

The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation

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Continental crust is too Si-rich and Mg-poor to derive directly from mantle melting, which generates basaltic rather than felsic magmas. Converting basalt to more felsic compositions requires a second step involving Mg loss, which is thought to be dominated by internal igneous differentiation. However, igneous differentiation alone may not be able to generate granites, the most silicic endmember making up the upper continental crust. Here, we show that granites from the eastern Peninsular Ranges Batholith (PRB) in southern California are isotopically heavy in Mg compared with PRB granodiorites and canonical mantle. Specifically, Mg isotopes correlate positively with Si content and O, Sr, and Pb isotopes and negatively with Mg content. The elevated Sr and Pb isotopes require that a component in the source of the granitic magmas to be ancient preexisting crust making up the prebatholithic crustal basement, but the accompanying O and Mg isotope fractionations suggest that this prebatholithic crust preserved a signature of low-temperature alteration. The protolith of this basement rock may have been the residue of chemical weathering, which progressively leached Mg from the residue, leaving the remaining Mg highly fractionated in terms of its isotopic signature. Our observations indicate that ancient continental crust preserves the isotopic signature of compositional modification by chemical weathering.

batholith | granite | isotope | magnesium | California

The Earth's continental crust is poor in Mg compared with the basaltic magmas derived from melting of the Earth's ultramafic mantle (1). The objective of this study is to better understand how basaltic, mantle-derived magma compositions are transformed into felsic continental crust by tracking the origin and fate of Mg in continental arcs. Continental arcs represent one environment where continental crust is being refined (2–4). Here, crust formation is ultimately driven by juvenile magmatism (mantle-derived magmatism), but the final aliquot of magmas that reaches the surface to form the continental crust is the end-product of (i) deep fractional crystallization of basalt or partial remelting of basaltic crust and (ii) assimilation or partial melts of preexisting crustal basement. These differentiation processes are responsible for the low Mg contents of evolved arc magmas, such as granodiorites and granites. For example, remelting of basaltic crust or the direct crystallization of basaltic magmas at depth generate Mg-rich residues and cumulates, respectively (1, 5), which, being denser than peridotitic mantle, delaminate and recycle back into the mantle, leaving behind a felsic continental crust (1, 2, 6). There is indeed clear geochemical, petrologic, and geologic evidence that such processes play a key role in the evolution of continental crust (3, 4, 7). However, low Mg contents can also be inherited by remelting preexisting crust, previously depleted of Mg by the above-mentioned magmatic processes or low-temperature processes, such as chemical weathering (2, 8). In the context of weathering, physical and chemical interaction of rocks (e.g., erosion and soil formation) with the atmosphere and hydro-

sphere results in the preferential dissolution of Mg-bearing minerals from the surface of continents while more chemically and physically resistant minerals, such as quartz, remain in the weathering residue. Transport of this dissolved Mg (and Ca) to the oceans leads to sequestration of Mg into the oceanic crust during hydrothermal alteration (9, 10), while the quartz-rich weathering residues are left behind in the continental crust in the form of soils or altered rock, which are subsequently eroded and deposited as sediments in continent shelf or slope. These sediments are later metamorphosed to form the crustal basement. Remelting of such metamorphic rocks can then generate granites (2).

Continental arc crust can thus be derived from magmatic differentiation of juvenile magmas or by recycling of ancient crust that is, remelting of preexisting crustal basement that may have been previously modified by chemical weathering. It is well known that some granites, generally referred to as S-type granites, are the partial melts of clay- or mica-rich sedimentary protoliths and are easily identified by their high aluminum contents (peraluminous) and the presence of two micas (biotite and muscovite) and cordierite (11). However, S-type granites are rare, even in batholiths associated with continental arcs (11). The more common types of granitoids, known as I-type, are thought to be dominated by juvenile sources, that is, their high Si and low Mg contents are the result of extreme fractional crystallization of a basaltic parent or extreme low-degree remelting of basaltic crust. Such granitoids are undoubtedly more important to crustal growth than S-type granitoids. However, I-type granitoids may still contain recycled components. For example, some I-type granites have heavy oxygen isotopic compositions compared with the mantle and thus require components within the granite source regions to have interacted with water at low temperatures (<300 °C) some time before melting because only low-temperature processes can lead to significant isotopic fractionation (12). The question here is to what extent I-type granites, previously thought of as being primarily juvenile, require a component of preexisting crust, in particular crust that has been compositionally modified by chemical weathering (e.g., depletion in Mg and Ca).

Assessing the contribution of ancient preexisting crust to the source regions of granitic magmas is traditionally approached with radiogenic isotope systems (e.g., ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ¹⁷⁶Hf/¹⁷⁷Hf) (12). However, because we are interested in the role of chemical weathering on modifying the crust, we are more

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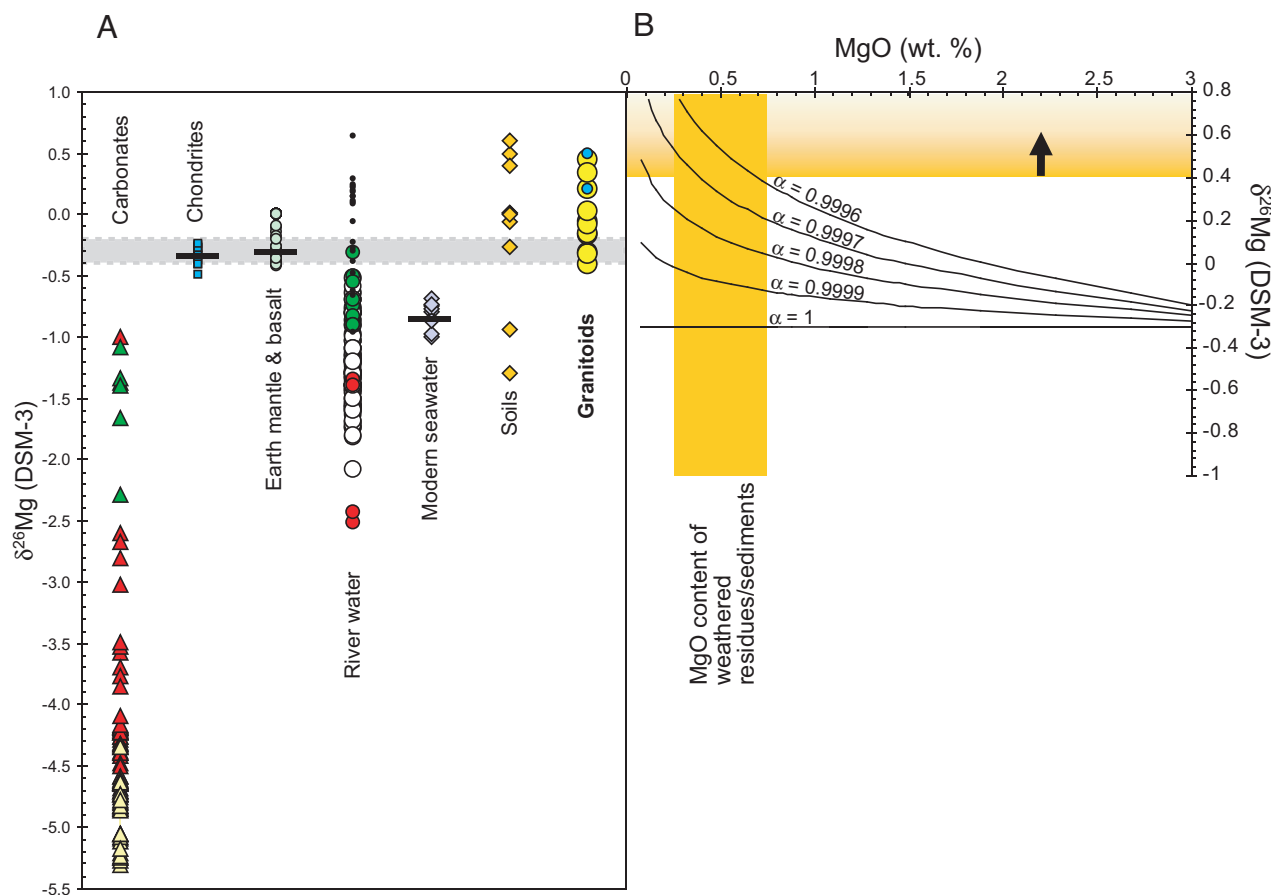


Fig. 1. Mg isotopic compositions of different reservoirs and Mg isotope fractionation during chemical weathering. (A) Global compilation of Mg isotope data for carbonates, undifferentiated meteorites [chondrites (13, 39)], terrestrial mantle and basalts (13, 14, 39), dissolved load in rivers, seawater (40), soils, and granitoid. The horizontal gray bar represents the best estimate of terrestrial mantle (13). Data are expressed in $\delta^{26}\text{Mg}$ notation relative to DSM-3 standard (15). For granitoids, PRB granitoids (this study) are yellow circles, and literature data on granites are blue circles (19). For carbonates, dolomite, limestone, and foraminifera shell are separately marked as green, red, and yellow triangles, respectively (41–43). For rivers, dissolved Mg draining silicate-dominated and carbonate-dominated regions are denoted as green and red circles, respectively (18, 19); rivers draining Icelandic basalt are shown by black dots (34); all other riverine Mg are indicated as open circles (16–19). Values for soils come from refs. 18, 19, and 34. Average values of different materials are denoted as small horizontal bars. (B) Predicted variation of $\delta^{26}\text{Mg}$ in soil residues as a function of fractional loss of Mg by weathering for given fractionation factors between aqueous Mg and Mg in soil residue (see *SI Text*). Fractional loss of Mg has been replaced by absolute concentrations of MgO by assuming unweathered protolith has MgO content of 3–4 wt.%. The horizontal orange bar shows the minimum $\delta^{26}\text{Mg}$ of the weathered endmember (sediments or metamorphic basement) that was assimilated into the PRB granitoids. The vertical orange bar represents a possible range of MgO contents for the weathered endmember. Intersection of the orange bars gives the range of permissible fractionation factors.

interested in the major-element or lithological composition of potential granitoid sources. Radiogenic isotopes, unfortunately, are not sensitive to major-element variations, but sensitive to protolith age and trace element fractionations. In this regard, stable isotopic variations involving the major elements are critical. For example, oxygen isotopes are very sensitive to low-temperature processes and provide an insight not provided by radiogenic isotopes. However, oxygen isotopes alone may not be sufficient to answer the questions posed in this article. Oxygen is a major element in water and all silicate rocks, hence fractionated oxygen isotopes can reflect either incorporation of sedimentary lithologies or the exchange of oxygen during water–rock interaction without significant lithological modification. To complement these approaches, we use Mg isotopes as a more direct constraint on the lithological nature of the sources of granitic magmas.

Mg Isotopes as a Tool for Assessing Chemical Weathering

Mg isotopes are well suited for detecting the effects of chemical weathering on lithology and major element composition because there is no significant isotopic fractionation during high-

temperature processes, such as during melting of the mantle to form basalts and during magmatic differentiation (13, 14) (Fig. 1A). However, measurable fractionations occur during low-temperature processes, particularly if such processes involve considerable leaching of Mg as in the case of chemical weathering. For example, it can be seen in Fig. 1A that the Mg isotopic compositions [expressed as $\delta^{26}\text{Mg}$, which is the per-mil deviation of a sample's $^{26}\text{Mg}/^{24}\text{Mg}$ relative to a universal standard, which by convention is Dead Sea Magnesium (DSM-3) standard (15)] of dissolved Mg in global river waters (-1.1‰) average lighter than seawater (-0.8‰), the Earth's mantle (-0.3‰), and juvenile igneous rocks (-0.3‰) (13, 14, 16–18), indirectly suggesting that leaching of Mg during deep continental weathering of silicates preferentially releases light Mg into rivers and leaves heavy Mg behind in the weathering residues. One caveat of this interpretation of the global Mg isotope data is that the low Mg isotopic composition of river waters may in part be influenced by weathering of carbonates (19), which are extremely light (we will return to this issue later). Nevertheless, the majority of soil residues have heavy Mg isotopes (Fig. 1A). Thus, independent of the Mg isotope signature of river waters and

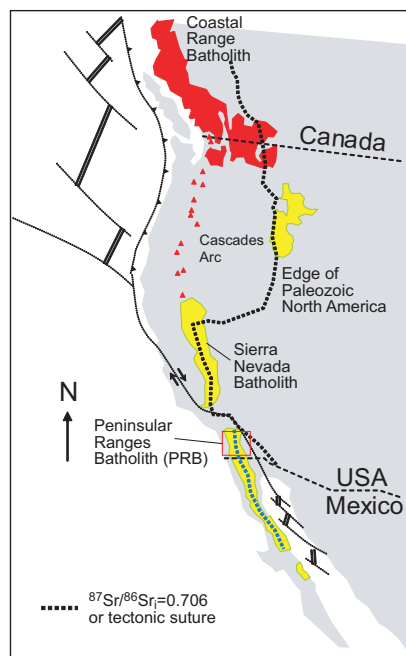


Fig. 2. Schematic geological map of western North America, showing the locality of continental arc plutons. Samples were collected from the northern PRB (red rectangle), which represents the eroded remnants of a late Cretaceous continental arc formed by the subduction of the Farallon Plate beneath North America (*Inset*). The blue dashed line indicates the boundary between the eastern and western blocks of PRB.

seawater, we can conclude that if one of the components of continental crust (e.g., metamorphosed sedimentary basement) has a weathering residue protolith, then the $\delta^{26}\text{Mg}$ of the crust would be expected to be heavier than that of the mantle or the basaltic parent to continental crust. Arguably, Mg isotopes are likely to be controlled more by chemical weathering than by isotope exchange during water–rock interactions because Mg, being a trace element in water, does not give water alone much leverage in resetting the Mg isotopic signature of a rock. In the case of chemical weathering, progressive leaching of Mg leaves behind a soil residue characterized by a magnified isotopic fractionation caused by Rayleigh distillation-like effects (the leachate counterpart, e.g., riverine water, will be lighter than the parent rock, but the degree of fractionation should be less).

Application to Continental Arc Granitoids

We now turn to continental arc magmas for a case study of Mg isotopes. At least during post-Archean times, continental arcs are thought to represent the final and most important stage in converting basaltic crust into the felsic composition characteristic of continents (4). It is in these environments where basaltic island arcs, one of the main building blocks of continents (6), are accreted onto the margins of preexisting continents, resulting in thickened lithosphere. Continued subduction generates juvenile basaltic magmas from the mantle wedge, which rise up into the overlying lithosphere and assimilate or remelt preexisting crust, followed by the formation of mafic cumulates and felsic crust.

We investigate here the Mg isotopic compositions of granitoid plutons from the eastern part of the northern Peninsular Ranges Batholith (PRB) in southern California (Fig. 2). We selected 11 representative samples in this region. The geology of the PRB has been described in detail (20–26). The PRB represents part of the north–south trending Cordilleran batholiths emplaced through the western margin of North America during Cretaceous subduction of the Farallon plate. The eastern PRB rep-

resents the part of the continental arc that was emplaced through the Paleozoic margin of North America and hence represents mixtures of juvenile magmas and melts of older metamorphic basement (27); this is suggested by trends toward heavy $\delta^{18}\text{O}$, radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, and unradiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ (4, 20, 26). Despite the involvement of older, metamorphic basement, all of the granitic rocks studied here belong to the I-type granitic series (11).

Results

Mg isotopes were determined on fresh (e.g., no chloritization) biotites, which dominate the Mg budget in these granitoids (biotite 10–15%; hornblende 0–5%); in the case of the granites, biotites are the only Mg-bearing mineral (26). Analyzing mafic minerals rather than the whole rock greatly simplifies chemical procedures for the purification of Mg (see *SI Text*). Mg isotopic compositions, $\delta^{26}\text{Mg}$, vary between -0.404 and $+0.441$ ‰ (Table S1 and Figs. 1A and 3), which exceed the range measured for terrestrial igneous rocks or minerals reported so far. The most positive values are represented by four granite samples ($\text{SiO}_2\% > 70\%$), whereas all other samples (tonalites and granodiorites) have values indistinguishable from mantle values. The heavy Mg isotopes in our granites are similar to those reported in other granites (19). Using previously published elemental and isotopic data on the same samples (4, 22), we found $\delta^{26}\text{Mg}$ shows a positive correlation with whole-rock SiO_2 , initial $^{87}\text{Sr}/^{86}\text{Sr}$, initial $^{206}\text{Pb}/^{204}\text{Pb}$, and $\delta^{18}\text{O}$ (per-mil deviation from standard mean ocean water), but shows a negative correlation with MgO (Fig. 3). Because we measured only biotite, the question arises as to whether our observed fractionations in biotite are artifacts of Mg isotope fractionations between minerals. In the case of the granites, other mafic minerals are almost nonexistent (biotite/hornblende ratios > 10), which means that biotite dictates the Mg budget and isotopic signature of the whole rock. Furthermore, the correlations of Mg isotopic compositions with radiogenic isotopic and whole-rock elemental abundances cannot be interpreted by internal isotopic fractionation between minerals and instead requires a source effect, which we will discuss in the next section. Finally, the mantle-like Mg isotopic compositions of the biotites in the more primitive granitoids (granodiorites) are fully consistent with the observation that whole-rock measurements of granodiorites and basalts all have mantle-like Mg isotopic signatures (13, 14). This implies that there is little internal fractionation of Mg isotopes between minerals at granite-formation temperatures (600 °C). Based on this discussion, we conclude that the biotite Mg isotopic compositions are representative of the PRB granitoids.

Origin of Heavy Mg Isotopes in Granites. Three possible scenarios for the origin of heavy Mg isotopes in the granites are discussed: (i) high-temperature kinetic isotope effects associated with chemical diffusion driven by thermal gradients in magma chambers (28), (ii) isotopic fractionation between source and partial melts, and (iii) source heterogeneity. The first scenario is motivated by experimentally based observations (29) that thermal gradients can give rise to chemical zonation (e.g., Soret diffusion) with accompanying stable isotope fractionations in Mg, Ca, Fe, and Si. It has recently been suggested that thermal gradients in plutons could lead to analogous compositional and isotopic gradients on the pluton-length scale (28). However, two observations argue against such large-scale diffusion-driven processes in our study: (i) the isotopic variability occurs over the entire eastern PRB and hence on > 10 -km length scales, too large for diffusive exchange to occur, and (ii) correlations with radiogenic isotopes cannot be explained by internal diffusion. We recognize that diffusion effects could operate on cm to m length scales, but these effects also will not generate correlations with radiogenic isotopes.

juvenile magmas and magmas derived from highly evolved, previously weathered components that preserve their low-temperature stable isotope signatures. This latter component most likely represents the Paleozoic North American metamorphic basement through which the Cretaceous batholith was emplaced (26, 27). The protoliths of these metamorphic rocks were probably highly weathered sediments shed off the North American continent and later metamorphosed during subduction well before Cretaceous plutonism. A detailed Mg isotope survey of these metamorphic lithologies is necessary but beyond the scope of the present article because of the high lithological variety in exposed metamorphic basement rocks.

We note that simple mixing between juvenile and “recycled” magmas is not likely to control all of the observed geochemical variations. For example, binary mixing should lead to linear trends on a MgO versus SiO₂ plot, but a hyperbolic curve is seen (Fig. 3A). The concave upwards shape of the MgO versus SiO₂ plot suggests that fractional crystallization was also occurring during magma mixing. Because Mg is slightly compatible and Si slightly incompatible in the crystallizing assemblage (mafic minerals + plagioclase), Mg is rapidly depleted from the differentiating magma while Si increases. The rapid depletion of Mg in the magma renders the Mg isotopic composition of the magma more susceptible to assimilation of the Mg-poor metamorphic basement or melts of such basement. The isotopic and elemental covariations thus require simultaneous fractional crystallization and magma mixing, which we refer to in Fig. 3 as a hybrid origin [analogous to assimilation and fractionation crystallization (31); also see *SI Text*]. Modeling this process involves many free variables, such as the composition of endmember components, crystal–liquid partition coefficients, and the ratio of crystallization to magma mixing. Nevertheless, crude constraints on some of these variables can be had by best-fitting the model to several geochemical observables, e.g., MgO and SiO₂ contents and Sr, Pb, O, and Mg isotopes as shown in Fig. 3. In the case of Sr and Pb isotopes, two different prebatholithic source rocks are needed (Fig. 3B, C, F, and G). However, only one source lithology is needed to explain Mg and O isotope covariation (Fig. 3D and H), underscoring the decoupling of radiogenic isotopes from major elements and showing that the processes that fractionate O and Mg isotopes in the protoliths of the metamorphic basement are the same. Our calculations show that to reproduce the geochemical trends in Fig. 3 the mass ratio of weathered Mg-poor preexisting crust to juvenile granodioritic magma must be ≈1 (Fig. 3, red arrows point to a mass ratio of 1). One way to interpret this calculation is that juvenile and nonjuvenile sources contribute equally in generating the magmas necessary for formation of granites in the eastern PRB. This ratio is large, but not unreasonable, because the energy needed to partially melt preexisting country rock is provided by juvenile magmatic underplates or intrusions, which are abundant in continental arc environments. We recognize that the uncertainties in this modeling are difficult to quantify. However, two robust conclusions can still be made: (i) a considerable amount of nonjuvenile material contributes to granite formation, and (ii) this nonjuvenile component preserves an ancient weathering signature. We speculate that fractionated Fe isotopes reported in granites may have a similar origin (32, 33).

Insights Into the Global Mg Cycle. Our observations may shed indirect light on a problem in the global mass balance of Mg isotopes. Seawater and some river waters are known to be considerably lighter in Mg than the mantle and primary igneous rocks, which is believed to be caused by the preferential leaching of light Mg from the continents (Fig. 1A). As pointed out above, this implies that somewhere in the continental crust exists a reservoir characterized by low Mg content and heavy δ²⁶Mg. The results of our study indicate that the basement rocks involved in

generating granites in the eastern PRB must have a δ²⁶Mg of at least +0.4‰ (Figs. 1A and 3). The few published measurements on weathering residues, such as soils, show a wide range of δ²⁶Mg values: soils from the high Himalayas have δ²⁶Mg of only ≈0‰ (16) (Fig. 1A), soils from granite weathering in the Moselle River Basin range from 0‰ to 0.5‰ (19), and Icelandic basalt soils show much lower values (−0.94‰ and −0.26‰) (34). We envision that soils are eroded and then deposited on the continental shelf or slope along with authigenic clays. These sediments are then converted into metamorphic rocks during continental arc formation. We suggest that the missing heavy Mg reservoir in the continental crust may be represented by siliciclastic sediments (i.e., eroded weathering residues) that have since been converted into metamorphic rocks.

Assuming ≈3–4 wt.% MgO for the parent rock (e.g., an intermediate lithology, such as granodiorite or diorite) and ≈0.5 wt.% MgO for the weathered residue, Fig. 1B shows that the fractionation factor of ²⁶Mg/²⁴Mg between aqueous Mg and Mg in the weathered residue ($\alpha_{\text{aqueous residue}}$) should be <0.9997. We chose a value of 0.5 wt.% MgO for the residue because it approaches values observed for highly weathered and Mg-depleted soils (35). The integrated weathering residues, however, will be represented by detrital sediments, which are mixtures of soil residues and authigenic clays, the latter of which have higher Mg contents. The MgO contents of detrital sediments are in the range of 1 to 2 wt.% (36), hence our choice of 0.5 wt.% is a lower bound for Mg of the integrated weathering residue. Importantly, assuming a residual MgO >0.5 wt.% would only amplify the fractionation effect ($\alpha_{\text{aqueous residue}}$ would be even lower). In other words, aqueous Mg in instantaneous equilibrium with a weathered residue should be at least ≈0.3‰ lighter (see *SI Text*). Given this small fractionation factor, one would expect that the cumulative Mg isotope signature of river waters draining silicate watersheds to be only slightly less than the canonical mantle value of −0.3‰.

The question that remains is to what extent the low Mg content of global continental crust is caused by chemical weathering losses or the formation of mafic cumulates and residues. Our study suggests that granites record a weathering signature, but represent only the most evolved endmember of continental crust. To answer this question will require an estimate of the average Mg isotopic composition of the continental crust. The Mg isotopic composition of river waters and seawater should also help our understanding of the global Mg cycle. However, even though on average global riverine flow has lighter Mg than seawater, there is significant variability that has not yet been fully explained. Global rivers may be biased toward lighter values because of weathering of carbonates, which are unusually light in Mg (Fig. 1). Indeed, smaller rivers, such as those draining Icelandic basaltic substrates, have similar or even heavier Mg than canonical mantle values (34). These observations complicate the interpretation of global riverine Mg isotopes as a simple recorder of silicate weathering. Our results, nevertheless, indicate that ancient weathering appears to play a significant role in granite formation. Whether this can be generalized to the entire continental crust will require a more detailed understanding of the global Mg cycle.

Conclusions

In conclusion, our observations require that granites in the PRB represent mixtures of juvenile magmas and partial melts of preexisting crust, which preserves a chemical weathering signal in the form of O and Mg isotopes. Because the PRB is representative of Cordilleran-style batholiths, which dominate continental arc magmatism in the Phanerozoic, our observations imply that the low Mg content of Phanerozoic upper continental crust may not just be caused by igneous fractional crystallization but also the incorporation of sediments and metamorphic rocks

that were previously processed through the weathering cycle (37).

Methods

Approximately 2–10 mg of biotite minerals was handpicked from coarse-crushed rock samples viewed under a binocular microscope. The biotites were dissolved in Savillex beakers in a mixture of HF and HNO₃. The Mg was purified by cation exchange chromatography (38). The column was loaded with 0.5 mL of Bio-Rad 200–400 mesh AG50W-X12 resin. Sample solutions containing ≈5–20 μg of Mg were dissolved in 0.2 mL of 1 N HCl. After the sample were completely adsorbed by the resin, 1 N HCl, 1 N HNO₃ + 0.5 N HF, 1 N HNO₃, and 2 N HNO₃ were added sequentially to elute Cr, Al, Fe, Na, V, and K. Mg was collected with 3 mL of 2 N HNO₃. To ensure a clean Mg fraction, the chemistry was repeated five times for each sample. All chemistry was conducted at Rice University. After five passes, Na/Mg, Al/Mg, K/Mg, Ca/Mg, and Fe/Mg were <0.05. The Mg yield, after five passes was >96%. Mg isotope ratios were measured at the University of California, Davis with a Nu Plasma high-resolution MC-ICP-MS. Solutions containing ≈800 ppb Mg were introduced to the plasma via a DSN-100 desolvating nebulizer. Analyses were made in static

mode simultaneously measuring ²⁶Mg, ²⁵Mg, and ²⁴Mg isotopes (in pseudo high mass resolution to avoid isobaric interferences). Instrumental drift was corrected by bracketing each sample analysis with a standard. Each sample was measured multiple times on different days to ensure reproducible results at different times. Isotope ratios are expressed in δ notation as per-mil (‰) deviation from the DSM-3 standard (15).

$$\delta^{26}\text{Mg} = \left[\frac{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{sample}}}{(^{26}\text{Mg}/^{24}\text{Mg})_{\text{standard}}} - 1 \right] \times 1,000.$$

The external precision on the ²⁶Mg/²⁴Mg ratio was determined by repeated measurements of the Cambridge-1 standard ($n = 11$; $\delta^{26}\text{Mg} = -2.613 \pm 0.172\text{‰}$ and $\delta^{25}\text{Mg} = -1.352 \pm 0.081\text{‰}$) and the J11-olivine standard ($n = 8$; $\delta^{26}\text{Mg} = -0.19 \pm 0.19\text{‰}$ and $\delta^{25}\text{Mg} = -0.10 \pm 0.10\text{‰}$). Multiple measurements on all samples have comparable precisions, all <0.2‰ (2 SD).

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