



Magnesium isotopic composition of igneous rock standards measured by MC-ICP-MS

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ABSTRACT

To provide inter-lab comparison for high-precision Mg isotope analysis, Mg isotope compositions (expressed as $\delta^{26}\text{Mg}$ relative to DSM-3) for commercially accessible peridotite, basalt, andesite, and granite geo-standards have been measured by multi-collector inductively coupled mass spectrometry (Nu-Plasma) using sample-standard bracketing method. There is a large tolerance of matrix cations during the measurement of Mg isotopes, as intensity ratios of $^{23}\text{Na}/^{24}\text{Mg}$ and $^{27}\text{Al}/^{24}\text{Mg}$ of about 20% only change the $\delta^{26}\text{Mg}$ by less than 0.1‰, and low $^{55}\text{Mn}/^{24}\text{Mg}$ (<0.1) and $^{58}\text{Ni}/^{24}\text{Mg}$ (<0.01) do not cause significant mass bias either. Concentration match between samples and standards within 90% is adequate to obtain accurate isotope analysis, which also mitigates the isobaric interference of $^{12}\text{C}^{14}\text{N}^+$ on ^{26}Mg . Organic matrix from chemical purification can cause significant analytical errors when the mass of Mg processed is small. The long-term reproducibility of $\delta^{26}\text{Mg}_{\text{DSM-3}}$ for samples with relatively higher MgO content is about 0.11‰ (2SD), and granites with lower MgO content is about 0.2‰ (2SD). Although the standards in this study have wide ranges of major element compositions with SiO_2 from 40 to 70 wt.% and MgO from 0.75 to 49.6 wt.%, they exhibit a variation of Mg isotopic compositions with $\delta^{26}\text{Mg}$ from -0.07 to -0.40 ‰. $\delta^{26}\text{Mg}$ do not correlate with SiO_2 or MgO contents, suggesting homogenous Mg isotope compositions in igneous rocks at the level of current precision, relative to low temperature samples including sediments and riverine and sea waters. Our data do not support a non-chondritic Mg isotope composition of the Earth.

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1. Introduction

Magnesium is one of the most abundant elements in the mantle, a major element of the crust and also an abundant species in seawater. It has three stable isotopes, ^{24}Mg , ^{25}Mg , and ^{26}Mg with abundances of 78.99%, 10.00%, and 11.01%, respectively. The development of analytical techniques using multi-collector inductively coupled mass spectrometry (MC-ICP-MS) allows measurement of Mg isotope ratios to high precision, enabling Mg isotopes to be used to address a variety of fundamental geological processes; these include weathering of continental crust and Mg geochemical cycling (Galy et al., 2002; Tipper et al., 2006a,b; Strandmann et al., 2008a,b; Tipper et al., 2008a; Teng et al., 2009), biogeochemical processes (e.g., plant photosynthesis (Black et al., 2006) and biomineralization (Chang et al., 2003, 2004)), magma differentiation by fractional crystallization (Teng et al., 2007) or thermal diffusion (Richter et al., 2008; Huang et al., 2009), and the origin of planets, Moon, and chondrules (Norman et al., 2006; Wiechert and Halliday, 2007). Because Mg isotope ratios can provide new insight into these fields, there is a critical need for analyses of

widely available reference materials in order to facilitate comparison of techniques and thus data between different laboratories.

The low atomic number of Mg means that the instrumental mass bias during measurement by MC-ICP-MS is relatively large, leading to the possibility of significant analytical bias due to matrix effects or incomplete yields. Thus, accurate measurement of Mg isotope ratios on natural samples remains very challenging. Indeed, recent investigations of Mg isotope ratios in terrestrial igneous rock and mineral samples indicate conflicting results. For instance, using solution based MC-ICP-MS, Wiechert and Halliday (2007) observed that samples from Earth, Mars, and Vesta have a relatively homogenous Mg isotopic composition that is isotopically offset to heavier compositions than most chondrules, suggesting a non-chondritic composition for the inner terrestrial planets. In contrast, Teng et al. (2007) found that the Mg isotopic composition of basalts from Kilauea Iki lava lake did not change with extent of differentiation and were identical to that of chondrules, supporting a chondritic composition for Earth. This observation is confirmed by the study of Tipper et al. (2008b) who showed that the Mg isotopic composition of the terrestrial Earth showed a limited range, overlapping the published range for chondrites (Young and Galy, 2004; Teng et al., 2007; Wiechert and Halliday, 2007). Ultimately, a great deal remains to be discovered about the homogeneity of both high temperature terrestrial samples and extra-terrestrial samples before this can be clearly resolved.

Reporting of Mg isotope ratio data for commercially accessible rock powder standards thus represents an ideal way to assess inter-laboratory

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biases and improve the overall accuracy of Mg isotope ratio measurements. However, published Mg isotope ratio data for standards to date are limited and inconsistent. Ratio data from different MC-ICP-MS laboratories show a relatively large range of values for the same sample, even slightly outside a typically reported error of 0.1‰ (2 σ). For instance, $\delta^{26}\text{Mg}$ (where $\delta^{26}\text{Mg} = [({}^{26}\text{Mg}/{}^{24}\text{Mg})_{\text{sample}}/({}^{26}\text{Mg}/{}^{24}\text{Mg})_{\text{DSM-3}} - 1] \times 1000$) of one of the most commonly analyzed USGS standards, BCR-1 or its second generation equivalent BCR-2, varies from -0.09% (BCR-1, [Wiechert and Halliday, 2007](#)) to -0.37% (BCR-1, [Young and Galy, 2004](#)) to -0.36% (BCR-2, [Teng et al., 2007](#)) to -0.15% (BCR-2, [Tipper et al., 2008b](#)). The variation in $\delta^{26}\text{Mg}$ for a given standard limits the ultimate accuracy of the method, hindering comparison of results between laboratories and thus the application of Mg isotope geochemistry to many fundamental problems in geology.

Here, we report Mg isotope ratio data for 11 international rock standard powders, all of which have been widely used as major and trace element and, sometimes, isotopic standards. The standards include two peridotites (DTS-1, PCC-1), four mafic samples (basalts BCR-1, BCR-2, BHVO-1, and gabbro W-1), one andesite (AGV-1), and four granites (GSN-1, GSP-1, G2, and GA), spanning a wide range of MgO content. We also report Mg isotope ratios for three andesitic samples (two andesitic high-Mg adakites from Eastern China and Mt. Hood andesite, MHA) and a Fo₉₀ crystal of San Carlos olivine. Our result shows that the terrestrial igneous rocks and San Carlos olivine have a restricted range in Mg isotope composition with $\delta^{26}\text{Mg}$ from -0.07 to -0.40 .

2. Analytical methods

The chemical purification methods in this study were slightly modified from those used in [Teng et al. \(2007\)](#). Approximately 10 mg of rock powder or 2 mg of olivine crystals were dissolved in capped teflon beakers using a mixture of 0.5 ml concentrated HNO₃ and 1.5 ml concentrated HF on a hotplate for 2 days. To remove residual fluorides and achieve complete solution, the sample was repeatedly taken to dryness with 0.5 ml aqua regia and then 0.5 ml concentrated HNO₃ (2 \times). Samples were then dissolved in 2 ml 1 N HNO₃ prior to chromatographic purification using a column filled with 0.5 ml Biorad AG50-X12 (200–400 mesh) cation resin, which was batch cleaned prior to any use through repeated rinses with methanol and then H₂O. Before loading 0.1 ml sample, the column with resin was cleaned by adding 1 ml 0.5 N HF and 1 ml H₂O, then 5 ml 8 N HNO₃, followed by conditioning with 2 ml 1 N HNO₃.

In order to assess the efficiency of separation and routinely check yields, we collected solutions off the column in the 0 to 4.5 ml interval (1 N HNO₃), in the 4.5 to 12 ml interval (the Mg cut, 1 N HNO₃), and the 2 ml 8 N HNO₃ + 0.2 ml 2.8 N HF added after the Mg cut to wash the column. The two solutions without Mg (the before and after solutions) were combined and then measured for Mg content as a check on the yield of the chemical separation. By comparing of signal of Mg in both the Mg cut and the combined solution, the yield and completeness of solution could be assessed. The ${}^{23}\text{Na}/{}^{24}\text{Mg}$ and ${}^{27}\text{Al}/{}^{24}\text{Mg}$ signal intensity ratios were generally lower than 5%, ${}^{55}\text{Mn}/{}^{24}\text{Mg}$ lower than 10%, and ${}^{58}\text{Ni}/{}^{24}\text{Mg}$ lower than 1%. Although Na and Al are the most abundant matrix cations, other cations (i.e., Si, K, Ca, Ti, Mn, Ni, and Fe) were also routinely checked to verify chemical purification. In general, a high yield Mg solution with little matrix can be obtained by two passes through this column separation procedure.

Total procedural blanks were measured in every purification session and ranged from 1 to 20 ng of Mg with a long-term average ~ 10 ng; this is insignificant relative to the amount of Mg loaded to the column for most samples ($>10 \mu\text{g}$); however, the contribution from blank could become significant if the amount of Mg loaded is only a few μg (see [Section 3.5](#) for details).

Mg isotopes were measured by sample-standard bracketing using DSM-3 as the bracketing standard on a Nu-Plasma HR MC-ICP-MS in the Department of Geology at the University of Illinois at Urbana-Champaign. Analyses were automated by using a Cetac ASX-110 auto-

sampler and introduced to the instrument through a DSN-100 desolvating nebulizer. Prior to sample introduction, samples and standards were diluted to produce ~ 0.2 ppm solutions in 0.3 N double-distilled HNO₃ solution, keeping the ${}^{24}\text{Mg}$ intensity variation to within 5%. For the samples here, the purified Mg off the columns brought up in 5 ml of acid was then diluted ~ 200 times to produce the running solution. This produces a ${}^{24}\text{Mg}$ signal of 16 V in the low resolution mode (resolution ~ 400) at an uptake rate of 0.1 ml/min with higher sensitivity (~ 80 V/ppm) than a few recent studies such as [Handler et al. \(2009\)](#) and [Humayun and Huang \(2009\)](#). The high sensitivity in this study is particularly important for measurement of samples with small amount of Mg (2 to 10 μg) such as Soret diffusion experiment samples obtained by micro-drilling technique ([Huang et al., 2008a](#)). Although the DSN-100 reduces the sizes of interferences relative to wet plasma conditions, a ${}^{12}\text{C}{}^{14}\text{N}^+$ interference always persists and varies from 0.2 to 1 mV in different sessions, which was not resolved from ${}^{26}\text{Mg}$ by using a big ΔM or peak centering. Peak parallelism measurement was performed to assess the flatness of signals. Prior to each analysis, sequential rinses of two separate 0.75 N HNO₃ (5%) of 60 s each were followed by two 0.3 N HNO₃ rinses to reduce baselines to <1 mV on the ${}^{24}\text{Mg}$ channel. The beams of ${}^{26}\text{Mg}$, ${}^{25}\text{Mg}$, and ${}^{24}\text{Mg}$ were measured on the H6, Ax, and L5 Faraday channels, respectively. Baselines for each measurement were measured on each cup by diverting the beam into the flight tube using ESA deflection. A given measurement consists of 10 ratios, and each measurement of a sample was bracketed

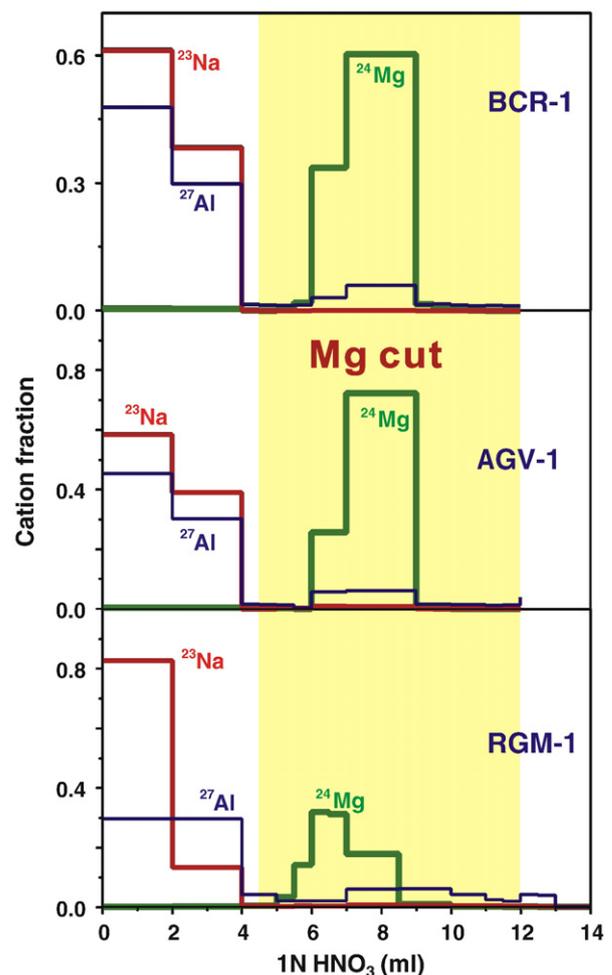


Fig. 1. Elution curves of Mg, Na, and Al for basalt (BCR-2), andesite (AGV-1), and rhyolite (RGM-1). Na and Al are eluted before Mg cut. Despite each having a different matrix of rock forming elements, the Mg peak consistently falls between 5 and 11 ml of 1 N HNO₃ eluent if the cation resin column is not overloaded. Eluent from 4.5 to 12 ml of 1 N HNO₃ is the Mg cut.

by a measurement of DSM-3, with the final average value and error on a given sample normally reflecting 4 bracketed measurements.

3. Results

In the following sections, we address several issues that can lessen accuracy and precision of Mg isotope ratio analysis. These issues include storage of Mg standard solution, the effects of matrix (Na, Al, Mn, and Ni) on the instrumental mass bias of Mg isotopes, the influence of concentration mismatch and isobaric interference ($^{12}\text{C}^{14}\text{N}^+$), and the effect of Mg blank and organics leached from resin during chemical purification.

3.1. Column elution tests

Previous work has shown that Mg isotopes can be fractionated by incomplete yield (Chang et al., 2003). To eliminate possible isotope fractionation during the chemical separation process and to decrease the effect of matrix elements during MC-ICP-MS analysis, a 100%

recovery and effective separation of Mg from matrix elements is necessary. Fig. 1 shows elution curves for dissolved rock solutions of varying composition. Despite dramatically differing chemical compositions, BCR-1, AGV-1, and RGM-1 elution curves have similar elution peaks for Na and Al (they consistently elute earlier than Mg). In all three compositions, Mg elutes from the column during the 5 to 11 ml interval of 1 N HNO_3 . Other matrix cations are also well separated from Mg, with Ti and K removed earlier and Ca and Fe later than the Mg cut (not shown). This is particularly useful if the same sample is further used for Ca and Fe isotope measurement after Mg separation because Ca and Fe can be eluted from cation resin column using 2 ml 8 N HNO_3 . In order to avoid elution curve drifting, we collected solutions from 4.5 to 12 ml 1 N HNO_3 as the Mg cut.

In order to examine the effect of overloading the cation column with sample, we deliberately added ~2 mg equivalent of BCR-2 solution to the column. The resulting Mg yield was 86% with the Mg peak being eluted earlier than the normal Mg cut. The $\delta^{26}\text{Mg}$ of this BCR-2 was ~0.2‰ lighter than our BCR-2 analyses where yields were 100% (Table 1). This is consistent with previous work showing that Mg

Table 1

Tests of influences of Na-Al and Mn-Ni cation matrix, concentration mismatch, and chemical purification on Mg isotope analyses.

Name	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	Comments	
In-house mono-element standards								
CAM-1	-2.63	0.11	-1.36	0.07	1.93	44		
UIMg-1	-2.00	0.12	-1.03	0.06	1.95	21		
Na-Al doping test								
Test ^a	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	$^{23}\text{Na}/^{24}\text{Mg}$	$^{27}\text{Al}/^{24}\text{Mg}$
DSM-Na-Al-1	0.01	0.02	-0.02	0.02	-0.53	2	0.048	0.002
DSM-Na-Al-2	0.00	0.01	0.00	0.04	5.73	2	0.142	0.006
DSM-Na-Al-3	0.02	0.03	0.04	0.10	0.58	2	0.213	0.010
DSM-Na-Al-4	-0.03	0.23	-0.03	0.08	0.89	2	0.498	0.034
DSM-Na-Al-5	-0.13	0.08	-0.06	0.05	2.18	2	1.510	0.101
DSM-Na-Al-6	-0.32	0.00	-0.09	0.07	3.60	2	7.111	7.111
Mn-Ni doping test								
Test ^a	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	$^{55}\text{Mn}/^{24}\text{Mg}$	$^{58}\text{Ni}/^{24}\text{Mg}$
DSM-Mn-Ni-1	-0.44	0.18	-0.27	0.31	1.63	4	0.875	0.098
DSM-Mn-Ni-2	-0.25	0.11	-0.16	0.08	1.56	4	0.452	0.049
DSM-Mn-Ni-3	-0.06	0.07	-0.05	0.06	1.32	4	0.191	0.020
DSM-Mn-Ni-4	0.00	0.15	0.00	0.08	-1.77	4	0.099	0.011
Concentration match test								
Test	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	$^{24}\text{Mg}_{\text{sample}}/^{24}\text{Mg}_{\text{DSM-3}}$	
DSM-DI-1	0.37	0.08	-0.26	0.12	-1.45	2	0.176	
DSM-DI-2	-0.22	0.07	-0.20	0.02	1.08	4	0.220	
DSM-DI-3	0.04	0.11	-0.18	0.03	-0.25	2	0.334	
DSM-DI-4	-0.18	0.08	-0.11	0.06	1.60	4	0.478	
DSM-DI-5	-0.05	0.05	-0.03	0.02	1.76	4	0.740	
DSM-DI-6	-0.02	0.17	-0.04	0.07	0.51	4	0.875	
DSM-DI-7	0.07	0.11	0.03	0.04	2.15	2	0.891	
DSM-DI-8	0.01	0.14	0.00	0.03	5.45	2	1.000	
DSM-DI-9	0.02	0.17	0.01	0.10	3.80	4	1.036	
DSM-DI-10	0.17	0.08	0.12	0.06	1.41	4	1.527	
Chemical purification test								
Test ^b	$\delta^{26}\text{Mg}$	2SD	$\delta^{25}\text{Mg}$	2SD	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	N	Mg (μg)
DSM-3 + blk	-0.37	0.07	-0.20	0.04	1.80	4	-	0.6
UIMg-1-A	-2.61	0.06	-1.37	0.04	1.91	4	2	0.32
UIMg-1-B	-2.53	0.04	-1.28	0.13	1.98	4	2	0.67
UIMg-1-C	-2.44	0.06	-1.27	0.05	1.92	4	2	0.66
UIMg-1-D	-2.57	0.10	-1.32	0.05	1.95	4	2	1.38
UIMg-1-E	-1.99	0.11	-1.03	0.07	1.94	4	2	3.17
UIMg-1-F	-2.06	0.13	-1.06	0.07	1.95	3	3	62.81
UIMg-1-G	-2.07	0.08	-1.08	0.07	1.92	4	5	11.12
BCR-1-A	-0.08	0.02	-0.03	0.02	2.41	4	2	2.20
BCR-1-B	-0.26	0.06	-0.13	0.04	2.03	4	2	0.72
BCR-2 low yield	-0.57	0.11	-0.29	0.06	1.97	4	2	40.2

^a $^{23}\text{Na}/^{24}\text{Mg}$, $^{27}\text{Al}/^{24}\text{Mg}$, $^{55}\text{Mn}/^{24}\text{Mg}$, and $^{58}\text{Ni}/^{24}\text{Mg}$ refer to ratio of intensity measured by MC-ICP-MS.

^b The amount of Mg (μg) was calculated based on the intensity of running solution and sensitivity of the MC-ICP-MS. N is the number of chemical purifications by cation resin column and n is the number of repeat analysis.

lost from the beginning of the elution peak is enriched in heavy isotopes (Chang et al., 2003; Teng et al., 2007).

3.2. Mg solution storage

To avoid an important systematic bias, it is critical to ensure that no isotopic changes occur to the bracketing standard. One primary concern is the effect of long-term storage of standards in plastic bottles. Storage of a pure, concentrated Mg standard (~500 ppm) in clean polypropylene or high density polyethylene (HDPE) bottles for up to 6 years has not caused any deviations in ratio (A. Galy, personal communication). However, we consistently observe that weak Mg standard solutions at 0.2 ppm stored in 500 ml fluorinated plastic (PTFE or Teflon®) bottles will deviate with time, with the $\delta^{26}\text{Mg}$ shifting to lighter values by -0.2% . The reason for the isotopic shift is not quite clear. It could be due to absorption of heavy isotopes by the container or leaching organic matrix from the container. Therefore, fresh running standard solutions were used for sample-standard bracketing method because older standard solutions can result in positively shifted ^{26}Mg for samples although the relative isotopic

offsets among the three weak standard solutions can remain constant. Prior to any isotopic measurement of samples, we ensure proper offsets between three standard solutions made fresh from concentrated stocks (i.e., 20 ppm UIMg-1 in a 7 ml Teflon beaker, 0.2 ppm CAM-1 in a 60 ml Teflon beaker, and 6 ppm chemically purified BCR-1 in a 7 ml Teflon beaker) and the DSM-3 standard.

3.3. The matrix effects

Most matrix elements (Na, Al, Si, K, Ti, Ca, and Fe) in typical rock samples are well separated by our chemical procedure. Before Mg isotope analysis, we monitor the matrix elements to assess chemical purification. However, because a few percent Na and Al relative to Mg still can persist in the running solution, we need to assess the matrix effect of Na and Al on the measurement of Mg isotope ratios. We test this by doping of Na and Al into the DSM-3 solution (Fig. 2). Although a few studies suggest that the cation/Mg ratios for running solution should be lower than 5% (Galy et al., 2001; Teng et al., 2007; Wiechert and Halliday, 2007), the standard-sample bracketing method using the Nu-Plasma allows a surprisingly high tolerance of matrix bias with

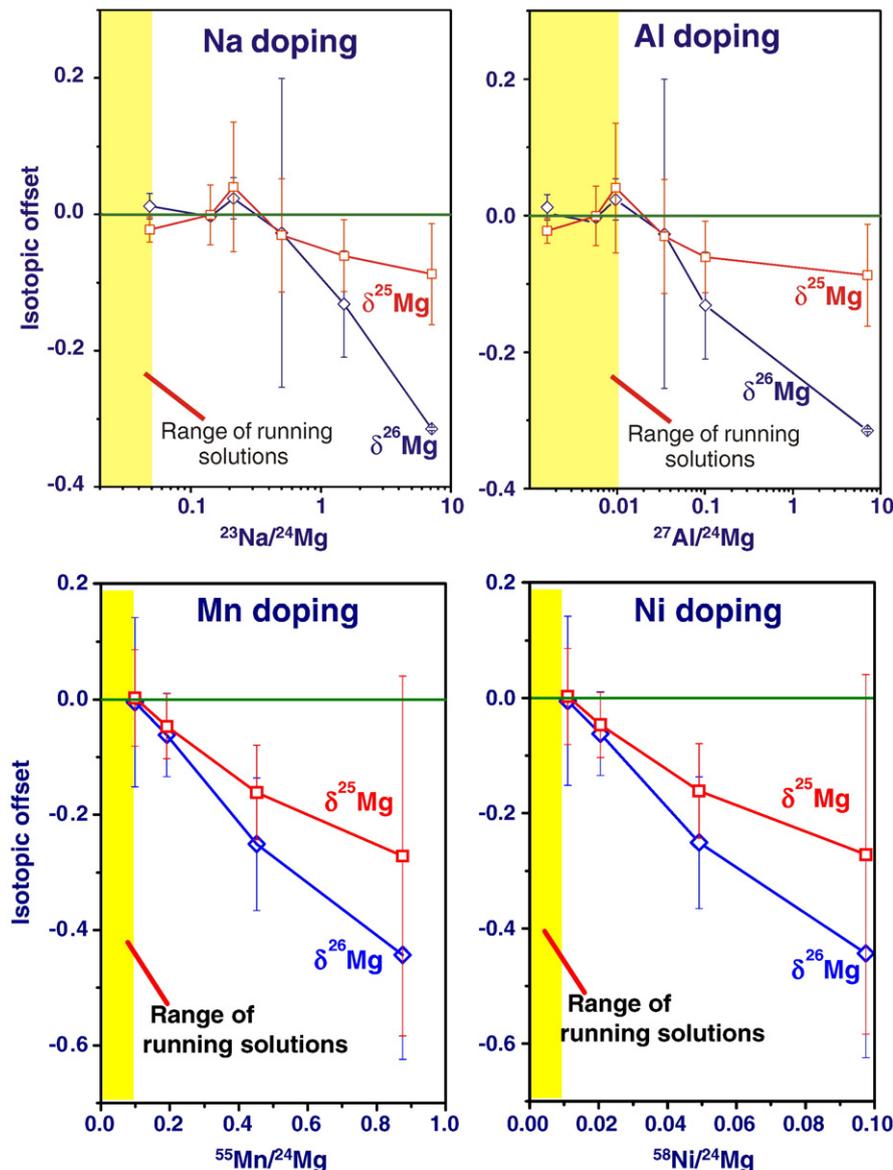


Fig. 2. Cation doping tests show that instrumental mass bias of Mg isotopes caused by Na–Al and Mn–Ni matrix is not significant if the intensity ratio of $^{23}\text{Na}/^{24}\text{Mg}$ and $^{27}\text{Al}/^{24}\text{Mg} < 0.2$, $^{55}\text{Mn}/^{24}\text{Mg} < 0.1$, and $^{58}\text{Ni}/^{24}\text{Mg} < 0.01$.

an intensity ratio of ($^{23}\text{Na} + ^{27}\text{Al}$) over ^{24}Mg of about 0.2 changing the $\delta^{26}\text{Mg}$ by less than 0.1‰. We did not take extra steps to remove Mn and Ni, which could be important matrix elements in purified Mg solution. However, a Mn–Ni doping test shows that, if an intensity ratio of $^{55}\text{Mn}/^{24}\text{Mg}$ and $^{58}\text{Ni}/^{24}\text{Mg}$ is less than 0.2 and 0.01, respectively, the matrix effect caused by Mn and Ni is insignificant (<0.1‰). Notably, when matrix/Mg is big, the isotopic offset caused by matrix effect is always negative (Fig. 2). This is not consistent with the space-charge effects in the skimmer cone region, which may cause positive isotopic offset due to the preferential transmission of heavier isotopes than lighter ones, suggesting that the matrix effects are more complicated than the simple space-charge effects. Nonetheless, ($^{23}\text{Na} + ^{27}\text{Al}$)/ ^{24}Mg of all measurements reported here were always <5%, $^{55}\text{Mn}/^{24}\text{Mg}$ <10%, and $^{58}\text{Ni}/^{24}\text{Mg}$ <1% (Fig. 2), well below the level where ^{23}Na , ^{27}Al , ^{55}Mn , and ^{58}Ni play an important role. However, a step to separate Mn and Ni from Mg is recommended for samples with high Mn/Mg and Ni/Mg.

3.4. The concentration mismatch and isobaric interference effect

The sample-standard bracketing method assumes identical mass bias between the standard and samples (e.g., Dauphas et al., in press). For light stable isotope measurements, the mass bias factor during analysis is sensitive to the concentration of running solutions. To better constrain the influence of concentration mismatch between samples and standards, we systematically tested a series of DSM-3 dilutions bracketed to the typical running concentration DSM-3 solution.

Lowering the analysis solution concentration leads to differing behaviors for $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ (Fig. 3 and Table 1). Decreasing Mg concentration leads to consistent lowering of the measured $\delta^{25}\text{Mg}$, which we interpret to reflect a mass bias change due to the different beam sizes passing through the interface region. The sense of change is opposite to similar tests on deviation of Fe isotopes by Dauphas et al. (in press) which show a negative correlation between $\delta^{56}\text{Fe}$ and the concentration ratio of sample over standard. Fig. 3 shows that mismatch in Mg signal intensity of greater than 30% can cause an error greater than 0.1‰, but a difference less than 20% does not appear to cause a significant deviation. Notably, the $\delta^{26}\text{Mg}$ of diluted solutions does not always decrease with decreasing sample concentration in a manner similar to $\delta^{25}\text{Mg}$ as solutions with 0.33 \times and 0.25 \times concentrations of the bracketing standard show positive offsets in $\delta^{26}\text{Mg}$. This is well explained by the effect of the isobaric interference on mass 26 (mainly $^{12}\text{C}^{14}\text{N}^+$) as the overall Mg signal decreased. As

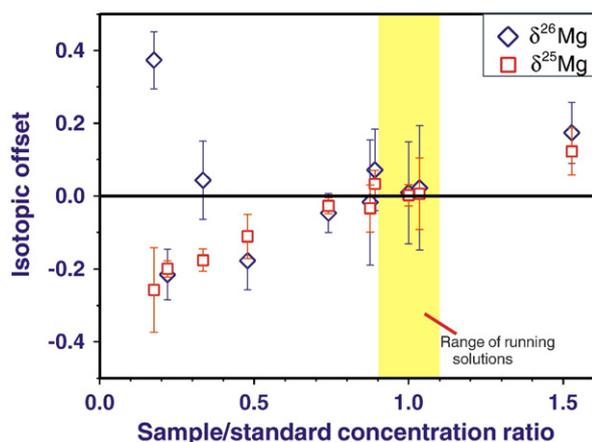


Fig. 3. Signal intensity match between the samples and standards of less than $\pm 10\%$ difference is sufficient for accurate Mg isotope analysis. The concentration ratios were obtained by comparison of signal intensity of samples and standards. The $^{12}\text{C}^{14}\text{N}^+$ isobaric interference has no measurable effect on the ^{26}Mg signal and does not need to be resolved.

mentioned above, $^{12}\text{C}^{14}\text{N}^+$ signal varies in different sessions from 0.2 to 1 mV. When $^{12}\text{C}^{14}\text{N}^+$ signal is low, the effect of concentration mismatch on variation of $\delta^{26}\text{Mg}$ is similar to that of $\delta^{25}\text{Mg}$. However, if $^{12}\text{C}^{14}\text{N}^+$ signal is significant (e.g., 1 mV) relative to ^{26}Mg signal, the isobaric interference results in a positive offset of ^{26}Mg . Therefore, it is important to ensure that solution concentrations are high enough that the contribution from $^{12}\text{C}^{14}\text{N}^+$ is minimal relative to the ^{26}Mg signal and that different solution concentrations are closely matched. The concentration mismatches of most samples used in this study were adjusted to within 5% of the DSM-3 standard, similar to the approach of a simple time interpolation introduced in Dauphas et al. (2004). A magnesium three-isotope plot of all samples and in-house Mg standards defines a single fractionation line with a slope of 0.519 ± 0.004 (Fig. 4), close to the theoretical values for equilibrium and kinetic fractionation of 0.521 and 0.510, respectively (Young et al., 2002; Young and Galy, 2004).

3.5. Deviations of measured ratios under conditions of small column load

Our early results on igneous rocks with very low MgO content (<0.5 wt.% MgO; results not reported here) showed a systematic change to significantly lighter isotopic composition (up to 1‰ lighter). With these samples, the amount of Mg added to the column was small because the total rock solution was limited to avoid overloading the cation resin column. Thus, the amount of purified Mg after chemistry was low such that the dilutions to run solutions were much less (1/10 or less compared to 1/200 for most samples).

Because of the implications of an offset to lower $\delta^{26}\text{Mg}$ for low MgO samples if it were true, we further investigated possible biases in our method by performing tests under conditions relevant to these samples. A test using a solution made by mixing a low concentration of DSM-3 and a procedure blank with low <10 ng Mg content (DSM-3 + blk, Table 1) produced a strongly negatively biased $\delta^{26}\text{Mg}$, $-0.37 \pm 0.07\%$ (2SD, $n = 4$). The likely cause of this is a matrix effect due to a higher relative amount of residual organics from the column but blank contribution could in principle also play a role. The possibility of matrix effects due to organic molecules leaching from the cation resin presents a complicated issue in these analyses although the purified Mg solutions were evaporated twice using concentrated HNO_3 . Even though the resin was pre-cleaned with methanol, residual organics are continuously leached from resins, which can produce significant mass bias effects and yet are virtually undetectable using the mass spectrometer.

Although Mg blank is consistently low in our chemical procedure (~ 10 ng), this amount can cause analytical errors if the amount of Mg

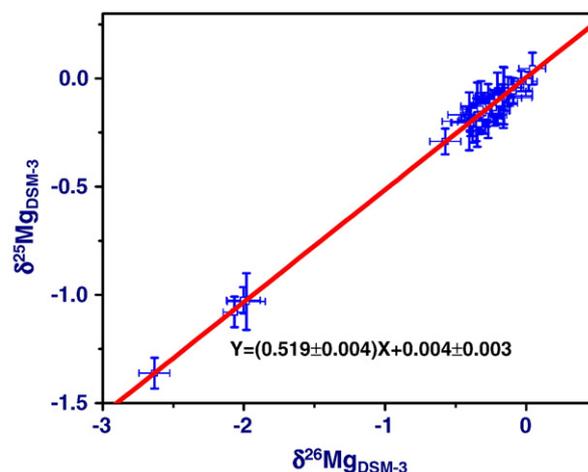


Fig. 4. Magnesium three isotope plot of all standards and samples analyzed in this study defines a line with slope of 0.519 ± 0.004 , close to the theoretical equilibrium and kinetic fractionation values for Mg isotopes (0.521 and 0.510, respectively) (Young et al., 2002).

that is purified is $<10\mu\text{g}$. We further tested the influence of Mg blank and the concentration of organic matrix effect by passing diluted BCR-1 solutions (down to a few μg Mg) and a mono-elemental standard (UIMg-1, a spex ICP-MS Mg concentration standard) through cation resin columns with differing amounts of total Mg (Table 1). The $\delta^{26}\text{Mg}$ of BCR-1-A, containing $2.2\mu\text{g}$ Mg, is $-0.08\pm 0.02\%$, is significantly higher than the long-term average of BCR-1 measured in our lab ($-0.34\pm 0.12\%$). However, $\delta^{26}\text{Mg}$ of BCR-1-B, with $0.72\mu\text{g}$ Mg, ($-0.26\pm 0.06\%$) is consistent with the average BCR-1 value within error, opposite to the expectation that the organic matrix and blank effect should have greater effect on lower amount of Mg loaded. This could be due to that the cation resin columns are slightly different in terms of leaching organics or Mg blank during purification.

Result of systematic test on the mono-elemental standard is more straightforward. UIMg-1-E ($3.2\mu\text{g}$ Mg), UIMg-1-F ($63\mu\text{g}$ Mg), and UIMg-1-G ($11\mu\text{g}$ Mg) had average $\delta^{26}\text{Mg}$ of $-1.99\pm 0.11\%$ ($n=4$), $-2.06\pm 0.15\%$ ($n=5$), and $-2.07\pm 0.08\%$ ($n=3$), respectively, in good agreement with the pure UIMg-1 within error (-2.00 ± 0.12) (Fig. 5). However, when the amount of Mg processed through chemistry is reduced to $1.4\mu\text{g}$ or less, $\delta^{26}\text{Mg}$ of the UIMg-1-A, B, C, and D are significantly and consistently negatively shifted by $\sim 0.6\%$. Evaporating UIMg-1-C and B in the presence of concentrated HNO_3 to try to remove organics did not eliminate the isotopic offset relative to the mono-elemental UIMg-1 standard. It is not known whether this reflects the inability to remove recalcitrant organics by this method or the effect reflects something else such as blank. Although it is not exactly clear how the blank and organic matrix cause biases in Mg isotope ratio measurements, increasing the amount of Mg processed through chemistry to at least $5\mu\text{g}$ can effectively eliminate the error. This is easily achieved in samples with MgO content higher than 1 wt.% without overloading the columns. However, it is quite challenging for low MgO content samples. For instance, we have measured RGM-1 (MgO of 0.28 wt.%) for six times with $\delta^{26}\text{Mg}$ varying from -0.31% to -0.93% , suggesting that great caution needs to be taken for measurement of low MgO rocks.

4. Mg isotope ratios of igneous rock and mineral standards

4.1. Precision and accuracy

Repeat analyses of in-house mono-elemental standards (CAM-1 and UIMg-1) and well-studied rock standards (e.g., BCR-1 and BCR-2) allow evaluation of our long term precision and accuracy. The average $\delta^{26}\text{Mg}$ of CAM-1 over a six month period is $-2.63\pm 0.11\%$ (2σ , $n=36$), consistent with the literature values (-2.60%) (Galy et al.,

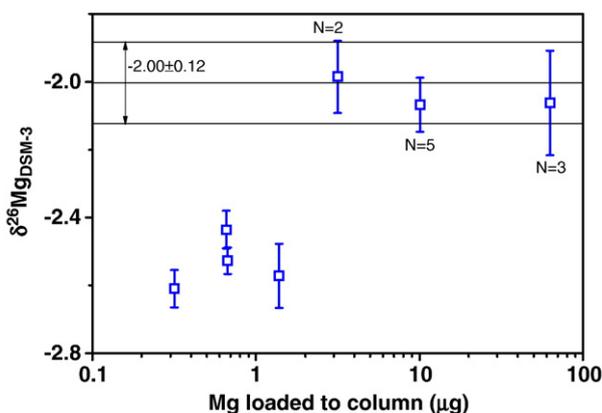


Fig. 5. Tests of analytical error induced by chemical purification. If the amount of Mg loaded to the column is small (i.e., $<3\mu\text{g}$), chemical purification can cause significant negative bias of Mg isotopes. N stands for the number of column procedure.

2003), while the average $\delta^{26}\text{Mg}$ of UIMg-1 over 3 months is $-2.00\pm 0.12\%$ (2σ , $n=21$). These precisions of $\sim 0.1\%$ reflect the long-term external precision of pure Mg solution measurements. UIMg-1 processed through chemistry up to five times produced $\delta^{26}\text{Mg}_{\text{DSM}-3}$ of $-2.07\pm 0.08\%$ (2σ , $n=4$), indicating that the purification process does not result in an accuracy bias nor a change in the overall analysis precision.

Precision and accuracy of sample Mg isotope measurements for silicate rocks are indicated by repeated analyses of the Columbia River basalt standard (BCR-1 and BCR-2) over a period of 10 months. These analyses include independent digestions of the same rock powder, duplicate column chemistry using aliquots of the same bulk raw solution, and re-measurements of purified Mg solutions on different days (Table 2). $\delta^{26}\text{Mg}$ of BCR-1 from five different digestions ranges from $-0.25\pm 0.06\%$ to $-0.40\pm 0.08\%$ and results in an average value of $-0.34\pm 0.12\%$ (2σ). Assessment of the long-term stability of processed BCR solutions was performed by diluting a purified solution to $\sim 6\text{ppm}$ (stored in 0.3 N HNO_3 in a 7 ml Saville screw-top PTFE beaker) and measuring repeatedly over 3 months; and no significant isotopic bias was observed over this time period.

Our analyses fail to find any significant difference in $\delta^{26}\text{Mg}$ between BCR-1 and BCR-2. This should be expected since these reference materials were collected from the same quarry, located approximately 29 miles east of Portland, Oregon (United States Geological Survey, Certificate of Analysis, <http://minerals.cr.usgs.gov/geochem/basaltbcr2.pdf>) and only represent different samplings and grindings of this rock. If the two basalt standards have identical Mg isotopic composition, the average $\delta^{26}\text{Mg}$ of BCR is $-0.33\pm 0.12\%$ (2SD , $n=64$) and $\delta^{25}\text{Mg}$ is $-0.16\pm 0.08\%$ (2SD). Individually, the average $\delta^{26}\text{Mg}$ of BCR-1 measured over 14 sessions is $-0.34\pm 0.12\%$ (2SD , $n=48$). This average is consistent with the values reported by Teng et al. (2007) ($-0.34\pm 0.06\%$), Young and Galy (2004) ($-0.37\pm 0.11\%$), and Wiechert and Halliday (2007) ($-0.09\pm 0.27\%$) within errors. $\delta^{26}\text{Mg}$ of two separate BCR-2 digestions over four sessions ranges from $-0.28\pm 0.05\%$ to $-0.30\pm 0.14\%$ with an weighted average of $-0.30\pm 0.11\%$ (2SD , $n=18$). These values are also consistent with Teng et al. (2007), but slightly lighter than those reported in Baker et al. (2005), Bizzarro et al. (2005), Wiechert and Halliday (2007), Tipper et al. (2008b), and Wombacher et al. (2009) although still within their reported error.

At least two duplicate measurements were performed for all standards in this study, with all duplicates being within errors of each other. The two standard deviation precision for measurements of peridotites, olivine, basalts, and andesites varies from 0.08% to 0.14% with an average of $\sim 0.11\%$ (Table 2), representing our long-term external precision for high temperature terrestrial samples with relatively higher MgO content. This is greater than the external precision published by Tipper et al. (2008b) (0.05 to 0.075%) for $\delta^{26}\text{Mg}$, which was obtained by the more time-consuming standard-addition method. The size of the measurement precisions increases for granites to $\sim 0.2\%$ (2SD), reflecting the greater difficulty in measuring lower MgO content samples.

4.2. Mg isotopic composition of standards and some igneous rock samples

In this study, rock standards and terrestrial igneous rock samples include peridotite (DTS-1 and PCC-1), basalt (BCR-1, BCR-2, and BHVO-1) and diabase (W-1), andesite (AGV-1), and granite (French granite standard GA and USGS granite standards G-2, GSP-1, and GSN-1). The MgO contents of these materials vary from 49.6 (DTS-1) to 0.75 wt.% (G-2), and SiO_2 from 70.0 (GA) to 40.4 wt.% (DTS-1) (Henderson, 1967), covering the range of compositions found in most igneous rocks. Two andesitic high-Mg adakites (00CT-1 and 00CT-6) from the Dabie orogen, Eastern China (Huang et al., 2008b) and one andesite from Mt. Hood (MHA) (Leshner and Walker, 1986) were also measured.

Table 2

Mg isotopic composition of igneous rock and mineral standards as well as some rock samples (to be continued).

Standard/sample	Session	$\delta^{26}\text{Mg}$	2SD	2SE ^a	$\delta^{25}\text{Mg}$	2SD	2SE	$\delta^{26}\text{Mg}/\delta^{25}\text{Mg}$	n	Comments
<i>Peridotite</i>										
DTS-1	1	−0.30	0.16		−0.13	0.02		2.36	4	1–2 used the same bulk raw solution
	2	−0.37	0.06		−0.15	0.02		2.41	4	
Average		−0.33	0.14	0.09	−0.14	0.03	0.02	2.38	8	
PCC-1	1	−0.22	0.10		−0.15	0.07		1.49	4	1–2 used the same bulk raw solution
	2	−0.21	0.12		−0.11	0.06		1.85	4	
Average		−0.22	0.10	0.07	−0.13	0.07	0.05	1.64	8	
<i>Mantle mineral</i>										
San Carlos olivine	1	−0.32	0.14		−0.13	0.12		2.45	5	1–3 used the same bulk raw solution
	2	−0.23	0.08		−0.14	0.06		1.70	4	
	3	−0.28	0.14		−0.15	0.05		1.90	4	
	4	−0.27	0.15		−0.15	0.13		1.79	4	New digestion
Average		−0.27	0.14	0.06	−0.15	0.09	0.04	1.84	17	
<i>Basalt</i>										
BCR-1	1	−0.40	0.08		−0.19	0.05		2.07	4	New digestion
	2	−0.36	0.06		−0.18	0.04		1.96	5	New digestion
	3	−0.35	0.10		−0.19	0.10		1.86	5	New digestion
	4	−0.33	0.01		−0.21	0.03		1.59	2	4–8 are a new digestion measured in different days
	5	−0.32	0.13		−0.16	0.08		1.94	4	
	6	−0.38	0.15		−0.20	0.09		1.86	2	
	7	−0.25	0.06		−0.12	0.01		2.06	3	
	8	−0.33	0.14		−0.15	0.10		2.25	2	
	9	−0.26	0.07		−0.11	0.07		2.42	3	9–14 are a new digestion measured in different days
	10	−0.35	0.05		−0.17	0.05		2.08	2	
	11	−0.28	0.09		−0.15	0.07		1.84	4	
	12	−0.36	0.08		−0.18	0.04		1.98	4	
	13	−0.33	0.13		−0.17	0.09		1.95	4	
	14	−0.31	0.12		−0.16	0.04		1.91	4	
Average		−0.34	0.12	0.03	−0.17	0.08	0.02	1.97	48	
BCR-2	1	−0.31	0.14		−0.14	0.08		2.15	8	1–2 used the same bulk raw solution
	2	−0.29	0.12		−0.17	0.08		1.67	4	
	3	−0.28	0.05		−0.13	0.02		2.17	2	New digestion
	4	−0.29	0.06		−0.13	0.02		2.28	4	New digestion
Average		−0.30	0.11	0.05	−0.15	0.07	0.03	2.03	18	
Average of BCR		−0.33	0.12	0.03	−0.16	0.08	0.02	1.98	64	
BHVO-1	1	−0.31	0.08		−0.16	0.03		1.95	5	New digestion
	2	−0.30	0.10		−0.14	0.06		2.15	4	New digestion
Average		−0.30	0.08	0.06	−0.14	0.04	0.03	2.13	8	
W-1	1	−0.17	0.05		−0.09	0.06		1.98	4	New digestion
	2	−0.09	0.13		−0.06	0.06		1.57	4	New digestion
Average		−0.13	0.13	0.08	−0.07	0.06	0.04	1.82	8	
<i>Andesite</i>										
AGV-1	1	−0.30	0.11		−0.13	0.07		2.23	4	1–2 used the same bulk raw solution
	2	−0.31	0.09		−0.13	0.02		2.34	4	
	3	−0.34	0.07		−0.17	0.03		1.97	4	New digestion
	4	−0.33	0.05		−0.14	0.05		2.29	4	New digestion
Average		−0.32	0.08	0.04	−0.16	0.05	0.02	2.02	16	
MHA ^b		−0.40	0.09		−0.20	0.05		1.98	4	
00CT-1 ^c		−0.40	0.04		−0.17	0.03		2.34	4	
00CT-2 ^c		−0.33	0.05		−0.16	0.04		2.04	4	
<i>Granite</i>										
G-2	1	−0.18	0.04		−0.09	0.04		1.98	4	New digestion
	2	−0.16	0.20		−0.09	0.14		1.84	4	New digestion
	3	−0.39	0.13		−0.20	0.06		1.93	4	New digestion
	4	−0.13	0.13		−0.06	0.07		2.15	4	New digestion
Average		−0.22	0.25	0.11	−0.07	0.14	0.06	2.91	16	
GA	1	−0.35	0.21		−0.17	0.15		2.07	4	1–2 used the same purified solution
	2	−0.34	0.10		−0.17	0.07		2.01	4	
Average		−0.34	0.15	0.10	−0.17	0.11	0.07	2.04	8	
GSN-1	1	−0.16	0.20		−0.08	0.13		1.97	4	1–2 used the same purified solution
	2	−0.32	0.11		−0.16	0.06		1.97	4	
Average		−0.24	0.23	0.16	−0.12	0.13	0.09	1.97	8	
GSP-1	1	0.04	0.10		0.05	0.07		0.94	4	New digestion
	2	−0.04	0.07		−0.01	0.05		3.11	4	New digestion
	3	−0.19	0.13		−0.11	0.07		1.70	4	New digestion
	4	−0.11	0.09		−0.04	0.05		2.45	4	New digestion
Average		−0.07	0.20	0.09	−0.03	0.13	0.06	2.66	16	

^a 2SE = 2SD × Students T/n^{1/2}.^b MHA (Mt. Hood andesite) is from [Lesher and Walker \(1986\)](#).^c Sample 00CT-1 and 00CT-2 are high-Mg adakite from [Huang et al. \(2008b\)](#).

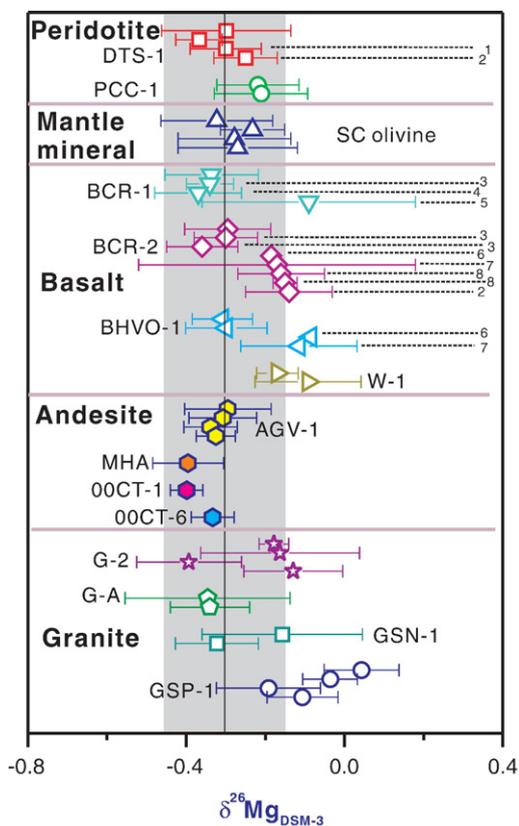


Fig. 6. Comparison of rock standard data analyzed in this study with the literature values. San Carlos olivine (SC olivine), two andesitic high-Mg adakites (OOCT-1 and OOCT-6), and MHA are also plotted. The grey band represents the average $\delta^{26}\text{Mg}$ of all the samples except granite, $-0.30 \pm 0.15\%$ (2SD). Data sources for BCR-1, BCR-2, and BHVO-1: 1, Teng et al. (2009); 2, Wombacher et al. (2009); 3, Teng et al. (2007); 4, Young and Galy (2004); 5, Wiechert and Halliday (2007); 6, Baker et al. (2005); 7, Bizzarro et al. (2005); and 8, Tipper et al. (2008b).

$\delta^{26}\text{Mg}$ of all igneous rock samples range from -0.07 to -0.40% (Table 2, Fig. 6). This range is consistent with that previously reported for silicate rocks (Young and Galy, 2004; Tipper et al., 2006a; Teng et al., 2007; Wiechert and Halliday, 2007; Strandmann et al., 2008a) and olivines (Norman et al., 2006; Handler et al., 2009), but much smaller than the range found in olivines from mantle xenoliths using LA-MC-ICP-MS (Pearson et al., 2006). Given the long-term precision for samples with relatively high MgO content (0.11%) and granites ($\sim 0.2\%$), this small range suggests that fresh magmatic rocks appear to vary little in their Mg isotope compositions. The average $\delta^{26}\text{Mg}$ of San Carlos olivine in this study is $-0.27 \pm 0.14\%$ (2SD, $n = 17$), higher than $-0.06 \pm 0.07\%$ reported in Wiechert and Halliday (2007) but lower than $\sim -0.6\%$ of Pearson et al. (2006) and Teng et al. (2007). Because the measured samples differ between laboratories, it is not clear whether this variation reflects real variations in olivines from the San Carlos locality or if it is analytical. Clearly, more measurements of mantle samples are needed to determine the Mg isotope composition of the mantle, the largest Mg reservoir for the Earth. The average $\delta^{26}\text{Mg}$ of all samples except granites in this study is $-0.30 \pm 0.15\%$ (2SD), identical to that of chondrites within error (Young and Galy, 2004; Teng et al., 2007; Wiechert and Halliday, 2007). Therefore, the chondritic origin of terrestrial Mg cannot be ruled out based on the current data and analytical precision. Finally, Mg isotopes in igneous rocks are significantly heavier than riverine and sea water samples (Tipper et al., 2006a,b; Strandmann et al., 2008a,b; Tipper et al., 2008a; Zhang et al., 2008), but lighter than soil (Tipper et al., 2006a) and weathered igneous rocks (Teng et al., 2009), suggesting that weathering of igneous rocks can fractionate Mg isotopes probably due

to incorporation of ^{26}Mg preferentially into secondary phases that generates an enrichment in ^{24}Mg in rivers (Tipper et al., 2006a).

5. Conclusions

We measured a set of 11 silicate rock standard powders for their Mg isotopic composition by sample-standard bracketing methods using MC-ICP-MS and examined a number of factors which can cause analytical biases during analysis. The long-term reproducibility of $\delta^{26}\text{Mg}$ for samples with relatively higher MgO content is 0.11‰ (2SD) and $\sim 0.2\%$ for granites with lower MgO content. We evaluated the influence of standard solution storage, cation matrix, concentration mismatch, isobaric interference, and isotopic fractionation during chemical purification on Mg isotope measurement. As long as the $^{23}\text{Na}/^{24}\text{Mg}$ and $^{27}\text{Al}/^{24}\text{Mg}$ was <0.2 , $^{55}\text{Mn}/^{24}\text{Mg} < 0.1$, and $^{58}\text{Ni}/^{24}\text{Mg} < 0.01$, $\delta^{26}\text{Mg}$ was unaffected within measurement precision. Concentration mismatch can produce significant error when the concentration difference between samples and standards is greater than 30%. The $^{12}\text{C}^{14}\text{N}^+$ isobaric interference does not significantly affect the measurement if concentrations of standard and samples are matched to within 90% intensity. The organic residue off the chromatographic column appears to affect the measurement of low MgO content samples, producing a negatively biased Mg isotope ratio if the amount of Mg purified is small ($<3 \mu\text{g}$). Since the organic matrix leached from storage containers and absorption of Mg by storage containers appear to affect weak Mg solutions over time, the use of fresh bracketing standard solutions is encouraged. The rock standards and samples in this study exhibit limited variation of Mg isotopic compositions with $\delta^{26}\text{Mg}$ ranging from -0.07 to -0.40% , and appear to be consistent with a chondritic Mg isotope composition of the Earth.

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