Magnesium isotopic systematics of metapelite in the deep crust and implications for granite petrogenesis

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Abstract

Fluid-absent reactions that involve the breakdown of hydrous minerals produce granites in the continental crust. The minerals in the deep continental crust thus play a significant control on the chemical compositions of granites, but how and to what extent it may influence their isotopic signatures is poorly understood. Here we present Mg isotope data for a suite of amphibolite- to granite-facies metapelites as well as the biotite and garnet minerals therein from the Ivrea Zone, NW Italy. The mineralogy of metapelites changes from biotite-dominated in the amphibolite-facies to garnet-dominated in the granite-facies. The bulk Mg isotopic compositions (δ26Mg = -0.23 to +0.20 ‰) do not correlate with metamorphic grade, indicating negligible Mg isotope variation caused by metamorphism of metapelites. By contrast, the δ26Mg values of biotite vary widely from -0.98 to +1.10 ‰, and increase with metamorphic grade. Correspondingly, coexisting garnets become isotopically heavy (-1.22 to +0.10 ‰) as metamorphism proceeds, in order to equilibrate with the biotite, with a fractionation equation of $\ln\left(\frac{T_{\text{biotite}}}{T_{\text{garnet}}}\right) = 0.96 \times 10^{\delta_{26}Mg}$, which can be used as a novel geothermometer. Our results indicate a nearly closed system for Mg isotopes of metapelites with metamorphic grade. Correspondingly, coexisting garnets become isotopically heavy (-0.25 to 0.07 ‰; Teng et al., 2010a). While protolith heterogeneity (i.e., sedimentary vs. igneous protoliths) partially explains this Mg isotopic variation (Shen et al., 2009), metamorphic overprints on potential granitoid sources, with concomitant changes of source mineralogy, may play an important, but poorly understood, role as well.

Here, we present Mg isotope data for 12 well-characterised metapelites and 13 mineral separates (biotite and garnet) therein from the Ivrea Zone, NW Italy (Bea and Montero, 1999; Qiu et al., 2011). These metapelites represent a typical prograde metamorphic sequence from middle amphibolite- to granulite-facies, and thus are ideal samples for studying the behaviour of Mg isotopes under the middle-lower crustal conditions. Our results indicate that the bulk metapelites display a considerable Mg isotopic variation (δ26Mg = -0.23 to +0.20 ‰) that does not correlate with metamorphic grade. By contrast, the δ26Mg values of garnet (+1.08 to +1.10 ‰) vary more significantly and increase as metamorphism proceeds, which makes Mg isotopes a potential tracer for crustal melting and granite petrogenesis.

Ivrea Zone Metapelites

The Ivrea Zone, NW Italy, represents an exposed section of the middle to lower crust and preserves a transition from amphibolite- to granulite-facies metapelites (e.g., Zingg, 1984). The metamorphic condition for these metapelites ranges from ca. 4 kbar at 300 °C to ca. 12 kbar at >900 °C (Henk et al., 1997; Bea and...
Montero, 1999; Luvisotto and Zack, 2009; Redler et al., 2011). The modal abundance of garnet in metapelites increases at the expense of biotite with increasing metamorphic grade following the metamorphic reaction: biotite + sillimanite + plagioclase + quartz → garnet + K-feldspar + rutile + melt. This reaction proceeds until the biotite is almost entirely consumed in granulite-facies metapelites (Bertolani and Garutti, 1970; Schmid and Wood, 1976). The metapelites in the Ivrea Zone are divided into three zones from low to high metamorphic grade based on the biotite/garnet ratio (Bea and Montero, 1999): the kinzigite zone that corresponds to metapelites with modal biotite/garnet >2, the transition zone in which the modal biotite/garnet is between 0.5 and 2, and the stonalite zone where modal biotite/garnet is <0.5 (Fig. S-1). Twelve representative samples of metapelites and garnet-biotite mineral pairs from the three zones were studied for Mg isotopes (Fig. S-1).

### Results

The Mg isotopic data, along with details of the analytical methods, are presented in the Supplementary Information and summarised in Figure 1. The bulk metapelites display a considerable variation in Mg isotopic composition, with δ²⁶Mg ranging from -0.23 to +0.20 ‰ for the kinzigite zone, from -0.10 to +0.14 ‰ for the transition zone, and from -0.10 to +0.12 ‰ for the stonalite zone. No correlation between bulk δ²⁶Mg and metamorphic grade is observed (Fig. 1). By contrast, δ²⁶Mg values of the associated mineral separates display wider ranges and increase systematically with metamorphic grade (Fig. 1). The Mg isotopic compositions of garnet become progressively heavier from the transition zone to the stonalite zone (δ²⁶Mg = -1.10 to -1.22 ‰) to the transition zone (δ²⁶Mg = -0.34 ‰) and finally to the kinzigite zone (δ²⁶Mg = -0.03 to +0.10 ‰; Fig. 1). The biotite is isotopically heavier than coexisting garnet, with δ²⁶Mg increasing from the kinzigite zone (-0.08 to +0.30 ‰) through the transition zone (+0.58 ‰) to the stonalite zone (+1.00 to +1.10 ‰; Fig. 1).

### Discussion and Conclusion

Minerals with low Mg coordination numbers (CN) and thus strong Mg-O bonds preferentially incorporate heavy Mg isotopes. Given the difference in Mg coordination geometry between biotite (CN = 6) and garnet (CN = 8), substantial inter-mineral isotope fractionation is expected, but the exact fractionation factor has not been determined. Our study shows that the Mg isotope fractionation between biotite and garnet is significant, in the range of 0.92 ~ 1.48 ‰ (Fig. 2). Different mineral fragments from the same metapelite yield identical Mg isotopic compositions (Table S-1), suggesting negligible intra-mineral Mg isotopic variations and thus implying the equilibrium Mg isotope fractionation. The degree of equilibrium isotope fractionation is a function of temperature, during metamorphism, the majority of Mg in rocks is inherited by newly formed minerals without significant loss, hence Mg isotope variations in the bulk metamorphic rocks are not directly related to metamorphic grade. Therefore, the heavy Mg isotopic compositions of the studied metapelites indicate that their protoliths were the residues of chemical weathering, from which light Mg isotopes had been progressively leached to the hydrosphere (e.g., Tipper et al., 2006; Teng et al., 2010b).

Figure 1 Magnesium isotopic compositions versus metamorphic grade for the bulk metapelites, biotites and garnets. The average value of bulk upper continental crust (δ²⁶Mg = -0.22 ‰) is represented by the blue line (Li et al., 2010). Data are reported in Table S-1.

with 10⁸lnδ²⁶Mg₀₂⁶Mg = 0.96 × 10⁸/T² (R² = 0.7; Fig. 2). This fractionation equation is very similar to those previously reported for garnet-clinopyroxene pairs from eclogites (Fig. 2) (Li et al., 2011; Wang et al., 2012, 2014a,b; Huang et al., 2013), which is reasonable since the Mg coordination geometry in biotite is the same as in clinopyroxene. The relatively high scatter of data may reflect an additional but small effect from pressure, as first-principles calculations suggest that the equilibrium inter-mineral Mg isotope fractionation is also pressure-dependent; i.e., the degree of fractionation is suppressed as pressure decreases (Huang et al., 2013). Nevertheless, our results indicate for the first time that Mg isotopes might be used as a novel geothermometer for garnet and biotite-bearing rocks.

The δ²⁶Mg values of the bulk-rock do not correlate with metamorphic grade (Fig. 1), suggesting that metamorphic dehydration/partial melting during the transition from amphibolite- to granulite-facies caused negligible change of Mg isotopes of metapelites. This conclusion is consistent with previous studies that show limited Mg isotope fractionation by either low- or high-temperature metamorphic dehydration (Teng et al., 2013; Li et al., 2014; Wang et al., 2014b). During metamorphism, the majority of Mg in rocks is inherited by newly formed minerals without significant loss, hence Mg isotope variations in the bulk metamorphic rocks are not directly related to metamorphic grade. Therefore, the heavy Mg isotopic compositions of the studied metapelites indicate that their protoliths were the residues of chemical weathering, from which light Mg isotopes had been progressively leached to the hydrosphere (e.g., Tipper et al., 2006; Teng et al., 2010b).
The systematic variation of mineral Mg isotopic compositions during middle-lower crustal metamorphism indicates the possibility of Mg isotope fractionation during crustal melting. As temperature rises, metapelites in the deep continental crust undergo two stages of dehydration melting: first as muscovite, and second as biotite (e.g., Le Breton and Thompson, 1988; Clemens, 2003). Muscovite dehydration melting (e.g., muscovite + plagioclase + quartz → melt + K-feldspar + sillimanite + biotite) would not produce significant Mg isotope fractionation between melts and residues because minerals participating in the melting reactions have the same Mg coordination geometry and hence would display limited inter-mineral Mg isotope fractionations. By contrast, dehydration melting of biotite at higher temperatures as discussed above (e.g., biotite + sillimanite + plagioclase + quartz → garnet + K-feldspar + rutile + melt) is able to generate highly variable δ26Mg for the melt. Melting reaction consistent with the biotite dehydration melting experiment of Patiño Douce and Johnston (1991) is modelled to investigate the behaviour of Mg isotopes during crustal melting (Fig. S-3). With progressive melting, Mg isotopic compositions of residual biotite become heavier accompanied by the growth of peritectic garnet. Correspondingly, the resulting melts become isotopically heavier (Fig. S-3). Therefore, multiple pulses of granitic magmas generated from the same protolith could have δ26Mg values that vary by up to ~1‰ (Fig. S-3).

Our results also have important implications on tracing intra-crustal differentiation by using Mg isotopes. The granulite-facies lower crustal rocks that have undergone a previous melt extraction would contain only small amounts of hydrous minerals (e.g., biotite and amphibole) coexisting with a garnet-dominated solid peritectic mineral assemblage (Fig. 3). As expected from the closed-system Mg isotopic evolution during metamorphism, these
biotites and amphiboles would have heavier Mg isotopic compositions than those in the amphibolite-facies middle crust. Hence, dehydration melting of a granulite-facies source in the lower crust at high temperatures (>850 °C) would generate melts that have higher δ²⁶Mg values than those derived from dehydration melting of an amphibolite-facies source in the middle crust. Further studies of Mg isotopes in granites may help to fingerprint their source and melting mechanism in the deep continental crust.

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Additional Information

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References


Methods

Prior to sample dissolution, biotite and garnet grains were handpicked under a binocular microscope with extra care taken to avoid any alteration products during separation. The mineral separates were then ultrasonicated for three times with each in Milli-Q Water for 10 minutes. Chemical procedures including sample dissolution, column chemistry, and instrumental analyses were carried out at the Isotope Laboratory of University of Washington, Seattle, USA. These mineral separates together with the rock powders were digested using a mixture of Optima-grade HF-HNO$_3$-HCl acids. After complete dissolution, dried residues were taken up in 1N HNO$_3$ ready for column chemistry. Detail procedures have been reported elsewhere (Teng et al., 2007, 2010, 2015; Yang et al., 2009; Teng and Yang, 2014), and only a brief description is given below.

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Supplementary Information

The Supplementary Information includes:

➣ Methods

➣ Figures S-1 to S-3

➣ Table S-1

➣ Supplementary Information References