Magnesium isotopic variations in cratonic eclogites: Origins and implications

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Abstract

Cratonic eclogites play an important role in the formation and dynamic evolution of the subcontinental lithospheric mantle. However, their origin, whether as fragments of subducted oceanic crust or high-pressure mantle cumulates, remains controversial. Here, we report Mg isotopic compositions (δ^{26}Mg) for cratonic eclogites from Kaalvallei and Bellsbank kimberlite pipes, South Africa. We find that clinopyroxene is 0.375 ± 0.069 to 0.676 ± 0.075 ‰ heavier than coexisting garnet, which reflects equilibrium isotope fractionation between these phases, primarily driven by the difference in Mg coordination between clinopyroxene and garnet. Bulk eclogites have strikingly variable Mg isotopic compositions, which range from -0.797 ± 0.075 to -0.139 ± 0.061 ‰, values that are significantly lighter than the range displayed by global mantle peridotites to date (-0.25 ± 0.07 ‰, 2SD). As significant Mg isotope fractionation is only known to occur during low-temperature water-rock interaction, our results provide further evidence for the derivation of cratonic eclogites from subducted altered oceanic crust. In addition, the lack of correlation between Δ^{26}Mg and Δ^{57}Fe provides evidence for redox control on equilibrium inter-mineral Fe isotope fractionation.

Keywords: magnesium isotopes, iron isotopes, isotope fractionation, cratonic eclogite, mantle

1. Introduction

Cratonic eclogites hosted by kimberlite are samples of relict subcontinental lithospheric mantle preserved beneath ancient continental cratons. As such, they have the potential to provide fundamental information on the genesis of continental cratons and the recycling and preservation of subducted oceanic crust into the deep mantle. Their origin, however, is still a subject of controversy (Smyth et al., 1989; Caporuscio and Smyth, 1990; Ireland et al., 1994; Jacob et al., 1994, 2004; Schulze et al., 1997; Barth et al., 2001; Griffin and O'Reilly, 2007; Gréau et al., 2011). The “mantle hypothesis” interprets cratonic eclogites as products of high-pressure cumulates from mantle melts based on cumulate textures, mineralogical layering, and exsolution of garnet from pyroxene in cratonic eclogites (Smyth et al., 1989; Caporuscio and Smyth, 1990). By contrast, the “crustal hypothesis” states that cratonic eclogites represent products of ancient subducted oceanic crust (either basaltic melts or cumulates) and their protoliths have experienced surface processes such as water-rock interaction and/or hydrothermal alteration prior to subduction and stacking beneath pre-existing continental lithosphere (Ireland et al., 1994; Jacob et al., 1994; Barth et al., 2001, 2002). The most compelling evidence in support of the “crustal hypothesis” comes from studies of oxygen (O) and carbon (C) isotopes. The large variations in O isotopic composition in many cratonic eclogites have been interpreted to inherit from altered oceanic crust, where O isotopes deviated from those of the Earth’s mantle are produced through seawater-rock interactions (Jacob et al., 1994) and similar arguments apply to C isotopes (Schulze et al., 1997). Recent studies show, however, that partial melting and fluid-solid reaction processes could also produce the large O isotopic variations in cratonic eclogites (Griffin and O'Reilly, 2007; Williams et al., 2009), and C isotopes can be as well fractionated by different degrees of oxidation at mantle environment (Cartigny et al., 1998). Accordingly, new tracers are therefore needed in order to resolve the debate on the origin of cratonic eclogites.

Magnesium (Mg) stable isotopes have strong potential as such a tracer. Magnesium has only one oxidation state hence Mg isotopes do not fractionate during redox-related processes. High-temperature fractionation of Mg isotopes is generally limited, as peridotites and unaltered oceanic basalts have quite homogenous Mg isotopic compositions (average δ^{26}Mg = -0.25 ± 0.07 ‰, 2SD; Teng et al., 2007, 2010a; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Pogge von Strandmann et al., 2011). On the contrary, Mg isotopes are highly fractionated during low-temperature surface processes (Fig. 1). For example, both continental and oceanic crustal rocks have highly heterogeneous Mg isotope compositions (Fig. 1; Shen et al., 2009; Higgins and Schrag, 2010; Li et al., 2010; Liu et al., 2010; Wombacher et al., 2011), due to various degrees of water-rock interaction (Tipper et al., 2006a; Pogge von Strandmann et al., 2008; Teng et al., 2010b; Wimpenny et al., 2010). On these grounds, cratonic eclogites are expected to have mantle-like Mg isotopic compositions if the “mantle hypothesis” holds true, whereas the opposite is true should the “crustal hypothesis” account for the origin of cratonic eclogites.

Specific conditions (e.g., diffusion) can, however, generate large Mg isotopic variations in igneous rocks (Richter et al., 2008; Huang et al., 2009, 2010; Dauphas et al., 2010; Pogge von Strandmann et al., 2011; Teng et al., 2011). For example, diffusion-related process has produced isotope fractionations up to 0.4 ‰ in Mg and 1.6 ‰ in Fe isotopes from Hawaii olivine (Teng et al., 2011). Significant high-temperature equilibrium inter-mineral Mg isotope fractionations can also take place between coexisting minerals (e.g., between garnet and omphacite in eclogite; spinel and olivine in peridotite; Young et al., 2009; Li et al., 2011; Liu et al., 2011). These effects have been predominantly attributed to the distinct bonding environment of Mg in these minerals (coordination number of Mg is 8 and 4 in garnet and spinel, respectively compared to 6 in pyroxene and olivine), as lower Mg coordination with stronger Mg-O bonds prefers the heavier Mg isotopes (Bigeleisen and Mayer, 1947; Urey, 1947).

Here, we present Mg isotopic data for a set of well-characterized cratonic eclogites from Kaalvallei and Bellsbank kimberlite pipes in Kaapvaal craton, South Africa (Nielsen et al., 2009; Williams et al., 2009). Our results yield up to 0.676 ± 0.075 ‰ Mg isotope fractionation (calculated as $\delta^{26}\mathrm{Mg}_{\mathrm{clinopyroxene}} - \delta^{26}\mathrm{Mg}_{\mathrm{garnet}}$; errors are propagated using the standard sum-of-squares approach) between coexisting garnet and clinopyroxene. The bulk eclogites have Mg isotopic compositions (recalculated from mineral separate data) ranging from -0.797 ± 0.075 to -0.139 ± 0.061 ‰, values that are significantly lighter than the range displayed by global mantle peridotites, hence supporting the "crustal hypothesis" for the origin of cratonic eclogites. Decoupled Mg and Fe isotope variations suggest that the observed Fe isotope fractionation is highly redox-controlled.

2. Geological Setting and Samples

The Cretaceous Kaalvallei and Bellsbank kimberlite pipes are located on the Kaapvaal craton, South Africa. Five cratonic eclogite samples (382, 402, 423, Kaalvallei-A, and 375) were collected from concentrates at the Kaalvallei kimberlite pipe. They are from the same suite as samples studied by Viljoen (2005). Additionally one cratonic eclogite sample (Bellsbank) from the Bellsbank kimberlite pipe was analyzed. These six cratonic eclogites have been the subject of previous studies (Nielsen et al., 2009; Williams et al., 2009) and a detailed description of these samples has been provided in Williams et al. (2009).

All the samples studied here are bimineralic with garnet: clinopyroxene ratios ranging from 0.20 : 0.80 to 0.65 : 0.35 and are texturally identical to Group I and Group II eclogite xenoliths described in Roberts Victor (Macgregor and Carter, 1970). Replacement textures and new mineral phases such as amphibole and phlogopite are absent, indicating limited modal metasomatic overprinting. Minor oxide inclusions are occasionally observed in both garnet and clinopyroxene. Significantly, clinopyroxenes have Al^{VI}/Al^{IV} ratios > 2 (Fig. 2), which imply high-pressure equilibration (Aoki and Shiba, 1973), and garnets have higher $Mg^{\#}$ numbers [0.62 - 0.83, $Mg^{\#}$ = molar

$MgO/(MgO + FeO)$] and Cr_2O_3 contents (0.07 - 0.42 %) relative to orogenic eclogite garnets (Fig. 2; Li et al., 2011). Both garnet and clinopyroxene are compositionally homogenous and record equilibration temperatures from 935 ^{o}C to 1401 ^{o}C (Williams et al., 2009).

Because these eclogite xenoliths are too small to provide representative samples for whole-rock chemical analysis, as well as the potential existence of contamination by kimberlite infiltration, bulk powder samples of the eclogites were not prepared and whole-rock compositions of these eclogites were instead calculated by combining the chemistry of both garnet and clinopyroxene according to the mineral abundance estimation (Williams et al., 2009). The re-constructed whole-rock compositions are characterized by higher MgO (8.46 - 17.9 %) and lower SiO_2 (45.9 - 52.1 %) contents compared to those of eclogites from orogenic massifs (Li et al., 2011) and broadly similar to those of gabbroic cumulates (Barth et al., 2002).

3. Analytical Methods

Eclogite samples were provided as coarse gravels and were subsequently crushed in an agate mortar with an agate pestle to ~50 mesh size. Fresh garnet and clinopyroxene grains were handpicked under a binocular microscope with extra care taken to avoid any alteration products during separation. Before dissolution, 0.34 - 2.1 mg separated minerals were ultrasonicated for 3 times with each 10 minutes in Milli-Q water (18.2 MΩ cm) at room temperature. All chemical procedures including mineral dissolution and column chemistry were carried out in the clean laboratory at the Isotope Laboratory of the University of Arkansas, Fayetteville, following established procedures (Yang et al., 2009; Li et al., 2010; Teng et al., 2010a).

Minerals were digested in Savillex screw-top beakers in a 6:1 (v/v) mixture of Optima-grade HF and HNO_3 acids on a hotplate in an exhaust hood. After about one week, the sample solutions were dried at 120 ^oC and the dried residues were refluxed with a 1:3 (v/v) mixture of Optima-grade HNO_3 and HCl acid, followed by heating at 160 ^oC to dryness. Concentrated HNO_3 was then added at 160 ^oC to ensure complete dissolution. Finally, the solution was evaporated to dryness at 160 ^oC, and the dried residue was dissolved in 1N HNO_3 for ion exchange column chemistry.

Chemical separation and purification of Mg were achieved by cation exchange chromatography with Bio-Rad 200 - 400 mesh AG50W-X8 resin in 1N HNO_3 media (Teng et al., 2007). The same column procedure was performed twice in order to obtain pure Mg solutions for mass spectrometry. The total procedural blank is < 10 ng, which represented < 0.1 % of Mg loaded on the column (Teng et al., 2010a).

Magnesium isotopic compositions were analyzed by the sample-standard bracketing method using a *Nu Plasma* MC-ICPMS at low resolution mode, with ^{26}Mg, ^{25}Mg and ^{24}Mg measured simultaneously in separated Faraday cups (H5, Ax, and L4). No molecular interferences or double charge interferences were observed during analyses. The background Mg signals for the ^{24}Mg were < 10^{-4} V, which is negligible relative to sample signals of 3 - 4 V. Each batch of sample analysis contains at least one well-characterized standard. Sample solutions were re-measured > 4 times per analytical session. The long-term precision was better than 0.07 ‰ (Teng et al., 2010a), based on the replicate analyses of synthetic solution, mineral and rock standards. Magnesium isotope results are reported in the conventional δ notation in per mil relative to DSM-3 (Galy et al., 2003), $\delta^{x}\mathrm{Mg} = [(^{x}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}}/(^{x}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{DSM\text{-}3}}-1] \times 1000$, where x refers to 25 or 26.

4. Results

Magnesium isotopic compositions of the mineral separates and whole rocks, together with the well-characterized international (seawater) and in-house (KH-olivine) standards are reported in Table 1. Different batches of garnets and clinopyroxenes from the same eclogite sample have identical Mg isotopic compositions within analytical uncertainty (Table 1).

The δ^{26}Mg values span a considerable range from -1.083 to -0.608 ‰ in garnet and from -0.622 to +0.013 ‰ in clinopyroxene (Fig. 3). Clinopyroxene is always heavier than coexisting garnet, with $\Delta^{26}\mathrm{Mg}_{\mathrm{clinopyroxene\ -\ garnet}}$ (= $\delta^{26}\mathrm{Mg}_{\mathrm{clinopyroxene}} - \delta^{26}\mathrm{Mg}_{\mathrm{garnet}}$) ranging from 0.375 ± 0.069 to 0.676 ± 0.075 ‰. The δ^{26}Mg values of whole-rock eclogites, calculated based on δ^{26}Mg values and modal abundance of clinopyroxene and garnet, vary from -0.798 ± 0.075 to -0.139 ±

0.061 ‰ (Fig. 3, Table 1), of which four exhibit significantly lighter Mg isotopic compositions than the mantle value (Fig. 3, Teng et al., 2010a). The constructed whole-rock δ^{26}Mg values are not susceptible of variation of the mineral modes, as changes in the modal abundance of garnet and clinopyroxene by ± 10 % can only shift the whole-rock δ^{26}Mg values within ± 0.07 ‰, which is still within analytical uncertainty.

5. Discussion

5.1 Equilibrium inter-mineral Mg isotope fractionation

Both equilibrium (Young et al., 2009; Li et al., 2011; Liu et al., 2011) and chemical diffusion-driven kinetic (Richter et al., 2008; Huang et al., 2009; Dauphas et al., 2010; Teng et al., 2011) Mg isotope fractionation could occur at high temperature and potentially produce large Mg isotope fractionations between clinopyroxene and garnet. Kinetic isotope fractionation during inter-diffusion of Mg and Fe should generate a negative linear correlation between δ^{26}Mg and δ^{56}Fe (Dauphas et al., 2010; Teng et al., 2011). No such correlations were observed (Fig. 4). Furthermore, no elemental variations exist within single mineral grain or among different grains from an individual eclogite sample (Williams et al., 2009). Analysis of different mineral fragments from the same sample yield identical Mg isotope compositions (Table 1), suggesting that there is minimal intra-mineral Mg isotopic variation at the mineral scale (< 0.2 mm) and implying equilibrium Mg isotope fractionation. The final support for equilibrium inter-mineral Mg isotope fractionation comes from the linear correlation between $\Delta^{26}Mg_{clinopyroxene\text{-}garnet}$ and $1/T^2$ (Fig. 5). An equilibrium fractionation line is defined on $\Delta^{26}Mg – 1/T^2$ diagram for all cratonic eclogites studied here and orogenic eclogites that formed at lower temperatures from Dabie Mountain, China (Li et al., 2011), with the following equilibrium fractionation equation $\Delta^{26}Mg_{clinopyroxene\text{-}garnet} = 0.86 \times 10^6/T^2$ ($R^2 = 0.84$, Fig. 5). This equilibrium inter-mineral Mg isotope fractionation may reflect the distinct bonding environment of Mg in garnet [coordination number (CN) of Mg is 8] compared to clinopyroxene (CN of Mg is 6), where stronger Mg - O bonds in lower Mg coordination sites prefer heavier Mg isotopes to lighter ones (Li et al., 2011).

5.2 Crustal origin of cratonic eclogites

When compared to mantle peridotites and unaltered oceanic basalts (Teng et al., 2007, 2010a; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Pogge von Strandmann et al., 2011), cratonic eclogites have distinct, extremely light Mg isotopic compositions (Fig. 3). Providing that prograde metamorphism does not significantly fractionate Mg isotopes (Li et al., 2011), and the rapid eruption of kimberlitic magma does not allow for extensive interaction between eclogite minerals and host magma (Kelley and Wartho, 2000), the large Mg isotopic variations in these eclogites must therefore result from other, open-system processes. These include melt extraction and diffusion processes associated with eclogite-peridotite interaction and melt/fluid metasomatism, or, alternatively protolith heterogeneity.

Diffusion processes can generate large Mg isotope fractionations due to the faster diffusion of lighter Mg isotopes relative to heavier isotopes (e.g., Richter et al., 2008). It is, however, unlikely to be the main process responsible for producing the light δ^{26}Mg values observed in the bulk eclogites as the eclogite sample with the highest Mg$^{\#}$ also has the heaviest Mg isotopic composition, opposite to what would be expected from diffusion. In addition, diffusion processes alone (i.e. without any mineral recrystallization) should generate disequilibrium inter-mineral Mg isotope fractionation. This is inconsistent with the equilibrium Mg isotope fractionation between clinopyroxene and garnet observed here.

Metasomatism can also alter the chemical and isotopic compositions of eclogites at different scales and obscure their primary features. Although metasomatic overprinting has been demonstrated to be of limited importance in producing variations in stable Fe, O and Tl isotope signatures observed in these samples (Viljoen, 2005; Nielsen et al., 2009; Williams et al., 2009), it is necessary to evaluate its impact on Mg isotope systematics. Mg isotopic compositions of global oceanic basalts are homogenous (Teng et al., 2010a), thus silicate metasomatism, in the absence of any additional fractionation processes, cannot produce the light Mg isotopic compositions of these cratonic eclogites. Mantle carbonatite melt is another important metasomatic agent with the potential to change the Mg isotopic compositions of target rocks towards light values, as both theoretical studies and analysis of crustal carbonates suggest that they have isotopically light Mg isotope signatures (Galy et al., 2002; Young and Galy, 2004; Brenot et al., 2008; Higgins and Schrag, 2010; Jacobson et al., 2010; Schauble, 2011). Carbonatite metasomatism should, however, be readily identifiable through an increase in the values of metasomatic indices such as Sr, Sr/Y, and LREE. There are however no correlations between δ^{26}Mg and such indices of metasomatism (Fig. 6). For example, the sample with the highest ratio of Sr/Y has a relative unfractionated δ^{26}Mg value of -0.164 ‰. Furthermore, the eclogites studied here have δ^{18}O values ranging from 4.49 - 5.58 ‰ (Williams et al., 2009), slightly below the mantle value (5.5 - 5.9 ‰), but much lower than values exhibited by mantle carbonatites (Deines, 1989), which provides further evidence against carbonatite metasomatism as the primary cause of Mg isotope heterogeneity.

The most likely explanation for these isotopically light cratonic eclogites is therefore protolith heterogeneity. As Mg isotopes can only be significantly fractionated during surface processes such as carbonate precipitation (Galy et al., 2002; Higgins and Schrag, 2010) and silicate weathering (Tipper et al., 2006a; Pogge von Strandmann et al., 2008; Teng et al., 2010b; Wimpenny et al., 2010), these protoliths must have had a surface origin. For example, oceanic dolomite is deeply depleted in Mg isotopes (< -2 ‰) with δ^{26}Mg values 2.0 - 2.7 ‰ lighter than the precipitating pore fluid (Higgins and Schrag, 2010). Marine sediments have highly variable but isotopically extremely light Mg isotopic compositions (Higgins and Schrag, 2010). While fresh oceanic basalts such as MORBs and OIBs have homogenous Mg isotopic compositions around the mantle value (defined by unaltered peridotites), the bulk altered oceanic crust is inferred to have a lighter Mg isotopic composition. This is based on the systematics of Mg isotopes during weathering: the δ^{26}Mg value of seawater (δ^{26}Mg = -0.83 ± 0.09 ‰, Foster et al., 2010; Ling et al., 2011 and references therein) is higher than that of the global runoff (δ^{26}Mg = -1.09 ± 0.05 ‰, Tipper et al., 2006b), which requires the uptake of light Mg isotopes by alteration of oceanic crust as suggested by Tipper et al (2006b). During oceanic alteration, carbonates form by the uptake of Mg and Ca in seawater that were originally released from oceanic basalts (Wilkinson and Algeo, 1989). A significant portion of carbonate resides in the top 300 m of altered oceanic crust with an average CO_2 content of ~3 % (Alt and Teagle, 1999). Local enrichment of carbonate veins (as high as 75 % modal abundance) can account for > 10 % of the CO_2 content of altered basalt (Staudigel et al., 1996). Considering the extremely light Mg isotopic compositions of carbonates, at least parts of the altered oceanic crust should have a distinct, light Mg isotopic composition relative to the primitive mantle. Subduction should subsequently transform this isotopically light altered oceanic crustal material into carbonated eclogites during prograde metamorphism (Green and Ringwood, 1967). Carbonates in eclogites, due to their higher solidus than the geothermal gradient of even hot subduction, can be preserved in the form of dolomite at intermediate depths (60 – 120 km) and magnesite at greater depths (> 120 – 150 km), potentially surviving processes such as subduction-related partial melting (e.g., Dasgupta et al., 2010, and references therein). This subducted carbonate material may ultimately react with the silicates to form reduced carbon (diamond or graphite) and release Mg into silicates (e.g., Knoche et al., 1999; Pal'vanov et al., 2002), providing a mechanism by which the light Mg isotopic composition of altered oceanic crust can be inherited by its metamorphic equivalents in mantle conditions.

Further evidence for subducted altered oceanic crust as protolith of these cratonic eclogites comes from coupled variations of Mg and Tl isotopes (Fig. 7). The variable Mg and Tl isotopic compositions of these eclogites can be explained by mixing of a mantle end-member with an altered component. Oceanic crust altered at low temperature by seawater is characterized by light Tl isotopic composition (ε^{205}Tl = -15), in great contrast to mantle rocks (ε^{205}Tl = -2; Nielsen et al., 2006a, b). Accordingly, sample 375 with ε^{205}Tl value of -5 and δ^{26}Mg value of -0.779 ‰ is chosen to represent the altered oceanic crust, and sample 402 with primary mantle-like Tl and Mg isotopic signatures is selected to represent the mantle end-member. All other samples fall on the mixing line between these two end-members, further suggesting the involvement of altered oceanic crust into the formation of cratonic eclogites (Fig. 7).

5.3 Redox-controlled inter-mineral Fe isotope fractionation

Large inter-mineral Fe isotope fractionations between garnet and clinopyroxene have been previously observed in mantle rocks such as garnet peridotites, pyroxenites and eclogites (Beard and Johnson, 2004; Williams et al., 2005, 2009; Weyer et al., 2007). Although the observed fractionations can be ascribed to equilibrium processes (Beard and Johnson, 2004; Williams et al., 2009), the underlying mechanisms are not yet fully resolved. As in the case of Mg isotopes, contrasts in the bonding environment of Fe, here involving both Fe redox state and coordination, in minerals and melts are predicted to be responsible for the inter-mineral Fe isotope fractionation (Polyakov and Mineev, 2000; Polyakov et al., 2007; Schuessler et al., 2007; Hill and Schauble, 2008; Shahar et al., 2008). Resolving the effects of Fe redox state (Williams et al., 2004, 2005, 2012; Weyer et al., 2007; Weyer and Ionov, 2007; Dauphas et al., 2009; Teng et al., 2008; Sossi et al., 2012) from coordination has so far proved difficult.

Combined Mg and Fe isotopic analyses of the same samples may help to evaluate the relative roles of oxidation state and coordination on Fe isotope fractionation, as Mg isotopes do not fractionate during redox reactions and Mg^{2+} and Fe^{2+} have identical charge and similar ionic radii, and occupy the same site in common rock-forming minerals. For example, in garnet with general chemical formula of $X_3Y_2Z_3O_{12}$, Mg^{2+} and Fe^{2+} have ionic radii of 0.890 Å and 0.920 Å (Shannon and Prewitt, 1969; Shannon, 1976), respectively, and occupy the same X site with eight-fold coordination, whereas the Fe^{3+} has ionic radii of only 0.645 Å and goes into the Y site with six-fold coordination. It then follows that if inter-mineral Fe isotope fractionation is controlled purely by the coordination and bonding environment of Fe^{2+}, then positive correlations between δ^{26}Mg and δ^{57}Fe for an individual mineral and between Δ^{26}Mg and Δ^{57}Fe are expected. No such correlations however are observed in samples investigated here (Fig. 8). This implies that Fe^{3+} also plays a critical role in inter-mineral Fe isotope fractionation, while the proportions of Fe^{3+} and Fe^{2+} in minerals is largely related to the oxidation state. Considering that equilibrium Fe isotope fractionation has been achieved for the studied cratonic eclogites (Williams et al., 2009), the change of redox state of Fe thus accounts for the fractionation of Fe isotopes. This conclusion is further supported by literature studies where coupled Mg and Fe isotopic analyses of clinopyroxene and olivine in peridotites were conducted (Yang et al., 2009; Huang et al., 2011; Zhao et al., 2012). Theoretical calculation suggests that, clinopyroxene should be heavier than coexisting olivine for both Mg and Fe isotopes (Polyakov and Mineev, 2000; Polyakov et al., 2007; Schauble, 2011), hence a positive correlation between Δ^{26}Mg and Δ^{57}Fe is expected if bonding environment of Mg^{2+} and Fe^{2+} alone accounts for the effect. The fractionation of Mg isotopes between clinopyroxene and olivine in mantle rocks is, however, relatively small (<0.2 ‰, Fig. 8) and within the theoretical prediction at mantle temperature (Schauble, 2011). By contrast, the magnitude of Fe isotope fractionation between clinopyroxene and olivine (up to 0.54 ‰ for Δ^{57}Fe, Zhao et al., 2012) is variable and beyond that predicted by theory (Polyakov and Mineev, 2000; Polyakov et al., 2007), leading to a lack of correlation between Δ^{26}Mg and Δ^{57}Fe for clinopyroxene and olivine (Fig. 8). This decoupled behavior of Mg and Fe isotopes during high-temperature processes further suggests that bonding environment of Fe^{2+}

alone is unlikely to be the major control on Fe isotope fractionation. Our study thus suggests that coupled Mg and Fe isotopic analyses on mineral pairs may provide a novel way to identify the mechanism responsible for Fe isotope fractionation.

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Table 1 Magnesium isotopic composition of mineral separates and constructed whole-rock for cratonic eclogites and reference materials (KH-olivine and seawater)

Sample	Mineral/rock[a]	Mode[*]	Wt.(mg)	δ^{26}Mg	2SD[g]	δ^{25}Mg	2SD
375	Cpx	0.65	1.26	-0.622	0.061	-0.336	0.051
	Grt^{1} [b]	0.35	1.07	-1.014	0.051	-0.541	0.052
	Grt^{2}		1.44	-0.973	0.082	-0.504	0.054
	Duplicate [c]			-0.990	0.051	-0.533	0.052
	Ave. Grt [d]			-0.997	0.033	-0.526	0.030
	Whole-rock[e]			-0.779	0.069	-0.416	0.059
382	Cpx^{1}	0.8	0.93	0.001	0.051	-0.002	0.052
	Cpx^{2}		2.1	-0.025	0.051	-0.025	0.052
	Ave. Cpx			-0.012	0.036	-0.014	0.037
	Grt^{1}	0.2	1.57	-0.681	0.061	-0.328	0.039
	Grt^{2}		0.34	-0.652	0.061	-0.340	0.039
	Ave. Grt			-0.666	0.043	-0.334	0.028
	Whole-rock			-0.164	0.056	-0.088	0.046
402	Cpx^{1}	0.8	1.32	-0.015	0.061	-0.002	0.051
	Cpx^{2}		0.72	0.040	0.061	0.010	0.051
	Ave. Cpx			0.013	0.043	0.004	0.036
	Grt^{1}	0.2	0.9	-0.647	0.061	-0.338	0.051
	Grt^{2}		0.63	-0.568	0.061	-0.306	0.051
	Ave. Grt			-0.608	0.043	-0.322	0.036
	Whole-rock			-0.139	0.061	-0.076	0.051
423	Cpx^{1}	0.35	1.84	-0.101	0.061	-0.030	0.051
	Cpx^{2}		0.62	-0.044	0.051	-0.055	0.052
	Ave. Cpx			-0.068	0.039	-0.042	0.036
	Grt	0.65	1.64	-0.723	0.061	-0.377	0.051
	Whole-rock			-0.520	0.072	-0.273	0.062
Bellsbank	Cpx	0.55	1.4	-0.407	0.061	-0.206	0.039
	Grt^{1}	0.45	0.78	-1.091	0.061	-0.555	0.051
	Grt^{2}		0.86	-1.075	0.061	-0.565	0.051
	Ave. Grt			-1.083	0.043	-0.560	0.036
	Whole-rock			-0.798	0.075	-0.411	0.053
Kaalvallei-A	Cpx^{1}	0.4	0.5	-0.565	0.082	-0.259	0.054
	Duplicate			-0.523	0.051	-0.280	0.052
	Cpx^{2}		0.34	-0.579	0.082	-0.285	0.054
	Duplicate			-0.511	0.051	-0.279	0.052
	Ave. Cpx			-0.533	0.031	-0.276	0.026
	Grt^{1}	0.6	1.27	-0.920	0.082	-0.450	0.054
	Duplicate			-0.939	0.051	-0.484	0.052
	Grt^{2}		1.79	-0.962	0.082	-0.461	0.054
	Duplicate			-0.911	0.051	-0.488	0.052
	Ave. Grt			-0.929	0.031	-0.471	0.026

	Whole-rock	-0.794	0.044	-0.404	0.037
KH-Olivine	Ol	-0.276	0.061	-0.151	0.039
	Replicate[f]	-0.274	0.043	-0.124	0.039
	Replicate	-0.236	0.043	-0.150	0.039
	Replicate	-0.251	0.075	-0.135	0.049
	Replicate	-0.235	0.055	-0.116	0.050
	Replicate	-0.237	0.052	-0.128	0.040
	Replicate	-0.250	0.054	-0.133	0.047
	Replicate	-0.227	0.050	-0.111	0.049
	Replicate	-0.248	0.063	-0.142	0.054
	Replicate	-0.270	0.043	-0.106	0.039
	Replicate	-0.289	0.061	-0.155	0.051
	Ave. Ol	-0.253	0.016	-0.132	0.013
Seawater	Seawater	-0.879	0.082	-0.431	0.054
	Replicate	-0.827	0.051	-0.413	0.052
	Replicate	-0.825	0.063	-0.412	0.035
	Replicate	-0.849	0.056	-0.415	0.052
	Replicate	-0.861	0.061	-0.418	0.056
	Replicate	-0.842	0.043	-0.410	0.039
	Ave. Seawater	-0.844	0.023	-0.415	0.019

Notes:

[*] Mineral modal abundances are taken from Williams et al. (2009).

[a] Grt = garnet; Cpx = clinopyroxene; Ol = olivine.

[b] The number on the upper-right corner denotes different batches of mineral grains from the same eclogite sample.

[c] Duplicate: repeated measurement of Mg isotopic ratios on the same solution.

[d] Ave. = weighted average value.

[e] Whole-rock Mg isotopic compositions that are calculated based on the mineral data. Variations in the modal abundance of garnet and clinopyroxene by ± 10 % can shift the whole-rock δ^{26}Mg values within ± 0.07 ‰, which is still within the analytical uncertainty.

[f] Replicate: repeat sample dissolution, column chemistry and instrumental analysis

[g] 2SD = 2 times the standard deviation of the population of n (n > 20) repeat measurements of the standards during an analytical session.

Figure captions

Fig. 1. Magnesium isotopic compositions of major reservoirs: carbonates (Young and Galy., 2004; Tipper et al., 2006a; Brenot et al., 2008; Higgins and Schrag., 2010; Jacobson et al., 2010), upper continental crust (Li et al., 2010), marine sediment & pore fluid (Higgins and Schrag., 2010; Wombacher et al., 2011), global oceanic basalt (Teng et al., 2007, 2010a; Bourdon et al., 2010), global peridotite (Bourdon et al., 2010; Teng et al., 2010a;), seawater and global runoff (Tipper et al., 2006b; Foster et al., 2010; Ling et al., 2011). δ^{26}Mg values for carbonates and marine sediments can be as low as -5.29 ‰ and -5.57 ‰, respectively.

Fig. 2. Major element compositions of clinopyroxene and garnet from cratonic eclogites. In the Al^{VI} versus Al^{IV} diagram, all the clinopyroxene from cratonic eclogites plot in the eclogite field defined by $Al^{VI}/Al^{IV} > 2$. Fields and ratio are from Aoki and Shiba (1973). Data of Dabie granulites are from Wang et al. (2012); In the Cr_2O_3 - $Mg^{\#}$ diagram, all garnets from cratonic eclogites are distinct from orogenic eclogite in higher Cr_2O_3 content and $Mg^{\#}$ number. Data of Bixiling orogenic eclogite are from Li et al. (2011).

Fig. 3. Variations of δ^{26}Mg values as a function of whole-rock MgO contents. The horizontal gray band represents the Mg isotopic composition of the mantle (-0.25 ± 0.07‰, 2SD, Teng et al., 2010a).

Fig. 4. δ^{26}Mg vs. δ^{57}Fe diagrams for garnet and clinopyroxene from cratonic eclogites. Fe isotopic compositions are from Williams et al. (2009). δ^{57}Fe value of the clinopyroxene from sample 382 is not available.

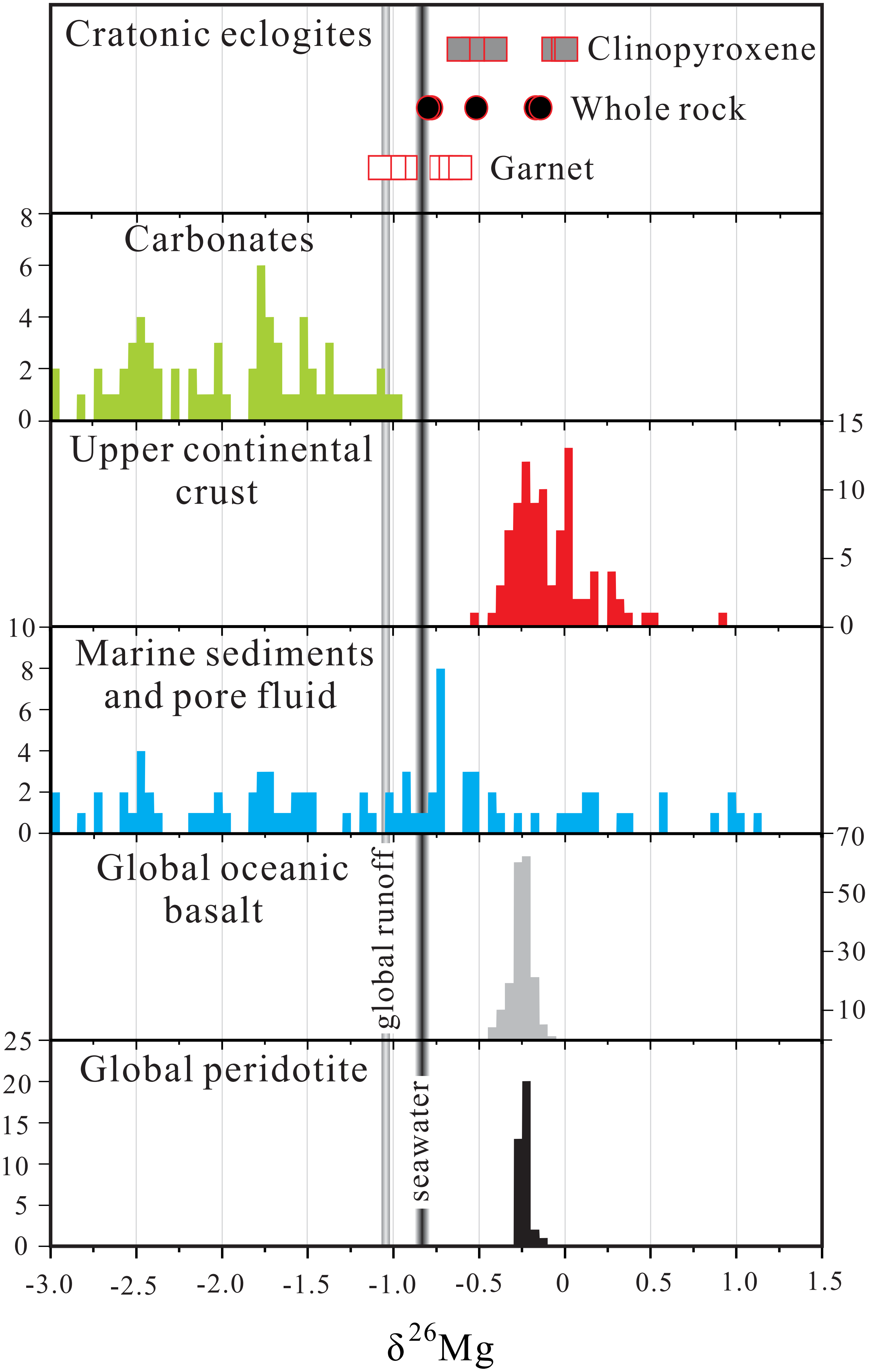
Fig. 5. Equilibrium Mg isotope fractionation between clinopyroxene and garnet ($\Delta^{26}Mg_{clinopyroxene\text{-}garnet} = \delta^{26}Mg_{clinopyroxene} - \delta^{26}Mg_{garnet}$) as a function of $1/T^2$. The orogenic eclogites data are from Li et al (2011).

Fig. 6. Variations of bulk eclogite δ^{26}Mg values as a function of elemental indices of metasomatism. Trace element data are from Williams et al. (2009). Sample labeled with "×" is the Bellsbank eclogite. The high Sr/Nb ratio of Bellsbank resulted from the low Nb content, which is under the detect limitation.

Fig. 7. Correlation of δ^{26}Mg and ε^{205}Tl values for eclogite samples. Sample 402 and 375 are taken to represent the end-member of mantle and altered oceanic crust, respectively. Tl contents and Tl isotopic compositions of the end-member components are taken from Nielsen et al. (2009) and as follows. Sample 402: Tl = 80 ppb, ε^{205}Tl =

-1.8; Sample 375: Tl = 464 ppb, ε^{205}Tl = -5.1. Mg contents are taken from Williams et al. (2009) and Mg isotopic compositions are from Table 1. Mixing line represents simple mixing between the mantle and altered oceanic that have lost 90 % original Tl during subduction-related dehydration.

Fig. 8. Δ^{26}Mg - Δ^{57}Fe diagram for minerals from the cratonic eclogites and peridotites. Mg and Fe isotopic compositions for the clinopyroxene and garnet in cratonic eclogites are from this study and Williams et al. (2009), respectively. Mg and Fe isotopic compositions for the clinopyroxene and olivine pairs in peridotites are from Huang et al. (2011), Zhao et al. (2012) and Yang et al. (2009).


Cratonic eclogites
Clinopyroxene
Whole rock
Garnet
Carbonates
Upper continental crust
Marine sediments and pore fluid
Global oceanic basalt
Global peridotite
global runoff
seawater
8
6
4
2
0
15
10
5
0
10
8
6
4
2
0
70
50
30
10
25
20
15
10
5
0
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0
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1.0
1.5
δ26Mg

Figure 1

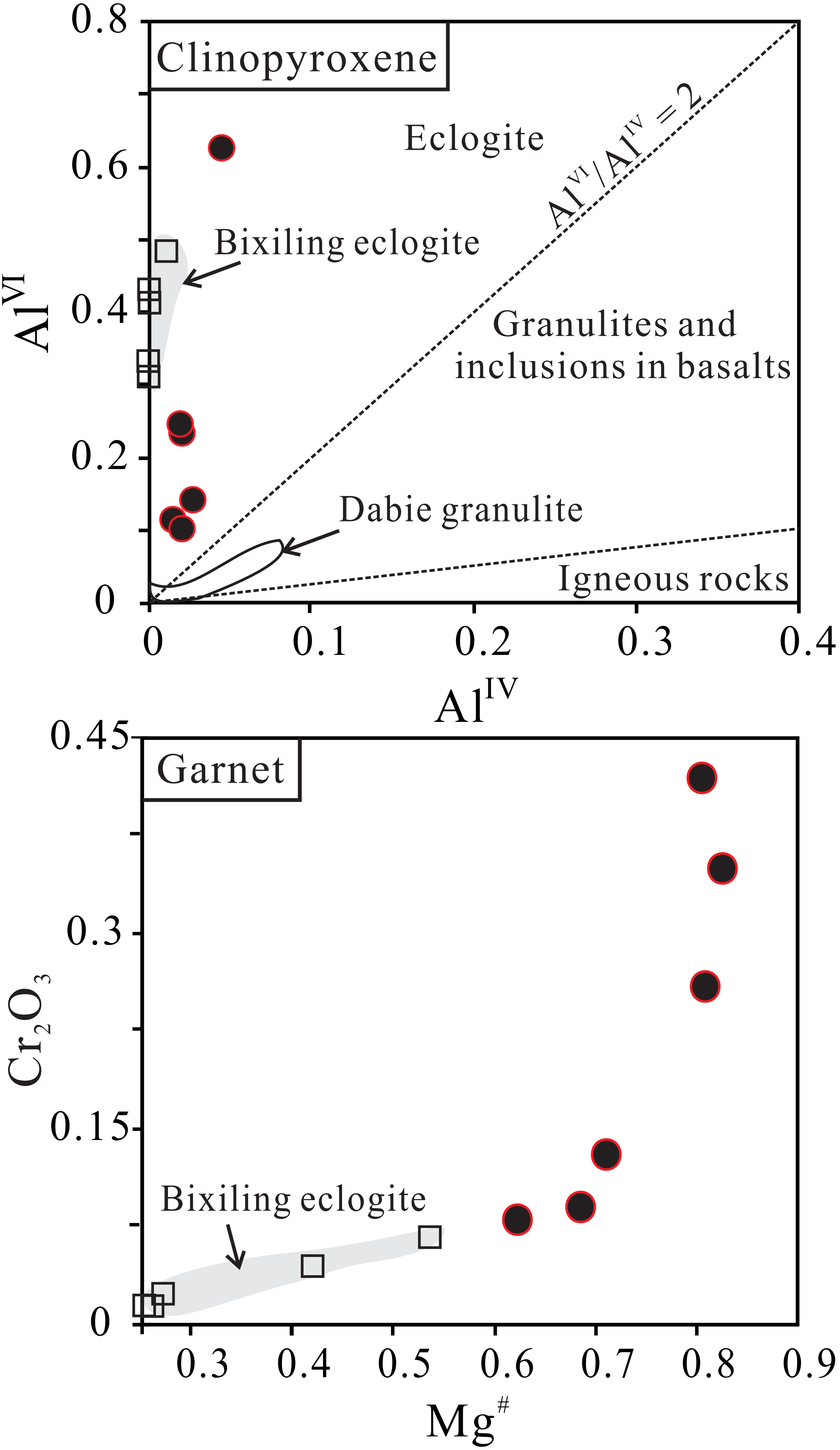
Clinopyroxene
Eclogite
$Al^{VI}/Al^{IV} = 2$
Bixiling eclogite
Granulites and inclusions in basalts
Dabie granulite
Igneous rocks
Al^{VI}
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
Al^{IV}
Garnet
Bixiling eclogite
Cr_2O_3
0.45
0.3
0.15
0
0.3
0.4
0.5
0.6
0.7
0.8
0.9
$Mg^{\#}$

Figure 2

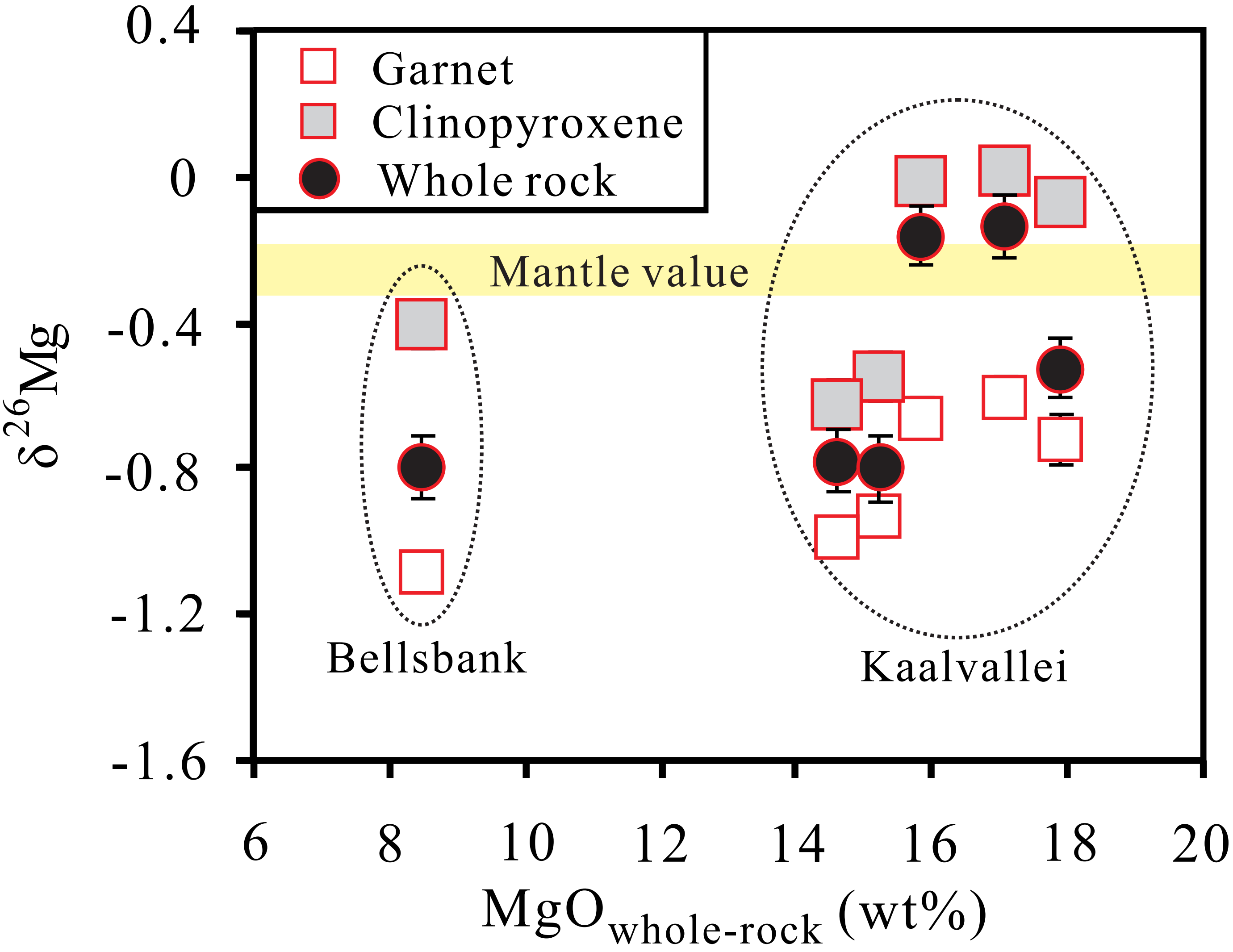
0.4
0
-0.4
-0.8
-1.2
-1.6
δ^{26}Mg
Garnet
Clinopyroxene
Whole rock
Mantle value
Bellsbank
Kaalvallei
6
8
10
12
14
16
18
20
MgO$_{\text{whole-rock}}$ (wt%)

Figure.3

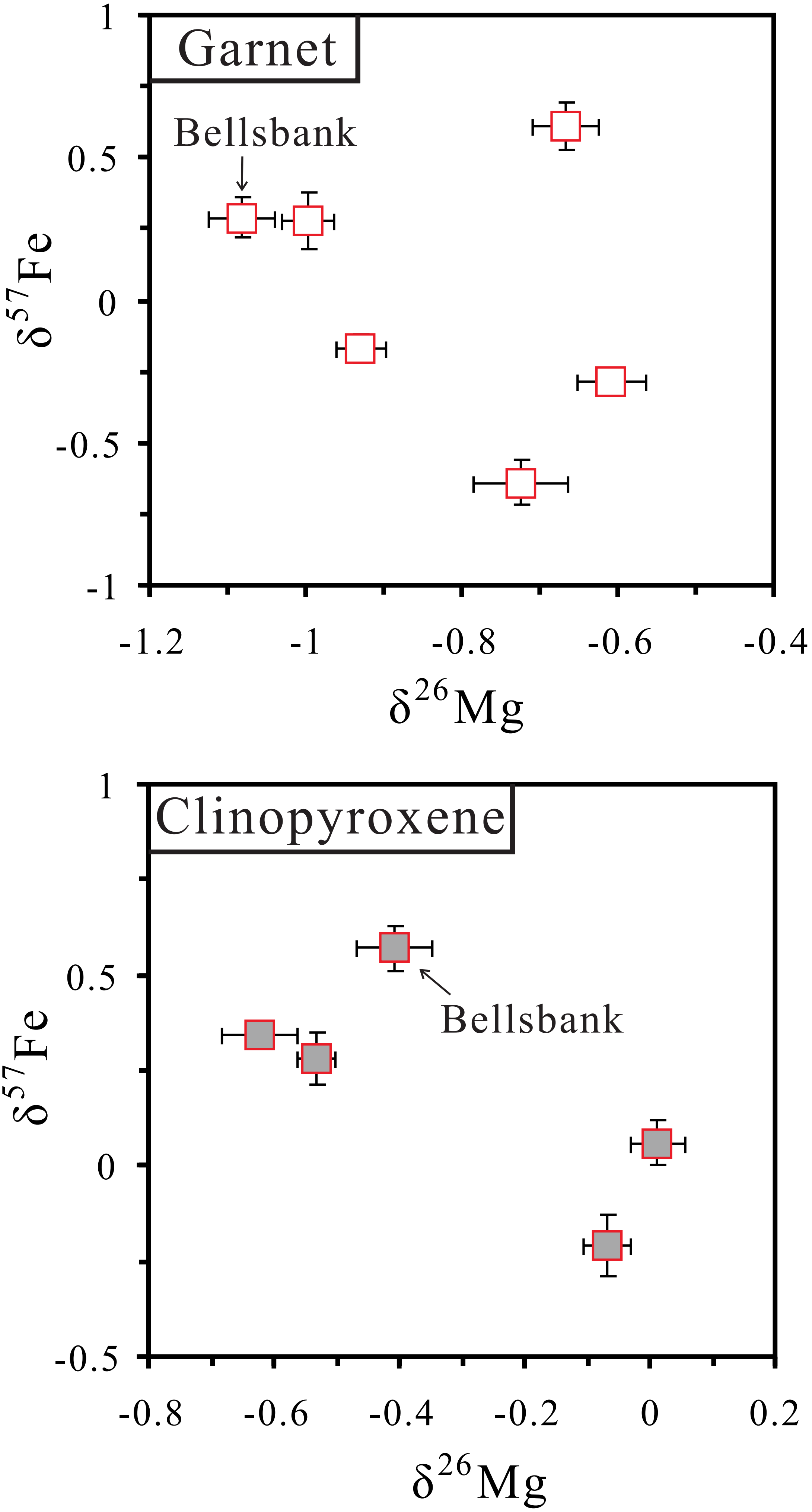
Garnet
Bellsbank
1
0.5
0
-0.5
-1
δ^{57}Fe
-1.2
-1
-0.8
-0.6
-0.4
δ^{26}Mg
Clinopyroxene
Bellsbank
1
0.5
0
-0.5
δ^{57}Fe
-0.8
-0.6
-0.4
-0.2
0
0.2
δ^{26}Mg

Figure 4

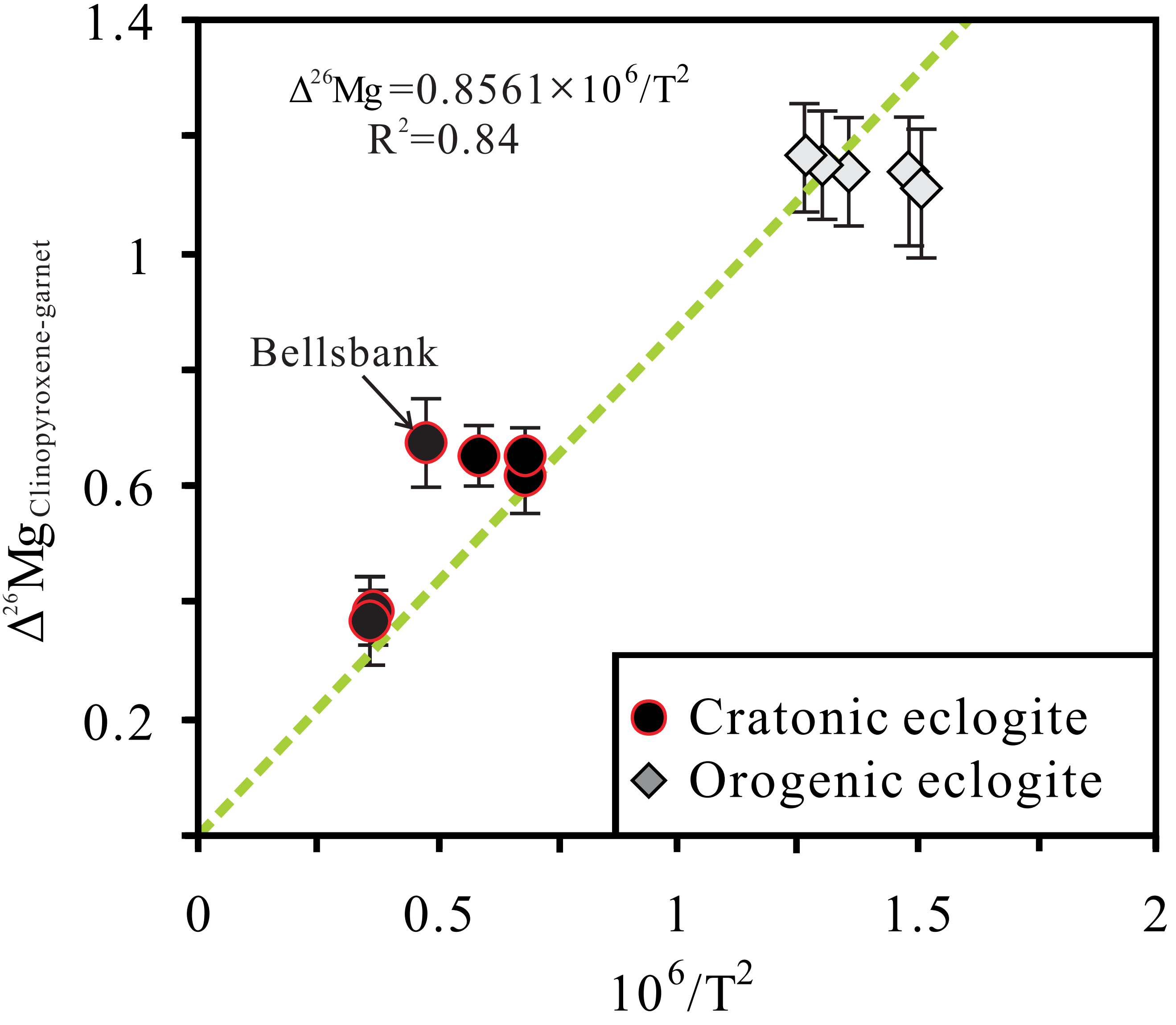
1.4
1
0.6
0.2
0
0.5
1
1.5
2
$\Delta^{26}Mg_{Clinopyroxene\text{-}garnet}$
$10^6/T^2$
$\Delta^{26}Mg = 0.8561 \times 10^6/T^2$
$R^2 = 0.84$
Bellsbank
● Cratonic eclogite
◆ Orogenic eclogite

Figure 5

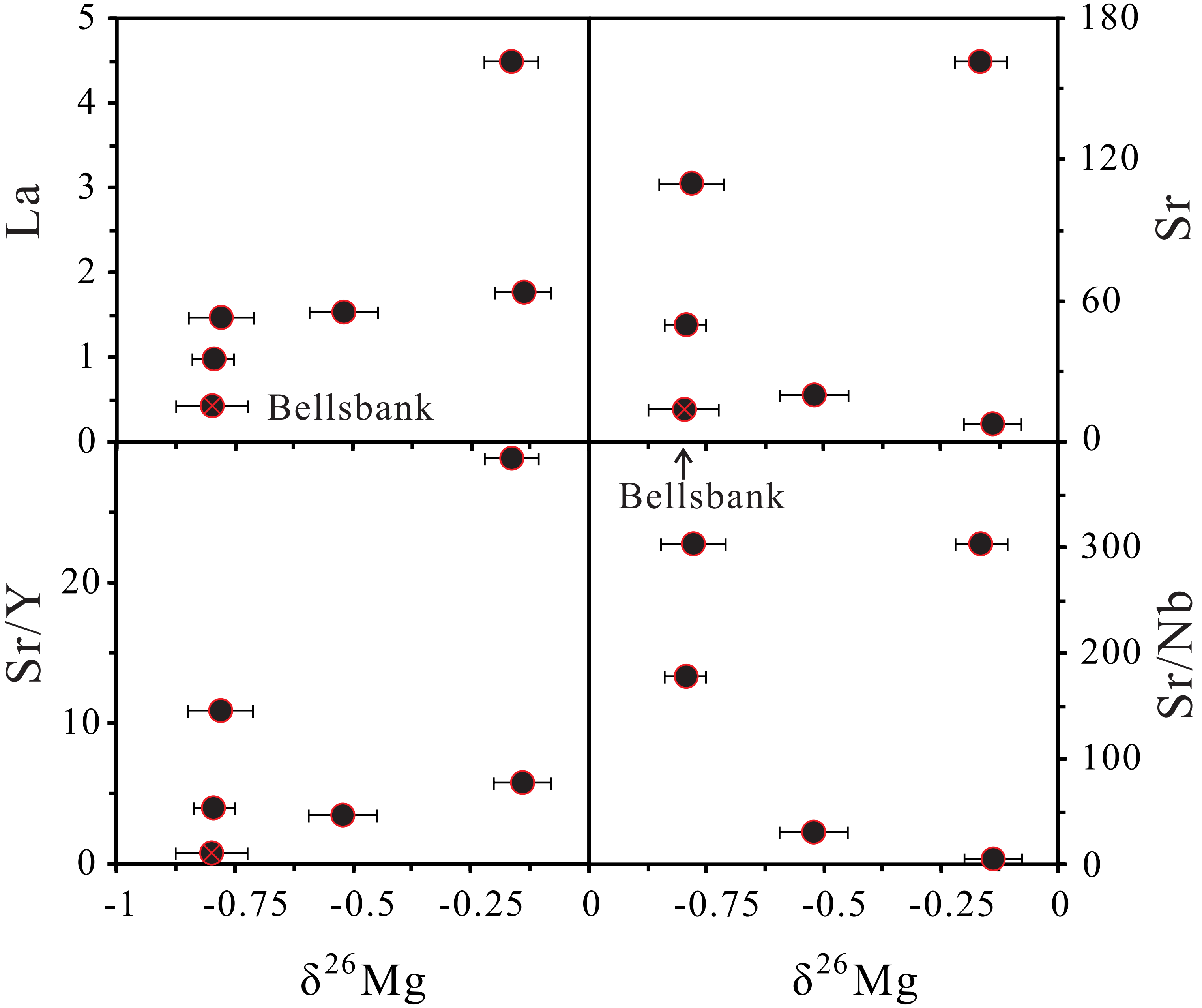
La
Sr
Sr/Y
Sr/Nb
Bellsbank
Bellsbank
5
4
3
2
1
0
180
120
60
0
20
10
0
300
200
100
0
-1
-0.75
-0.5
-0.25
0
-0.75
-0.5
-0.25
0
δ26Mg
δ26Mg

Figure 6

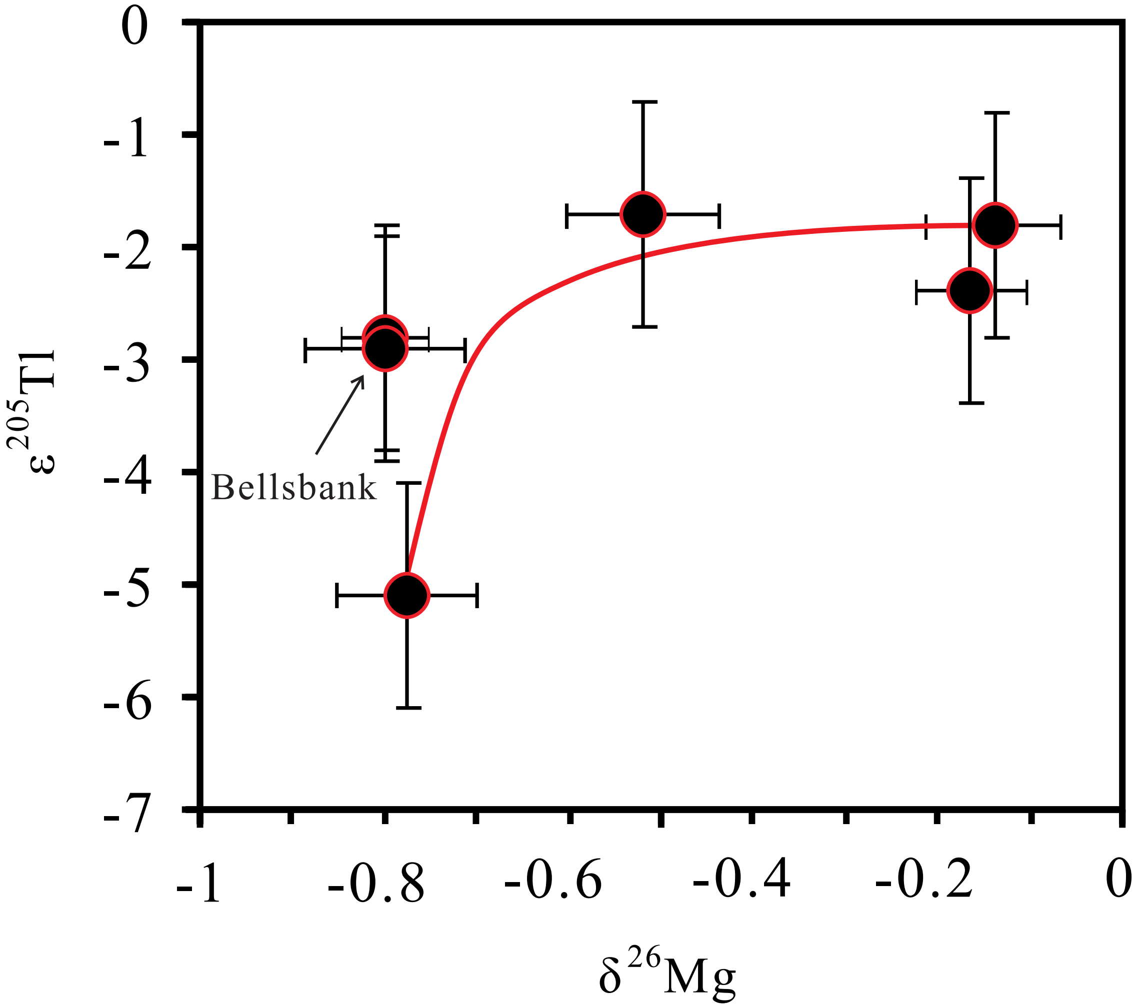

Figure 7

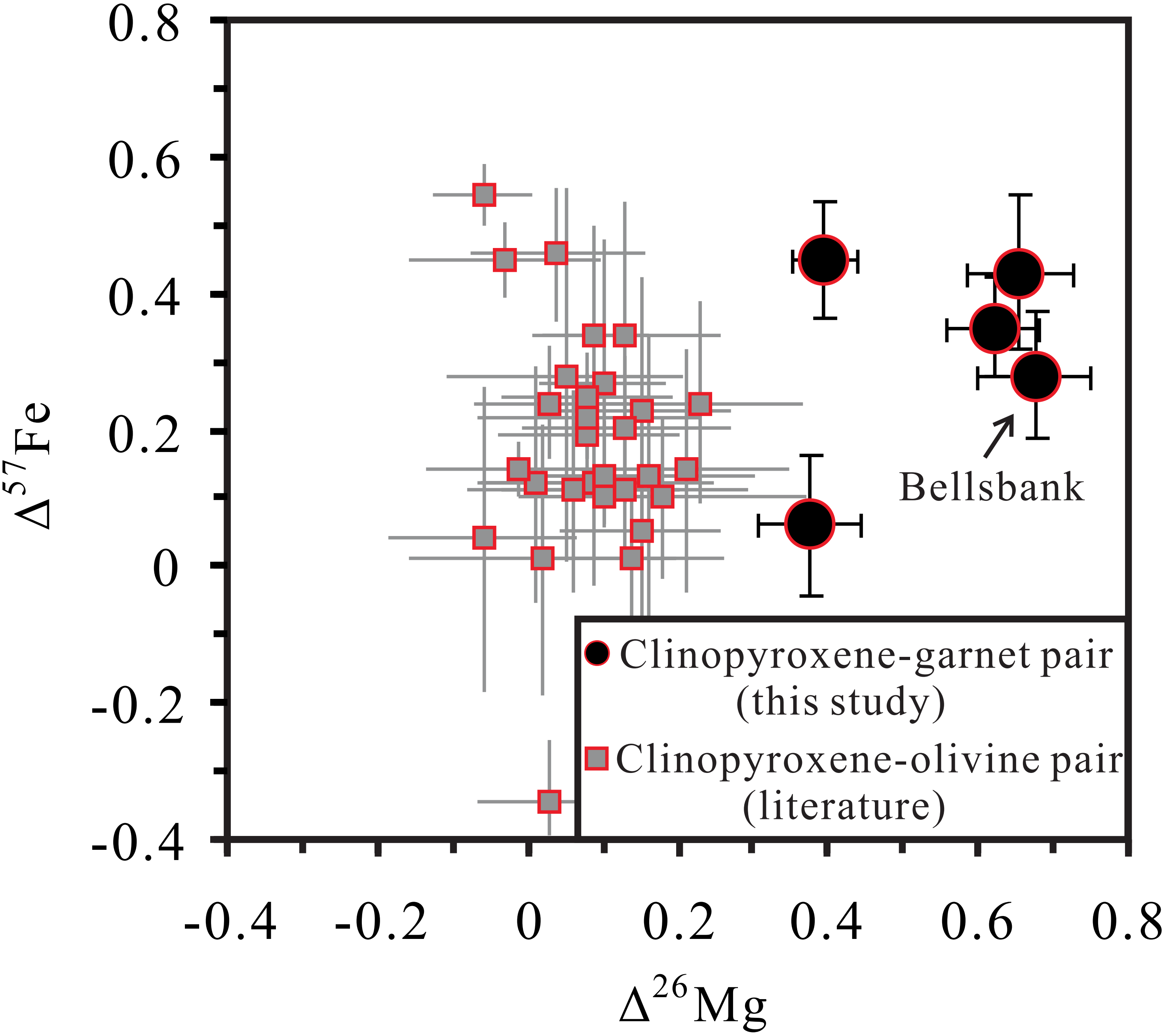
0.8
0.6
0.4
0.2
0
-0.2
-0.4
Δ^{57}Fe
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Δ^{26}Mg
Bellsbank
● Clinopyroxene-garnet pair (this study)
■ Clinopyroxene-olivine pair (literature)

Figure 8