

Heterogeneous magnesium isotopic composition of the upper continental crust

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Abstract

High-precision Mg isotopic data are reported for ~100 well-characterized samples (granites, loess, shales and upper crustal composites) that were previously used to estimate the upper continental crust composition. Magnesium isotopic compositions display limited variation in eight I-type granites from southeastern Australia ($\delta^{26}\text{Mg} = -0.25$ to -0.15) and in 15 granitoid composites from eastern China ($\delta^{26}\text{Mg} = -0.35$ to -0.16) and do not correlate with SiO_2 contents, indicating the absence of significant Mg isotope fractionation during differentiation of granitic magma. Similarly, the two S-type granites, which represent the two end-members of the S-type granite spectrum from southeastern Australia, have Mg isotopic composition ($\delta^{26}\text{Mg} = -0.23$ and -0.14) within the range of their potential source rocks ($\delta^{26}\text{Mg} = -0.20$ and $+0.15$) and I-type granites, suggesting that Mg isotope fractionation during crustal anatexis is also insignificant. By contrast, $\delta^{26}\text{Mg}$ varies significantly in 19 A-type granites from northeastern China (-0.28 to $+0.34$) and may reflect source heterogeneity.

Compared to I-type and S-type granites, sedimentary rocks have highly heterogeneous and, in most cases, heavier Mg isotopic compositions, with $\delta^{26}\text{Mg}$ ranging from -0.32 to $+0.05$ in nine loess from New Zealand and the USA, from -0.27 to $+0.49$ in 20 post-Archean Australian shales (PAAS), and from -0.52 to $+0.92$ in 20 sedimentary composites from eastern China. With increasing chemical weathering, as measured by the chemical index of alternation (CIA), $\delta^{26}\text{Mg}$ values show a larger dispersion in shales than loess. Furthermore, $\delta^{26}\text{Mg}$ correlates negatively with $\delta^7\text{Li}$ in loess. These characteristics suggest that chemical weathering significantly fractionates Mg isotopes and plays an important role in producing the highly variable Mg isotopic composition of sedimentary rocks.

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Based on the estimated proportions of major rock units within the upper continental crust and their average MgO contents, a weighted average $\delta^{26}\text{Mg}$ value of -0.22 is derived for the average upper continental crust. Our studies indicate that Mg isotopic composition of the upper crust is, on average, mantle-like but highly heterogeneous, with $\delta^{26}\text{Mg}$ ranging from -0.52 to $+0.92$. Such large isotopic variation mainly results from chemical weathering, during which light Mg isotopes are lost to the hydrosphere, leaving weathered products (e.g., sedimentary rocks) with heavy Mg isotopes.

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1. INTRODUCTION

Magnesium is a fluid-mobile, major element in both the mantle and the crust and has three isotopes, ^{24}Mg , ^{25}Mg and ^{26}Mg . The mass differences between its isotopes ($>8\%$ between ^{26}Mg and ^{24}Mg) can potentially produce large Mg isotope fractionation during low-temperature processes (e.g., Young and Galy, 2004). Consequently, Mg isotopes may be excellent tracers of geological processes that occur at the Earth's surface. Relative to the mantle (Teng et al., 2007, 2010a; Wiechert and Halliday, 2007; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Chakrabarti and Jacobsen, 2010; Dauphas et al., 2010), the hydrosphere, as represented by seawater and rivers, has a much lighter Mg isotopic composition ($\delta^{26}\text{Mg} = -0.8 \pm 0.1$ in present-day seawater and mainly within -1.2 to -0.6 in rivers draining silicates, Chang et al., 2003; Young and Galy, 2004; Tipper et al., 2006a,b; Brenot et al., 2008). The large variation in Mg isotopic composition of rivers has been partially attributed to isotope fractionation during weathering processes, with heavy Mg isotopes retained in the solid residue and light isotopes lost to the rivers and, ultimately, the oceans (Tipper et al., 2006a,b, 2008a; Brenot et al., 2008; Pogge von Strandmann et al., 2008; Teng et al., 2010b).

Compared to our knowledge of the Mg isotopic composition of the mantle and hydrosphere, little is known about the Mg isotopic composition of the continental crust. To date, only two studies on Mg isotopic composition of I-type granites have been carried out and they report contrasting results. Shen et al. (2009) found $\sim 0.8\%$ variation in biotites from I-type granitoids from southern California. By contrast, Liu et al. (2010) found limited Mg isotopic variation in I-type granitoids and associated minerals from the Dabie Orogen, central China.

To further constrain the Mg isotopic composition of the upper continental crust, investigate the behavior of Mg isotopes during granite differentiation and chemical weathering, and explore the processes that influence the composition of the continental crust, we have analyzed ~ 100 well-characterized upper crustal samples including granites, loess, shales and upper crustal composites from around the world. Our results demonstrate that Mg isotope fractionation is limited during crustal differentiation but is large during chemical weathering. Overall, the upper continental crust has a highly heterogeneous but, on average, mantle-like Mg isotopic composition.

2. SAMPLES

Two methods have generally been applied to determine the composition of the upper continental crust (for details,

see Rudnick and Gao, 2003). One is to establish weighted averages of the wide variety of rocks that crop out at the Earth's surface (e.g., Clarke, 1889; Clarke and Washington, 1924; Shaw et al., 1967, 1976; Eade and Fahrig, 1973; Ronov and Yaroshevsky, 1976; Gao et al., 1992, 1998; Condie, 1993; Borodin, 1999; Hu and Gao, 2008). Estimates of upper crustal concentrations of all major elements and a number of soluble trace elements rely upon this method. The other is to analyze fine-grained clastic sedimentary rocks (e.g., shale) or aeolian/glacial deposits (e.g., loess) to derive average upper crustal compositions for insoluble elements (e.g., Goldschmidt, 1933; Taylor and McLennan, 1985; Plank and Langmuir, 1998; Barth et al., 2000; McLennan, 2001; Hu and Gao, 2008).

Both methods are used here to characterize the Mg isotopic composition of the upper continental crust. Samples investigated here cover all major types of upper crustal rocks, including the classic I (igneous)- and S (sedimentary)-type granites from southeastern Australia (Chappell and White, 1974), A (anorogenic)-type granites from northeastern China (Wu et al., 2002), loess from New Zealand and the USA (Taylor et al., 1983), post-Archean Australian shales (PAAS) (Nance and Taylor, 1976), as well as upper crustal composites from eastern China, which include graywacke, pelite, tillite, granite, granodiorite and diorite (Gao et al., 1998). All of these samples were previously used to derive the average chemical composition (Nance and Taylor, 1976; Taylor et al., 1983; Taylor and McLennan, 1985, 1995; Gao et al., 1991, 1992, 1998; Barth et al., 2000; Hu and Gao, 2008) and Li and Cu isotopic composition (Teng et al., 2004, 2009; Li et al., 2009) of the upper continental crust (major element compositions of the samples analyzed here are available in the online supplement).

2.1. Granites

Granite is a major rock type of the crystalline upper continental crust and its Mg isotopic composition can directly reflect that of the upper crust. If Mg isotopes do not significantly fractionate during magmatic differentiation (Teng et al., 2007, 2010a; Liu et al., 2010), granites can further be used to constrain the Mg isotopic compositions of their sources in the middle and lower continental crust. To date, only a few $\delta^{26}\text{Mg}$ data have been published for granites, with $\delta^{26}\text{Mg}$ ranging from -0.83 to -0.07 for whole-rock samples (Tipper et al., 2006b, 2008b; Bolou-Bi et al., 2009; Huang et al., 2009a; Liu et al., 2010), from -0.40 to $+0.44$ for biotite separates (Shen et al., 2009) and from -0.31 to -0.12 for hornblende and biotite separates (Liu et al., 2010).

2.1.1. I-type and S-type granites from southeastern Australia

I-type granites are inferred to derive from melting of meta-igneous middle- to lower-crustal source rocks, whereas S-type granites are inferred to derive from melting of deep-seated sedimentary source rocks (Chappell and White, 1974, 1992, 2001; Chappell, 1984). Eight I-type granites from the Bega Batholith and two S-type granites from the Wagga Batholith in the Lachlan Fold Belt (LFB) were analyzed here. The ~400 Ma old Bega Batholith is the largest dominant I-type granite complex in the LFB and can be grouped into seven supersuites, within which the rocks share similar petrographic and chemical features (Chappell, 1996). Two samples from the Moruya supersuite and one each from the other six supersuites (the Cobargo, Kameruka, Candelo, Bemboka, Glenbog and Tonghi supersuites), ranging from monzogranite through granodiorite to tonalite, were chosen for this study. S-type granites are dominant in the Wagga Batholith, which was emplaced ~430 Ma (Chappell et al., 1988; Collins and Hobbs, 2001). Samples analyzed here represent the two end-members of the S-type granite spectrum from the Koetong suite, i.e., the most mafic rock (VB30) and the most felsic rock (VB98). For comparison, two Ordovician sedimentary rocks from the LFB were also analyzed, one clay-rich shale (OS35) and one quartz-rich graywacke (OS38). They are considered as the potential source rocks for the S-type granites in the LFB, although they are less feldspathic (Chappell et al., 2000). All samples were collected far from weathered surfaces and are fresh. Lithium isotopic compositions of these samples were previously reported in Teng et al. (2004).

2.1.2. A-type granites from northeastern China

A-type granites, first defined by Loiselle and Wones (1979), refer to granites emplaced in anorogenic settings. A-type granites may provide constraints on the contribution of post-collisional/intraplate extensional magmatism to the upper continental crust (Eby, 1990, 1992). Nineteen A-type granites were analyzed here. They are widely distributed within the Xing'an-Mongolia orogenic belt ($\geq 200,000 \text{ km}^2$) in northeastern China and were emplaced during three major episodes: Permian, late Triassic to early Jurassic, and early Cretaceous (Jahn et al., 2001; Wu et al., 2002). These A-type granites can be divided into two subgroups: aluminous and peralkaline, based on the presence or absence of alkali mafic minerals (Wu et al., 2002). These samples are highly siliceous ($\text{SiO}_2 > 72\%$), alkali-rich ($\text{K}_2\text{O} + \text{Na}_2\text{O} > 8\%$) and MgO-poor ($< 0.5\%$) (Wu et al., 2002). Based on their low initial $^{87}\text{Sr}/^{86}\text{Sr}$ and positive $\varepsilon_{\text{Nd}}(t)$ values, these A-type granites were considered to be partial melting products of underplated lower crust (Wu et al., 2002, 2003). The samples are fresh, as indicated by petrographic studies (Wu et al., 2002). Lithium isotopes for these samples were previously reported in Teng et al. (2009).

2.2. Loess

Loess is wind-blown dust derived from glacial outwash plains and desert environments that was deposited during

cold-dry conditions (Taylor et al., 1983). It is comprised of fine, silt-sized rock flour that has been transported by wind over long distances, providing us with a natural sampling of large regions of the surface. Thus, loess has been studied to determine the average chemical composition of the upper continental crust (e.g., Taylor et al., 1983; Gallet et al., 1998; Barth et al., 2000; Peucker-Ehrenbrink and Jahn, 2001; Teng et al., 2004; Hu and Gao, 2008). Until now, the only $\delta^{26}\text{Mg}$ value reported for loess is for one sample from China ($\delta^{26}\text{Mg} = -0.60 \pm 0.22$, Young and Galy, 2004).

Nine loess samples from New Zealand and the USA, which were previously used to investigate the composition of the upper continental crust (Taylor et al., 1983; Barth et al., 2000; Teng et al., 2004; Hu and Gao, 2008), were analyzed here. Samples from Banks Peninsula, New Zealand, are mainly derived from mountain glacial erosion, while samples from Kansas and Iowa, the midwestern USA, are probably derived from river outwash from the Rocky Mountains (Taylor et al., 1983). These loess samples are dominated by quartz, feldspar and muscovite, along with a small amount (generally $< 10\%$) of clay minerals, mainly illite and smectite (Taylor et al., 1983). The chemical index of alteration (CIA, defined as molar $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})$, where CaO^* is the amount of CaO in silicates only) gives a practical way to measure the transformation of feldspars to clay minerals, i.e., the extent of chemical weathering (Nesbitt and Young, 1982; McLennan, 1993). The loess studied here show relatively low and restricted CIA values between 57 and 64, with an average of 59 (cf. unweathered igneous rocks, which typically have CIA around 50 ± 5 , Nesbitt and Young, 1982), consistent with previous conclusions that, in general, loess is derived from areas of moderate weathering (Gallet et al., 1998). Lithium isotopic compositions of these samples were previously reported in Teng et al. (2004).

2.3. Shales

Shales are fine-grained sedimentary rocks deposited in a quiet-water environment. They derive from large volumes of land masses that are weathered and eroded under generally humid and high-rainfall conditions. Thus, shales are also widely used for estimating the average composition of the upper continental crust (e.g., Nance and Taylor, 1976; Taylor and McLennan, 1985; Barth et al., 2000; Teng et al., 2004; Hu and Gao, 2008). Compared to the formation of loess, which involves simple physical abrasion and aeolian transport, the formation of shales involves more complicated process, e.g., chemical and physical erosion, transportation, deposition and diagenesis. However, one advantage of studying shales is that they exist in stratigraphic sections throughout most of geological time, while loess occurs mainly within the Pleistocene. To our knowledge, no Mg isotopic data have previously been reported for shales.

Twenty post-Archean Australian shale (PAAS) samples, originally used by Nance and Taylor (1976) to constrain the rare earth element (REE) contents of the upper continental crust, have been analyzed here. These shales were collected

from three separate basins (the Perth Basin, Canning Basin and Amadeus Basin), the Camp Hill and the Mt. Isa Group, with ages ranging from middle Proterozoic (~1500 Ma) to Triassic (Taylor and McLennan, 1985). The samples studied here show variable and high CIA values between 66 and 80, with an average of 74 (cf. 59 in the loess studied here), reflecting the higher degree of weathering experienced by their protoliths and possibly during transport of the sediments prior to deposition. All samples come from drill cores and have not been subjected to recent weathering and leaching. Lithium isotopes for these samples were previously reported in Teng et al. (2004).

2.4. Upper crustal composites

Upper crustal composites are weighted averages of exposed rock types sampled over large areas. Thus, their compositions provide direct estimates of the upper crust composition for a given region (Shaw et al., 1967, 1976; Gao et al., 1998). Such systematic sampling should include, in theory, all rock units in both crystalline basement and sedimentary cover, as well as intrusive bodies within the studied region. In practice, large composite samples of a given rock unit are made by mixing relevant rock types according to their thickness, determined from seismic and aeromagnetic data and exposure area measured from geological maps (Gao et al., 1998).

Thirty-five upper crustal composites were studied here. They are part of the 905 composite samples utilized to study the chemical composition of the continental crust in eastern China (Gao et al., 1998; Hu and Gao, 2008). These 35 large composites were produced from over 750 individual rock samples derived from Precambrian cratons (the North China Craton and Yangtze Craton) and the Phanerozoic Qinling fold belt. Samples can be divided into two subgroups: sedimentary composites (including graywackes, pelites and one tillite) and granitoid composites (including granites, granodiorites and one diorite). Each composite was made from different numbers of individual rock samples (mostly 10–100) of the same age and lithology in a given tectonic unit. Samples were collected from sections along roadcuts, riverbanks or mountain valleys and selected by petrographic examination to insure freshness (Gao et al., 1998). Lithium isotopes for these samples were previously reported in Teng et al. (2004).

3. ANALYTICAL METHODS

Magnesium isotope analyses were performed at the Isotope Laboratory of the University of Arkansas, Fayetteville, following the methods reported in Teng et al. (2007, 2010a,b), Yang et al. (2009) and Liu et al. (2010). All chemical procedures were carried out in the class 10,000 clean laboratory, equipped with class 100 laminar flow exhaust hood. Ultra-pure Optima acids or acids prepared by sub-boiling distillation, and 18.2 M Ω Milli-Q[®] water were used throughout. Based on the Mg contents of samples, 1–20 mg of sample powder was dissolved in Savillex screw-top beakers in order to have ~25 μ g Mg in the solution. Acids added to the beakers for sample dissolution, in turn, are: (I) a mixture of con-

centrated HF–HNO₃ (~3:1, v/v). For loess and shale samples, a few drops of HClO₄ were also added; (II) a mixture of concentrated HCl–HNO₃ (~3:1, v/v) and (III) concentrated HNO₃. In each step, the capped beakers were heated at a temperature of ~160 °C on a hot plate for 1–2 days, and then the solutions were evaporated to dryness overnight in an exhaust hood. The dried residue of step III was finally dissolved in 1 N HNO₃, in preparation for column chemistry.

3.1. Column chemistry and instrumental analysis

Chemical separation of Mg was achieved by cation exchange chromatography with Bio-Rad 200–400 mesh AG50W-X8 resin in 1 N HNO₃ media following the established procedures (Teng et al., 2007, 2010a,b; Yang et al., 2009; Liu et al., 2010). The resin was rinsed with >20 times volume of 6 N HCl, 1 N HNO₃ and Milli-Q[®] water before being filled into the column. Sample solutions already in 1 N HNO₃ were loaded on the resin and eluted by 1 N HNO₃. The Mg elution curves were calibrated using pure Mg, granite, basalt and chondrite samples, and the results indicate that the Mg cuts do not shift measurably (Teng et al., 2007, 2010a). The Mg yield, based on multiple analyses of pure Mg and synthetic Mg standard solutions, is 100 ± 0.2% and the procedure blank is <10 ng (Teng et al., 2010a). The same column procedure was performed twice or four times (for some A-type granites with low MgO content) in order to obtain a pure Mg solution for mass spectrometry and to test the accuracy of the data. To further assure accuracy of our data, at least two reference materials (synthetic solution, seawater, mineral and rock reference materials, see Table 1) were processed with each batch of unknown samples at comparable levels of Mg. For example, 4.2 μ g Mg was loaded on the resin when the in-house standard solution IL-Mg-1 was processed, comparable to ~5 μ g Mg loaded for sample solutions.

Magnesium isotopic compositions were analyzed by the standard bracketing method using a Nu Plasma MC-ICP-MS at the University of Arkansas, following previously published procedures (Teng et al., 2010a). A “wet” plasma, using a quartz cyclonic spray chamber and a micro-uptake glass concentric nebulizer, was utilized in order to achieve higher precision. The difference in Mg concentrations between the sample and the bracketed standard during each analysis is within ±10%. Analyses were conducted in low resolution mode, with ²⁶Mg, ²⁵Mg and ²⁴Mg measured simultaneously in separate Faraday cups (H5, Ax and L4) and no molecular interferences or double charge interferences were observed. The background Mg signals for ²⁴Mg (<10⁻⁴ V) were negligible relative to the sample signals (3–4 V).

3.2. Precision and accuracy

Samples with different matrices, including the pure Mg Cambridge standard solution, seawater, a synthetic in-house multi-element standard solution (IL-Mg-1 with concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:0.1) as well as previously well-studied mineral and rock reference materials, were analyzed in order to evaluate the precision and accuracy of our Mg isotope measurements.

Table 1
Magnesium isotopic composition of synthetic solution, Cambridge1, seawater, mineral and rock reference materials.

Standard	<i>n</i>	$\delta^{26}\text{Mg}^{\text{a}}$	2SD ^b	$\delta^{25}\text{Mg}^{\text{a}}$	2SD ^b	$\Delta^{25}\text{Mg}'^{\text{c}}$	Reference
IL-Mg-1 ^d		-0.03	0.08	+0.01	0.10	+0.03	
		-0.04	0.09	-0.04	0.05	-0.02	
		-0.06	0.08	0.00	0.06	+0.03	
		-0.07	0.08	-0.03	0.05	+0.01	
		0.09	0.07	+0.01	0.06	-0.04	
		-0.02	0.07	-0.03	0.06	-0.02	
		+0.07	0.07	+0.01	0.06	-0.03	
		0.00	0.09	-0.01	0.05	-0.01	
		0.00	0.04	+0.01	0.04	+0.01	
		-0.06	0.09	0.00	0.04	+0.03	
		-0.08	0.06	-0.05	0.06	-0.01	
		-0.03	0.06	-0.02	0.06	0.00	
		-0.04	0.08	-0.02	0.05	0.00	
		-0.01	0.08	0.00	0.04	+0.01	
		0.00	0.07	0.00	0.06	0.00	
		-0.01	0.07	-0.01	0.06	0.00	
		0.00	0.07	-0.03	0.06	-0.03	
		0.00	0.07	-0.05	0.06	-0.05	
		-0.07	0.12	-0.04	0.08	0.00	
		-0.03	0.12	-0.04	0.08	-0.02	
	+0.05	0.12	-0.02	0.08	-0.05		
Average	21	-0.02	0.09	-0.02	0.04	-0.01	This study
Cambridge1		-2.61	0.07	-1.35	0.05	+0.01	
		-2.65	0.09	-1.38	0.06	0.00	
		-2.64	0.07	-1.36	0.05	+0.02	
		-2.61	0.09	-1.35	0.06	+0.01	
Average	4	-2.63	0.04	-1.36	0.03	+0.01	This study
	35	-2.58	0.14	-1.33	0.07		Galy et al. (2003)
	168	-2.60	0.14	-1.34	0.08		Tipper et al. (2006a)
	67	-2.59	0.09	-1.34	0.05		Tipper et al. (2008b)
	18	-2.62	0.13	-1.34	0.10		Bolou-Bi et al. (2009)
	56	-2.58	0.04	-1.34	0.02		Hippler et al. (2009)
	44	-2.63	0.11	-1.36	0.07		Huang et al. (2009a)
Seawater		-0.86	0.09	-0.45	0.06	0.00	
		-0.87	0.09	-0.46	0.04	-0.01	
		-0.85	0.07	-0.43	0.06	+0.01	
		-0.87	0.07	-0.45	0.06	0.00	
		-0.86	0.10	-0.46	0.05	-0.01	
Average	5	-0.86	0.02	-0.45	0.02	0.00	This study
	4	-0.82	0.08	-0.42	0.09		Chang et al. (2003)
	3	-0.84	0.06	-0.42	0.02		Young and Galy (2004)
	1	-0.84	0.13	-0.43	0.15		Tipper et al. (2006a)
	14	-0.89	0.10	-0.47	0.08		Bolou-Bi et al. (2009)
	10	-0.80	0.05	-0.42	0.02		Hippler et al. (2009)
	4	-0.83	0.06	-0.43	0.03		Teng et al. (2010a)
Allende chondrite		-0.32	0.10	-0.15	0.05	+0.02	
		-0.34	0.06	-0.19	0.04	-0.01	
		-0.31	0.08	-0.17	0.05	-0.01	
		-0.33	0.10	-0.19	0.06	-0.02	
		-0.31	0.07	-0.22	0.06	-0.06	
		-0.31	0.07	-0.22	0.06	-0.06	
		-0.34	0.06	-0.18	0.05	0.00	
		-0.32	0.06	-0.17	0.04	0.00	
Average	8	-0.32	0.03	-0.19	0.05	-0.02	This study
	5	-0.30	0.07	-0.16	0.03		Galy et al. (2003)
	8	-0.36		-0.18	0.03		Baker et al. (2005)
	4	-0.37	0.06	-0.19	0.07		Teng et al. (2007)

(continued on next page)

Table 1 (continued)

Standard	<i>n</i>	$\delta^{26}\text{Mg}^{\text{a}}$	2SD ^b	$\delta^{25}\text{Mg}^{\text{a}}$	2SD ^b	$\Delta^{25}\text{Mg}'^{\text{c}}$	Reference
	14	−0.25	0.26	−0.13	0.15		Wiechert and Halliday (2007)
	2	−0.39	0.04	−0.21	0.01		Young et al. (2009)
	9	−0.30	0.05	−0.15	0.04		Teng et al. (2010a)
Kilbourne Hole (KH) olivine		−0.27	0.08	−0.15	0.07	−0.01	
		−0.29	0.07	−0.14	0.05	+0.01	
		−0.33	0.06	−0.18	0.05	−0.01	
		−0.30	0.09	−0.14	0.04	+0.02	
		−0.32	0.07	−0.18	0.05	−0.01	
		−0.33	0.08	−0.15	0.06	+0.02	
		−0.36	0.12	−0.20	0.08	−0.01	
Average	7	−0.31	0.06	−0.16	0.05	0.00	This study
	24	−0.31	0.09	−0.14	0.08		Teng et al. (2007)
	16	−0.27	0.07	−0.14	0.04		Teng et al. (2010a)
	1	−0.27	0.04	−0.12	0.05		Liu et al. (2010)
GSN granite		−0.22	0.07	−0.10	0.05	+0.01	This study
		−0.21	0.09	−0.13	0.07	−0.02	
	8	−0.24	0.23	−0.12	0.13		Huang et al. (2009a)
GA granite		−0.26	0.07	−0.14	0.05	0.00	This study
		−0.29	0.09	−0.12	0.07	+0.03	
	8	−0.34	0.15	−0.17	0.11		Huang et al. (2009a)
	1	−0.75	0.14	−0.36	0.08		Bolou-Bi et al. (2009)
SCo-1 shale		−0.94	0.08	−0.50	0.06	−0.01	This study

^a $\delta^X\text{Mg} = [(^X\text{Mg}/^{24}\text{Mg})_{\text{sample}} / (^X\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1] \times 1000$, where $X = 25$ or 26 and DSM3 is Mg solution made from pure Mg metal (Galy et al., 2003).

^b 2SD = 2 times the standard deviation of the population of n repeat measurements of a simple solution.

^c $\Delta^{25}\text{Mg}' = \delta^{25}\text{Mg}' - 0.521\delta^{26}\text{Mg}'$, where $\delta^X\text{Mg}' = 1000 \times \ln[(\delta^X\text{Mg} + 1000)/1000]$ with $X = 25$ or 26 (Young and Galy, 2004).

^d IL-Mg-1 is a synthetic solution with concentration ratios of Mg:Fe:Al:Ca:Na:K:Ti = 1:1:1:1:1:1:0.1.

The in-run precision on the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio for a single measurement run of one block of 40 ratios is $\leq \pm 0.02\%$ (2SD, i.e., two times the standard deviation of the population of n repeat measurements of a sample solution). The internal precision on the measured $^{26}\text{Mg}/^{24}\text{Mg}$ ratio, based on ≥ 4 repeat runs of the same sample solution during a single analytical session, is $\leq \pm 0.1\%$ (2SD). For example, 21 total procedural replicates (repeat column chemistry and measurement of different aliquots) of IL-Mg-1 performed during analytical sessions conducted over the course of this study yield an average $\delta^{26}\text{Mg}$ value of -0.02 ± 0.09 (2SD, Table 1). This is consistent with the expected value of 0. A-type granites that were processed through columns twice and four times yield identical $\delta^{26}\text{Mg}$ values (Table 3), further assuring the accuracy and precision of our data. Results for other solution, rock and mineral reference materials analyzed during the course of this study are compared with previously reported data in Table 1. When the equivalent 2SD uncertainties are considered, Mg isotopic compositions reported here are similar to previously published values for Cambridge1, seawater, the Allende chondrite, Kilbourne Hole olivine (KH) and the granite standard GSN (Chang et al., 2003; Galy et al., 2003; Young and Galy, 2004; Baker et al., 2005; Tipper et al., 2006a, 2008b; Teng et al., 2007, 2010a,b; Wiechert and Halliday, 2007; Bolou-Bi et al., 2009; Hippler et al.,

2009; Huang et al., 2009a; Young et al., 2009; Liu et al., 2010). The $\delta^{26}\text{Mg}$ value of -0.21 ± 0.06 for the granite standard GA is within uncertainty of the value (-0.34 ± 0.15) reported by Huang et al. (2009a), but is significantly different from the value (-0.75 ± 0.14) reported by Bolou-Bi et al. (2009). The reason for this discrepancy is unknown. To our knowledge, $\delta^{26}\text{Mg}$ of -0.94 ± 0.08 presented here is the first published data for the shale standard SCo-1 (USGS reference material).

4. RESULTS

Magnesium isotopic compositions are reported in Table 1 for reference materials, Table 2 for I-type and S-type granites, Table 3 for A-type granites, Table 4 for loess, Table 5 for shales and Table 6 for upper crustal composites, along with selected chemical compositions (Nance and Taylor, 1976; Taylor et al., 1983; Chappell, 1984; Gao et al., 1998; Barth et al., 2000; Wu et al., 2002; Teng et al., 2004, 2009). All samples analyzed in this study fall on a single isotopic mass-dependent fractionation line with a slope of 0.505 (Fig. 1), with all of the $\Delta^{25}\text{Mg}'$ values $\leq \pm 0.06\%$ (Table 1–6, see Young and Galy, 2004 for the definitions of $\Delta^{25}\text{Mg}'$ notation). Overall, Mg isotopic compositions of the upper crustal rocks are highly heterogeneous, with $\delta^{26}\text{Mg}$ values ranging from -0.52 to $+0.92$ (Fig. 2).

Table 2
Magnesium isotopic composition of granites and sedimentary rocks from southeastern Australia.

Sample ID	SiO ₂ ^a (wt%)	MgO ^a (wt%)	δ ⁷ Li ^b	δ ²⁶ Mg	2SD	δ ²⁵ Mg	2SD	Δ ²⁵ Mg ^c
<i>Lachlan fold belt S-type granites</i>								
VB30	66.1	2.57	-1.4	-0.23	0.07	-0.12	0.05	0.00
VB98	73.5	0.21	-1.1	-0.14	0.10	-0.05	0.05	+0.02
Replicate ^d				-0.15	0.08	-0.04	0.07	+0.04
<i>Lachlan fold belt I-type granites</i>								
MG14	67.2	1.80	+0.3	-0.15	0.09	-0.11	0.06	-0.03
Replicate				-0.20	0.08	-0.08	0.07	+0.02
MG20	74.9	0.24	+0.8	-0.24	0.09	-0.15	0.06	-0.02
Repeat ^e				-0.22	0.09	-0.13	0.02	-0.02
AB40	68.8	1.29	-2.5	-0.18	0.09	-0.10	0.06	-0.01
Replicate				-0.25	0.08	-0.12	0.07	+0.01
AB105	67.9	1.49	-2.1	-0.17	0.09	-0.11	0.06	-0.02
Replicate				-0.24	0.08	-0.11	0.07	+0.02
AB128	64.5	2.52	+0.1	-0.24	0.06	-0.14	0.06	-0.01
Replicate				-0.24	0.07	-0.10	0.05	+0.03
Repeat				-0.23	0.07	-0.10	0.05	+0.02
AB249	66.2	1.98	+2.7	-0.16	0.09	-0.06	0.06	+0.02
Replicate				-0.20	0.08	-0.12	0.07	-0.02
AB289	73.8	0.47	+1.8	-0.21	0.08	-0.11	0.07	0.00
Repeat				-0.26	0.11	-0.15	0.06	-0.01
AB293	63.6	2.59	-0.1	-0.20	0.07	-0.10	0.05	0.00
<i>Ordovician sedimentary rocks</i>								
OS35	56.8	2.85	+1.2	+0.15	0.10	+0.07	0.04	-0.01
Replicate				+0.12	0.08	+0.08	0.07	+0.02
OS38	78.1	1.33	-0.7	-0.20	0.10	-0.10	0.04	0.00
Repeat				-0.18	0.07	-0.08	0.05	+0.01

^a Data from Chappell (1984).

^b Data from Teng et al. (2004).

^c $\Delta^{25}\text{Mg}' = \delta^{25}\text{Mg}' - 0.521\delta^{26}\text{Mg}'$, where $\delta^X\text{Mg}' = 1000 \times \ln[(\delta^X\text{Mg} + 1000)/1000]$ with $X = 25$ or 26 (Young and Galy, 2004).

^d Replicate = repeat column chemistry and measurement of different aliquots of a stock solution.

^e Repeat = repeat dissolution and column chemistry of individual samples.

4.1. Granites from Australia and China

4.1.1. I-type and S-type granites from southeastern Australia

Regardless of their bulk compositions, e.g., SiO₂ contents ranging from 64.5% to 74.9% (Fig. 3a), δ²⁶Mg values of I-type granites from the LFB, southeastern Australia, are indistinguishable and range from -0.25 to -0.15, with the MgO-weighted average value of -0.21 ($n = 8$). This variation is within analytical uncertainties of oceanic basalts (Fig. 3b). Two S-type granites have Mg isotopic compositions of -0.23 for the mafic end member (VB30) and -0.14 for the felsic end member (VB98), respectively, both within uncertainty of that of the Ordovician graywacke (OS38, δ²⁶Mg = -0.20 ± 0.10). The Ordovician shale sample is heavier (OS35, δ²⁶Mg = +0.15) than both granites and graywacke.

4.1.2. A-type granites from northeastern China

In contrast to I-type and S-type granites from southeastern Australia, Mg isotopic compositions of A-type granites from northeastern China vary by more than 0.6‰, although their SiO₂ content varies by only ~4%, from 72.8% to 77.0% (Fig. 2). δ²⁶Mg values vary from -0.21 to +0.12 in the aluminous subgroup and from -0.28 to +0.34 in the peralkaline subgroup (Fig. 4b), with the

weighted average value of -0.01 for all these A-type granites ($n = 19$).

4.2. Loess from New Zealand and the USA

Magnesium isotopic compositions are relatively constant for loess samples from a given area but vary significantly from one area to another (Fig. 5). The δ²⁶Mg values of five samples from Banks Peninsula, New Zealand, vary from -0.07 to +0.05, compared to -0.32 to -0.23 of three samples from Kansas and -0.01‰ of the only sample from Iowa, USA. The weighted average δ²⁶Mg value for loess samples analyzed here is -0.10 ($n = 9$).

4.3. Shales from Australia

Magnesium isotopic compositions vary by >0.7‰ in PAAS samples, with δ²⁶Mg values ranging from -0.27 to +0.49 (weighted average = +0.05, $n = 20$) and different among the five sampling areas (Fig. 5). The two samples from the Canning Basin have identical Mg isotopic compositions (δ²⁶Mg = -0.13 and -0.14). Similarly, the seven State Circle shale samples have similar δ²⁶Mg values (from -0.05 to +0.07). On the other hand, Mg isotopic compositions are highly heterogeneous for samples from the other

Table 3

Magnesium isotopic composition of aluminous and peralkaline A-type granites from northeastern China.

Sample ID	SiO ₂ ^a (wt%)	MgO ^a (wt%)	δ ⁷ Li ^b	ε _{Nd} (t) ^a	T _{DM2} ^a (Ma)	δ ²⁶ Mg	2SD	δ ²⁵ Mg	2SD	Δ ²⁵ Mg ^c
<i>Aluminous</i>										
9715-1 ^e	74.1	0.20	+2.8	+2.34	781	−0.04	0.11	−0.02	0.06	0.00
Replicate ^{d,e}						+0.01	0.08	−0.01	0.05	−0.02
9717-1	73.0	0.47	+3.2			−0.10	0.08	−0.04	0.04	+0.01
9718-1	72.8	0.46	+0.8	+1.34	862	−0.08	0.08	−0.04	0.04	0.00
9767-1 ^e	77.0	0.21	+0.8	−0.16	987	−0.21	0.11	−0.13	0.06	−0.02
9801-2 ^e	75.7	0.16	+6.9	+2.62	835	+0.12	0.09	+0.08	0.06	+0.02
9832-2	76.3	0.29	+3.1			−0.18	0.06	−0.09	0.04	0.00
9849-1	74.4	0.28	+5.1	+2.09	710	+0.01	0.10	−0.06	0.06	−0.07
Replicate ^e						−0.03	0.09	−0.04	0.05	−0.02
<i>Peralkaline</i>										
DW-2	72.9	0.28	−1.8			+0.28	0.10	+0.12	0.06	−0.03
Replicate ^e						+0.20	0.09	+0.11	0.05	+0.01
DW-3	74.5	0.30	+2.9	+3.09	752	+0.18	0.07	+0.11	0.04	+0.02
Replicate						+0.13	0.09	+0.06	0.05	−0.01
9757-3 ^e	75.9	0.14	+0.7	+0.25	969	−0.18	0.09	−0.11	0.06	−0.02
9757-4	76.2	0.10	+1.2	−0.89	1103	−0.12	0.08	−0.08	0.05	−0.02
9780-1 ^e	76.2	0.17	+4.6	−1.93	1134	+0.17	0.09	+0.06	0.06	−0.03
9781-1 ^e	76.3	0.13	+0.7	−1.20	1170	+0.27	0.09	+0.12	0.06	−0.02
9781-4 ^e	75.8	0.14	+0.5			+0.34	0.09	+0.15	0.06	−0.03
9781-5 ^e	76.8	0.12	+1.5	−0.81	1040	+0.18	0.09	+0.08	0.07	−0.01
9782-1 ^e	76.6	0.11	+1.7	−0.86	1046	−0.01	0.09	−0.01	0.06	0.00
Baishi-1	76.1	0.18	+2.4	+2.01	752	−0.12	0.06	−0.07	0.04	−0.01
9843-1	74.9	0.17	+1.1	+5.06	666	−0.10	0.07	−0.04	0.05	+0.01
9843-6 ^e	75.7	0.14	+3.2	+4.24	710	−0.28	0.09	−0.10	0.05	+0.05
Replicate ^e						−0.27	0.09	−0.11	0.07	+0.03

^a Data from Wu et al. (2002), T_{DM2} = two-stage Nd model ages.^b Data from Teng et al. (2009).^c Δ²⁵Mg' = δ²⁵Mg' − 0.521δ²⁶Mg', where δ^XMg' = 1000 × ln[(δ^XMg + 1000)/1000] with X = 25 or 26 (Young and Galy, 2004).^d Replicate = repeat column chemistry and measurement of different aliquots of a stock solution.^e Results for samples processed through columns four times.

Table 4

Magnesium isotopic composition of loess from New Zealand and the USA.

Sample ID	SiO ₂ ^a (wt%)	MgO ^a (wt%)	δ ⁷ Li ^b	δ ²⁶ Mg	2SD	δ ²⁵ Mg	2SD	Δ ²⁵ Mg ^c	CIA ^d
<i>Banks Peninsula, New Zealand</i>									
BP-1	72.7	0.95	−2.6	−0.04	0.07	0.00	0.05	+0.02	59
BP-2	74.0	0.97	−1.7	+0.02	0.07	+0.02	0.05	+0.01	59
BP-3	72.5	0.88	−3.1	+0.05	0.07	−0.01	0.05	−0.04	61
BP-4	74.0	1.07	+1.4	−0.01	0.07	−0.01	0.05	0.00	57
BP-5	72.5	1.06	−0.7	−0.07	0.07	−0.06	0.05	−0.02	57
<i>Kansas, USA</i>									
CY-4a-A	80.4	0.86	+4.5	−0.23	0.08	−0.12	0.06	0.00	59
CY-4a-B	80.8	0.95	+4.8	−0.31	0.08	−0.18	0.06	−0.02	59
CY-4a-C	79.9	0.88	+4.2	−0.32	0.08	−0.19	0.06	−0.02	58
<i>Iowa, USA</i>									
I	79.5	1.01	−0.3	−0.01	0.08	−0.03	0.06	−0.02	64

^a Data from Taylor et al. (1983).^b Data from Teng et al. (2004).^c Δ²⁵Mg' = δ²⁵Mg' − 0.521δ²⁶Mg', where δ^XMg' = 1000 × ln[(δ^XMg + 1000)/1000] with X = 25 or 26 (Young and Galy, 2004).^d CIA refers to the chemical index of alteration and is the molar ratio of Al₂O₃/(Al₂O₃ + CaO* + Na₂O + K₂O) as defined by Nesbitt and Young (1982), where CaO* refers to Ca that is not contained in carbonate and phosphate. Here, correction for Ca in phosphate cannot be made as the P₂O₅ contents for these loess samples are not available. Moreover, all samples have the molar CaO/Na₂O < 1, suggesting little carbonate is present and thus no correction is needed for Ca in carbonate (McLennan, 1993). The major element data for CIA calculations are from Taylor et al. (1983).

Table 5
Magnesium isotopic composition of post-Archean Australian shales.

Sample ID	SiO ₂ ^a (wt%)	MgO ^a (wt%)	δ ⁷ Li ^b	δ ²⁶ Mg	2SD	δ ²⁵ Mg	2SD	Δ ²⁵ Mg ^c	CIA ^d
<i>Perth Basin</i>									
PW-4	57.9	1.80		+0.03	0.08	-0.02	0.06	-0.04	79
PW-5	55.3	1.68	+2.0	-0.07	0.07	+0.02	0.04	+0.06	80
PW-7	59.6	1.99		-0.22	0.08	-0.14	0.06	-0.03	75
Replicate ^e				-0.27	0.08	-0.13	0.05	+0.01	
<i>Canning Basin</i>									
PL-1	63.5	1.53	-0.9	-0.13	0.07	-0.10	0.05	-0.03	80
PL-6	61.1	1.86		-0.14	0.07	-0.07	0.05	0.00	76
<i>State Circle</i>									
SC-1	65.1	2.77		-0.05	0.08	-0.03	0.05	0.00	76
SC-2	65.3	2.63		+0.04	0.07	+0.03	0.05	+0.01	76
SC-3	67.0	2.67		+0.03	0.07	-0.01	0.05	-0.03	76
SC-4	64.7	2.81		+0.03	0.07	+0.01	0.05	-0.01	77
SC-5	65.3	2.68		+0.07	0.07	+0.04	0.05	0.00	76
SC-7	65.6	2.80	-0.7	+0.02	0.07	+0.01	0.05	0.00	77
SC-8	65.6	2.63	-0.2	+0.03	0.07	+0.02	0.05	0.00	75
<i>Amadeus Basin</i>									
AO-6	61.1	3.48	-3.0	-0.18	0.08	-0.11	0.05	-0.02	66
AO-8	70.0	1.52		+0.34	0.08	+0.18	0.05	0.00	71
AO-9	65.8	2.29	-2.6	+0.05	0.07	+0.01	0.04	-0.02	70
AO-10	63.0	1.92	-0.7	+0.37	0.07	+0.20	0.04	+0.01	72
AO-12	56.6	3.13	+3.4	+0.49	0.07	+0.23	0.04	-0.03	66
Replicate				+0.48	0.08	+0.25	0.05	0.00	
<i>Mt. Isa Group</i>									
M-11	71.0	2.46		+0.28	0.07	+0.18	0.04	+0.03	70
Replicate				+0.23	0.08	+0.12	0.05	0.00	
M-14	69.8	1.48		+0.05	0.08	+0.03	0.05	0.00	66
M-15	65.9	2.46		+0.05	0.07	+0.02	0.04	-0.01	76

^a Data from Nance and Taylor (1976).

^b Data from Teng et al. (2004).

^c Δ²⁵Mg' = δ²⁵Mg' - 0.521δ²⁶Mg', where δ^XMg' = 1000 × ln [(δ^XMg + 1000)/1000] with X = 25 or 26 (Young and Galy, 2004).

^d CIA refers to the chemical index of alteration and is the molar ratio of Al₂O₃/(Al₂O₃ + CaO* + Na₂O + K₂O) as defined by Nesbitt and Young (1982), where CaO* refers to Ca that is not contained in carbonate and phosphate. Correction for Ca in phosphates is done with CaO* = CaO - 10/3 P₂O₅ (all in the molar ratio). Moreover, McLennan's (1993) correction for Ca in carbonates, i.e., assuming molar CaO/Na₂O ≤ 1, is used here, as no CO₂ contents are available for these samples. The major element data for CIA calculations are from Nance and Taylor (1976).

^e Replicate = repeat column chemistry and measurement of different aliquots of a stock solution.

three areas, i.e., δ²⁶Mg values vary from -0.27 to +0.03 in three samples from the Perth Basin, from -0.18 to +0.49 in five samples from the Amadeus Basin and from +0.05 to +0.28 in three samples from the Mt. Isa Group.

4.4. Upper crustal composites from eastern China

Magnesium isotopic compositions of granitoid composites from eastern China including diorites, granodiorites and granites, are indistinguishable, within analytical uncertainties, of oceanic basalts (Fig. 3c and d). Among them, granitoid composites (the only diorite composite is included) have δ²⁶Mg values ranging from -0.34 to -0.20 (weighted average = -0.29, n = 8), while granite composites have δ²⁶Mg values ranging from -0.30 to -0.16 (weighted average = -0.24, n = 7). By contrast, sedimentary composites from eastern China display the largest isotopic variation among all 95 samples studied

here (Fig. 2). δ²⁶Mg values vary from -0.52 to +0.92 (weighted average = -0.16, n = 20), with the range bracketed by one pelite composite (D100) at the lower end (-0.52) and another pelite composite (D085) at the higher end (+0.92).

5. DISCUSSION

The highly variable Mg isotopic composition of the upper crustal rocks reflects Mg isotope fractionation during different geological processes that occurred within the crust. In this section, we first evaluate the behavior of Mg isotopes during granite differentiation and chemical weathering, and then use our dataset to estimate the average Mg isotopic composition of the upper continental crust. Finally, we provide a preliminary picture of the Mg isotopic budget among three major Earth reservoirs, i.e., the mantle, upper continental crust and hydrosphere.

Table 6
Magnesium isotopic composition of upper crustal composites from eastern China.

Sample ID	<i>n</i> ^a	SiO ₂ ^b (wt%)	MgO ^b (wt%)	δ ⁷ Li ^c	δ ²⁶ Mg	2SD	δ ²⁵ Mg	2SD	Δ ²⁵ Mg ^d
<i>Graywackes</i>									
D059	82	63.8	2.63	−1.1	−0.35	0.08	−0.19	0.07	−0.01
Repeat ^e					−0.36	0.06	−0.21	0.05	−0.02
D060	36	65.5	2.72	+0.4	−0.40	0.07	−0.21	0.05	0.00
Replicate ^f					−0.43	0.07	−0.17	0.04	+0.05
D062	5	67.5	1.50	+0.6	−0.17	0.07	−0.10	0.05	−0.01
D075	16	64.7	2.03	−0.1	−0.02	0.09	−0.04	0.06	−0.03
Replicate					−0.06	0.08	−0.03	0.06	0.00
<i>Pelites</i>									
D085	5	71.2	0.69		+0.92	0.07	+0.49	0.04	+0.01
Replicate					+0.88	0.09	+0.45	0.05	−0.01
D086	8	60.1	2.61		+0.16	0.06	+0.13	0.05	+0.05
D088	8	58.2	0.57		−0.22	0.07	−0.10	0.04	+0.01
D090	11	61.2	1.68		+0.50	0.07	+0.25	0.04	−0.01
Replicate					+0.45	0.10	+0.24	0.07	+0.01
D097	28	64.2	2.15		−0.32	0.07	−0.16	0.04	+0.01
D100	16	60.9	3.55	+0.9	−0.52	0.07	−0.26	0.05	+0.01
Replicate					−0.52	0.07	−0.26	0.04	+0.01
D103	10	66.8	1.68		+0.06	0.08	+0.05	0.06	+0.02
D104	2	59.8	0.95	−5.2	+0.28	0.08	+0.13	0.05	−0.02
Replicate					+0.30	0.08	+0.16	0.06	0.00
Repeat ^f					+0.27	0.06	+0.14	0.05	0.00
D107	9	60.1	3.40		−0.34	0.08	−0.14	0.06	+0.04
D111	24	65.4	2.09	−0.1	−0.26	0.07	−0.13	0.05	+0.01
D119	15	62.4	2.47	+1.2	+0.11	0.08	+0.03	0.05	−0.03
Replicate					+0.08	0.08	+0.07	0.06	+0.03
D122	25	66.2	1.98	−2.1	+0.04	0.07	+0.01	0.05	−0.01
D124	7	64.0	1.90	+0.1	−0.12	0.07	−0.06	0.05	0.00
D355	172	61.3	2.93	−2.6	−0.44	0.08	−0.20	0.05	+0.03
Replicate					−0.44	0.08	−0.17	0.06	+0.06
D359	1	64.7	1.93		−0.27	0.10	−0.12	0.06	+0.02
<i>Tillite</i>									
D325	7	64.8	2.33		−0.23	0.10	−0.13	0.07	−0.01
<i>Diorite</i>									
D284	21	56.8	4.07	−3.4	−0.28	0.08	−0.15	0.03	0.00
Replicate					−0.23	0.07	−0.14	0.04	−0.02
<i>Granodiorites</i>									
D239	36	67.5	1.01		−0.20	0.08	−0.11	0.06	−0.01
D276	23	64.7	1.37	+1.3	−0.31	0.07	−0.20	0.05	−0.04
Replicate					−0.26	0.07	−0.16	0.04	−0.02
D293	21	64.6	3.05		−0.35	0.08	−0.15	0.06	+0.03
Replicate					−0.33	0.08	−0.15	0.05	+0.02
D306	7	65.1	1.23		−0.26	0.08	−0.15	0.06	−0.01
D308	12	58.9	3.15	+0.2	−0.27	0.07	−0.14	0.05	0.00
D309	3	60.9	2.82		−0.33	0.08	−0.14	0.06	+0.03
D311	20	63.6	2.08		−0.31	0.09	−0.15	0.04	+0.01
<i>Granites</i>									
D240	35	70.4	0.38		−0.16	0.09	−0.09	0.04	−0.01
D256	26	70.7	0.62		−0.21	0.06	−0.11	0.05	0.00
D274	23	69.3	0.83		−0.28	0.08	−0.14	0.06	+0.01
D295	22	70.4	1.00		−0.30	0.06	−0.11	0.05	+0.05
D312	12	68.5	0.71	−0.5	−0.27	0.08	−0.13	0.04	+0.01
D313	5	72.0	0.62		−0.16	0.09	−0.08	0.04	0.00
D314	15	74.7	0.32	+3.0	−0.14	0.08	−0.07	0.04	0.00
Repeat					−0.22	0.10	−0.12	0.06	−0.01
Replicate					−0.18	0.08	−0.08	0.05	+0.01

^a *n* = number of individual samples comprising the composite.

^b Data from Gao et al. (1998).

^c Data from Teng et al. (2004).

^d Δ²⁵Mg' = δ²⁵Mg' − 0.521δ²⁶Mg', where δ^XMg' = 1000 × ln[(δ^XMg + 1000)/1000] with X = 25 or 26 (Young and Galy, 2004).

^e Repeat = repeat dissolution and column chemistry of individual samples.

^f Replicate = repeat column chemistry and measurement of different aliquots of a stock solution.

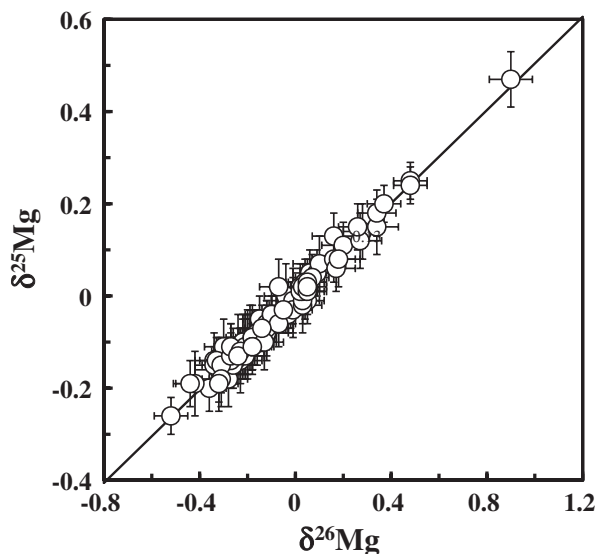


Fig. 1. Magnesium three-isotope plot of all samples analyzed in this study. The solid line represents the fractionation line with a slope of 0.505. Error bars represent 2SD uncertainties. Data are from Tables 2–6.

5.1. The absence of Mg isotope fractionation in I-type and S-type granites

Teng et al. (2007, 2010a) showed that Mg isotope fractionation is insignificant during differentiation of basaltic magma. Recently, Liu et al. (2010) found limited Mg isotope fractionation during I-type granite differentiation. The data collected here allow further investigations of the behavior of Mg isotopes during intra-crustal melting and subsequent granitic magma differentiation.

Although the eight I-type granites are from different supersuites of the Bega Batholith from the LFB, formed at various temperatures ranging from 750 to 800 °C and display a negative correlation between SiO₂ and MgO contents (Fig. 3a), their Mg isotopic compositions are indistinguishable within our analytical uncertainties (Fig. 3b). Such limited variation suggests a lack of Mg isotope fractionation during magmatic differentiation of these granites, with temperatures down to 750 °C, a conclusion similar to that of Liu et al. (2010).

The two end-member S-type granites from the LFB have δ²⁶Mg values (−0.23 and −0.14, respectively) that are within the range of their potential source rock, the Ordovician graywacke (−0.20 ± 0.10), as well as I-type granites (from −0.25 to −0.15) from the LFB, suggesting Mg isotope fractionation during crustal anatexis of these granites is also insignificant.

The homogeneous Mg isotopic compositions of granitoid composites from eastern China further support this conclusion. These granitoid composites display a negative correlation between SiO₂ and MgO contents, with SiO₂ varying from 55% to 75% (Fig. 3c), whereas their Mg isotopic compositions are uniform (Fig. 3d), suggesting that little Mg isotope fractionation occurred during differentiation of granitic magma.

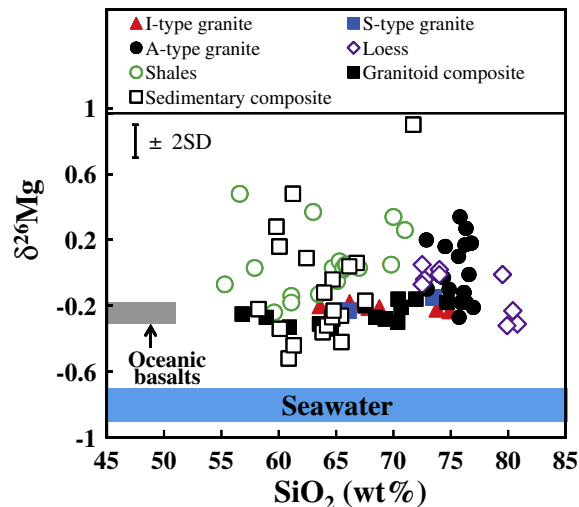


Fig. 2. δ²⁶Mg vs. SiO₂ (wt%) for all samples studied here. The blue bar represents the Mg isotopic composition of seawater (δ²⁶Mg = −0.8 ± 0.1, Chang et al., 2003; Young and Galy, 2004; Tipper et al., 2006a; Bolou-Bi et al., 2009; Hippler et al., 2009; Teng et al., 2010a). The shaded area represents oceanic basalts (δ²⁶Mg = −0.26 ± 0.07, Teng et al., 2010a). Data are from Tables 2–6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To summarize, Mg isotope fractionation during granite differentiation is limited, hence Mg isotopic composition of granites may record their crustal sources, i.e., the middle and lower crust.

5.2. Significant Mg isotopic variation in A-type granites

In contrast to the relatively homogeneous Mg isotopic compositions of I-type and S-type granites from southeastern Australia and granitoid composites from eastern China, δ²⁶Mg varies significantly (>0.6‰ variation) in A-type granites from northeastern China, and some heavy values, up to +0.34, are observed (Fig. 2). These A-type granites are highly evolved, with very high SiO₂ contents (from 72.8% to 77.0%). Hence, the variable and heavy Mg isotopes might result from crystallization of certain minerals with light Mg isotopes in the later stages of granite differentiation. However, no such mineral has yet been reported and no correlation exists between δ²⁶Mg and MgO contents among our samples (not shown). Therefore, similar to the conclusion in Section 5.1, it seems unlikely that significant Mg isotope fractionation occurred during differentiation of these A-type granites and, thus, other processes must be responsible for the large Mg isotope variation observed here. Since all samples analyzed here are fresh (Wu et al., 2002), weathering effects after intrusion of these granites can also be excluded.

Recently, Lundstrom (2009) predicted that heavy Mg isotopes will be enriched in highly siliceous granites formed by a “thermal migration zone refining” process. However, the A-type granites studied here have high SiO₂ contents, yet contain both heavy and light Mg isotopes. This is inconsistent with the results of thermal diffusion experiments, where the felsic end-member is always enriched in heavy

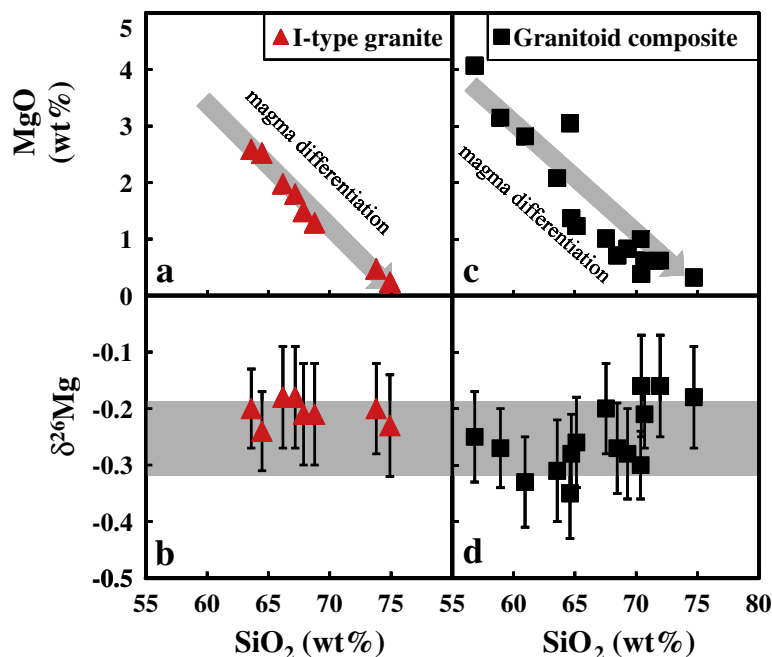


Fig. 3. (a) MgO (wt%) vs. SiO₂ (wt%) and (b) δ²⁶Mg vs. SiO₂ (wt%) for I-type granites from the Lachlan Fold Belt, southeastern Australia. (c) MgO (wt%) vs. SiO₂ (wt%) and (d) δ²⁶Mg vs. SiO₂ (wt%) for granitoid composites from eastern China. The gray bar represents oceanic basalts (δ²⁶Mg = -0.26 ± 0.07, Teng et al., 2010a). Error bars represent 2SD uncertainties. Data are from Tables 2 and 6.

Mg isotopes (Richter et al., 2008, 2009; Huang et al., 2009b, 2010). The homogeneous Li isotopic composition of these A-type granites (Teng et al., 2009) also argues against thermal diffusion processes, as significant Li isotope fractionation should occur (Lundstrom and Bindeman, 2010). Additionally, it seems unlikely that diffusion effects could operate on such a large scale and continue over such a long period of time; these A-type granites come from a ≥200,000 km² area and have ages spanning more than 180 Ma (Wu et al., 2002). Therefore, thermal diffusion-driven Mg isotope fractionation is unlikely to produce the large Mg isotopic variation in A-type granites.

The most likely explanation for the large Mg isotopic variation in these A-type granites is source heterogeneity. Based on the negative correlation between the initial $\epsilon_{\text{Nd}}(t)$ values and two-stage Nd model ages ($T_{\text{DM}2}$) (Fig. 4a), Wu et al. (2002) suggested that these A-type granites formed from mixing between juvenile and old crustal components. The juvenile crustal component has mantle-like Nd isotopes (Fig. 4a). It also has mantle-like Mg isotopes, as shown by the lowest δ²⁶Mg value of -0.28 among these A-type granites (Fig. 4b), which falls within the range of the mantle (δ²⁶Mg = -0.25 ± 0.07, Teng et al., 2010a). Therefore, the large Mg isotope variation and the heavy Mg isotopes seen in some A-type granites studied here may reflect contributions from old crustal components that have variable Mg isotopic compositions (ranging from mantle-like to extremely high δ²⁶Mg; Fig. 4b). Old crustal components might have experienced low-temperature weathering cycles that fractionated Mg isotopes and, thus, may be enriched in heavy Mg isotopes (see Section 5.3) before they were melted to produce A-type granites. A similar mechanism was suggested to be responsible for the >0.8‰ variation in δ²⁶Mg

within a set of I-type granites from California (Shen et al., 2009).

5.3. Magnesium isotope fractionation during continental weathering

The behavior of Mg isotopes during continental weathering has been inferred on the basis of river compositions and associated bedrocks in riverine catchments (Tipper et al., 2006a,b, 2008a; Brenot et al., 2008; Pogge von Strandmann et al., 2008) and the isotopic systematics of source materials for granites (Shen et al., 2009). It has also been measured directly from weathering profiles (Teng et al., 2010b). These studies show that continental weathering can significantly fractionate Mg isotopes via release of light Mg to the hydrosphere and formation of isotopically heavy Mg in the weathered products. Data on sedimentary rocks collected here allow us to further evaluate the effects of weathering on Mg isotope fractionation.

In contrast to the homogeneous Mg isotopic composition of the mantle (Teng et al., 2007, 2010a; Handler et al., 2009; Yang et al., 2009; Bourdon et al., 2010; Dauphas et al., 2010), the upper crust is highly heterogeneous. Such heterogeneity is best seen in sedimentary rocks, while most granitoids analyzed here have mantle-like Mg isotopic composition (Fig. 2). Except for a few sedimentary composites, in most cases the sedimentary rocks analyzed here have heavier Mg isotopic compositions than the mantle (Fig. 6), with the weighted average δ²⁶Mg value of -0.10 for loess, +0.05 for shales and -0.16 for sedimentary composites, respectively. The heavy Mg isotopic compositions of sedimentary rocks are opposite to the light Mg isotopic compositions of rivers draining silicates (Fig. 6). This observation

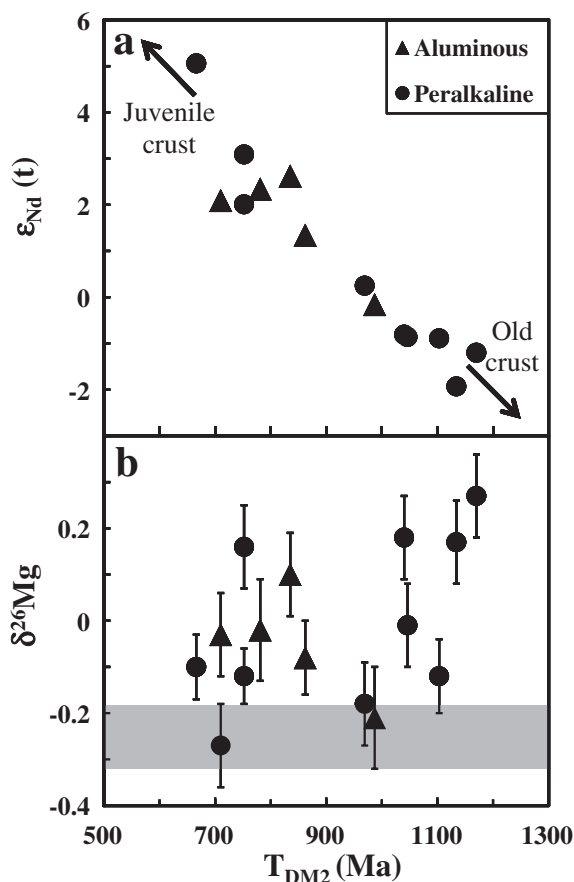


Fig. 4. (a) $\epsilon_{Nd}(t)$ (deviation in Nd isotopes from the chondritic value in parts per 10,000) vs. T_{DM2} (two-stage Nd model age in Ma) and (b) $\delta^{26}Mg$ vs. T_{DM2} (Ma) for A-type granites from northeastern China. The gray bar represents the average $\delta^{26}Mg$ values of the mantle ($-0.25 \pm 0.07\%$, Teng et al., 2010a). Error bars represent 2SD uncertainties. Data are from Table 3.

is consistent with the release of light Mg to water and the retention of heavy Mg in the solid residue during chemical weathering (Tipper et al., 2006a,b, 2008a; Brenot et al., 2008; Pogge von Strandmann et al., 2008; Teng et al., 2010b). The light Mg isotopes of some sedimentary composites are distinctive, and one possible explanation is that these composites contain a small amount of dolomite, which has very light Mg isotopic compositions ($\delta^{26}Mg$ of -1.3 to -1.6 , Tipper et al., 2008a).

The effects of weathering on Mg isotope fractionation can be further demonstrated through comparison of Mg isotopic systematics between loess and shale (Fig. 5). Compared to shales, loess is produced by physical abrasion and aeolian transport with less fluid–rock interaction, and therefore generally has lower CIA values. On the $\delta^{26}Mg$ vs. CIA diagram, $\delta^{26}Mg$ values show a larger dispersion in shales than loess ($>0.7\%$ vs. $<0.4\%$, Fig. 5), suggesting that heavy Mg isotopes are more likely to be enriched in samples that experienced more intensive weathering. Hence, old crustal components that generally experienced more weathering cycles are more likely to have heavy Mg isotopes, as hypothesized for the old crustal components seen in some granites discussed above.

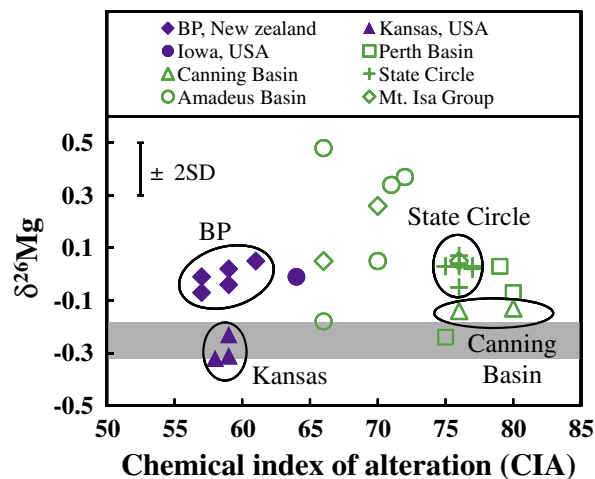


Fig. 5. $\delta^{26}Mg$ vs. chemical index of alteration (CIA) for loess from New Zealand and the midwestern USA (purple and solid symbols) as well as PAAS (green and void symbols). The gray bar represents oceanic basalts ($\delta^{26}Mg = -0.26 \pm 0.07$, Teng et al., 2010a). Data are from Tables 4 and 5. See text for definition of CIA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

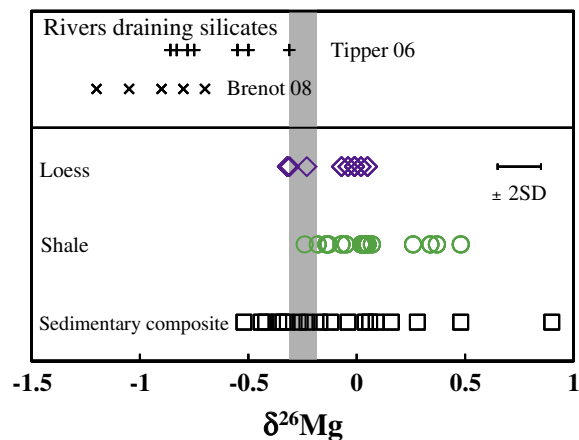


Fig. 6. Range in $\delta^{26}Mg$ for sedimentary rocks analyzed in this study. The upper panel shows literature data for some rivers draining silicates (Tipper et al., 2006b; Brenot et al., 2008). The gray bar represents the average $\delta^{26}Mg$ values of the mantle ($\delta^{26}Mg = -0.25 \pm 0.07$, Teng et al., 2010a). Data are from Tables 4–6.

Further support for Mg isotope fractionation during weathering comes from coupled Li isotope studies. δ^7Li roughly correlates with $\delta^{26}Mg$ in loess (Fig. 7), which is consistent with the inferred mechanism controlling Li and Mg isotopes during weathering, i.e., light Li isotopes prefer secondary minerals to fluids during low-temperature fluid–rock interaction (Pistiner and Henderson, 2003; Huh et al., 2004; Kisakürek et al., 2004; Rudnick et al., 2004), while light Mg isotopes preferentially partition into fluids, leaving heavy Mg isotopes in the weathered products.

Collectively, the combined studies indicate that chemical weathering significantly fractionates Mg isotopes and, thus, may be the dominant process producing the highly hetero-

geneous Mg isotopic composition of the upper continental crust.

5.4. Magnesium isotopic composition of the upper continental crust

Based on samples studied here, the upper continental crust has a highly heterogeneous Mg isotopic composition, with two peaks corresponding to $\delta^{26}\text{Mg}$ values of -0.35 to -0.10 (“Peak I”) and -0.05 to $+0.05$ (“Peak II”) (Fig. 8). “Peak I” is mainly dominated by I-type granites and granitoid composites while “Peak II” is mainly dominated by loess and shales. Although “Peak I” is indistinguishable from the range of $\delta^{26}\text{Mg}$ of the mantle, “Peak II” is clearly beyond the mantle range toward heavier $\delta^{26}\text{Mg}$ values (Fig. 8).

The dataset achieved in this study is used to estimate the average Mg isotopic composition of the upper continental crust. The difficulty in precisely estimating an average $\delta^{26}\text{Mg}$ value of the upper crust lies in estimating the exact proportion of major rock units within the upper continental crust, and limited Mg isotopic data of crustal samples. The proportions of rock units within the upper continental crust, as well as average MgO content and Mg isotopic composition of each rock unit, are the key parameters for such estimates.

Following Wedepohl (1995), upper crustal rocks are divided into six major rock units, i.e., sediments, granites, granodiorites, tonalities, gabbros and metamorphic rocks. Among these six units, the average Mg isotopic composition of sediments, granites and granodiorites can be directly estimated from our data. Weighted by MgO content of each sample for the total 51 loess, shales and sedimentary composite samples studied here, an average $\delta^{26}\text{Mg}$ value of -0.05 is derived for the “sediments” unit. Based on the 37 granites (I-type, S-type and A-type) and granite composite samples and the eight granodiorite and diorite composite samples, -0.18 and -0.29 are estimated for the “granites” and “granodiorites” units, respectively. Comprehensive studies on both basalts (Teng et al., 2007, 2010a) and gran-

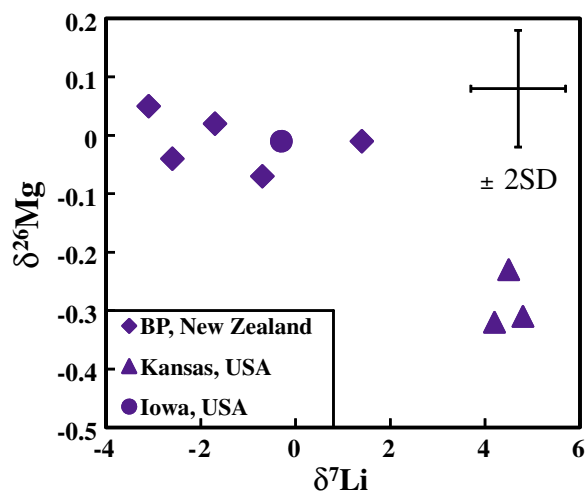


Fig. 7. $\delta^{26}\text{Mg}$ vs. $\delta^7\text{Li}$ for loess from New Zealand and the midwestern USA. Data are from Table 4.

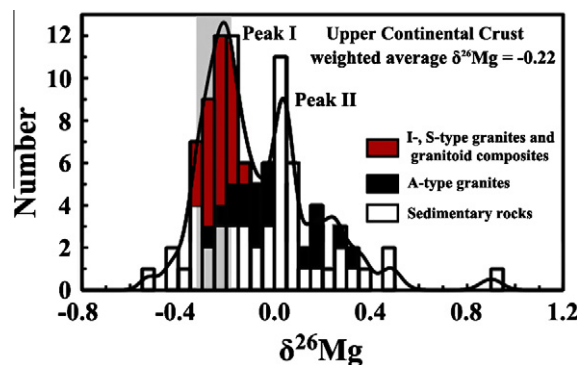


Fig. 8. Histogram of $\delta^{26}\text{Mg}$ values of all samples studied here. Based on this dataset, a weighted average $\delta^{26}\text{Mg}$ value of -0.22 is estimated for the upper continental crust. See text for details about how this weighted average is derived. The gray bar represents the average $\delta^{26}\text{Mg}$ values of the mantle ($-0.25 \pm 0.07\text{‰}$, Teng et al., 2010a). Data are from Tables 2–6.

ites (Liu et al., 2010, and this study) indicate insignificant Mg isotope fractionation during magmatic differentiation. Therefore, the average $\delta^{26}\text{Mg}$ value of -0.26 of oceanic basalts (Teng et al., 2010a) is used to represent that of the “tonalities” and “gabbros” units. Furthermore, if Mg isotopes do not fractionate during high-temperature metamorphism (Li et al., 2010), then the Mg isotopic composition of oceanic basalts ($\delta^{26}\text{Mg} = -0.26$, Teng et al., 2010a) could also represent the average value of the “metamorphic rocks” unit. Weighting the average Mg isotopic composition of these six units by the estimated proportion and average MgO content of each unit (Wedepohl, 1995), the average Mg isotopic composition of the upper continental crust is estimated to be -0.22 (Table 7). This value is indistinguishable from the average mantle value (-0.25 , Teng et al., 2010a), within current analytical uncertainties (e.g., ± 0.10).

Though the upper continental crust has, on average, a mantle-like Mg isotopic composition, most of the sedimentary rocks analyzed here have heavier Mg isotopes than both the mantle and seawater (Fig. 9). Teng et al. (2004) estimated the average Li isotopic composition of the upper continental crust, which is isotopically lighter ($\delta^7\text{Li}$ of ~ 0) than the mantle ($\delta^7\text{Li}$ of ~ 4 , Chan et al., 1992; Chan and Frey, 2003; Elliott et al., 2006; Tomascak et al., 2008) and seawater ($\delta^7\text{Li}$ of ~ 32 , Chan et al., 1992), and concluded that chemical weathering plays an important role in the Li isotopic budget of the crust. Our findings suggest that chemical weathering can also significantly fractionate Mg isotopes and, thus, plays an important role in generating the highly variable and relatively heavier Mg isotopic composition of the sedimentary rocks. It is also noteworthy that the behavior of Mg isotopes during weathering is the opposite to that of Li isotopes, i.e., light Mg isotopes are lost to the hydrosphere, leaving weathered products with heavy Mg isotopes. Such contrasting behavior accounts for the relative position of the seawater, mantle and crustal rocks on the $\delta^{26}\text{Mg}$ vs. $\delta^7\text{Li}$ diagram (Fig. 9).

Finally, our results may shed light on the Mg isotopic composition of the deep continental crust. Based on the I-type and S-type granites studied here and the I-type granitoids

Table 7
Mass balance model for Mg in the upper continental crust (UCC).

Rock units ^a	Proportions in the UCC ^a	Average MgO contents (%) ^a	MgO percentage in the UCC (%)	Weighted average $\delta^{26}\text{Mg}$
Sediments ^b	14	3.3	19	-0.05
Granites ^c	25	0.57	6	-0.18
Granodiorites ^d	20	1.74	14	-0.29
Tonalites ^e	5	2.6	5	-0.26
Gabbros ^e	6	7.6	19	-0.26
Metamorphic rocks ^e	30	2.91	36	-0.26
UCC ^f		2.41	100	-0.22

^a Division of rock units, their proportions in the upper continental crust and average MgO contents are from Wedepohl (1995).

^b Weighted average $\delta^{26}\text{Mg}$ value derived from Mg isotopic compositions of sedimentary rock ($n = 2$, Table 2), loess ($n = 9$, Table 4), shales ($n = 20$, Table 5) and sedimentary composite (graywackes, pelites and tillite, $n = 20$, Table 6) samples analyzed here.

^c Weighted average $\delta^{26}\text{Mg}$ value derived from Mg isotopic compositions of I-type and S-type granite ($n = 10$, Table 2), A-type granite ($n = 19$, Table 3) and granite composite ($n = 7$, Table 6) samples analyzed here.

^d Weighted average $\delta^{26}\text{Mg}$ value derived from granodiorite and diorite composite ($n = 8$, Table 6) samples analyzed here.

^e Assume tonalities, gabbros and metamorphic rocks have the same average $\delta^{26}\text{Mg}$ values as oceanic basalts ($\delta^{26}\text{Mg} = -0.26 \pm 0.07$, Teng et al., 2010a). See text for the details.

^f Weighted average $\delta^{26}\text{Mg}$ value derived from mass balance calculation, using MgO percentage in the UCC of each rock unit as the weight.

studied in Liu et al. (2010), the deep continental crust should, on average, have a mantle-like Mg isotopic composition. On the other hand, the large Mg isotopic variation of A-type granites studied here, as well as of I-type granitoids studied in Shen et al. (2009), suggests that the deep crust may be highly heterogeneous in Mg isotopic composition due to the involvement of materials previously processed through weathering cycle. In any case, more Mg isotopic data on deep crustal samples (e.g., granulite xenoliths and high-grade metamorphic terranes) are needed in order to better characterize the average Mg isotopic composition of the deep crust.

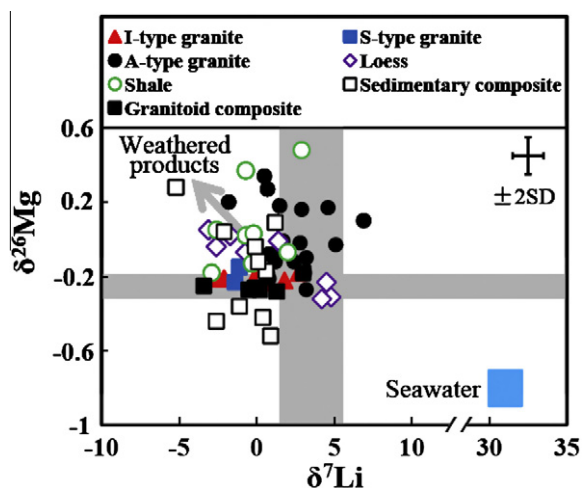


Fig. 9. Magnesium and lithium isotopic compositions of the upper continental crust. The gray bars represent the average Li ($+3.7 \pm 1.9\text{‰}$) and Mg ($-0.25 \pm 0.07\text{‰}$) isotopic compositions of the upper mantle (Tomascak et al., 2008; Teng et al., 2010a). The blue square represents Li and Mg isotopic compositions of seawater (Chan et al., 1992; Young and Galy, 2004). Data are from Tables 2–6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6. CONCLUSIONS

The main conclusions that can be drawn from the ~ 100 high-precision Mg isotopic analyses of well-characterized upper crustal rocks are:

1. Magnesium isotopic compositions show a limited ($<0.2\text{‰}$) variation in both I-type and S-type granites from southeastern Australia ($\delta^{26}\text{Mg} = -0.25$ to -0.14) and granitoid composites from eastern China ($\delta^{26}\text{Mg} = -0.35$ to -0.16), despite the wide variation in SiO_2 content, suggesting insignificant Mg isotope fractionation during crustal anatexis and differentiation of granitic magma.
2. $\delta^{26}\text{Mg}$ shows substantial variation in loess from New Zealand and the USA (-0.32 to $+0.05$), shales from Australia (-0.27 to $+0.49$) and sedimentary composites from eastern China (-0.52 to $+0.92$). Most of these sedimentary rocks have heavier Mg isotopic composition than the mantle and rivers draining silicates, indicating the release of light Mg to the hydrosphere and formation of isotopically heavy Mg in the weathered products.
3. Loess displays less Mg isotopic variation ($<0.4\text{‰}$ vs. $>0.7\text{‰}$) than shales, with $\delta^{26}\text{Mg}$ negatively correlating with $\delta^7\text{Li}$ in loess. These observations, together with the heavier Mg isotopes in sedimentary rocks, further suggest that continental weathering significantly fractionates Mg isotopes and plays an important role in producing the highly variable Mg isotopic composition of sedimentary rocks.
4. A-type granites from northeastern China display large ($>0.6\text{‰}$) Mg isotopic variation, with $\delta^{26}\text{Mg}$ ranging from -0.28 to $+0.34$, reflecting incorporation of ancient, weathered materials in their source regions.
5. Our granite data indicate that the deep continental crust, on average, may have a mantle-like Mg isotopic composition, although it is likely to be very heterogeneous.

6. Overall, the upper continental crust has a highly heterogeneous ($\delta^{26}\text{Mg} = -0.52$ to $+0.92$) Mg isotopic composition, with a mantle-like weighted average ($\delta^{26}\text{Mg} = -0.22$).

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2010.08.030.

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