



Introduction

Fluid-absent incongruent melting of hydrous minerals such as muscovite, biotite, and amphibole that takes place in the continental crust give rise to large volumes of granitoids (Clemens and Vielzeuf, 1987; Clemens and Watkins, 2001). Pelitic rocks containing abundant mica minerals are the most fertile lithologies in the deep (middle and lower) continental crust, and can produce as much as 50 vol.% melt as the temperature rises above 700 °C (Le Breton and Thompson, 1988; Vielzeuf and Holloway, 1988). Dry, granulitic residues after an early melt extraction are relatively refractory but may still be melted at higher temperatures (e.g., >830 °C; Whalen *et al.*, 1987). Consequently, the elemental and isotopic diversity of granitoids results from a combination of protolith heterogeneities, melting reaction patterns, melt extraction and ascending processes (Barbero *et al.*, 1995; Bea, 1996; Patiño Douce, 1999; Brown, 2007; Stevens *et al.*, 2007; Clemens and Stevens, 2012; Lee and Morton, 2015).

Magnesium (Mg) in anatexic melts may come exclusively from the mafic hydrous minerals participating in the melting reactions. Taking anatexis of the metapelitic system as an example, micas (mainly muscovite and biotite) in the source play the first order control on the Mg isotopic composition ($\delta^{26}\text{Mg}$) of resulting melts. The $\delta^{26}\text{Mg}$ values of global granites range from -0.45 to +0.44 ‰ (Shen *et al.*, 2009; Li *et al.*, 2010; Liu *et al.*, 2010; Telus *et al.*, 2012; Ling *et al.*, 2013; Wang *et al.*, 2014b), far exceeding that of normal mantle rocks (-0.25 ± 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 ($\delta^{26}\text{Mg} = -0.23$ to +0.20 ‰) that does not correlate with metamorphic grade. By contrast, the $\delta^{26}\text{Mg}$ values of biotite (-0.08 to +1.10 ‰) and garnet (-1.22 to +0.10 ‰) 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 500 °C to *ca.* 10 ~ 12 kbar at >900 °C (Henk *et al.*, 1997; Bea and

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 granulite-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 granulite-facies. The bulk Mg isotopic compositions ($\delta^{26}\text{Mg} = -0.23$ to +0.20 ‰) do not correlate with metamorphic grade, indicating negligible Mg isotopic variation caused by metamorphism of metapelites. By contrast, the $\delta^{26}\text{Mg}$ values of biotite vary widely from -0.08 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 $10^3 \ln \alpha_{\text{biotite-garnet}} = 0.96 \times 10^6/T^2$, which can be used as a novel geothermometer. Our results indicate a nearly closed system for Mg isotopes of metapelites during metamorphism, and the bulk Mg isotopic compositions are therefore reconciled by the shifting garnet and biotite modes accompanied by increasing mineral $\delta^{26}\text{Mg}$ values. The systematic Mg isotopic variation in the biotite and garnet implies a possible Mg isotope fractionation between melts and residues during biotite dehydration melting, which makes Mg isotopes a potential monitor of crustal melting and a tracer of granite petrogenesis.

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Montero, 1999; Luvizotto 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 Garuti, 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 stronalite 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 $\delta^{26}\text{Mg}$ 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 stronalite zone. No correlation between bulk $\delta^{26}\text{Mg}$ and metamorphic grade is observed (Fig. 1). By contrast, $\delta^{26}\text{Mg}$ 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 heavy from the kinzigite zone ($\delta^{26}\text{Mg} = -1.10$ to -1.22 ‰) to the transition zone ($\delta^{26}\text{Mg} = -0.34$ ‰) and finally to the stronalite zone ($\delta^{26}\text{Mg} = -0.03$ to +0.10 ‰; Fig. 1). The biotite is isotopically heavier than coexisting garnet, with $\delta^{26}\text{Mg}$ increasing from the kinzigite zone (-0.08 to +0.30 ‰) through the transition zone (+0.58 ‰) to the stronalite 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,

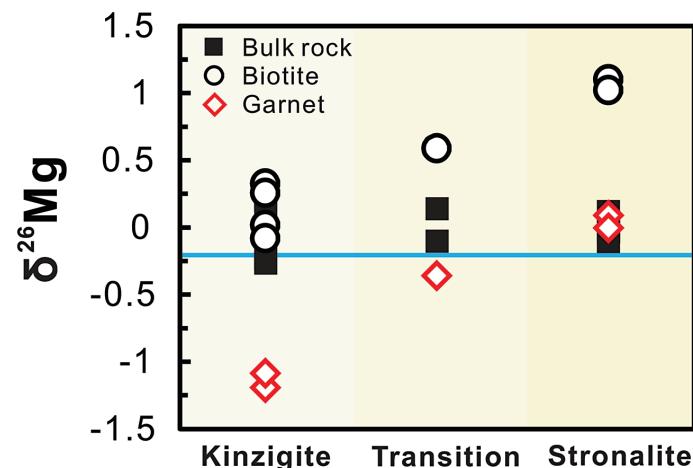


Figure 1 Magnesium isotopic compositions versus metamorphic grade for the bulk metapelites, biotites and garnets. The average value of bulk upper continental crust ($\delta^{26}\text{Mg} = -0.22$ ‰) is represented by the blue line (Li *et al.*, 2010). Data are reported in Table S-1.

with $10^3 \ln \alpha_{\text{biotite-garnet}} = 0.96 \times 10^6 / T^2$ ($R^2 = 0.7$; 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 $\delta^{26}\text{Mg}$ 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).



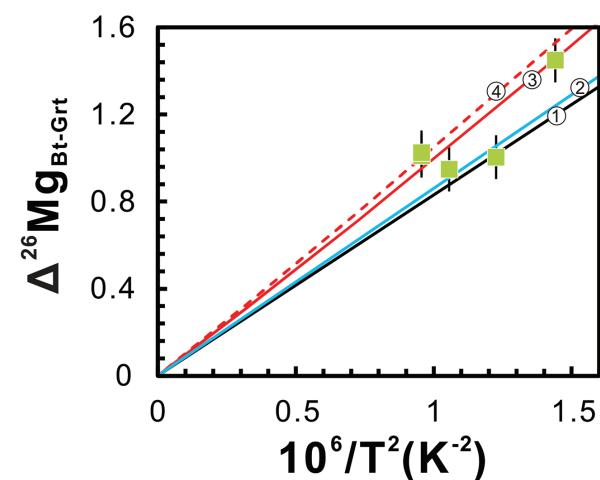


Figure 2 Magnesium isotope fractionation between biotite and garnet ($\Delta^{26}\text{Mg}_{\text{Bt-Grt}} = \delta^{26}\text{Mg}_{\text{Bt}} - \delta^{26}\text{Mg}_{\text{Grt}}$) as a function of $1/T^2$. Empirically and theoretically determined equilibrium equations of clinopyroxene-garnet Mg isotope fractionation are also shown for comparison. ① is an empirical equilibrium fractionation equation of $\Delta^{26}\text{Mg}_{\text{clinopyroxene-garnet}} = 0.83 \times 10^6/T^2$ from Li *et al.* (2011); ② is also an empirical equilibrium fractionation equation of $\Delta^{26}\text{Mg}_{\text{clinopyroxene-garnet}} = 0.86 \times 10^6/T^2$ from Wang *et al.* (2012); ③ and ④ represent the theoretically determined equilibrium fractionation equations at pressures of 0 and 10 kbar (Huang *et al.*, 2013), respectively. The temperatures for the studied metapelites, estimated using biotite-garnet Mg-Fe exchange geothermometer, are from Bea and Montero (1999). Data are reported in Table S-1.

The Mg budget in metapelites is exclusively controlled by biotite and garnet, which is opposite to other isotopic systems (such as Sr, Nd, Li, and O) that are hosted in other minerals in addition to biotite and garnet. Due to the prograde reaction of biotite + sillimanite + plagioclase + quartz \rightarrow garnet + K-feldspar + rutile + melt (Schnetger, 1994; Luvizotto and Zack, 2009), the mineralogy of metapelites changes from biotite-dominated at amphibolite-facies to garnet-dominated at granulite-facies (Fig. S-2). At the same time, both biotite and garnet $\delta^{26}\text{Mg}$ values become more positive (Fig. S-2). The coherent garnet - biotite Mg isotopic variations mainly result from the fact that the partitioning of Mg and its isotopes between garnet and biotite proceeds in accordance with their modal abundance within a nearly closed system. For example, biotites dominate the Mg budget in amphibolite-facies pelites, and consequently biotite $\delta^{26}\text{Mg}$ values are, as expected from mass balance, similar to the bulk-rock values, whereas garnet $\delta^{26}\text{Mg}$ values are significantly lighter because of the coordination geometry controlled inter-mineral fractionation (Fig. 1). During prograde metamorphism, isotopically heavy Mg released from the breakdown of biotite is progressively incorporated into the garnet, driving garnets towards high $\delta^{26}\text{Mg}$, close to the bulk-rock values (Fig. 1), and simultaneously shifting residual biotites to more ^{26}Mg enriched.

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 \rightarrow 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 \rightarrow garnet + K-feldspar + rutile + melt) is able to generate highly variable $\delta^{26}\text{Mg}$ 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 $\delta^{26}\text{Mg}$ values that vary by up to $\sim 1\text{‰}$ (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

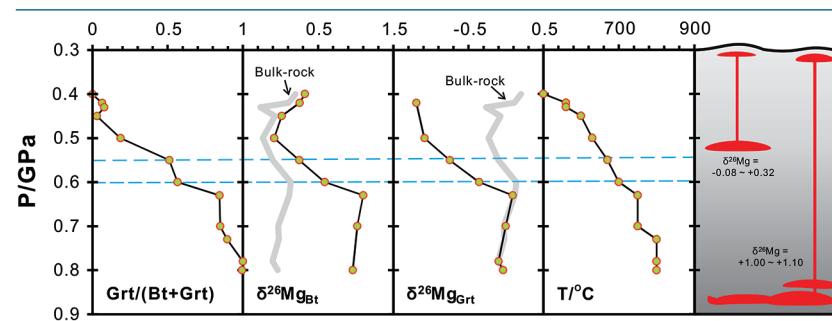


Figure 3 The variation of Grt/(Bt+Grt) ratio, $\delta^{26}\text{Mg}_{\text{Bt}}$, $\delta^{26}\text{Mg}_{\text{Grt}}$ and temperature as a function of pressure (crustal depth). Also shown is a cartoon illustrating the generation of granitic melts at different crustal depths. For those samples whose mineral separates are unavailable, Mg isotopic compositions of biotite and garnet are calculated based on the mineral modes and chemistries, assuming an inter-mineral Mg isotope fractionation of $\sim 1.00\text{‰}$. The mineral modes, compositions and temperatures are from Bea and Montero (1999).



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 ($>850^{\circ}\text{C}$) would generate melts that have higher $\delta^{26}\text{Mg}$ 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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Magnesium isotopic systematics of metapelite in the deep crust and implications for granite petrogenesis

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Supplementary Information

The Supplementary Information includes:

- Methods
- Figures S-1 to S-3
- Table S-1
- Supplementary Information 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-HNO₃-HCl acids. After complete dissolution, dried residues were taken up in 1N HNO₃ 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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Chemical separation and purification of Mg were achieved by cation exchange chromatography with Bio-Rad AG50W-X8 resin in 1N HNO₃ media. The same column procedure was performed twice in order to obtain the pure Mg recovery. The pure Mg solutions were then dried down, and re-dissolved in 3 % HNO₃ ready for mass spectrometry. An additional chromatographic step was processed for some garnets containing high Mn concentrations, using Bio-Rad AG50W-X8 200-400 mesh resin in 0.5N HCl-95 % acetone media (Bizzarro *et al.*, 2011).

The Mg isotopic compositions were analysed by the sample-standard bracketing method using a Nu Plasma MC-ICPMS at low resolution mode (Teng and Yang, 2014). Each batch of sample analysis contains at least one well-characterised standard. Sample solution was repeated on ratio measurements for >4 times within a session. The long-term precision is better than $\pm 0.07\text{‰}$ (2SD) for the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio. Magnesium isotopic results are reported in the conventional δ notation in per mille relative to DSM-3:

$$\delta^{26}\text{Mg} = [(^{26}\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^{26}\text{Mg}/^{24}\text{Mg})_{\text{DSM-3-1}}] \times 1000 \quad \text{Eq. S-1}$$

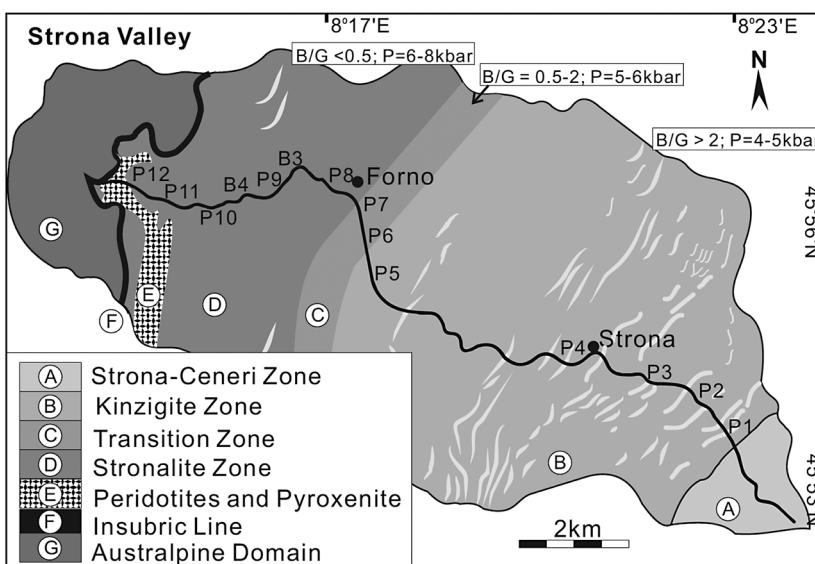


Figure S-1 Sketch map showing the location of Ivrea Zone, NW Italy (modified from Bea and Montero, 1999). The labels indicate the samples listed in Table S-1.

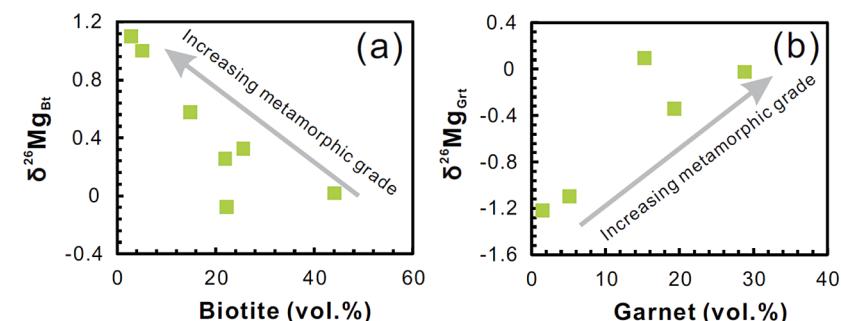


Figure S-2 Plots of biotite $\delta^{26}\text{Mg}$ versus biotite mode (a) and garnet $\delta^{26}\text{Mg}$ versus garnet mode (b) in metapelites. The modal abundances of biotite and garnet are from Bea and Montero (1999). The Mg isotopic data are reported in Table S-1.

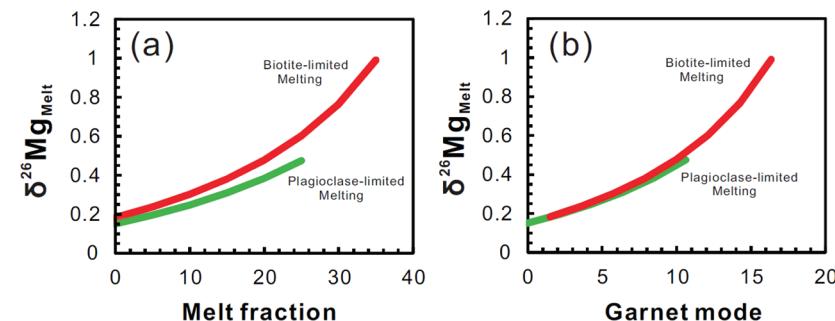


Figure S-3 Modelling showing the evolution of melt $\delta^{26}\text{Mg}$ values as a function of melt fraction (a) and peritectic garnet mode (b) during progressive biotite dehydration melting. The stoichiometry of biotite dehydration melting reaction is: 1 biotite + 0.55 plagioclase + 0.14 aluminosilicate + 0.76 quartz = 1.72 melt + 0.73 garnet (Patiño Douce and Johnston, 1991). Biotite-limited melting and plagioclase-limited melting indicate that melting terminates when biotite and plagioclase in the source is exhausted, respectively. In the modelling, the protoliths are assumed to have $\delta^{26}\text{Mg}$ value of $+0.15\text{‰}$ and MgO of 3 wt.%; the partition coefficient of Mg between biotite and garnet ($D_{\text{biotite/garnet}}$) is roughly assumed to be 2 based on the mineral compositions (Bea and Montero, 1999). The mineral modes in P1 (biotite : plagioclase : aluminosilicate : quartz : others = 0.26 : 0.09 : 0.11 : 0.49 : 0.05) and P2 (biotite : plagioclase : aluminosilicate : quartz : garnet : others = 0.22 : 0.17 : 0.04 : 0.52 : 0.015 : 0.035) are taken as examples to model plagioclase-limited melting and biotite-limited melting, respectively. The inter-mineral Mg isotope fractionation between biotite and garnet is assumed to be $\sim 1.00\text{‰}$.



Table S-1 Magnesium isotopic compositions (‰) of bulk rocks and mineral separates for the metapelites from the Ivrea Zone, NW Italy.

Sample	Bulk/Mineral	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	Grt/ (Bt+Grt)*	P (GPa)*	T(°C)*
<i>Kinzigit Zone</i>								
P1	Bulk rock	+0.205	0.070	+0.100	0.068	0	0.40	500
	Replicate ^a	+0.201	0.048	+0.141	0.044			
	average	+0.202	0.040	+0.129	0.037			
	Biotite	+0.329	0.076	+0.189	0.052			
	Replicate	+0.275	0.076	+0.156	0.052			
	average	+0.302	0.054	+0.173	0.037			
P2	Bulk rock	+0.110	0.048	+0.075	0.044	0.064	0.42	560
	Biotite	+0.255	0.073	+0.132	0.074			
	Garnet	-1.194	0.093	-0.631	0.094			
	Duplicate ^b	-1.258	0.064	-0.614	0.049			
	Replicate	-1.197	0.064	-0.615	0.050			
	Duplicate	-1.225	0.098	-0.598	0.098			
	average	-1.221	0.039	-0.620	0.031			
P3	Bulk rock	-0.265	0.048	-0.155	0.044	0.078	0.43	560
P4	Bulk rock	-0.073	0.048	-0.048	0.044	0.029	0.45	600
	Biotite	+0.017	0.073	+0.049	0.074			
P5	Bulk rock	-0.234	0.048	-0.124	0.044	0.187	0.50	630
	Biotite	-0.082	0.073	-0.054	0.074			
	Duplicate	-0.072	0.064	-0.078	0.049			
	average	-0.076	0.048	-0.071	0.041			
	Garnet	-1.086	0.073	-0.624	0.074			
	Duplicate	-1.108	0.064	-0.605	0.049			
	average	-1.099	0.048	-0.611	0.041			
<i>Transition Zone</i>								
P6	Bulk rock	-0.099	0.048	-0.046	0.044	0.511	0.55	670
	Replicate	-0.105	0.064	-0.036	0.054			
	average	-0.101	0.038	-0.042	0.034			

Sample	Bulk/Mineral	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	Grt/ (Bt+Grt)*	P (GPa)*	T(°C)*
P7	Bulk rock	+0.138	0.048	+0.090	0.044	0.566	0.60	700
	Biotite	+0.608	0.073	+0.323	0.074			
	Duplicate	+0.567	0.076	+0.316	0.052			
	Duplicate	+0.555	0.064	+0.290	0.049			
	average	+0.575	0.041	+0.306	0.032			
	Garnet	-0.360	0.076	-0.170	0.052			
	Duplicate	-0.330	0.064	-0.171	0.049			
	average	-0.343	0.049	-0.170	0.036			
<i>Stronalite Zone</i>								
P8	Bulk rock	+0.118	0.048	+0.048	0.044	0.845	0.63	750
	Biotite	+1.100	0.073	+0.579	0.074			
	Garnet	+0.090	0.073	+0.077	0.074			
	Duplicate	+0.098	0.064	+0.026	0.049			
	average	+0.095	0.048	+0.042	0.041			
P9	Bulk rock	-0.031	0.052	0.014	0.048	0.850	0.70	750
	Biotite	+1.020	0.073	+0.560	0.074			
	Duplicate	+0.983	0.064	+0.518	0.041			
	average	+0.999	0.048	+0.531	0.048			
	Garnet	-0.005	0.073	+0.009	0.074			
	Duplicate	-0.043	0.064	+0.001	0.049			
	average	-0.026	0.048	+0.003	0.041			
P10	Bulk rock	-0.022	0.052	+0.025	0.048	0.895	0.73	800
P11	Bulk rock	-0.105	0.052	-0.049	0.048	1.000	0.78	800
P12	Bulk rock	-0.035	0.052	-0.002	0.048	0.994	0.80	800

* Data are from Bea and Montero (1999).

a Repeat sample dissolution, column chemistry and instrumental analysis.

b Repeat measurement of Mg isotopic ratios on the same solution.

2SD 2 times the standard deviation of the population of n (n > 20) repeated measurements of the standards during an analytical session.



Supplementary Information References

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