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Article

Accurate Measurement of Mg Isotopes in Twenty-four Reference Materials by MC-ICP-MS with A Highly Efficient Optimized Method

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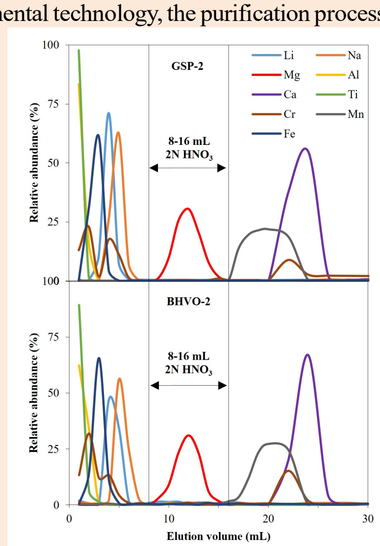
ABSTRACT: The purification of Mg requires the separation of Mg from matrix elements, which is the prerequisite for the accurate determination of Mg isotopic compositions. With the rapid development of instrumental technology, the purification process has played an important role in affecting the efficiency of isotopic measurement. This study reported a highly efficient optimized method based on the combination of precipitation process and chromatographic procedure to finish purification process within nine hours, which improved the purification efficiency. The precipitation procedure is used to remove K and optimized 2N HNO_3 is proposed for collecting Mg fraction, which shortens the time in chromatographic process. With the popularization of Mg isotope analytical method and the wide application of Mg isotope in the geosciences, the existing reference materials with confirmed δ^{26}Mg values are being consumed more, and there is a situation of short supply. After the verification of eleven different types of reference materials with confirmed Mg isotopic compositions using established purification process, the δ^{26}Mg values of thirteen reference materials were firstly reported for broadening the selection of reference materials. In addition, the Mg concentration mismatch effect and acid molarity mismatch effect were further evaluated using Neptune *Plus* MC-ICP-MS in wet plasma mode. The long-term instrumental stability was assessed by repeated analysis of the in-house standard GSB-Mg, which yielded δ^{25}Mg and δ^{26}Mg of 0.00 ± 0.02‰ (2 SD, n = 106) and 0. 00 ± 0.04‰ (2 SD, n = 106), respectively.



INTRODUCTION

Mg is an alkaline-earth metal and widely distributed in the silicate Earth.[1-3] Mg has three stable isotopes with masses of 24, 25, and 26 and typical abundances of 78.99%, 10.00% and 11.01%, respectively. The relatively large mass difference between ^{26}Mg and ^{24}Mg is commonly exploited to explore the distribution of Mg isotopes in extra-terrestrial and terrestrial reservoirs,[4, 5] magma differentiation by fractional crystallization or thermal diffusion,[6, 7] weathering of continental crust and geochemical recycling,[8, 9] environmental improvement, human risk assessment,[10, 11] and biogeochemical processes such as plant photosynthesis and biomineralization.[12, 13]

Matrix-matched reference materials is critical to ensure the data quality and enable inter-laboratory comparison.[14, 15] With the development of Mg isotopic analytical technology and wide application of Mg isotopes in various subject areas, a number of international geological standard rock and mineral powders including igneous rock, metamorphic and sedimentary rocks as well as minerals have been widely analyzed by different laboratories.[16] What followed is the consumption of well-characterized reference materials is increasing.[15-17] Therefore, it is necessary to confirm Mg isotopic compositions in more reference materials for quality assurance and reduce the consumption of existing reference materials.

Highly precise and accurate analysis of the Mg isotopes in unknown samples is essential for identifying various geological processes. Accurate determination of Mg isotopes in unknown samples requires ultrapure Mg solutions. The matrix elements that interfere with the accurate determination of Mg isotopes can be classified into two types depending on how easily the element is separated from the Mg in cation resin. The first type is element such Na, Al, Fe that are easily separated from Mg by using large quantities of eluent and long-time cost. For example, three column steps and near a hundred milliliters of eluent were used in the method established by Bolou-Bi *et al.* (2009)[18] and Wang *et al.* (2022)[19]. The second one is K, which has a distribution coefficient similar to that of Mg in cation resin and it is difficult to absolutely separate from Mg especially for high-K_2O samples. For example, An *et al.* (2014)[20] first reported the separation of K from Mg by using 1 N HNO_3, but there is still a small overlap of the elution curves of K and Mg in high- K_2O and low-MgO samples. For removing the above two types of matrix elements, different pioneers have proposed their own solutions, while not achieve the complete removal of K and small consumption of time and elutions. Bao *et al.* (2019)[21] utilized NaOH precipitation to totally remove K but two column steps were needed to remove other matrix elements. Huang *et al.* (2021)[22] reported one step purification method by using AG50W-X8 resin and 0.5 N HNO_3 to achieve the large gap between Mg and K elution profiles, but this method costs about 90 milliliters of elutes. To solve the above problems at the same time, we learned from the previous method of rapid removal of K and improved chromatographic processes. Bao *et al.* (2019)[21] conducted a detailed investigation of the isotopic fractionation, precipitation frequency, and precipitation efficiency during a precipitation process that overcomes the aforementioned issues and achieves the separation of K from the matrix within an hour. Here we use the same precipitation procedure to remove K prior chromatographic purification. The separation of other matrix elements was achieved by using a mixed acid consisting of 2N HNO_3 and 0.5 N HF to elute matrix elements within only 5 mL of eluent based on the advantage that the addition of the mixed acid an shift Ti, Al, Zr, and Y peaks far from the Mg cut quickly.[20] The optimized 2N HNO_3 was then used to collect the Mg fraction. The use of 2N HNO_3 halves the volume of eluent required to collect the entire Mg fraction (in comparison to 1N HNO_3) by lowering the Mg distribution coefficient on the cation resin but no worry about the overlapping of elution curves of Mg and K. In summary, a precipitation step to remove K and an optimized chromatographic procedure were combined to purify the sample solution within a few hours, allowing more samples to be processed in less time and with less eluent. This purification process is more efficient than most existing purification methods for geological samples.

In this study, an efficient Mg purification process was developed to precisely determine Mg isotopes and the Mg isotopic composition of thirteen different types of reference materials were firstly reported. Building on the earlier work of An *et al.* (2014)[20] and Bao *et al.* (2019),[21] matrix elements were removed by combining precipitation and calibrated elution steps. Following precipitation with NaOH to remove most of the K, a single column was used to remove other elements such as Na, Al, Fe, and Ti using an optimized elution acid. The Mg purification method was verified using various types of reference materials. The accurate determination of the Mg isotopes in these reference materials demonstrates that this novel purification procedure is suitable for the analysis of various rocks, including high-K_2O and low-MgO rocks. In addition, the factors that interfere with precise and accurate determination of Mg isotopes, including the Mg concentration and acid molarity mismatch effects, along with the matrix effect, were evaluated using Neptune *Plus* MC-ICP-MS in wet plasma mode.

EXPERIMENTAL

Reagents and reference materials. To reduce the process blank of Mg and avoid cross contamination, the digestion and purification of samples were performed under 100 clean laboratory conditions at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences in Wuhan. Ultrapure water (18.0 MΩ cm) was obtained using a Milli-Q Element purification system (Millipore, Bedford, MA, USA). Commercially available nitric acid (HNO_3 68%, GR grade), hydrofluoric acid (HF 40%, GR grade), and hydrochloric acid (HCl 68%, GR grade) were further distilled twice using a DST-1000 acid purification system (Savillex, Eden Prairie, MN, USA). All acids and mixed acids used for column elution were prepared by gravimetric dilution and their strength was precisely determined by titration with analytical grade Na_2CO_3. Sodium hydroxide (NaOH, AR grade) was purchased from Aladdin.

The standard solution of GSB-Mg (1000 µg g^{-1} in 5% HCl) was manufactured by Bao *et al.* 2020[33] and the δ^{25}Mg and δ^{26}Mg values of GSB-Mg relative to DSM3 were -1.056‰ and -2.049‰ with a combined expanded uncertainty of 0.028‰ and 0.049‰. The eleven reference materials with the confirmed Mg isotopes were chosen to verify the robustness of the developed method. The six reference materials from the United States Geological Survey composed of basalts: BHVO-2, and BCR-2; rhyolite: RGM-2; andesite: AGV-2; granodiorite: GSP-2; carbonate: COQ-1. Two rhyolite reference materials from Geological Survey of Japan with

Table 1. Details of the Mg purification procedure

	Eluent	Amount (mL)	Comments
Precipitation	Detailed information can be found in Bao *et al.* (2019)[21]		
Elution	6 N HNO_3 and H_2O	10	Resin cleaning
	2 N HNO_3 + 0.5 N HF	5	Resin conditioning
	2 N HNO_3 + 0.5 N HF	5	Removal of Na, Al, Fe, Ti, Cr, V, and Zr
	2 N HNO_3	2	Removal of Na
	2 N HNO_3	9	Mg collection
	6 N HCl	15	Resin cleaning and removal of Ca, Mn, and Cr

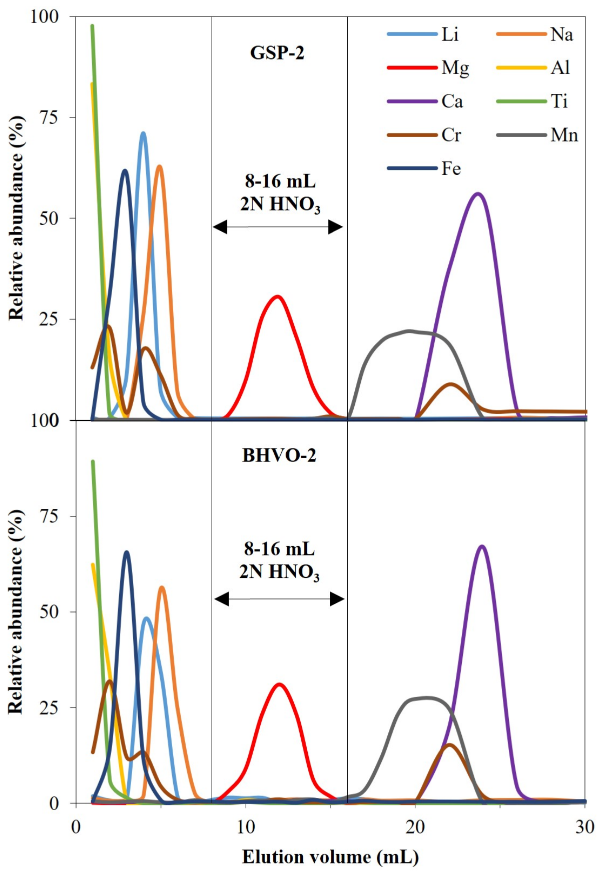


Fig. 1 Elution curves obtained during Mg purification procedures of GSP-2 and BHVO-2 rock standards.

extreme low MgO content were JR-1 and JR-3. Three reference materials from China Iron and Steel Research Institute Group (CRSRI) were GSS-2 (soil), GSR-11 (rhyolite), and GSR-15 (amphibolite). In addition, the Mg isotopic composition of thirteen standard materials (GSD-1, GSD-3A, GSD-4, GSD-5, GSS-1, GSS-9, GSS-15, GSS-16, GSR-4, GSR-5, GSR-6, GSR-7, and GSR-10) from CRSRI were firstly reported.

Sample preparation and Mg purification. Sample powders containing ~25 µg Mg based on the MgO content of samples were digested overnight in Teflon vessels containing a mixture of 1 mL HF and 1 mL HNO_3 at 120 °C. The dried samples were refluxed with concentrated HNO_3 to remove residual fluoride and dried again before being digested in a mixture of 1.5 mL HCl and 0.5 mL HNO_3 to ensure complete dissolution. The dried residue was refluxed with concentrated HNO_3 dissolved in 0.5 mL 1 N HNO_3 and transferred to a 2 mL centrifuge tube. 1.5 mL of 4 N NaOH was used to precipitate Mg^{2+} with the solution pH of about 14, and the ultrasonic bath for 15 min contributed to the formation of precipitation. To remove the unprecipitated K, the solution was centrifugated for 15 min at 8000 rpm and the supernatant was discarded. The whole precipitation process was repeated twice to make sure the remove of K and no Mg isotopic fractionation occurred.[21] After precipitation, one-column Mg purification was performed in Bio-Rad columns loaded with Bio-Rad 200-400 mesh AG50W-X12 cation-exchange resin (2 mL, Table 1). The resin was cleaned with 6 N HNO_3 at least three times and stored in ultrapure water until use. The resin was backwashed using a Pasteur pipette to remove air bubbles before purification. After precipitation, the samples were dissolved in 0.2 mL 2 N HNO_3 + 0.5 N HF and loaded into the resin that was conditioned with 5 mL of 2 N HNO_3 + 0.5 N HF. A mixture of 5 mL 2 N HNO_3 + 0.5 N HF along with 2 mL 2 N HNO_3 was loaded to efficiently remove Na, Al, Fe, Ti, V, Cr, and Zr. Elution was then performed using 13 mL 2 N HNO_3 to collect the Mg fraction (Fig. 1). The collected solutions were evaporated, and the residues were dissolved in 2% HNO_3 for Mg isotope determination.

Mass spectrometry. Mg isotopes were determined using double-focusing MC-ICP-MS (Neptune *Plus*, Thermo Fisher Scientific, Bremen, Germany)[23-31] at the China University of Geosciences, Wuhan. The sample solutions were nebulized and introduced using a Thermo Finnigan stable introduction system (SIS, ~ 50 µl min^{-1} PFA nebulizer and quartz glass spray chamber) coupled with an autosampler (ASX-112FR; Cetac Technologies, Omaha, NE, USA). The L3, C, and H3 Faraday cup configurations were used to analyze ^{24}Mg, ^{25}Mg, and ^{26}Mg, respectively. The five blocks of analysis consisted of four data cycles with an integration time of 4.094 s per cycle. Mg isotopes were analyzed in the low-resolution mode using the standard-sample bracketing method. To ensure accurate and precise determination of the Mg isotopic composition, the instrument was calibrated daily by repeated analyses of the GSB-Mg solution until stable results were obtained. All sample

Table 2. MC-ICP-MS operating parameters

Instrument parameter	Neptune *Plus* MC-ICP-MS
Cup configuration	L3: ^{24}Mg; C: ^{25}Mg; H3: ^{26}Mg
Resistor for the Faraday cup	$10^{11}\Omega$
RF power	1250W
Cool gas flow	16.00 L/min
Auxiliary gas flow	1.29 L/min
Argon make-up gas flow	1.065 L/min
Guard Electrode (GE)	On
Instrumental resolution	Low resolution
Sample uptake	50 μL/min
Cones	Jet + X
Block cycle	4 cycles / 5 blocks
Integration time	4.95 s

and standard solutions were diluted to 0.5 μg g^{-1} by the addition of 2% HNO_3 to ensure that the signal intensity of ^{24}Mg reached ~ 20 V. To eliminate the cross-contamination between samples, the sample-introduction system was repeatedly washed with 2% HNO_3 solutions until the ^{24}Mg signal intensity in the blank solution dropped to several mV. Interference from the polyatomic interferents formed by the carrier gas and reagents (which include $^{12}C^{12}C^{+}$, $^{12}C^{13}C^{+}$, $^{12}C^{14}N^{+}$, $^{12}C^{13}CH^{+}$, $^{48}Ti^{2+}$, and $^{48}Ca^{2+}$ etc.) was corrected by subtracting the signal from that of the blank solution. The operating parameters are listed in Table 2.

The Mg isotopic composition of all samples is expressed in standard notation according to the DSM3 standard. GSB-Mg was used as the bracketing standard and the conversion to DSM3 was calculated using the following equation:

$$\delta^{X}Mg_{DSM3}^{sample}(‰)=1000\times\left(\frac{(^{X}Mg/^{24}Mg)_{sample}}{(^{X}Mg/^{24}Mg)_{GSB\text{-}Mg}}-1\right)+\ \delta^{X}Mg_{DSM3}^{GSB\text{-}Mg}$$

Where X is 25 or 26 mass units, $\delta^{X}Mg_{DSM3}^{sample}$ means the Mg isotopic composition of samples relative to DSM3, $\delta^{X}Mg_{DSM3}^{GSB\text{-}Mg}$ means the Mg isotopic composition of GSB-Mg relative to DSM3, $(^{X}Mg/^{24}Mg)_{sample}$ means the measured Mg isotopes of sample and $(^{X}Mg/^{24}Mg)_{GSB\text{-}Mg}$ means the measured Mg isotopes of GSB-Mg.

RESULTS AND DISCUSSION

Purification of Mg. The total procedural blanks of Mg were less than 30 ng throughout sample digestion, precipitation, and chromatographic processes owing to the use of high-purity chemical reagents and thoroughly cleaned beakers and columns. The ratio of the procedural Mg blank to the Mg loaded onto the column was < 0.0012; thus, the Mg in the procedural blank was considered negligible compared to the 25 μg of Mg processed. ICP-MS analysis of the Mg blank indicated that the procedural blanks for all elements in the matrix were acceptable. Measurement of the Mg isotopes showed that the blank intensities of ^{24}Mg were typically lower than 5 mV in a 2% HNO_3 solution, while the Mg recovery from geological standards after precipitation with NaOH and chromatographic purification ranged from 99.5% to 101.4%, with an average of 99.8 ± 1.5%.

Approximately 99.9% K of the sample was efficiently removed by precipitation with NaOH, with no obvious Mg isotopic fractionation.[21] Building on a previous study,[20] the single-column procedure used in this study efficiently separates Mg from other matrix elements, including Na, Al, Fe, Ti, V, and Zr, using 5 mL of 2 N HNO_3 + 0.5 N HF and 2 mL of HNO_3. The distribution coefficient of Mg was reduced using an optimized step with 9 mL of 2 N HNO_3, allowing Mg to be collected more quickly than when using 1 N HNO_3. The matrix elements in the eluted solution were also determined using ICP-MS to verify the purification using the established method. The concentrations of matrix elements were much lower than that of Mg, such that the ratio of Mg to the sum of the major elements, (Na + K + Ca + Al + Fe)/Mg, was < 0.06. The individual ratios were as follows: Na/Mg < 0.02, Al/Mg < 0.005, K/Mg < 0.007, Ca/Mg < 0.009, Fe/Mg < 0.015, and Ti/Mg < 0.0005. The developed purification procedure therefore effectively removed the matrix elements, thus minimizing the matrix effect during the instrumental analysis.

Evaluation of matrix effects. Based on the established purification procedure, trace matrix elements were still present in the purified solution, and the ratio of each matrix element to Mg in the purified solution was not identical. Trace matrix elements in the purified solution may limit the accuracy and precision of the Mg isotope measurements. Furthermore, previous studies have confirmed that observed matrix effects are influenced by the type of instrument and experimental conditions.[34] For example, Liu *et al.* (2021)[32] observed a significant offset of $\delta^{26}Mg$ (0.2 – 0.3‰) when Ca/Mg was > 0.03 using Nu Plasma 3 MC-ICP-MS in wet plasma mode. Bao *et al.* (2019)[21] also used Nu Plasma 3 MC-ICP-MS in wet plasma mode and achieved a precise and accurate Mg isotope measurement when Ca/Mg was < 0.3. In the present study, the effects of Na, Al, K, Ca, Mn, Fe, Cu, and Zn on Mg isotopic analysis using Neptune *Plus* MC-ICP-MS in wet plasma mode were evaluated. Quantitative GSB-Mg solutions doped with different proportions of Na, Al, K, Ca, Mn, Fe, Cu, and Zn (matrix/Mg = 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10) were used to explore the influence of the matrix elements on the Mg isotopic analysis (Fig. 2). Among them, some elements are the main components of geological samples, and some are the matrix elements that are difficult to be separated from Mg in cation resin. Accordingly, these matrix elements are ideal for the doping experiment to determine the accuracy of our method. By employing pure GSB-Mg (0.5 μg g^{-1}) as the bracketing standard, the measurement Mg isotopic data can be considered sufficiently precise and accurate when Na/Mg ≤ 1,

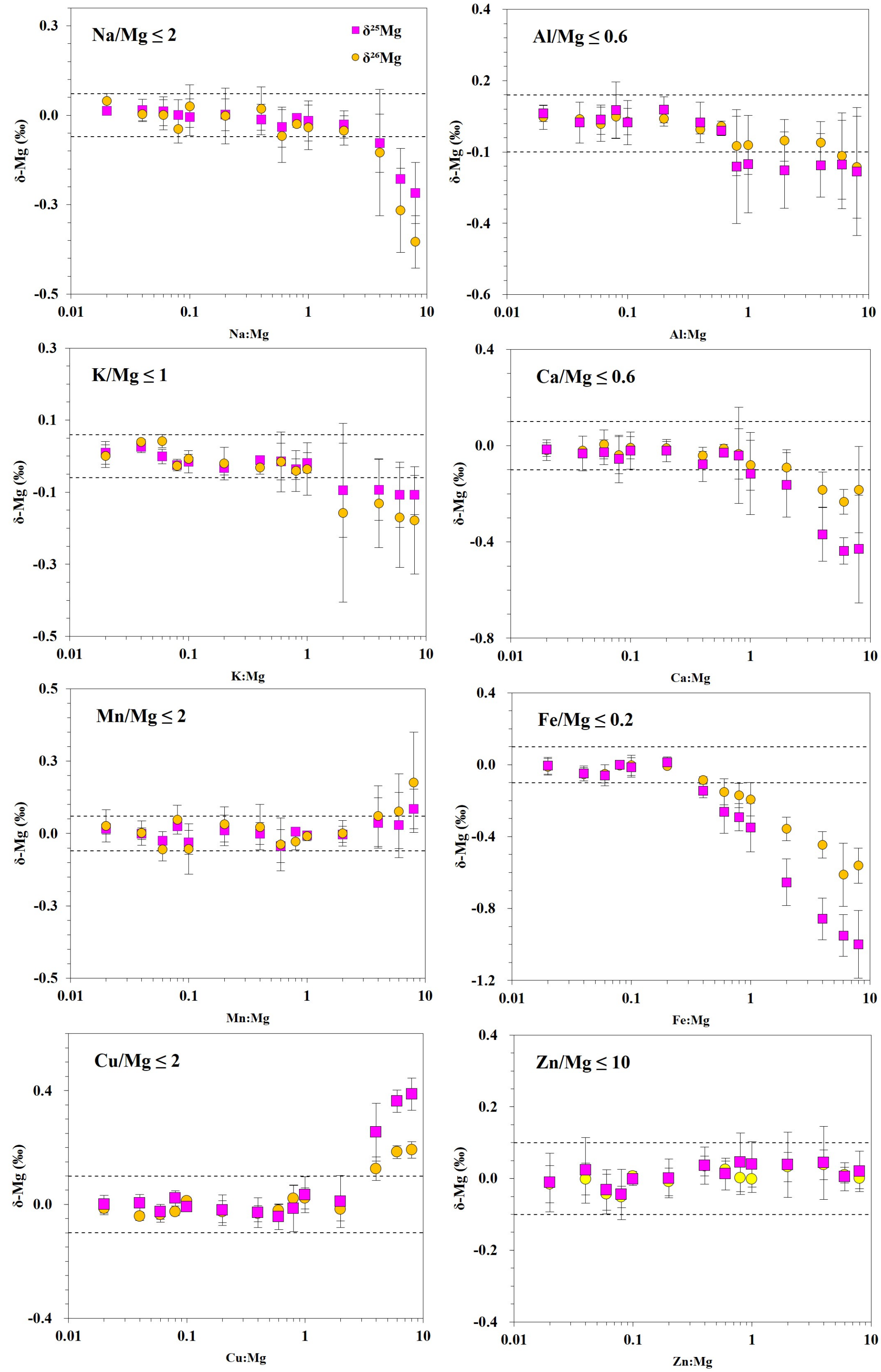


Fig. 2 Evaluation of the matrix effect on analysis of Mg isotopes by doping experiments. The Mg concentration of samples and bracketing standards were 0.5 μg g^{-1}. Error bars represent 2 SD. The measurement Mg isotopic data can be considered sufficiently precise and accurate when Na/Mg ≤ 1, Al/Mg ≤ 0.6, K/Mg ≤ 1, Ca/Mg ≤ 0.6, Mn/Mg ≤ 2, Fe/Mg ≤ 0.2, Cu/Mg ≤ 2, Zn/Mg ≤ 10 in the obtained solution.

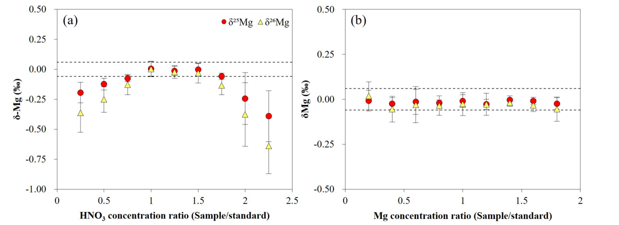


Fig. 3 Effect of acid molarity mismatch between sample and standard Mg concentrations. Error bars represent 2 SD. Each measurement was performed in triplicate.

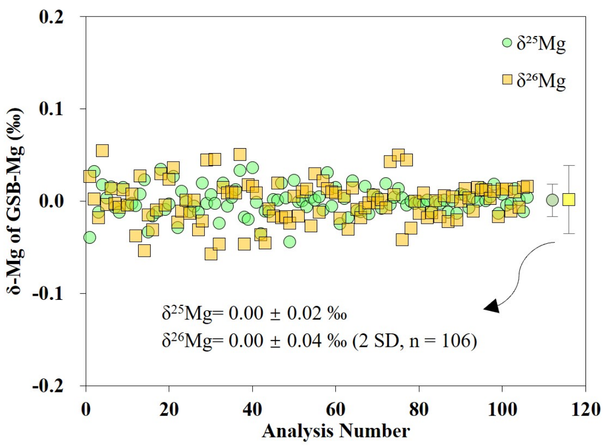


Fig. 4 Instrumental stability evaluation conducted by repeated analysis of GSB-Mg.

Al/Mg ≤ 0.6, K/Mg ≤ 1, Ca/Mg ≤ 0.6, Mn/Mg ≤ 2, Fe/Mg ≤ 0.2, Cu/Mg ≤ 2, Zn/Mg ≤ 10. (Fig. 2). The results indicated that the matrix effects of different elements were different. Excess Na, Al, K, Ca, and Fe induced a negative drift in Mg isotopes, whereas excess Mn and Cu induced a positive drift. For instance, with a Na/Mg ratio greater than 2, the deviation of δ^{25}Mg and δ^{26}Mg reached approximately - 0.2‰ and - 0.4‰ respectively. With a Cu/Mg ratio greater than 2, the deviation of δ^{25}Mg and δ^{26}Mg reach approximately + 0.2‰ and + 0.4‰ respectively. Various samples with different Mg content were prepared in accordance with international standards for separation and purification to evaluate the reliability of the purification method.

Evaluation of acid and concentration mismatch. Purified Mg samples and bracketing standard solutions were injected into the MC-ICP-MS instrument in diluted nitric acid. Mg isotopic fractionation is known to occur on different instruments owing to mass bias caused by acid molarity mismatch.[19-21] To verify the effect of Mg concentration mismatch on Mg isotope measurements, a series of 0.5 μg g^{-1} GSB-Mg solutions with different acid molarities (0.5% – 6% HNO_3) were measured using MC-ICP-MS using GSB-Mg (0.5 μg g^{-1}) in 2% HNO_3 as the bracketing standard. The difference in the acid molarities of the standards and samples resulted in an Mg isotope offset of approximately 0.5‰ (Fig. 3). The obtained δ^{25}Mg and δ^{26}Mg values were within the acceptable uncertainty interval of 2 SD (0.06‰) when $C_{sample}/C_{standard}$ was within 1.0 to 1.5 (concentration ratio). To avoid the mass bias difference produced by the acidity mismatch, the acid molarity ratio of the samples and standard must be as close to 1 as possible. Thus, the same batch of nitric acid should be used to dilute unknown samples and standards, and the changes in the acidity of running solutions due to evaporation during analysis should be monitored.[35]

Numerous studies have confirmed that the mass bias factor is also sensitive to the concentration of running solutions.[35] An *et al.* (2014)[20] reported that the δ-Mg values increased with Mg concentration using Neptune MC-ICP-MS in wet plasma mode. In contrast, Teng and Yang (2014) [35] observed a negative correlation between the δ^{26}Mg values and ratio of the Mg concentration in the sample and standard solution using Nu Plasma MC-ICP-MS in dry plasma mode. In this study, the effect of Mg concentration mismatch on Mg isotopic analysis in wet plasma mode was evaluated using a series of 2% HNO_3 GSB-Mg solutions with different concentrations (0.1 - 0.8 μg g^{-1}), with GSB-Mg (0.5 μg g^{-1}) in 2% HNO_3 as the bracketing standard. It showed that the δ^{25}Mg and δ^{26}Mg values did not vary with the concentration ratio of standard and sample (0.2 - 1.8). In summary, although different instruments and mode conditions (wet/dry) give rise to different Mg concentration mismatch effects, ensuring that the concentrations of the samples and standards are as similar as possible can minimize such effects.

Accurate determination of Mg isotopes of reference materials. To further verify the practicality of this purification method, eleven geological standards with MgO contents ranging from 0.05 to 7.23% were purified using the newly developed method using Neptune *Plus* MC-ICP-MS. These standards include basalts (BHVO-2 and BCR-2), rhyolite (RGM-2, JR-1, JR-3, GSR-11), andesite (AGV-2), granodiorite (GSP-2), soil (GSS-2), amphibolite (GSR-15) and carbonate (COQ-1). The long-term analysis of mono-standard solutions of GSB-Mg (δ^{25}Mg = 0.00 ± 0.02‰, δ^{26}Mg = 0.00 ± 0.04‰, n = 106) demonstrated the stability of the instrument prior to analysis of the standard solutions (Fig. 4). The Mg isotopic compositions of all reference materials are summarized in Table 3, and defined a single fractionation line ranged from 0.5108 to 0.5196, which were in good agreement with the theoretical equilibrium (0.521) and kinetic fractionation (0.510) values.[36] The mean δ^{26}Mg value of GSP-2 was 0.10 ± 0.03‰ (2 SD, n = 5), which is in good agreement with previously-determined values (0.09 ± 0.03‰).[20, 21] The δ^{26}Mg values of rhyolite RGM-2, JR-1, JR-3, and GSR-11 were - 0.14 ± 0.04‰ (2 SD, n = 6), - 0.19 ± 0.05‰ (2 SD, n = 3), - 0.10 ± 0.05‰ (2 SD, n = 3), and - 0.53 ± 0.10‰ (2 SD, n = 3), respectively and they were identical to published values within 2 SD uncertainties.[19, 20, 32, 37] The δ^{26}Mg value of AGV-2 was - 0.12 ± 0.07‰ (2 SD, n = 3), and the mean

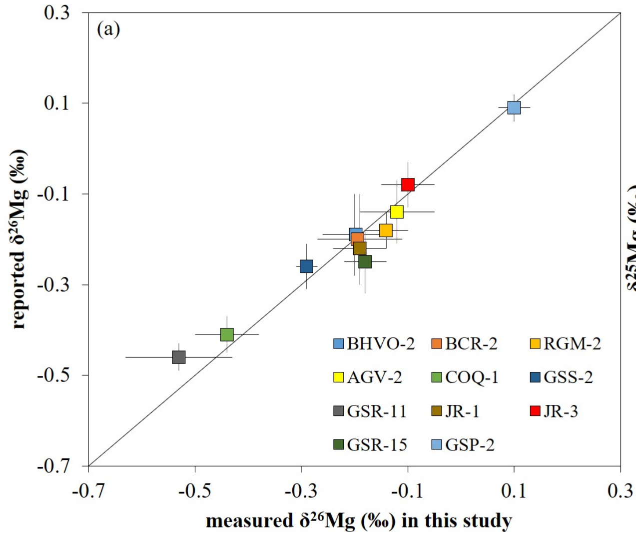


Fig. 5 (a) δ^{26}Mg values of eleven reference materials obtained in this study vs. reported values; (b) Mg three-isotope plot of twenty-four reference materials analyzed in this study, purified by established method, defines a line with a slope ranged from 0.5118, similar to the theoretical equilibrium (0.521) and kinetic fractionation (0.510) values. Error bars represent 2 SD.

δ^{26}Mg values of basalt BCR-2 and BHVO-2 were - 0.19 ± 0.08‰ (2 SD, n = 6) and - 0.20 ± 0.06‰ (2 SD, n = 6), respectively. The δ^{26}Mg values of BCR-2 and BHVO-2 were both consistent with the values measured by previous studies. [20,21,32] The measured δ^{26}Mg values of GSS-2, GSR-15, and COQ-1 were - 0.29 ± 0.02‰ (2 SD, n = 3), - 0.18 ± 0.04‰ (2 SD, n = 3), and - 0.44 ± 0.06‰ (2 SD, n = 3), respectively. In summary, the Mg isotopes of all eleven geological samples were accurately determined after purification (Fig. 5a).

For ensuring the data quality and data comparison of different laboratory, the matrix of reference materials should be matched with that of unknown samples.[14, 17, 38] In the last two decades, the consumption of reference materials with confirmed Mg isotopic composition has gradually increased. The determination of more reference materials of unknown Mg isotopes can broaden the selection range of standards and reduce the consumption of existing samples. Here, the Mg isotopic composition of a batch of CRSRI reference materials were firstly reported (Fig. 5b). Five sediment materials (GSD-1, GSD-3A, GSD-4, GSD-5, and GSS-9) were analyzed and their δ^{26}Mg values were -1.11 ± 0.12‰ (2 SD, n = 3), -0.08 ± 0.06‰ (2 SD, n = 3), -0.12 ± 0.04‰ (2 SD, n = 3), -0.24 ± 0.06‰ (2 SD, n = 3) and -0.54 ± 0.07‰ (2 SD, n = 3), respectively. Other various types of reference materials (GSR-6, GSS-1, GSS-15, GSS-16, GSR-4, GSR-5, GSR-7, and GSR-10) have δ^{26}Mg values of -1.11 ± 0.12‰ (2 SD, n = 3), -0.71 ± 0.12‰ (2 SD, n = 3), -0.40 ± 0.11‰ (2 SD, n = 3), -0.06 ± 0.01‰ (2 SD, n = 3), -0.07 ± 0.09‰ (2 SD, n = 3), 0.21 ± 0.08‰ (2 SD, n = 3), -0.50 ± 0.03‰ (2 SD, n = 3), and -0.33 ± 0.08‰ (2 SD, n = 3), respectively.

CONCLUSION

A novel highly efficient process for the purification of Mg in geological samples is presented. Most matrix elements (Ca, Ti, Na, Al, and Fe) were efficiently removed by combining the precipitation procedure after acid digestion and a column chromatography step using an optimized mixed acid ratio. This approach consumes fewer chemical reagents to achieve the efficient precipitation of K, and the entire process can be completed in a few hours. Parameters that commonly affect the accurate and precise analysis of Mg isotopes, including the matrix effect, Mg concentration, and molarity mismatch effects, were systematically investigated using the Neptune *Plus* MC-ICP-MS. No significant errors were introduced when the ratio of the HNO_3 concentrations of the sample and standards ranged from 1.0 – 1.5, and the Mg concentration ratio of the samples and standards ranged from 0.2 – 1.8. The accuracy and precision of the measurement of Mg isotopes were acceptable when Na/Mg ≤ 1, Al/Mg ≤ 0.6, K/Mg ≤ 1, Ca/Mg ≤ 0.6, Mn/Mg ≤ 2, Fe/Mg ≤ 0.2, Cu/Mg ≤ 2, Zn/Mg ≤ 10. The δ^{26}Mg values of eleven geological standard materials measured using the optimized purification method were in good agreement with published values. The Mg isotopes of thirteen CRSRI reference materials were firstly reported for quality assurance and reduce the consumption of existing reference materials. The optimized purification procedure for Mg isotope measurements is suitable for various geological samples and is less time-consuming than existing methods.

Table 3 Mg isotopic compositions for geological reference materials

Sample	Rock type	Data resource	K_2O/MgO	$\delta^{25}Mg$	2SD	$\delta^{26}Mg$	2SD	n
BHVO-2	basalt	this study	0.07	-0.10	0.05	-0.20	0.06	6
		Ref.[21]		-0.11	0.06	-0.19	0.09	
		Ref.[20]		-0.10	0.03	-0.21	0.04	
BCR-2	basalt	this study	0.50	-0.08	0.03	-0.19	0.08	6
		Ref.[21]		-0.11	0.05	-0.20	0.10	
		Ref.[20]		-0.08	0.02	-0.16	0.03	
GSP-2	granodiorite	this study	5.60	0.06	0.02	0.10	0.03	5
		Ref.[21]		0.05	0.02	0.09	0.03	
		Ref.[20]		0.03	0.01	0.04	0.02	
RGM-2	rhyolite	this study	15.3	-0.07	0.03	-0.14	0.04	6
		Ref.[21]		-0.12	0.03	-0.24	0.07	
		Ref.[20]		-0.09	0.03	-0.18	0.04	
AGV-2	andesite	this study	1.60	-0.05	0.04	-0.12	0.07	6
		Ref.[21]		-0.07	0.03	-0.14	0.07	
		Ref.[20]		-0.05	0.02	-0.11	0.01	
COQ-1	carbonate	this study	0.13	-0.23	0.03	-0.44	0.06	4
		Ref.[39]				-0.41	0.04	
		Ref.[32]				-0.47	0.07	
GSS-2	soil	this study	2.44	-0.14	0.05	-0.29	0.02	3
		Ref.[15]		-0.13	0.04	-0.26	0.05	
GSR-11	rhyolite	this study	38.8	-0.27	0.03	-0.53	0.10	3
		Ref.[38]		-0.24	0.03	-0.46	0.03	
JR-1	rhyolite	this study	44.1	-0.10	0.06	-0.19	0.05	3
		Ref.[19]		-0.12	0.03	-0.22	0.03	
JR-3	rhyolite	this study	86.0	-0.05	0.03	-0.10	0.05	3
		Ref.[19]		-0.04	0.05	-0.08	0.05	
GSR-15	amphibolite	this study	0.07	-0.09	0.03	-0.18	0.04	3
		Ref.[39]		-0.12	0.05	-0.25	0.07	
GSR-6	limestone	this study	0.15	-0.73	0.04	-1.42	0.02	3
		replicate		-0.70	0.02	-1.40	0.06	3
GSD-1	sediment	this study	0.67	-0.57	0.13	-1.11	0.12	3
GSD-3A	sediment	this study	3.98	-0.04	0.02	-0.08	0.06	3
GSD-4	sediment	this study	2.14	-0.07	0.05	-0.12	0.04	3
GSD-5	sediment	this study	2.15	-0.11	0.05	-0.24	0.06	3
GSS-1	soil	this study	1.43	-0.35	0.03	-0.71	0.12	3
GSS-9	sediment	this study	1.30	-0.28	0.05	-0.54	0.07	3
GSS-15	clay	this study	1.31	-0.21	0.04	-0.40	0.11	3
GSS-16	clay	this study	2.98	-0.02	0.04	-0.06	0.01	3
GSR-4	sandstone	this study	7.11	-0.04	0.06	-0.07	0.09	3
GSR-5	shale	this study	2.07	0.11	0.03	0.21	0.08	3
GSR-7	syenite	this study	11.5	-0.26	0.04	-0.50	0.03	3
GSR-10	gabbro	this study	0.03	-0.17	0.02	-0.33	0.08	3

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Notes

The authors declare no competing financial interest.

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