -0.02 ± 0.03 (2 SD; $n = 3$, Table 2), identical to the expected value of 0. The

analyzed results of standard solutions, therefore, confirm that our data are accurate.

San Carlos olivine standard studied by Charkrabarti and Jacobsen (2010) was also analyzed here for inter-laboratory comparison, which yielded a $\delta^{26}\text{Mg}$ value of -0.27 ± 0.07 (2 SD), similar to that ($\delta^{26}\text{Mg} = -0.19$) reported by Young et al. (2009), Kilbourne Hole olivine and global oceanic basalts and peridotites (Teng et al., 2007, 2010; Handler et al., 2009; Yang et al., 2009). Our value however, is much heavier than that ($\delta^{26}\text{Mg} = -0.55$) reported by Charkrabarti and Jacobsen (2010). The cause for these differences is unknown and further collaborative studies are needed.

4. Results

Major elemental concentrations of granitoids are reported in Table 1. Magnesium isotopic data of granitoid whole-rocks and hornblende and biotite separates, together with reference materials, are reported in Table 2. Samples including the synthetic granite standard (IL-granite) that were processed through both Ti column chemistry and main Mg column chemistry have similar Mg isotopic compositions to those that were only processed through the main Mg column chemistry (Table 2), suggesting that our main Mg column chemistry can effectively separate Ti from Mg.

The granitoids define a narrow range in $\delta^{26}\text{Mg}$ from -0.26 to -0.14 ($n = 11$), with an overall variation of 0.12 falling within our external precision of ± 0.07 (2 SD). $\delta^{26}\text{Mg}$ values vary from -0.26 to -0.14 in granites and from -0.24 to -0.18 in granodiorites, respectively (Fig. 2c). Hornblende and biotite separates in these granitoids have $\delta^{26}\text{Mg}$ values ranging from -0.31 to -0.14 and from -0.23 to -0.12 , respectively (Fig. 3a). Both hornblende and biotite have similar Mg isotopic compositions, within the analytical precision, to their whole-rocks (Fig. 3b, c).

The Mg isotopic compositions of the granitoids calculated using the modal abundances of minerals (hornblende and biotite) and their corresponding $\delta^{26}\text{Mg}$ values agree with the measured values within

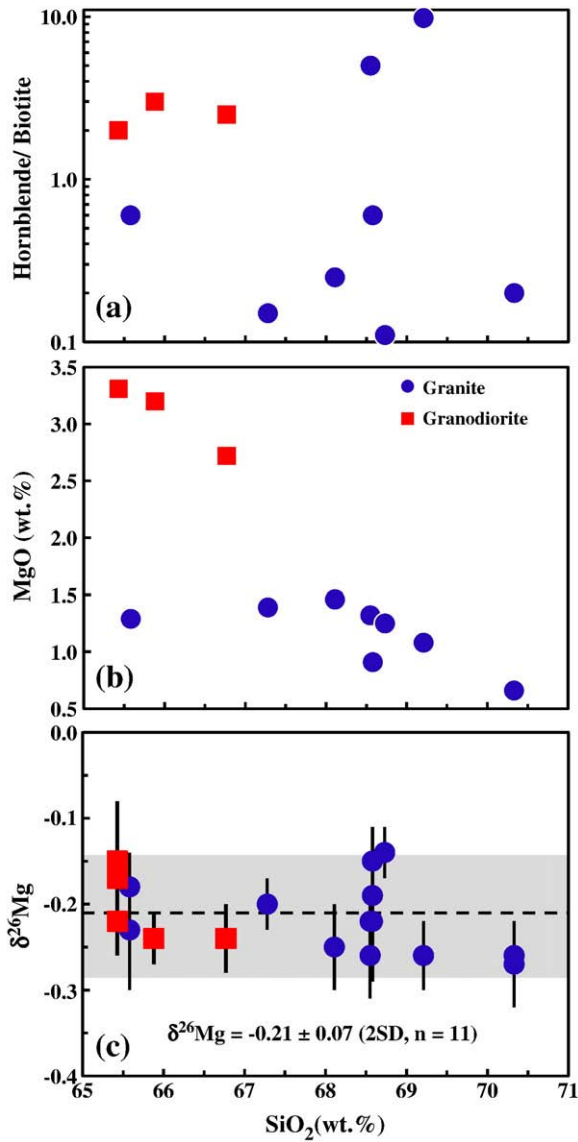


Fig. 2. Plots of SiO_2 contents of granitoids from the Dabie Orogen as a function of (a) modal abundance ratio between hornblende and biotite, which is calculated based on the intermediate value of modal abundance of hornblende and biotite in Table 1; (b) MgO contents from Table 1, and (c) $\delta^{26}\text{Mg}$ values from Table 2. The constant $\delta^{26}\text{Mg}$ over a wide range of SiO_2 and MgO contents and mineral abundance indicates a lack of crystal–melt Mg isotope fractionation. The dashed line and grey band represent averaged $\delta^{26}\text{Mg}$ of the granitoids from the Dabie Orogen (-0.21 ± 0.07 ; $n = 11$; 2SD). Error bars for all data are 2 SD.

$\pm 0.03\%$ (Table 2 and Fig. 4). This further suggests that hornblende and biotite dominate the Mg budget in granitoids analyzed here.

5. Discussion

Previous studies suggest that equilibrium Mg isotope fractionation during crystal–melt differentiation of basaltic magmas at high temperatures ($>1050^\circ\text{C}$) is analytically insignificant (Teng et al., 2007, 2010). It is however uncertain whether there is measurable Mg isotope fractionation during differentiation of granitic magmas that generally occurs at lower temperatures ($\leq 850^\circ\text{C}$), in particular considering that equilibrium isotope fractionation increases as the temperature decreases (Chacko et al., 2001). In this section, we first evaluate the behavior of Mg isotopes during granite differentiation and then use available Mg isotopic data of I-type granitoids to

Table 2
Magnesium isotopic compositions of minerals and whole-rocks of granitoids from the Dabie Orogen and reference materials.

Sample no.	Sample ^a	$\delta^{26}\text{Mg}^b$	2 SD ^c	$\delta^{25}\text{Mg}^b$	2 SD ^c
<i>Granite</i>					
07LD-1	Bt	-0.21	0.04	-0.11	0.05
	Wr	-0.26	0.04	-0.14	0.05
07LD-2	Bt	-0.22	0.04	-0.10	0.05
	Replicate-Ti ^d	-0.23	0.07	-0.16	0.05
	Average	-0.23	0.02	-0.13	0.08
	Hbl	-0.30	0.04	-0.18	0.05
	Replicate-Ti	-0.31	0.07	-0.12	0.05
	Average	-0.31	0.02	-0.15	0.08
	Wr	-0.22	0.04	-0.11	0.05
07ZB-1	Replicate-Ti	-0.26	0.05	-0.16	0.04
	Average	-0.24	0.06	-0.14	0.07
	Wr ^g	-0.27	0.04	-0.14	0.05
	Bt	-0.19	0.04	-0.08	0.05
	Replicate-Ti	-0.15	0.05	-0.08	0.05
	Duplicate ^e	-0.18	0.07	-0.06	0.04
	Average	-0.17	0.04	-0.07	0.02
07ZB-6	Hbl	-0.26	0.04	-0.12	0.05
	Replicate-Ti	-0.27	0.05	-0.17	0.05
	Duplicate	-0.29	0.07	-0.12	0.04
	Average	-0.27	0.03	-0.15	0.06
	Wr	-0.15	0.04	-0.06	0.05
	Replicate-Ti	-0.22	0.07	-0.10	0.05
	Duplicate	-0.19	0.07	-0.08	0.04
	Average	-0.19	0.03	-0.08	0.01
	Wr ^g	-0.20	0.04	-0.09	0.03
	Bt	-0.19	0.04	-0.08	0.05
07FJ-2	Replicate-Ti	-0.21	0.05	-0.11	0.04
	Average	-0.20	0.02	-0.10	0.04
	Wr	-0.18	0.04	-0.09	0.05
	Replicate-Ti	-0.23	0.07	-0.12	0.05
07FJ-6	Average	-0.21	0.06	-0.11	0.04
	Bt	-0.19	0.04	-0.09	0.05
	Replicate-Ti	-0.12	0.07	-0.09	0.05
	Duplicate	-0.14	0.07	-0.06	0.04
	Average	-0.15	0.05	-0.08	0.03
07DT-3	Wr	-0.26	0.04	-0.13	0.05
	Replicate-Ti	-0.27	0.05	-0.13	0.04
	Average	-0.27	0.02	-0.13	0.02
	Bt	-0.21	0.04	-0.09	0.05
	Replicate-Ti	-0.20	0.07	-0.10	0.05
	Average	-0.21	0.02	-0.10	0.02
	Hbl	-0.28	0.04	-0.12	0.05
YFD-8	Replicate-Ti	-0.28	0.05	-0.14	0.04
	Average	-0.28	0.02	-0.13	0.02
	Wr	-0.25	0.05	-0.14	0.05
	Wr ^g	-0.25	0.02	-0.12	0.02
	Bt	-0.22	0.03	-0.09	0.04
	Hbl	-0.25	0.03	-0.12	0.04
	Wr	-0.20	0.03	-0.10	0.04
07MC-1	Wr ^g	-0.22	0.03	-0.09	0.04
	Bt	-0.11	0.03	-0.05	0.04
	Replicate-Ti	-0.12	0.05	-0.06	0.04
	Average	-0.12	0.02	-0.06	0.02
	Hbl	-0.12	0.03	-0.05	0.04
	Replicate-Ti	-0.16	0.07	-0.04	0.05
	Average	-0.14	0.06	-0.05	0.02
07MC-3	Wr	-0.14	0.03	-0.05	0.04
	Wr ^g	-0.12	0.02	-0.06	0.02
	Bt	-0.19	0.03	-0.10	0.04
	Replicate-Ti	-0.20	0.05	-0.10	0.04
	Average	-0.20	0.03	-0.10	0.04
	Hbl	-0.27	0.04	-0.14	0.05
	Replicate-Ti	-0.28	0.07	-0.11	0.05
07MC-3	Average	-0.28	0.03	-0.13	0.05
	Wr	-0.24	0.03	-0.11	0.04
	Wr ^g	-0.26	0.03	-0.13	0.05
	Bt	-0.14	0.03	-0.06	0.04
07MC-3	Replicate-Ti	-0.20	0.07	-0.12	0.05
	Duplicate	-0.25	0.05	-0.12	0.04
	Average	-0.20	0.04	-0.12	0.02

(continued on next page)

Table 2 (continued)

Sample no.	Sample ^a	$\delta^{26}\text{Mg}^b$	2 SD ^c	$\delta^{25}\text{Mg}^b$	2 SD ^c
<i>Granodiorite</i>					
07MC-3	Wr	-0.22	0.04	-0.12	0.05
	Replicate-Ti	-0.15	0.07	-0.08	0.05
	Duplicate	-0.17	0.05	-0.09	0.04
	Average	-0.18	0.04	-0.10	0.02
07MC-6	Bt	-0.21	0.04	-0.11	0.05
	Hbl	-0.27	0.04	-0.13	0.05
	Wr	-0.24	0.04	-0.12	0.05
	Wr ^g	-0.26	0.04	-0.13	0.05
<i>Reference materials^f</i>					
	KH-1 olivine	-0.27	0.04	-0.12	0.05
	San Carlos olivine	-0.27	0.07	-0.13	0.04
	IL-granite	-0.01	0.03	0.00	0.04
	Replicate-Ti	-0.03	0.07	-0.01	0.06
	Duplicate	-0.03	0.05	-0.01	0.05
	Average	-0.02	0.03	-0.01	0.02

^a Bt = biotite, Hbl = hornblende, Wr = whole-rock.

^b Calculation relative to Mg isotope standard DSM-3 (Galy et al., 2003) (see text for definition).

^c 2 SD = 2 times the standard deviation of the population of n (times) repeat measurements of a sample solution.

^d Replicate-Ti: samples were processed through both main Mg column chemistry and Ti column chemistry.

^e Duplicate: repeated measurement of Mg isotopic ratios on the same solutions.

^f IL-granite is a synthetic solution with Mg:Al:Fe:Ca:K:Na:Ti:Ni = 1:30:5:5:20:10:0.1:0.1 and KH-1 olivine is an in-house standard that has been analyzed through whole-procedural column chemistry and instrumental analysis with $\delta^{26}\text{Mg} = -0.27 \pm 0.07$ and $\delta^{25}\text{Mg} = -0.14 \pm 0.04$ ($n = 16$; 2 SD) relative to DSM-3 (Teng et al., 2010).

^g Calculated values based on modal abundance and measured $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of biotite and hornblende in each sample.

estimate Mg isotopic composition of the continental crust in the Dabie Orogen. Finally we explore the potential application of Mg isotopes as a tracer for granite genesis and crustal recycling.

5.1. The limited Mg isotope fractionation during granite differentiation

Chemical and isotopic compositions of granitic rocks may be affected by multiple processes, e.g., source heterogeneity, surface weathering and magmatic processes including partial melting and subsequent magmatic differentiation (e.g., Chappell, 1996). Thus, before evaluating the roles of magmatic processes in Mg isotopic composition of granitoids, two aspects must be taken into consideration: 1) source heterogeneity caused by recycling of surface materials (e.g., sediments) and 2) surface weathering of granitoid samples, because low-temperature surface processes can significantly fractionate Mg isotopes (Tipper et al., 2006, 2008; Brenot et al., 2008; Poggendorf et al., 2008; Hippler et al., 2009).

Involvement of recycled components in the granitoid sources can be readily excluded, as these I-type granitoids generally exhibit metaluminous affinity ($A/\text{CNK} = 0.82$ to 0.96 ; Table 1). The metaluminous characteristic is distinctly different from that of peraluminous granites with sediment precursors, e.g., S-type granites (Chappell and White, 1992). The Sr and Nd isotopic compositions of one sample analyzed here (YFD-8) have initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51167$, which indicates that magmas were derived from an igneous source, i.e., the ancient lower continental crust (Wang et al., 2007). The early Cretaceous granitoids from the same areas in the Dabie Orogen are characterized by highly unradiogenic Pb isotopic compositions (e.g., initial $^{206}\text{Pb}/^{204}\text{Pb} < 16.4$; Huang et al., 2008) and homogeneous zircon $\delta^{18}\text{O}$ values ($5.10 \pm 0.42\%$) (Zhao et al., 2007). These features suggest no significant involvement of surface sediments during formation of these granitoids. Furthermore, these granitoid samples have very low chemical index of alteration (CIA) (< 49 , Table 1), suggesting that these samples are not significantly affected by chemical weathering (Nesbitt and Young 1982). This is identical with the petrographical observations,

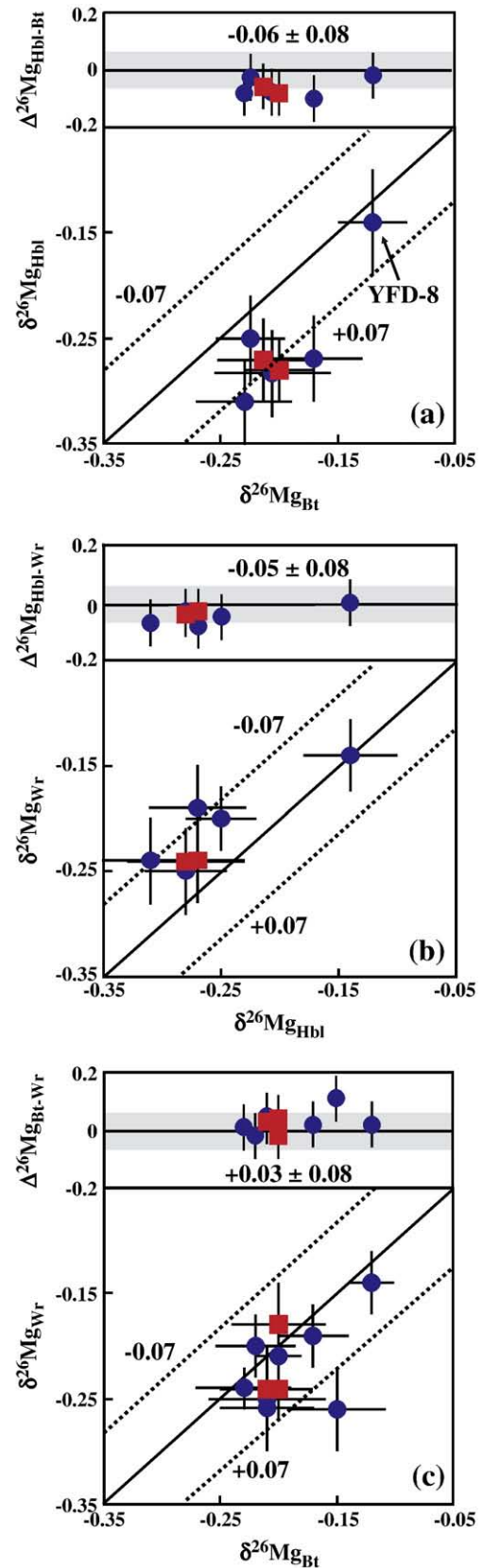


Fig. 3. Magnesium isotopic compositions of biotites, hornblendes and bulk granitoids from the Dabie Orogen. (a) hornblende vs. biotite; (b) hornblende vs. whole-rock; (c) biotite vs. whole rock. $\Delta^{26}\text{Mg}_{\text{X-Y}} = \delta^{26}\text{Mg}_{\text{X}} - \delta^{26}\text{Mg}_{\text{Y}}$, where X or Y = Hbl, Bt or Wr (whole rock). The horizontal lines and grey bands in the upper figures represent $0.00 \pm 0.07\%$ (our long-term external precision), which means that Δ values falling in the grey field are currently undetected. Data are from Table 2 and error bars for all data are 2 SD. The weighted average value is used for samples with multiple analyses.

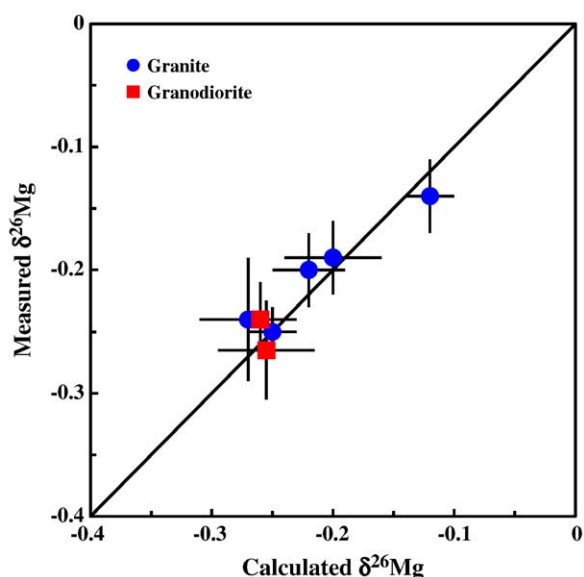


Fig. 4. Calculated versus measured $\delta^{26}\text{Mg}$ values of granitoid whole-rocks. The calculated values agree with the measured ones within 0.03%. Data are from Table 2.

which show no obvious mineral alteration (Fig. 1). Sediment recycling and surface weathering can thus be excluded and Mg isotopic variations among these samples, if any, should result from magmatic processes, i.e., partial melting and magmatic differentiation.

5.1.1. Magnesium isotopic systematics of whole-rock granitoids

The large variations in mineralogical and chemical compositions of the granitoids from the Dabie Orogen are coupled with variable degrees of partial melting of the deep continental crust and fractional crystallization (Fig. 2a, b). Nonetheless, these granitoids display a homogeneous Mg isotopic composition, with an average $\delta^{26}\text{Mg}$ of -0.21 ± 0.07 (2 SD) (Fig. 2c). The lack of measurable Mg isotopic variation in these granitoids, thus, suggests insignificant Mg isotope fractionation during crustal anatexis and subsequent magma differentiation. The constant granitoid Mg isotopic compositions, regardless of the two orders of magnitude variations in abundance ratios between hornblende and biotite (Fig. 2a, c), further indicate that fractional crystallization of either hornblende or biotite from magma does not significantly fractionate Mg isotopes.

5.1.2. Magnesium isotopic systematics of hornblende and biotite in granitoids

The homogeneous Mg isotopic composition of bulk granitoids from the Dabie Orogen indicates that crustal anatexis and granite differentiation do not cause significant Mg isotope fractionation. Nevertheless, studies of isotope behaviors during magmatic differentiation can be directly achieved by measuring minerals and their whole-rocks (e.g., Li isotopes, Teng et al., 2006; Marks et al., 2007; Fe isotopes, Schoenberg et al., 2008; Teng et al., 2008).

Coexisting hornblendes and biotites in the granitoids from the Dabie Orogen display similar Mg isotopic compositions (Fig. 3a). In details, the inter-mineral fractionation factors ($\Delta^{26}\text{Mg}_{\text{Hbl-Bt}} = \delta^{26}\text{Mg}_{\text{Hbl}} - \delta^{26}\text{Mg}_{\text{Bt}}$) vary from -0.10 to -0.02 , with a mean of -0.06 ± 0.08 (2 SD; $n=7$), and show no correlation with $\delta^{26}\text{Mg}$ values of hornblende or biotite (e.g., Fig. 3a). Hornblendes seem to be always slightly lighter in Mg isotopic composition than coexisting biotites in all samples, but the difference falls within our current analytical precision (Fig. 3a). These mineral data presented here thus confirm that limited Mg isotope fractionation occurs between coexisting biotite and hornblende, a conclusion consistent with studies of whole rocks.

5.2. Theoretic considerations of inter-mineral Mg isotope fractionation

Our results show that coexisting hornblende and biotite in granitoids have limited inter-mineral fractionation with a mean $\Delta^{26}\text{Mg}_{\text{Hbl-Bt}} = -0.06 \pm 0.08\%$ ($n=7$). Similar limited fractionation was also observed between coexisting pyroxene and olivine in mantle peridotites (Handler et al., 2009; Yang et al., 2009) (Fig. 5). For example, Yang et al. (2009) reported mean $\Delta^{26}\text{Mg}_{\text{opx-ol}} = +0.03 \pm 0.10\%$ ($n=12$) and $\Delta^{26}\text{Mg}_{\text{cpx-ol}} = +0.05 \pm 0.11\%$ ($n=15$) for a suite of peridotite xenoliths from the North China craton, and Handler et al. (2009) reported a mean $\Delta^{25}\text{Mg}_{\text{pyr-ol}} = +0.06 \pm 0.10\%$ ($n=5$) for mantle peridotites from a variety of locations. Pyroxenes from these studies are slightly isotopically heavier than coexisting olivines, but the difference was not resolvable at the current analytical uncertainty (Handler et al., 2009; Yang et al., 2009). By contrast, Young et al. (2009) reported that pyroxenes are significantly heavier than olivines by up to $\sim 0.4\%$ in $\delta^{26}\text{Mg}$ for two mantle xenoliths from San Carlos in southeastern Arizona (Fig. 5), which was interpreted as a result of kinetic isotope fractionation.

Equilibrium isotope fractionation is governed by the general rules of stable isotope fractionation and depends on differences in zero point energy (ΔZPE) between molecules with different isotopes (Bigeleisen and Mayer, 1947; Urey, 1947). Substances with stronger bonds will have larger ΔZPE during isotope substitution, and thus favor heavy isotopes (Chacko et al., 2001). The bond strength, in general, is inversely correlated with the coordination number of the cations in minerals, which depends on the radius ratio of cations and oxygen ($R_{\text{cation}}/R_{\text{oxygen}}$). Hence, substances with low Mg coordination are expected to be enriched in heavy isotopes.

Biotite is a sheet silicate with a general chemical formula of $[\text{K}(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})\text{Si}_3\text{O}_{10}(\text{OH}, \text{F})_2]$, where the basic structural group is $\text{Si}_2\text{O}_5^{2-}$ and Mg is bonded to six oxygen atoms and thus in octahedral coordination (Shannon, 1976). Hornblende is a double-chain silicate with a general chemical formula of $(\text{Na}, \text{K})_{0-1}\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_4\text{Al}(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$, where the basic structural group is $\text{Si}_4\text{O}_{11}^{6-}$. Magnesium in hornblende is also octahedrally coordinated with oxygen (Hawthorne and Oberti, 2007). To the first order, the same coordination of Mg in biotite and hornblende is not favorable for large inter-mineral Mg isotope fractionation. This is consistent with our observation of undetectable Mg isotope fractionation between coexisting biotite and hornblende in granitoids. Nevertheless, coordination circumstances of O bonded to Mg atoms in biotite and hornblende are slightly different (Fig. 5). Oxygen in biotite has two distinct sites, one in two-fold coordination and the other in three-fold coordination. In hornblende, oxygen also has two distinct coordinated sites, but is in three-fold coordination and four-fold coordination (Hawthorne and Oberti, 2007). Consequently, the higher coordination of oxygen in some Mg–O bonds in hornblende would lower the average Mg–O bond strength, making hornblende slightly enriched in light Mg isotopes. This may explain why hornblendes are always slightly lighter than coexisting biotites ($\Delta^{26}\text{Mg}_{\text{Hbl-Bt}} = -0.06 \pm 0.08\%$), although the difference is not resolvable at our current analytical precision.

This can also explain why mantle pyroxenes are always slightly ($\sim 0.06\%$) heavier than coexisting olivines although the difference is undetectable (Fig. 5). Pyroxene and olivine have the general chemical formula of XYSi_2O_6 (in which X and Y are two divalent cations or a monovalent and a trivalent) and $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, respectively. The basic structural group is SiO_6^{4-} in pyroxene and SiO_4^{4-} in olivine, and Mg in both minerals occupies octahedral sites. By contrast, oxygen bonded to Mg in olivine (an island silicate, where Si–O tetrahedrons are isolated) is in four-fold coordination, whereas oxygen in pyroxene has two different sites, one in three-fold sites and the other in four-fold sites (when bonded to a Si–O tetrahedron). The mean coordination number of oxygen in olivine and pyroxene is estimated to be 4.00 and 3.67, respectively (Brown and Gibbs, 1969). As a result of the lower mean coordination of oxygen in Mg–O bonds, pyroxene is expected to be

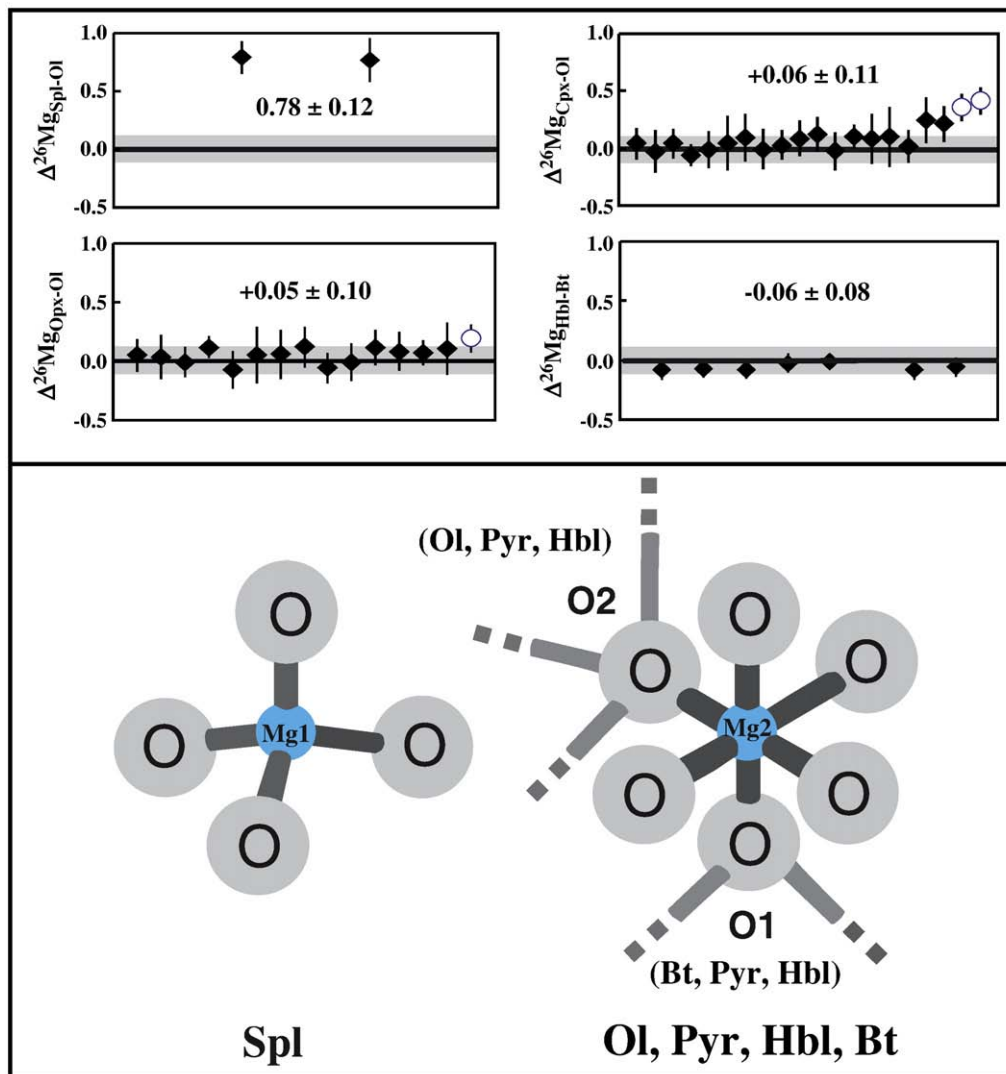


Fig. 5. Comparisons of observed inter-mineral Mg isotope fractionation among major Mg-hosting silicate minerals with theoretic considerations of coordination of Mg atoms and bonded oxygen atoms in these minerals. Top panel: the grey bars in all figures represent $\delta^{26}\text{Mg} = 0 \pm 0.1\%$ (2SD), which is similar to or better than the precision reported for those published data. Bt and Hbl data are from Table 2. Spinel (Spl) data are from Young et al. (2009). Clinopyroxene (Cpx), orthopyroxene (Opx) and olivine (Ol) data are from Handler et al. (2009), Yang et al. (2009) and Young et al. (2009). Data from Young et al. (2009) show large kinetic Mg isotope fractionation between Cpx and Ol and between Opx and Ol, as highlighted in open circles. Bottom panel: Mg1 site represents tetrahedrally coordinated Mg atoms (e.g., in spinel). Mg2 site represents octahedrally coordinated Mg atoms in major Mg-hosting silicate minerals (e.g., biotite, hornblende, pyroxene and olivine). O1 and O2 sites indicate different coordinated sites of oxygen in octahedrally coordinated minerals. O1 site is in three-fold coordination, e.g., some oxygen atoms in biotite, hornblende and pyroxene; O2 site is in four-fold coordination, e.g., in olivine and some oxygen atoms in pyroxene and hornblende.

slightly heavier in Mg isotopic composition than olivine. These limited fractionations between minerals with the same octahedral coordination are, however, much smaller than those occurring between tetrahedrally coordinated spinel and octahedrally coordinated olivine, with a difference up to $\sim 0.7\%$ as shown in Young et al. (2009) (Fig. 5).

In summary, theoretic considerations suggest that small inter-mineral Mg isotope fractionation may occur in peridotite and granitoid minerals in the following order: biotite > hornblende \approx pyroxene > olivine because of the difference in coordination of oxygen in these phases (Mg cations in all above minerals are six-fold coordinated with oxygen; Fig. 5). The magnitude of fractionation however is smaller than the current analytical precision based on this study of biotite and hornblende in granitoids and previous studies of olivine and pyroxene in mantle peridotites (Handler et al., 2009; Yang et al., 2009).

5.3. Implications

The limited Mg isotope fractionation between coexisting hornblendes and biotites in I-type granitoids implies that Mg isotopic

composition of either biotite or hornblende can represent that of their host granitoid. Hence measurement on one of them can directly yield information on Mg isotopic composition of the host granitoids. This greatly simplifies the procedure for chemical purification of Mg due to the high Mg concentrations in mafic minerals and makes it easier to study Mg isotopic compositions of granitoids, e.g., Shen et al. (2009).

Granitoid rocks constitute one of the most important lithological units in the upper continental crust. Since no significant Mg isotope fractionation occurs during I-type granite differentiation, Mg isotopic composition of granites can also reflect that of their sources (i.e. the deep continental crust). The average $\delta^{26}\text{Mg}$ of I-type granitoids studied here is -0.21 ± 0.07 (2 SD), which is taken to represent the average Mg isotopic composition of the continental crust in the Dabie Orogen. This estimated $\delta^{26}\text{Mg}$ value is, within error, in agreement with those of global oceanic basalts and peridotites analyzed in our lab ($\delta^{26}\text{Mg} = -0.25 \pm 0.07$, 2 SD; Teng et al., 2010), confirming that magmatic processes do not significantly fractionate Mg isotopes and suggesting that the continental crust in the Dabie Orogen, as sampled by I-type granitoids, has a mantle-like Mg isotopic composition.

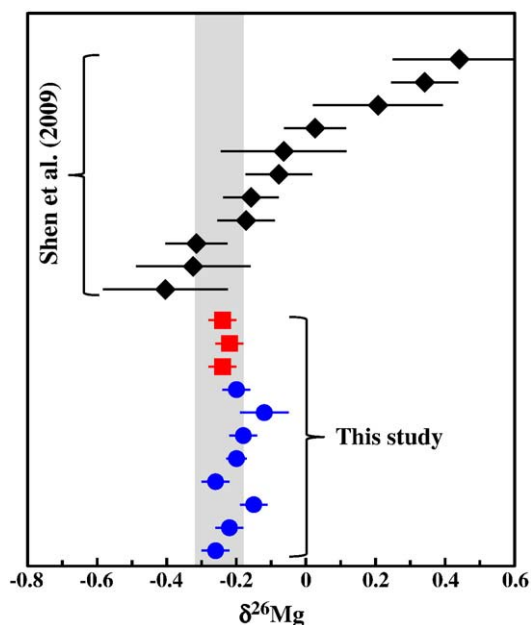


Fig. 6. Magnesium isotopic compositions of I-type granitoids from this study and Shen et al. (2009). The grey band represents Mg isotopic composition of the mantle based on studies of global oceanic basalts and peridotites ($\delta^{26}\text{Mg} = -0.25 \pm 0.07$, 2 SD; Teng et al., 2010). See text for details.

The homogeneous Mg isotopic composition of I-type granitoids from the Dabie Orogen is in sharp contrast to I-type granitoids in southern California, which displayed $\sim 0.8\%$ Mg isotopic variation (Shen et al., 2009) (Fig. 6). This large isotopic variation was interpreted as a result of source heterogeneity that involved recycled surface-weathered materials, as evidenced by the positive correlations of $\delta^{26}\text{Mg}$ values and radiogenic (Sr and Pb) isotopes as well as oxygen isotopes (Shen et al., 2009). When taking into account all these available Mg isotopic data in granites, the continental crust seems to have a heterogeneous Mg isotopic composition (Fig. 6). Considering the limited Mg isotope fractionation during granite differentiation, Mg isotopes can potentially be a great tracer for recycled sedimentary materials in granite sources.

6. Conclusions

The main conclusions to be drawn from high-precision Mg isotopic analysis of a suite of I-type granitoids and associated biotite and hornblende minerals from the Dabie Orogen in central China are:

1. Granitoids display a restricted range in Mg isotopic composition, with $\delta^{26}\text{Mg}$ varying from -0.26 to -0.14 , indistinguishable within our current analytical precision.
2. Coexisting hornblende and biotite in these granitoids have similar Mg isotopic compositions, with $\delta^{26}\text{Mg}$ varying from -0.31 to -0.14 in hornblendes and -0.23 to -0.12 in biotites.
3. The mean inter-mineral fractionation factor between hornblende and biotite ($\Delta^{26}\text{Mg}_{\text{Hbl-Bt}}$) is -0.06 ± 0.08 (2 SD). Although hornblendes might be slightly lighter than coexisting biotites, the difference is not resolved at current analytical resolution. This agrees with our theoretic studies that Mg cations occupy similar sites in both hornblendes and biotites but coordination circumstances of oxygen in them are slightly distinct.
4. Based on both whole-rocks and mineral separates, our study suggests that Mg isotope fractionation during I-type granite differentiation is small and undetectable at the current analytical uncertainty. Hence, Mg isotopes can potentially be used as a tracer for crustal recycling and origins of granites.

5. Granitoids from this study have an average $\delta^{26}\text{Mg}$ of -0.21 ± 0.07 (2 SD), which is considered as the average Mg isotopic composition of the continental crust in the Dabie Orogen.
6. Coupled with previous work on I-type granites from southern California (Shen et al., 2009), our study suggests that the continental crust has a heterogeneous Mg isotopic composition.

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