

RESEARCH ARTICLE

High-precision magnesium isotope analysis of geological and environmental reference materials by multiple-collector inductively coupled plasma mass spectrometry

Ting Gao^{1,2,3} | Shan Ke¹  | Ruiying Li¹ | Xu'nan Meng¹ | Yongsheng He¹ | Chengshuai Liu² | Yang Wang¹ | Zijian Li¹ | Jian-Ming Zhu¹

¹State Key Laboratory of Geological Process and Mineral Resources, School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China

²State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

³University of Chinese Academy of Sciences, Beijing 100049, China

Correspondence

Shan Ke, State Key Laboratory of Geological Process and Mineral Resources, School of Earth Science and Resources, China University of Geosciences, Beijing 100083, China.
Email: keshan@cugb.edu.cn

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Rationale: High-precision magnesium (Mg) isotopic analysis for geological and environmental reference materials is a prerequisite to ensure data quality before using Mg isotopes to trace geochemical and environmental processes. However, the Mg-isotopic ratios of many commonly used reference materials, especially sediments, have rarely been reported. Furthermore, published values for some commonly used reference materials exhibit a significant inconsistency across laboratories and thus need more data comparison.

Methods: We developed different Mg purification schemes for silicate rocks, high-Ca carbonates and carbonatites, and high-Mn samples because of their significantly different matrices. We then used synthetic solutions to evaluate potential effects on measurement using multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The accuracy and precision of our procedures were assessed by measurement on both synthetic solutions and well-studied geostandards.

Results: The three different schemes for routine, high-Ca, and high-Mn samples can remove matrices efficiently with nearly 100% Mg yield. However, the presence of acid molarity and concentration mismatch, matrix elements, and fluctuations in room temperature can significantly affect the precision and accuracy of Mg isotope analysis, and must be avoided. The Mg isotopic ratios of reference materials obtained in this study are identical to the previously published values within $\pm 0.06\%$, verifying that our procedures are robust.

Conclusions: This study presented a thorough set of tests for high precision and accuracy of Mg isotope measurements using MC-ICP-MS, which demonstrate reproducibility and accuracy better than 0.05‰ for $\delta^{25}\text{Mg}$ values and 0.06‰ for $\delta^{26}\text{Mg}$ values. We reported high-quality Mg isotopic data for 16 geological and environmental reference materials to aid the inter-laboratory calibration of Mg isotope measurements in the future.

1 | INTRODUCTION

Magnesium is one of the most abundant elements on Earth and it has three naturally occurring isotopes, ^{24}Mg , ^{25}Mg , and ^{26}Mg , with abundances of 78.99%, 10.00%, and 11.01%, respectively.

Magnesium isotopes fractionate in many geochemical processes, due to the ~8% mass difference between ^{24}Mg and ^{26}Mg .¹ Therefore, Mg isotope geochemistry has received particular interest in the last decade, as an important tool to trace geological and environmental processes such as deep carbon recycling (e.g.²⁻⁵),

paleo-climate/ocean reconstruction (e.g.⁶⁻⁸), and Mg cycling in the critical zone (e.g.⁹⁻¹⁴).

High precision and accuracy are required for Mg isotope measurement when it is applied to trace geological and environmental processes, especially in high-temperature systems, where isotope fractionation is generally small (see recent review by Teng¹). To date, most Mg isotopic data have been determined by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using the sample-standard bracketing method (e.g.¹⁵⁻¹⁸). This method relies on the assumption that samples and standards have the same instrumental mass bias over the short term.^{19,20} However, many factors can affect instrumental mass bias, which subsequently reduces the precision and accuracy of Mg isotope analysis. These factors may include mismatching in Mg concentration or acid molarity between samples and standards,^{18,21,22} spectral interferences,²³ matrix effects,^{18,19,21} and fluctuations in room temperature.²⁴ Such effects on measured Mg isotopic ratios have been reported to vary among different MC-ICP-MS laboratories (e.g.^{18,19,21,22,25}). An investigation should therefore be carried out to determine how and to what extent these factors affect precision and accuracy when optimizing Mg isotope analysis in a new laboratory.

Analysis of well-characterized reference materials that have matrices similar to unknown samples is commonly adopted to ensure data quality and to avoid analytical artifacts. To date, Mg isotopic data of a number of reference materials have been reported from different laboratories (e.g.²⁻¹⁹). Nevertheless, published values for some commonly used reference materials exhibit a significant inconsistency across laboratories, e.g., the $\delta^{26}\text{Mg}$ value of BCR-1 varies from -0.58‰ to -0.09‰ (e.g.^{1,17,18,26-28}), and this significantly exceeds the current precision of $<0.07\text{‰}$ for measurements of $\delta^{26}\text{Mg}$ values (e.g.^{4,17,21}). Furthermore, the Mg isotopic ratios of many commonly used geological reference materials (e.g. COQ-1, JB-3, JA-1, JA-2, and JA-3) and environmental reference materials (e.g. soil and sediment reference materials) have rarely been reported. Therefore, a better characterization of the Mg isotopic compositions of reference materials could help data quality control and interlaboratory calibration.

In this study, we report Mg purification procedures for routine, high-Mn (Mn-rich Fe-Mn nodules and shales), and high-Ca (calcite-rich carbonates and carbonatites) samples, and describe methods of optimizing Mg isotope analysis in our laboratory. We demonstrate that the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio can be precisely and accurately measured to within 0.06‰ (2SD) using MC-ICP-MS with a sample-standard bracketing technique. With the developed method, Mg isotopic data for 16 commonly used and commercially available geological and environmental reference materials are reported for future interlaboratory calibration and data quality control.

2 | REFERENCE MATERIALS

The reference materials used in this study are commercially available from the United States Geological Survey (USGS, Denver, CO, USA), the Geological Survey of Japan (GSJ, Tsukuba, Japan), and the

National Research Center for Certified Reference Materials of China (NRC CRM, Beijing, China). These reference materials vary greatly in matrix types, which include igneous and metamorphic rocks (JP-1, PCC-1, BHVO-2, BCR-2, JB-2, JB-3, GSR-3, W-2a, AGV-2, JA-1, JA-2, JA-3, GSP-2, COQ-1, GSR-1, GSR-14, and GSR-15), shale (GSR-5), kaolinite (GBW03121), dolomite (GBW07217a), and stream sediments (GSD-1, GSD-3, GSD-9, GSD-21, and GSD-23). Seawater from Hawaii (USA) was also analyzed.

3 | EXPERIMENTAL

3.1 | Chemical reagents and materials

In the experiments, BV-III grade HNO_3 , HCl, and HF, purchased from the Beijing Institute of Chemical Reagents (Beijing, China), were further distilled by sub-boiling distillation (DST-1000, Savillex, Eden Prairie, MN, USA). Ultrapure water ($18.2\text{M}\Omega$) was obtained using a Milli-Q Element system (Merck Millipore, Billerica, MA, USA). High-purity H_2O_2 (30%) was purchased from Alfa Aesar (Ward Hill, MA, USA). The mono-elemental standard solutions, including Mg, Al, Ca, Na, K, Fe, Ti, and Mn, were purchased from the China Iron and Steel Research Institute (Beijing, China). All the Teflon beakers (Savillex) were cleaned using HNO_3 (1:1), HCl (1:1) and Milli-Q water. Centrifuge tubes and pipette tips were cleaned by using 10% HNO_3 and Milli-Q water. AG50W-X8 resin (200–400 mesh) was purchased from Bio-Rad (Hercules, CA, USA) and cleaned using alternately 6 N HCl, 1 N HNO_3 , 1 N HF, and Milli-Q water before use. The customized quartz columns and renewed Teflon columns (4 mm ID \times 20 cm capillary, 15-mL reservoir, Savillex) were cleaned using 50% HNO_3 , 50% HCl and Milli-Q water. The chemical procedures were conducted in a class-1000 ultraclean room equipped with a class-100 hood at the China University of Geosciences, Beijing (China).

3.2 | Sample digestion

3.2.1 | Silicate igneous and metamorphic rocks

Typically, 0.2–20 mg powder was weighed into 7-mL Teflon vials in a 1:3 (v/v, similarly hereinafter) mixture of concentrated HF- HNO_3 and heated on a hot plate for 12 h at 130–150°C. Complete dissolution was carefully checked by naked eye, and the sample solutions were dried at 160°C. The dried residues were redissolved with a 3:1 mixture of HCl- HNO_3 , followed by heating at 130–150°C for 12 h and then evaporation until dry at 80°C. The samples were refluxed with concentrated HNO_3 at 130–150°C until complete digestion was achieved and subsequently evaporated until dry at 80°C. This dried residue was finally dissolved in 1 N HNO_3 prior to column chemistry.

3.2.2 | Sediments, shales and clays

Stream sediments, shales and clays were digested in a high-pressure bomb to remove organic materials. Approximately 10–40 mg of the sample powder was weighed into PTFE bomb vessels in a 1:4 mixture of concentrated HF-HNO₃. The vessels were then sealed into Parr bombs and placed in a preheated oven for 16 h at 180°C. After the samples had been allowed to cool, 1–2 mL of 30% H₂O₂ was added to each sample to remove further organic matter at 70°C for 1 h. The solutions were later transferred into Savillex beakers and treated with a 3:1 mixture of HCl-HNO₃ at 130–150°C for 1 to 2 days. The samples were evaporated until dry at 80°C and refluxed with concentrated HNO₃ at 130–150°C. The samples were then dissolved in 1 N HNO₃ for column chemistry. Complete digestion was checked in each step above.

3.2.3 | Carbonates and carbonatites

For carbonate and carbonatite reference materials, typically 0.5–5 mg of sample powder was weighed into 7-mL Teflon vials. Then 0.5 mL HNO₃ was added to dissolve carbonates, followed by HF-HNO₃ in a ratio of 1:3. The sealed vials were heated on a hot plate for 12 h at 130–150°C. When completely dissolved, the sample solutions were dried at 160°C. The dried residues were refluxed with a 3:1 mixture of HCl-HNO₃ and concentrated HCl at 130–150°C for 12 h sequentially. The samples were then evaporated until dry at 80°C, and were finally dissolved in 10 N HCl.

3.3 | Column chemistry

3.3.1 | Routine samples

The routine samples were mainly silicate igneous rocks, metamorphic rocks, and sedimentary rocks with low Mn (Mn/Mg <5, ppm/ppm, similarly hereinafter) and Ca (Ca/Mg <20). The magnesium in these sample was routinely purified using AG50W-X8 (200–400 mesh) resin in a HNO₃ media following the procedures modified from Teng et al.¹⁷ Approximately 10–20 µg of Mg dissolved in 100 µL of 1 N HNO₃ was loaded onto the quartz columns and eluted using 1 N HNO₃. Matrix elements were removed using 16 mL of 1 N HNO₃, and then Mg was collected using 19 mL of 1 N HNO₃ (Figure 1). However, because the quartz columns are prone to break, we select a durable perfluoroalkoxy-Teflon (PFA) column (Savillex) as a substitute. Details of the elution curves and the yield of Mg processed by the PFA column were reported in Li et al.²⁹ The differences between the quartz and Teflon columns are resin volumes (2.1 mL for the quartz column and 2.3 mL for the Teflon one) and collection cuts (17 to 35 mL for the quartz column and 24 to 38 mL for the PFA one, Figure S1, supporting information).

The elution sequence was further checked by the analysis of JP-1 (peridotite), BHVO-2 (basalt), AGV-2 (andesite), and GSP-2 (granodiorite) with MgO contents ranging from 44.60 wt% to 0.96 wt%. Despite each having a different matrix of rock-forming

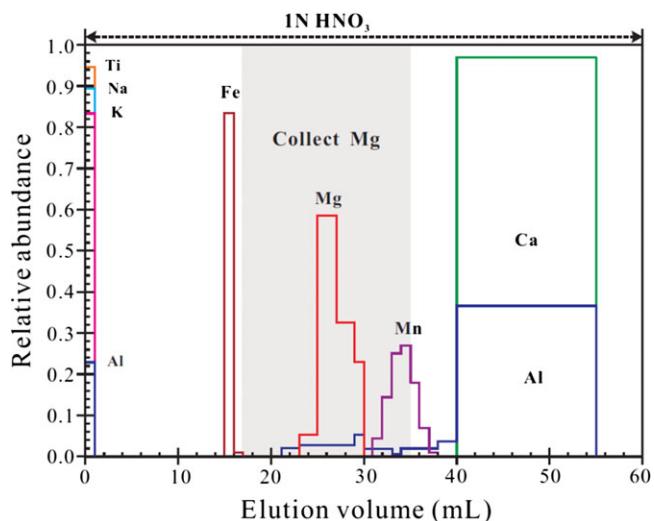


FIGURE 1 Elution curves of Mg and matrix elements for a mixed element solution with customized quartz columns [Color figure can be viewed at wileyonlinelibrary.com]

elements, the Mg peak consistently falls between 17 and 35 mL for quartz columns and between 24 and 38 mL for Teflon columns (Figure S1, supporting information). After one purification step, most of the matrix elements were efficiently removed. To obtain a sufficiently pure Mg fraction, all the samples were processed twice through the column. However, because Mn cannot be completely separated from Mg using this procedure, this may cause a problem for accurate Mg isotope analysis for samples with extremely high Mn/Mg ratios. A different column procedure was designed for these samples, as described below.

3.3.2 | High-Mn samples

Some Mn-rich samples such as Fe-Mn nodules and shales are depleted in MgO, which yields very high Mn/Mg ratios up to >20. In this study, samples with Mn/Mg ratios >5 were denoted as high-Mn samples. For these samples, Mg was separated from Mn using columns (Bio-Rad, 10 mL polypropylene column, denoted as “Mn-column”) filled with 1 mL of AG50W-X8 (200–400 mesh) resin in 0.5 N HCl-95% acetone media following the procedures modified from Bizzarro et al.³⁰ Manganese is eluted by 10 mL of 0.5 N HCl-95% acetone, with Mg quantitatively retained in the resin. Magnesium was then collected by 11 mL of 6 N HCl (Figure S2, supporting information).

3.3.3 | High-Ca samples

Calcite-rich carbonates and carbonatites are characterized by very high Ca/Mg ratios, such as COQ-1 where Ca/Mg=46, and defined as “high-Ca” samples. Although Mg and Ca can be separated (Figure S1, supporting information), the concentrations of Fe, Ti, Al, Mn, and Na were 30 times lower on average than the Mg concentration after a single separation, while the concentration of

Ca was 4 times lower. Therefore, we used another type of column (Bio-Rad, 10-mL polypropylene column, denoted as "Ca-column") using AG50W-X8 (200–400 mesh) resin in a 10 N HCl medium to efficiently remove Ca from the Mg. Magnesium was collected in the first 8 mL of 10 N HCl, while almost all the Ca was still held on the resin (Figure S3, supporting information).

3.4 | Whole procedure blank and yield

The whole procedural Mg blank is routinely less than 10 ng throughout dissolution, column purification, and measurement, and is negligible compared with the 10–20 µg of sample Mg processed. The column chemistry developed in this study also ensured, on average, a recovery of >99.6% of the Mg for the quartz column, >99.8% for the Teflon column, >99.6% for the Mn column, and >99.1 for the Ca column.

3.5 | Mass spectrometry

Isotopic analysis was performed using a Neptune Plus MC-ICP-MS instrument (Thermo Scientific, Waltham, MA, USA) at the China University of Geosciences, Beijing, China. Samples were introduced to the plasma using an ASX-110 autosampler (Cetac Technologies, Omaha, NE, USA) through a PFA self-aspiration micronebulizer (Thermo Scientific) with an uptake rate of 50–100 µL/min and a Scott double pass quartz glass spray chamber (Thermo Scientific). ^{24}Mg , ^{25}Mg , and ^{26}Mg were detected on the L3, C, and H3 Faraday cups, respectively. The isotope ratios were measured in low-resolution mode with the instrumental mass bias corrected by a standard-sample-standard bracketing method. Each measurement consisted of a 3 s idle time and 30 cycles of 4.19 or 8.39 s integration time. A blank of 3% HNO_3 was measured at the beginning of an analytical session for on-peak-zero (OPZ) correction.

The isotope ratio data are reported in the δ notation³¹ as:

$$\delta^x\text{Mg}_{\text{sample}} = \left(\frac{{}^x\text{Mg}/{}^{24}\text{Mg}}{\text{sample}} \right) / \left(\frac{{}^x\text{Mg}/{}^{24}\text{Mg}}{\text{DSM3}} \right) - 1 \quad (1)$$

where x refers to mass 25 or 26.

GSB Mg (a mono-elemental standard solution from the China Iron and Steel Research Institute) was routinely used as an in-house reference solution. The Mg isotopic compositions of reference materials are reported relative to DSM3, which can be readily converted from the $\delta^x\text{Mg}_{\text{GSB}}$ values using the following equation:

$$\delta^x\text{Mg}_{\text{DSM3}} = \delta^x\text{Mg}_{\text{GSB}} + \delta^x\text{Mg}_{\text{DSM3}}(\text{GSB}) + \delta^x\text{Mg}_{\text{GSB}} \times \text{Mg}_{\text{DSM3}}(\text{GSB}) \quad (2)$$

The $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of GSB relative to DSM3 are $-1.044 \pm 0.024\text{‰}$ and $-2.032 \pm 0.038\text{‰}$ (2SD, $n = 225$), respectively (Figure S4, supporting information). To achieve better measurement reproducibility and accuracy, the standard-sample sequences were repeated four times to reduce instrument-related random error. The

reported Mg isotopic composition for an unknown sample is the average value of the four repeat analyses. The uncertainties are reported as two standard deviation (2SD), calculated from the four repeated measurements of the sample.

4 | OPTIMIZATION OF Mg ISOTOPE ANALYSIS

4.1 | Acid molarity mismatching

Mismatching of acid molarity between samples and bracketing standards may cause difference in the instrumental mass bias between sample and standard measurements and break the fundamental principle of the standard-sample-bracketing method, leading to erroneous results (e.g.^{21,22,32–36}). The reason for this remains largely unknown but it may be caused by a difference in space charge effects when the acidity changes.^{32,37} Deviation from the true values in different degrees and directions has been previously observed for different instrument types (Neptune, Thermo Scientific; Nu Plasma, Nu Instrument, Wrexham, UK; and IsoProbe, GV Instruments, Manchester, UK) and sample introduction systems ("wet" and "dry" plasma).^{21,22} This effect was tested here by measurements of GSB Mg in 1% to 10% HNO_3 (m/m) against that in 3% HNO_3 (m/m), revealing a remarkable isotope variation up to $\sim 1.4\text{‰}$ in the $\delta^{26}\text{Mg}$ value (Figure 2). This observation further reinforces the importance of matching the acidity of blank, sample and standard solutions for accurate Mg isotope analysis.²² To minimize the effects of acid molarity mismatch, following Teng and Yang,²² all the solutions in a measurement sequence were prepared with the same batch of 3% HNO_3 in containers of identical shape and volume.

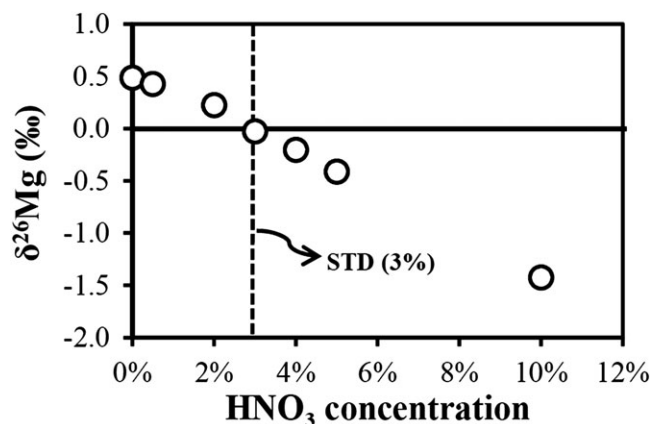


FIGURE 2 Magnesium isotopic composition variation of GSB Mg solutions with a varying acid molarity relative to the bracketing GSB Mg solution with certain acid molarity (3% HNO_3). Error bars represent 2SD uncertainties, the same as below

4.2 | Concentration mismatching

Matching of Mg concentration between samples and bracketing standards was suggested to be important for accurate Mg isotope determinations.^{18,21,22,34} To assess the effect of concentration mismatching on Mg isotope analysis, GSB Mg solutions with concentrations ranging from 40 to 2000 ppb were measured as samples against bracketing 400 ppb GSB Mg solutions. The results demonstrate that concentration mismatching (>10%) can dramatically affect the accuracy of Mg isotope measurements without OPZ corrections (Figure 3A). GSB solutions with $C_{\text{sample}}/C_{\text{standard}} > 1$ yield higher $\delta^{26}\text{Mg}$ values, whereas those with $C_{\text{sample}}/C_{\text{standard}} < 1$ yield lower $\delta^{26}\text{Mg}$ values than the true values of ~ 0 . Nevertheless, when the OPZ correction was utilized, no significant deviation from the true δ values is observed within analytical uncertainties for a $C_{\text{sample}}/C_{\text{standard}}$ range of 0.1–5 (Figure 3B). This suggests that the deviation of the measured δ values could be attributed to the contribution of the OPZ correction to the total intensities varying with C_{sample} . Similar observations were found when measuring Fe (e.g.³⁶) and Cu (e.g.³³) isotopes. Even with the OPZ correction, matching the sample and standard to within 10% is recommended to avoid potential analytical uncertainty.

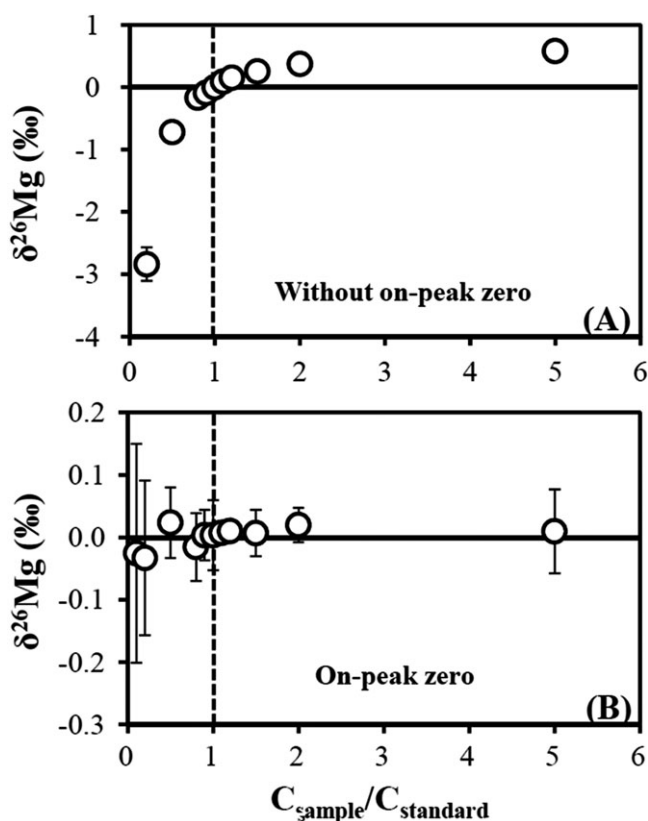


FIGURE 3 Magnesium isotopic composition variation of GSB Mg solutions with changing Mg concentrations relative to the bracketing GSB Mg solutions with known Mg concentration (400 ppb). The results obtained without on-peak zero (OPZ) A, and those obtained with OPZ correction B, are presented for comparison

4.3 | Effects of matrix elements

Matrix elements present in the analyzed solutions could reduce the precision and accuracy of Mg isotope determination (e.g.^{18,19,21,22,34}), because they can not only depress the ionization and throughput of Mg in the plasma and interface region, but also produce “isobaric interference” on the Mg isotopes. Polyatomic species such as $^{12}\text{C}^{12}\text{C}^+$, $^{12}\text{C}^{13}\text{C}^+$, $^{40}\text{Ar}^{12}\text{C}^{2+}$, $^{12}\text{C}^{14}\text{N}^+$, $^{12}\text{C}^{13}\text{CH}^+$, $^{23}\text{NaH}^+$ and doubly charged species such as $^{48}\text{Ti}^{2+}$, $^{48}\text{Ca}^{2+}$, $^{50}\text{Ti}^{2+}$, $^{50}\text{Cr}^{2+}$, $^{52}\text{Cr}^{2+}$ are the main isobaric interference for ^{24}Mg , ^{25}Mg , and ^{26}Mg . Polyatomic interferences formed by ^{12}C have been restrained efficiently since organic materials are eliminated during sample digestion. Furthermore, no resolvable ^{12}C has been detected in the low-resolution mode. To assess the effect of common elements on Mg isotope analysis, GSB Mg solutions doped with single elements (Na, Al, K, Ca, Ti, Mn and Fe) were measured. The results show that the presence of Na, Ca, Ti and Cr produces significant deviations in the $\delta^{26}\text{Mg}$ value when the ratios are $\text{Na}/\text{Mg} \geq 0.4$, $\text{Ca}/\text{Mg} \geq 1.5$, and $\text{Ti}/\text{Mg} > 0.1$ (Figure 4). The presence of Al and K also significantly shifts $\delta^{26}\text{Mg}$ towards lower values. The reason for this is not clear but might be because the mass bias is unstable when there is a high concentration of Al and K, since there is no known molecular spectral

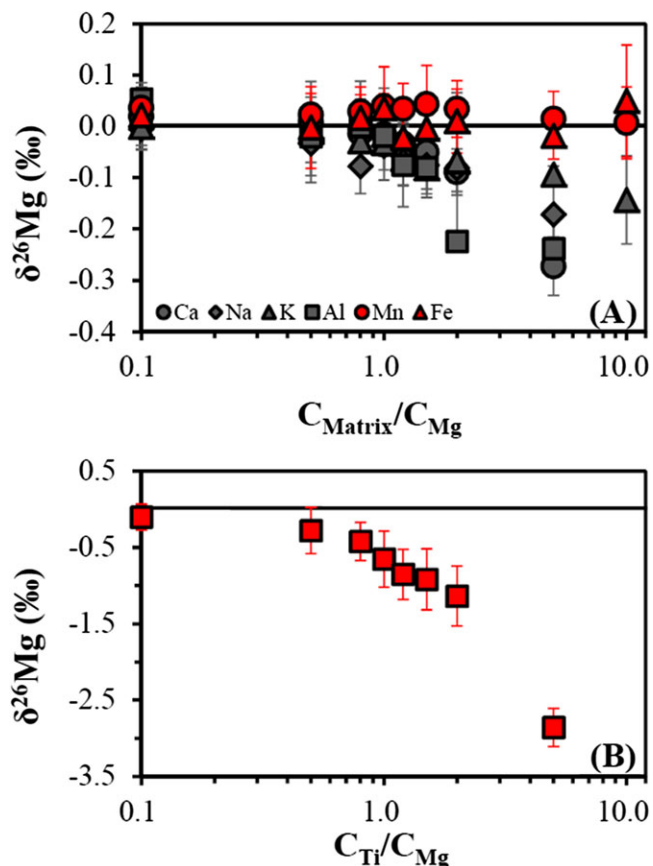


FIGURE 4 Magnesium isotope variations of GSB Mg solutions spiked with different amounts of Na, Al, K, Ca, Ti, Mn, and Fe relative to the unspiked GSB Mg solutions [Color figure can be viewed at wileyonlinelibrary.com]

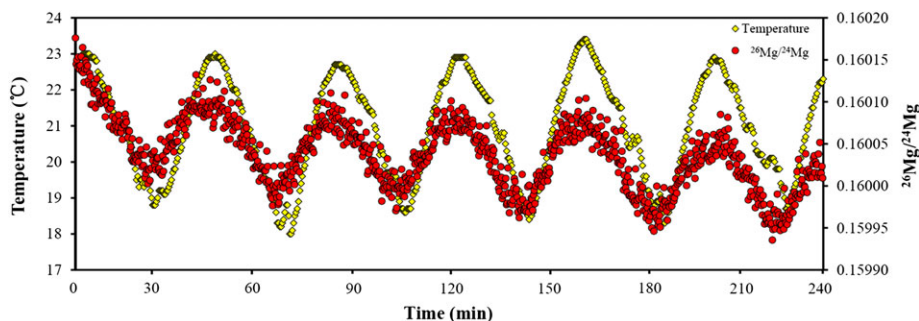


FIGURE 5 Magnesium isotopic ratios under oscillating room temperatures. The red circles are $^{26}\text{Mg}/^{24}\text{Mg}$ ratios that vary up to $\sim 0.06\%$ within 10 min, which exceeds the within-run precision of 0.02% in each measurement. The yellow rhombuses indicate room temperatures that decrease or increase by $\sim 1.3^\circ\text{C}$ within 10 min [Color figure can be viewed at wileyonlinelibrary.com]

interference from Al and K on the Mg isotopes. No significant deviation in the $\delta^{26}\text{Mg}$ value was observed within the uncertainty for the solutions doped with Fe and Mn with Fe/Mg and Mn/Mg ratios of up to 10, suggesting a high tolerance of Mn and Fe when using “wet” plasma in the low-resolution mode on the Neptune Plus instrument in our laboratory. After the digestion and purification procedures described above, all these matrix effects can be eliminated to ensure an accurate Mg isotope analysis.

4.4 | Effects of fluctuations in room temperature

The long-term stability of the temperature in the instrument laboratory is highly important, as any variation may influence the stability of the ICP torch or the ion transportation and further affect the instrumental mass bias, leading to a shift in the Mg isotopic ratios. In this study, we observed that the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio is well correlated with temperature in winter when the outside temperature changes dramatically from daytime to night (Figure 5). A change of 4°C within 30 min or less in the laboratory temperature can cause up to $\sim 0.9\%$ variation in $^{26}\text{Mg}/^{24}\text{Mg}$ that significantly

exceeds the relative variation of 0.1% in each measurement consisting of one block of 30 ratio measurements. When the temperature is oscillating rapidly, the instrumental mass bias cannot be stable or changing linearly, and this results in significant uncertainties for isotope analyses when using the sample-standard bracketing method. Similar effects were also observed by Zhang et al.²⁴ Therefore, the maintenance of a stable room temperature is essential for the acquisition of isotopic data with high precision and accuracy.

5 | REPRODUCIBILITY AND ACCURACY

The long-term external precision of our analytical method was evaluated by repeated analyses of the pure Mg solutions (GSB Mg) and well-characterized reference materials. Analyses of GSB Mg over a 4-year period yielded mean values of $-2.03 \pm 0.04\%$ for $\delta^{26}\text{Mg}$ and $-1.04 \pm 0.02\%$ (2SD, $n = 225$) for $\delta^{25}\text{Mg}$, suggesting that we are obtaining excellent instrument reproducibility for Mg isotope measurements (Figure S4, supporting information). The long-term

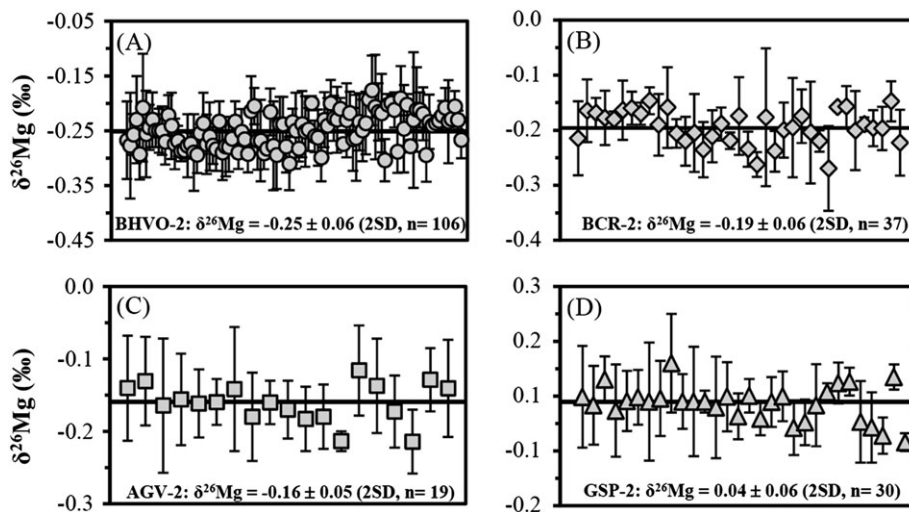


FIGURE 6 Magnesium isotopic compositions of geological reference materials (BHVO-2, BCR-2, AGV-2, and GSP-2) ranging from ultramafic rock to felsic rock for monitoring the long-term reproducibility of the whole procedure

external precision was further assessed by repeated analyses of BHVO-2, BCR-2, AGV-2, and GSP-2 with various matrices. These samples were processed through the entire chemistry procedure (sample dissolution, purification and instrumental analyses) and yielded 2SD of 0.06‰ ($n = 106$), 0.06‰ ($n = 37$), 0.05‰ ($n = 19$), and 0.06‰ ($n = 30$) for $\delta^{26}\text{Mg}$ values (Figure 6) over this period. These results ensure a whole-procedure reproducibility of 0.06‰ for $\delta^{26}\text{Mg}$ values.

The accuracy of the Mg-isotopic analytical procedure was checked by the analysis of well-studied reference materials (including JP-1, PCC-1, BHVO-2, BCR-2, W-2a, JB-2, AGV-2, GSP-2, and GSR-1) and seawater. The results and the literature data are listed in Table S1 (supporting information) for comparison. The $\delta^{26}\text{Mg}$ values obtained in this study are identical to the previously published values within $\pm 0.06\text{‰}$ (2SD, the long-term external precision, Figure 7). The measurements of reference materials and seawater verify that the purification procedure and the MC-ICP-MS measurement methodology developed in this study are robust and have an accuracy of 0.06‰ for $\delta^{26}\text{Mg}$ values. Furthermore, all these samples defined a mass-dependent fractionation line in a $\delta^{25}\text{Mg}$ versus $\delta^{26}\text{Mg}$ diagram, where $\delta^{25}\text{Mg} = 0.518 \times \delta^{26}\text{Mg} \pm 0.003$ (Figure S5, supporting

information). The slope of this line lies between the two theoretical mass fractionation coefficients for kinetic and equilibrium processes,¹ which suggests that there is no major influence of isobaric interferences on the measured Mg isotopic ratios.

6 | MAGNESIUM ISOTOPIC COMPOSITIONS OF NEW GEOLOGICAL AND ENVIRONMENTAL REFERENCE MATERIALS

The Mg isotopic compositions of 16 reference materials, including six igneous rocks, two metamorphic rocks, one shale, two minerals, and five stream sediments, were measured and are reported for the first time. The replicate results are presented in Table 1. The recommended Mg isotopic compositions for the 16 reference materials were calculated as an average of independent replicate analyses.

6.1 | Silicates

Three igneous rocks (JB-3, JA-2, and JA-3) yield $\delta^{26}\text{Mg}$ values of $-0.29 \pm 0.02\text{‰}$, $-0.29 \pm 0.00\text{‰}$, and $-0.26 \pm 0.06\text{‰}$ (2SD),

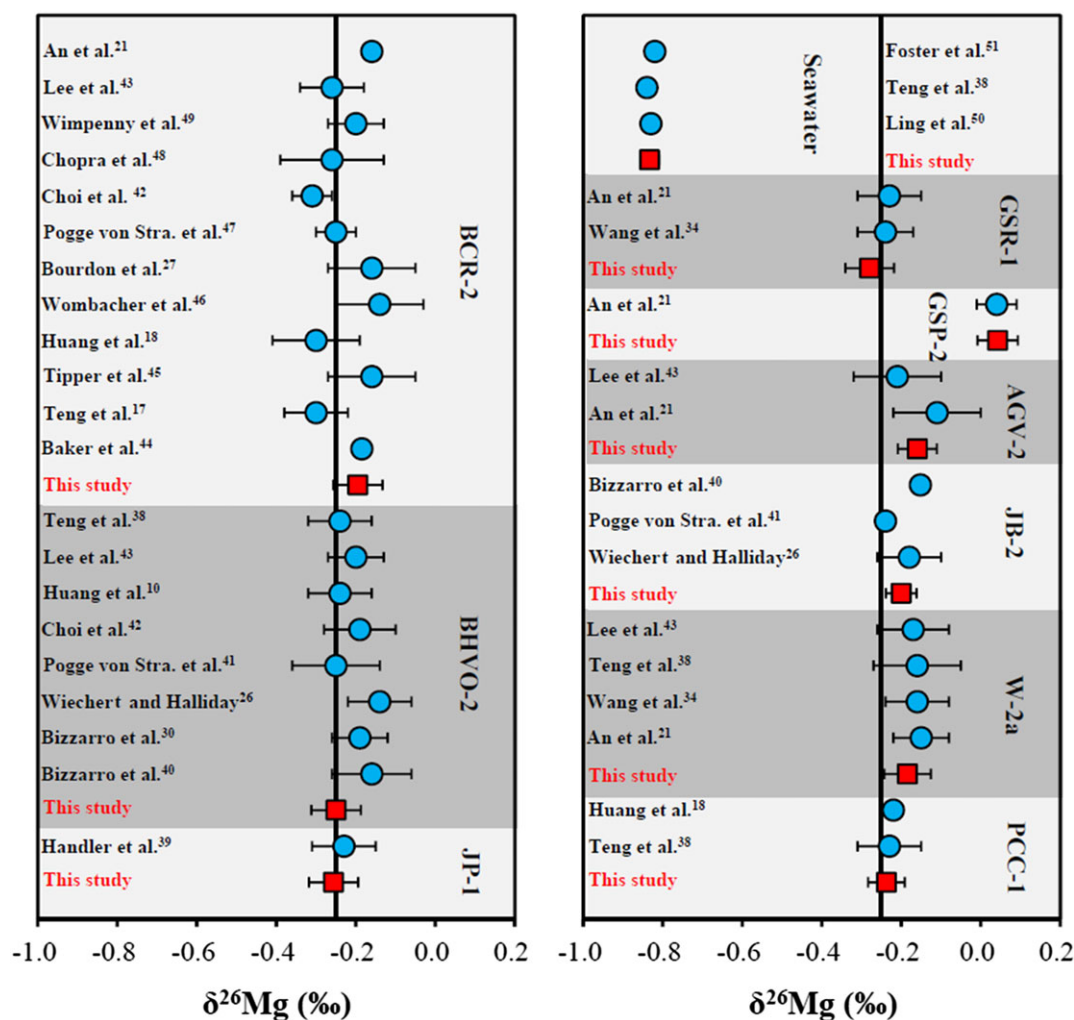


FIGURE 7 Comparison of Mg isotopic data of reference materials and seawater determined in the current study and values from the literature. The black line represents the average $\delta^{26}\text{Mg}$ value of the upper mantle from Teng et al.⁹ [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Magnesium isotopic compositions of geological and environmental RMs determined in this study

Sample	$\delta^{25}\text{Mg}$ value (‰)	2SD	$\delta^{26}\text{Mg}$ value (‰)	2SD
JB-3, basalt, GSJ				
Fuji (Japan)	-0.14	0.02	-0.28	0.03
	-0.13	0.06	-0.30	0.06
Average	-0.14	0.02	-0.29	0.02
GSR-3, basalt, NRCCRM				
Hebei (China)	-0.27	0.02	-0.50	0.10
	-0.23	0.05	-0.48	0.09
	-0.26	0.03	-0.52	0.07
	-0.26	0.06	-0.47	0.07
	-0.24	0.02	-0.48	0.03
	-0.28	0.04	-0.55	0.07
	-0.24	0.02	-0.47	0.03
	-0.22	0.05	-0.45	0.03
Average	-0.25	0.04	-0.49	0.06
JA-1, andesite, GSJ				
Hakone (Japan)	-0.06	0.04	-0.14	0.03
	-0.07	0.05	-0.13	0.04
	-0.06	0.04	-0.08	0.03
	-0.04	0.04	-0.09	0.05
Average	-0.06	0.02	-0.11	0.06
JA-2, andesite, GSJ				
Goshikidai (Japan)	-0.14	0.02	-0.29	0.04
	-0.16	0.03	-0.28	0.02
Average	-0.15	0.03	-0.29	0.00
JA-3, andesite, GSJ				
Asama (Japan)	-0.13	0.07	-0.24	0.05
	-0.14	0.04	-0.29	0.06
Average	-0.13	0.01	-0.26	0.06
COQ-1, carbonatite, USGS				
Montreal (Canada)	-0.27	0.02	-0.50	0.10
	-0.23	0.05	-0.48	0.09
	-0.26	0.03	-0.52	0.07
	-0.26	0.06	-0.47	0.07
	-0.24	0.02	-0.48	0.03
	-0.28	0.04	-0.55	0.07
	-0.24	0.02	-0.47	0.03
	-0.22	0.05	-0.45	0.03
	-0.27	0.05	-0.53	0.06
Average	-0.25	0.04	-0.50	0.06
GSR-14, granitic gneiss, NRCCRM				
	-0.09	0.04	-0.21	0.06
	-0.09	0.04	-0.18	0.07
Average	-0.09	0.00	-0.19	0.04
GSR-15, amphibolite, NRCCRM				
	-0.09	0.09	-0.18	0.04
	-0.11	0.04	-0.18	0.06
Average	-0.10	0.03	-0.18	0.01
GBW07217a, dolomite, NRCCRM				
	-1.12	0.02	-2.18	0.05
	-1.14	0.05	-2.19	0.05
	-1.15	0.04	-2.20	0.08
	-1.14	0.07	-2.21	0.07
Average	-1.14	0.02	-2.19	0.02
GBW03121, Kaolinite, NRCCRM				
	-0.10	0.07	-0.19	0.05
	-0.06	0.03	-0.15	0.02
	-0.06	0.03	-0.12	0.04
Average	-0.07	0.05	-0.15	0.08

(Continues)

TABLE 1 (Continued)

Sample	$\delta^{25}\text{Mg}$ value (‰)	2SD	$\delta^{26}\text{Mg}$ value (‰)	2SD
GSR-5, shale, NRCCRM				
	0.18	0.02	0.33	0.06
GSD-1, stream sediments, NRCCRM				
Shaanxi (China)	-0.12	0.04	-0.28	0.05
	-0.13	0.03	-0.26	0.08
	-0.13	0.03	-0.29	0.05
Average	-0.13	0.01	-0.28	0.02
GSD-3, stream sediments, NRCCRM				
Jiangxi (China)	0.10	0.03	0.19	0.03
	0.12	0.02	0.21	0.05
	0.09	0.03	0.18	0.05
Average	0.10	0.03	0.19	0.03
GSD-9, stream sediments, NRCCRM				
Hubei (China)	-0.42	0.01	-0.80	0.05
	-0.40	0.05	-0.79	0.04
	-0.41	0.02	-0.79	0.01
Average	-0.41	0.02	-0.79	0.01
GSD-21, stream sediments, NRCCRM				
Xinjiang (China)	-0.16	0.06	-0.31	0.02
	-0.15	0.08	-0.30	0.05
	-0.15	0.01	-0.31	0.02
Average	-0.16	0.01	-0.31	0.02
GSD-23, stream sediments, NRCCRM				
Jiangxi (China)	-0.26	0.04	-0.49	0.05
	-0.24	0.05	-0.45	0.06
	-0.23	0.01	-0.45	0.04
Average	-0.24	0.03	-0.46	0.05

USGS, United States Geological Survey; GSJ, Geological Survey of Japan; NRCCRM, National Research Center for Certified RMs of China.

respectively. Two metamorphic rocks, granitic gneiss (GSR-14) and amphibolite (GSR-15), have $\delta^{26}\text{Mg}$ values of $-0.19 \pm 0.04\text{‰}$ and $-0.18 \pm 0.01\text{‰}$ (2SD), respectively. These $\delta^{26}\text{Mg}$ values of igneous and metamorphic rocks are relatively homogeneous and identical to that of the upper mantle ($-0.25 \pm 0.07\text{‰}$) within the measurement uncertainty,³⁸ consistent with limited Mg isotope fractionation during magmatic and metamorphic processes (e.g.^{17,38,52}). GSR-3, a Cenozoic basalt from the Hannuoba volcanic group, eastern China, has a significantly lower $\delta^{26}\text{Mg}$ value of $-0.49 \pm 0.06\text{‰}$ (2SD) than the upper mantle. Previous studies showed the upper mantle in this area had been contaminated widely by recycled carbonates (e.g.^{2,3,5}). This is probably because the GSR-3 is from a carbonated mantle source. The andesite JA-1 is characterized by a high $\delta^{26}\text{Mg}$ value of $-0.11 \pm 0.06\text{‰}$ (2SD), similar to that reported for andesite AGV-2. The carbonatite COQ-1 yields an average $\delta^{26}\text{Mg}$ value of $-0.50 \pm 0.06\text{‰}$ (2SD), consistent with the inferred primary carbonatite melts being enriched in light Mg isotopes ($\leq -0.25\text{‰}$).⁵³

6.2 | Sediments, shales, clays and carbonates

Sediments and sedimentary rocks are important geological reservoirs of Mg in the upper continental crust and are critical to understanding the global Mg cycle in the surface environment. Five

stream sediments yield $\delta^{26}\text{Mg}$ values from -0.79 to 0.19‰ , a result of low-temperature processes which can induce large Mg isotope fractionation (e.g.⁹⁻¹³). The shale GSR-5 and kaolinite GBW03121 yield $\delta^{26}\text{Mg}$ values of $0.33 \pm 0.06\text{‰}$ (2SD) and $-0.15 \pm 0.08\text{‰}$ (2SD), respectively, similar to weathering residues with heavy Mg isotopes remaining.^{9,10} Dolomite (GBW07217a) has the lowest Mg isotopic ratio with a $\delta^{26}\text{Mg}$ value of $-2.19 \pm 0.02\text{‰}$ (2SD) among the reference materials, which is within the range of the global dolomite (-3.25 to -0.38‰) and close to the average $\delta^{26}\text{Mg}$ value of global dolomite (around 2‰).¹

7 | CONCLUSIONS

An analytical method has been developed for the high-precision and accuracy measurement of Mg isotopic ratios using a Neptune Plus MC-ICP-MS instrument. Flexible purification schemes were developed for silicate rocks, high-Mn ($\text{Mn}/\text{Mg} > 5$) and high-Ca ($\text{Ca}/\text{Mg} > 20$) samples. We systematically studied acid molarity and concentration mismatch, matrix effects, and fluctuations in room temperature, all of which potentially affect the precision and accuracy of Mg isotope analysis. Considering all these parameters fully, long-term external reproducibility better than $\pm 0.05\text{‰}$ for $\delta^{25}\text{Mg}$ values and $\pm 0.06\text{‰}$ (2SD) for $\delta^{26}\text{Mg}$ values was routinely obtained by

measurements of reference materials. The accuracy was further verified by analyses of well-studied reference materials with recommended Mg isotopic compositions but different matrices ranging from ultramafic to felsic igneous rocks. Additionally, with the developed method, we presented the high-quality Mg isotopic data for 16 geological and environmental reference materials, including silicates, carbonatite, shale, carbonate, clay, and stream sediments. This can aid the inter-laboratory calibration of Mg isotope measurement in the future.

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ORCID

Shan Ke  <https://orcid.org/0000-0001-8425-6393>

REFERENCES

- Teng F-Z. Magnesium isotope geochemistry. *Rev Mineral Geochem.* 2017;82(1):219-287.
- Yang W, Teng F-Z, Zhang H-F, Li S-G. Magnesium isotopic systematics of continental basalts from the North China craton: Implications for tracing subducted carbonate in the mantle. *Chem Geol.* 2012;328:185-194.
- Wang S-J, Teng F-Z, Li S-G. Tracing carbonate-silicate interaction during subduction using magnesium and oxygen isotopes. *Nat Commun.* 2014;5(1):5328.
- Ke S, Teng F-Z, Li S-G, et al. Mg, Sr, and O isotope geochemistry of syenites from Northwest Xinjiang, China: Tracing carbonate recycling during Tethyan oceanic subduction. *Chem Geol.* 2016;437:109-119.
- Li S-G, Yang W, Ke S, et al. Deep carbon cycles constrained by a large-scale mantle mg isotope anomaly in eastern China. *Natl Sci Rev.* 2017;4(1):111-120.
- Kasemann SA, Pogge von Strandmann PAE, Prave AR, Fallick AE, Elliott T, Hoffmann KH. Continental weathering following a Cryogenian glaciation: Evidence from calcium and magnesium isotopes. *Earth Planet Sci Lett.* 2014;396:66-77.
- Liu C, Wang Z, Raub TD, Macdonald FA, Evans DA. Neoproterozoic cap-dolostone deposition in stratified glacial melt water plume. *Earth Planet Sci Lett.* 2014;404:22-32.
- Saenger C, Wang Z. Magnesium isotope fractionation in biogenic and abiogenic carbonates: Implications for paleoenvironmental proxies. *Quaternary Sci Rev.* 2014;90:1-21.
- Teng F-Z, Li W-Y, Rudnick RL, Gardner LR. Contrasting lithium and magnesium isotope fractionation during continental weathering. *Earth Planet Sci Lett.* 2010;300(1-2):63-71.
- Huang K-J, Teng F-Z, Wei G-J, Ma J-L, Bao Z-Y. Adsorption- and desorption-controlled magnesium isotope fractionation during extreme weathering of basalt in Hainan Island, China. *Earth Planet Sci Lett.* 2012;359-360:73-83.
- Ma L, Teng F-Z, Jin L, et al. Magnesium isotope fractionation during shale weathering in the Shale Hills critical zone observatory: Accumulation of light mg isotopes in soils by clay mineral transformation. *Chem Geol.* 2015;397:37-50.
- Gao T, Ke S, Teng F-Z, Chen S, He Y, Li S-G. Magnesium isotope fractionation during dolostone weathering. *Chem Geol.* 2016;445:14-23.
- Gao T, Ke S, Wang S-J, et al. Contrasting Mg isotopic compositions between Fe-Mn nodules and surrounding soils: Accumulation of light Mg isotopes by Mg-depleted clay minerals and Fe oxides. *Geochim Cosmochim Acta.* 2018;237:205-222.
- Liu XM, Teng F-Z, Rudnick RL, McDonough WF, Cummings ML. Massive magnesium depletion and isotope fractionation in weathered basalts. *Geochim Cosmochim Acta.* 2014;135:336-349.
- Galy A, Bar-Matthews M, Halicz L, O'Nions RK. Mg isotopic composition of carbonate: Insight from speleothem formation. *Earth Planet Sci Lett.* 2002;201(1):105-115.
- Tipper ET, Galy A, Gaillardet J, Bickle MJ, Elderfield H, Carder EA. The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth Planet Sci Lett.* 2006;250(1-2):241-253.
- Teng F-Z, Wadhwa M, Helz RT. Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth Planet Sci Lett.* 2007;261(1-2):84-92.
- Huang F, Glessner J, Ianno A, Lundstrom C, Zhang Z. Magnesium isotopic composition of igneous rock standards measured by MC-ICP-MS. *Chem Geol.* 2009;268(1-2):15-23.
- Galy A, Belshaw NS, Halicz L, O'Nions RK. High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry. *Int J Mass Spectrom.* 2001;208(1-3):89-98.
- Zhu XK, Guo Y, Williams RJP, et al. Mass fractionation processes of transition metal isotopes. *Earth Planet Sci Lett.* 2002;200(1-2):47-62.
- An YJ, Wu F, Xiang YX, et al. High-precision Mg isotope analyses of low-Mg rocks by MC-ICP-MS. *Chem Geol.* 2014;390:9-21.
- Teng F-Z, Yang W. Comparison of factors affecting the accuracy of high-precision magnesium isotope analysis by multi-collector inductively coupled plasma mass spectrometry. *Rapid Commun Mass Spectrom.* 2014;28(1):19-24.
- Jacobsen B, Yin Q-Z, Moynier F, et al. ^{26}Al - ^{26}Mg and ^{207}Pb - ^{206}Pb systematics of Allende CAIs: Canonical solar initial $^{26}\text{Al}/^{27}\text{Al}$ ratio reinstated. *Earth Planet Sci Lett.* 2008;272(1-2):353-364.
- Zhang XC, Zhang AY, Zhang ZF, Huang F, Yu HM. Influence of room temperature on magnesium isotope measurements by multi-collector inductively coupled plasma mass spectrometry. *Rapid Commun Mass Spectrom.* 2018;32(13):1026-1030.
- Chang VTC, Makishima A, Belshaw NS, O'Nions RK. Purification of Mg from low-Mg biogenic carbonates for isotope ratio determination using multiple collector ICP-MS. *J Anal at Spectrom.* 2003;18(4):296-301.
- Wiechert U, Halliday AN. Non-chondritic magnesium and the origins of the inner terrestrial planets. *Earth Planet Sci Lett.* 2007;256(3-4):360-371.
- Bourdon B, Tipper ET, Fitoussi C, Stracke A. Chondritic Mg isotope composition of the earth. *Geochim Cosmochim Acta.* 2010;74(17):5069-5083.

28. Chakrabarti R, Jacobsen SB. The isotopic composition of magnesium in the inner solar system. *Earth Planet Sci Lett.* 2010;293(3-4):349-358.
29. Li RY, Ke S, He YS, Gao T, Meng XN. High precision magnesium isotope measurement for high-Cr samples. *Bull Mineral Petrol Geochem.* 2016;35(3):441-447.
30. Bizzarro M, Paton C, Larsen K, Schiller M, Trinquier A, Ulfbeck D. High-precision Mg-isotope measurements of terrestrial and extraterrestrial material by HR-MC-ICPMS – Implications for the relative and absolute Mg-isotope composition of the bulk silicate earth. *J Anal At Spectrom.* 2011;26(3):565-577.
31. Coplen TB. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Commun Mass Spectrom.* 2011;25(17):2538-2560.
32. Hu Y, Chen XY, Xu YK, Teng FZ. High-precision analysis of potassium isotopes by HR-MC-ICPMS. *Chem Geol.* 2018;493:100-108.
33. Liu S-A, Li DD, Li S-G, et al. High-precision copper and iron isotope analysis of igneous rock standards by MC-ICP-MS. *J Anal at Spectrom.* 2014;29(1):122-133.
34. Wang G, Lin Y, Liang X, et al. Separation of magnesium from meteorites and terrestrial silicate rocks for high-precision isotopic analysis using multiple collector-inductively coupled plasma-mass spectrometry. *J Anal at Spectrom.* 2011;26(9):1878-1886.
35. Teng F-Z, Li W-Y, Ke S, et al. Magnesium isotopic compositions of international geological RMs. *Geostand Geoanal Res.* 2015;39(3):329-339.
36. He Y, Ke S, Teng F-Z, et al. High-precision iron isotope analysis of geological RMs by high-resolution MC-ICP-MS. *Geostand Geoanal Res.* 2015;39(3):341-356.
37. Thomas R. A beginner's guide to ICP-MS – part V: The ion focusing system. *Spectroscopy.* 2001;16(9):38-44.
38. Teng F-Z, Li W-Y, Ke S, et al. Magnesium isotopic composition of the earth and chondrites. *Geochim Cosmochim Acta.* 2010;74(14):4150-4166.
39. Handler MR, Baker JA, Schiller M, Bennett VC, Yaxley GM. Magnesium stable isotope composition of Earth's upper mantle. *Earth Planet Sci Lett.* 2009;282(1-4):306-313.
40. Bizzarro M, Baker JA, Haack H, Lundgaard KL. Rapid timescales for accretion and melting of differentiated planetesimals inferred from ^{26}Al - ^{26}Mg chronometry. *The Astrophys J Lett.* 2005;632(1):L41-L44.
41. Pogge von Strandmann PAE, Burton KW, James RH, van Calsteren P, Gislason SR, Sigfússon B. The influence of weathering processes on riverine magnesium isotopes in a basaltic terrain. *Earth Planet Sci Lett.* 2008;276(1-2):187-197.
42. Choi MS, Ryu J-S, Lee S-W, Shin HS, Lee K-S. A revisited method for Mg purification and isotope analysis using cool-plasma MC-ICP-MS. *J Anal at Spectrom.* 2012;27(11):1955-1959.
43. Lee S-W, Ryu J-S, Lee K-S. Magnesium isotope geochemistry in the Han River, South Korea. *Chem Geol.* 2014;364:9-19.
44. Baker J, Bizzarro M, Wittig N, Connelly J, Haack H. Early planetesimal melting from an age of 4.5662 Gyr for differentiated meteorites. *Nature.* 2005;436(7054):1127-1131.
45. Tipper ET, Galy A, Bickle MJ. Calcium and magnesium isotope systematics in rivers draining the Himalaya-Tibetan-plateau region: Lithological or fractionation control? *Geochim Cosmochim Acta.* 2008;72(4):1057-1075.
46. Wombacher F, Eisenhauer A, Heuser A, Weyer S. Separation of Mg, Ca and Fe from geological RMs for stable isotope ratio analyses by MC-ICP-MS and double-spike TIMS. *J Anal at Spectrom.* 2009;24(5):627-636.
47. Pogge von Strandmann PAE, Opfergelt S, Lai YJ, Sigfússon B, Gislason SR, Burton KW. Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. *Earth Planet Sci Lett.* 2012;339:11-23.
48. Chopra R, Richter FM, Watson EB, Scullard CR. Magnesium isotope fractionation by chemical diffusion in natural settings and in laboratory analogues. *Geochim Cosmochim Acta.* 2012;88:1-18.
49. Wimpenny J, Colla CA, Yin Q-Z, Rustad JR, Casey WH. Investigating the behaviour of Mg isotopes during the formation of clay minerals. *Geochim Cosmochim Acta.* 2014;128:178-194.
50. Ling MX, Sedaghatpour F, Teng F-Z, Hays PD, Strauss J, Sun W. Homogeneous magnesium isotopic composition of seawater: An excellent geostandard for Mg isotope analysis. *Rapid Commun Mass Spectrom.* 2011;25(19):2828-2836.
51. Foster GL, Pogge von Strandmann PAE, Rae JWB. Boron and magnesium isotopic composition of seawater. *Geochem Geophys Geosy.* 2010;11(8):Q08015.
52. Wang S-J, Teng F-Z, Li S-G, Hong J-A. Magnesium isotopic systematics of mafic rocks during continental subduction. *Geochim Cosmochim Acta.* 2014;143:34-48.
53. Li W-Y, Teng F-Z, Halama R, Keller J, Klaudius J. Magnesium isotope fractionation during carbonatite magmatism at Oldoinyo Lengai, Tanzania. *Earth Planet Sci Lett.* 2016;444:26-33.

SUPPORTING INFORMATION

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