

A Review of Mg Isotope Analytical Methods by MC-ICP-MS

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ABSTRACT: Application of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has led to big breakthrough of analytical methods for metal stable isotopes, resulting in rapid progresses in non-traditional stable isotope geochemistry. As a new geological tracer, Mg isotopes have been widely applied in studies of almost all important disciplines of geochemistry. High precision Mg isotope data measured by MC-ICP-MS are now available with precision about 0.05‰ amu⁻¹ (2SD) or better. Because mass bias caused by chemical procedure and instrument can easily cause significant analytical error, it is still a challenge to obtain accurate Mg isotope data for natural samples. In this paper, we systematically review the development of analytical technique of Mg isotopes, with a detailed description of a series of important techniques used in the measurement process, including calibration of instrumental mass-bias, chemical purification process, matrix effect, and pitfalls for high precision isotope analyses. We compare standard data from different labs and establish a guideline for Mg isotope analysis procedure. Additionally, we briefly discuss the behaviors of Mg isotopes during geological processes including equilibrium and kinetic Mg isotope fractionations, such as magma differentiation, chemical and thermal diffusion, and continental weathering. Finally, we propose some future prospects for Mg isotope geochemistry in both high and low temperature geological processes.

KEY WORDS: magnesium isotope, MC-ICP-MS, isotope fractionation.

0 INTRODUCTION

Magnesium is the third-most abundant lithophile element in the Earth, one of the most abundant elements in the Earth's mantle (MgO=37.8 wt.%) (McDonough and Sun, 1995), the continental crust (MgO=4.66 wt.%) (Rudnick, 2003), and seawater (Mg%=~0.13 wt.%) (Millero, 1974). The mantle is the Earth's largest Mg reservoir containing >99% of Earth's Mg inventory. Mg is a non-gaseous element on an atomic basis in the solar system with a moderately refractory nature ($T_c(\text{Mg}_2\text{SiO}_4)=1\ 430\ ^\circ\text{C}$) (Lattimer et al., 1978). Volatility of Mg is between the most refractory elements (e.g., Al, Sr, Eu, and Ca) and the moderately volatile elements (e.g., Fe). Magnesium is also a fluid-mobile element and plays an important role in the fluid-rock interaction and hydrological and biological systems.

Mg has three stable isotopes, ²⁴Mg, ²⁵Mg, and ²⁶Mg, with natural abundances of 78.99%, 10.00% and 11.01%, respectively. The relatively mass difference between $\delta^{24}\text{Mg}$ and $\delta^{26}\text{Mg}$ is ~8%, large enough to produce significant Mg isotopic fractionations in geochemical processes. Magnesium stable isotope data are reported using the standard per mil (‰)

notation of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, i.e., the per mil deviation of the measured $^{26}\text{Mg}/^{24}\text{Mg}$ and $^{25}\text{Mg}/^{24}\text{Mg}$ ratios of the unknowns relative to those of the reference standard DSM-3. $\delta^x\text{Mg}=[(^x\text{Mg}/^{24}\text{Mg})_{\text{Sample}}/(^x\text{Mg}/^{24}\text{Mg})_{\text{Standard}}-1]\times 1\ 000$ (where $x=25$ or 26); in addition, Mg isotopic fractionation between two phases A and B is expressed as: $\Delta^{26}\text{Mg}_{\text{A-B}}=\delta^{26}\text{Mg}_{\text{A}}-\delta^{26}\text{Mg}_{\text{B}}\approx 10^3\ln\alpha_{\text{A-B}}$; the uncertainty is reported at 95% confidence level (2σ).

Measurements of Mg isotopic ratios by MC-ICP-MS revealed that there is approximately 5‰ range in the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio in terrestrial materials (Brenot et al., 2008; Pogge von Strandmann et al., 2008a; Tipper et al., 2008a, 2006a, b; Galy et al., 2002). The lightest values were observed in marine sediments and carbonates ($\delta^{26}\text{Mg}=-5.57$ – -1.09) (Wombacher et al., 2011; Higgins and Schrag, 2010; Hippler et al., 2009; Brenot et al., 2008; Pogge von Strandmann et al., 2008a; Tipper et al., 2006a; Young and Galy, 2004) and the heaviest isotopic ratios were found in shales and soils ($\delta^{26}\text{Mg}=+0.49$ to $+0.92$) (Huang et al., 2012; Li et al., 2010), likely reflecting low temperature aqueous processes such as chemical weathering reactions and kinetic mineral precipitation. Mg isotopes can also be significantly fractionated due to chemical or thermal diffusion, or equilibrium between minerals with different crystalline structure (Liu et al., 2011; Huang et al., 2010; Richter et al., 2008, 2003). Therefore, Mg isotopes could serve as a novel geochemistry tracer to address a variety of high- and low-temperature geological processes.

Variations of $\delta^{26}\text{Mg}$ in meteorites measured by thermal ionization mass spectrometry (TIMS) could be up to 10‰ in

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previous studies (Galy et al., 2000). However, low precision of ~1‰ of TIMS method is insufficient to resolve the small variations and mass-dependent fractionation of Mg isotopes in natural samples (Young and Galy, 2004). The advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and novel sample digestion and purification techniques have significantly improved analytical precision so that Mg isotopic variations in geological samples can be well resolved.

The light mass of Mg means larger instrumental mass bias than heavy elements during measurement by MC-ICP-MS. Significant analytical artifacts can also be derived from imperfect chemical procedure, standard solution storage problems, and contamination (Wang et al., 2011; Huang et al., 2009b; Wombacher et al., 2009; Young et al., 2009; Galy et al., 2001). Mg isotopic compositions of some widely studied standards measured in international labs are even inconsistent with each other, including San Carlos olivine, BCR-1, and BCR-2 (Fig. 1). Therefore, it is still challenging to obtain accurate and precise data for Mg isotopic compositions of natural samples.

In this paper, we review protocols of Mg isotope analytical procedure recently published in literature. Our purpose is to give a detailed description of the measurement process, especially focusing on calibration of instrumental mass-bias, chemical purification process, matrix effect, and other pitfalls for high precision isotope analyses. More studies are needed to improve the precision and accuracy of Mg isotope analyses for better understanding Mg isotopic variations in nature samples. The rapidly growing database will allow more applications of Mg isotope geochemistry to address the fundamental geological processes.

1 ANALYTICAL METHODS

1.1 Instrumentation

Preliminary studies of Mg isotope measurements using TIMS produced a poor precision of ~1‰–2‰, which is comparable to the extent of Mg isotope fractionation in nature systems (Lee and Papanastassiou, 1974; Catanzaro and Murphy, 1966). MC-ICP-MS offers the opportunity for high-precision measurements of Mg isotopes with two standard deviations of $\delta^{26}\text{Mg}$ better than 0.10‰.

Mg isotopic compositions have been determined by MC-ICP-MS using both laser ablation and solution aspiration. Although new instruments are also available in market during writing this paper, here we just summarize four types of MC-ICP-MS which were commonly used for Mg isotope measurement in the literature.

(1) The Nu-plasma is a double focusing magnetic sector instrument with variable dispersion ion optics and an array of Faraday collectors equipped with $10^{11} \Omega$ resistors (Belshaw et al., 1998). During isotopic measurement at a low resolution mode ($M/\Delta M \approx 400$), samples and standards were diluted with 3% double-distilled HNO_3 to ~0.2 ppm. The ^{24}Mg intensity variation is less than 5%. Samples are introduced into the argon plasma torch through an auto-sampler and aspirated via a desolvating nebulizer (DSN) (Huang et al., 2009b) or directly using wet-plasma method (Li et al., 2010; Teng et al., 2010a).

(2) The isoprobe is a single focusing magnetic sector

ICP-MS equipped with a hexapole collision cell (Rehkämper and Mezger, 2000). The collision cell was flushed with 99.999 9% purity helium gas for a collision gas (Chakrabarti and Jacobsen, 2010; de Villiers et al., 2005). Mg solutions are diluted to 0.5–5 ppm (Bolou-Bi et al., 2009; de Villiers et al., 2005). Similarly, sample solutions were introduced into the Ar plasma torch, then the ion beam passing the hexapole cell, and finally entering the magnetic analyser (Bolou-Bi et al., 2009).

(3) Mg isotopes were also measured on an Axiom MC-ICP-MS (Wombacher et al., 2011, 2009). Usually ~50 ng of Mg would be consumed for a single analysis. The superior washout characteristic of the glass spray chamber allows very fast alteration (one second) between samples and standards with good repeatability. The Apex-Q inlet system was employed for the majority of analyses because of its good washout features, signal stabilities and similar signal enhancement (Wombacher et al., 2009).

(4) The Neptune is a double focusing MC-ICP-MS with the capability of high mass resolution measurements in multi-collector mode. It was equipped with eight motorized Faraday cups and one fixed central channel where an ion beam can be switched between a Faraday detector and an ion counter. In-situ monitoring of the detector position at the optical bench of the multi-collector ensures precise and reproducible cup positioning (Weyer and Schwieters, 2003). Polyatomic interferences can be detected using the ion counter and low resolution entrance slit. The “moist” plasma introduction system (an Apex-Q chamber) yields a higher Mg sensitivity compared to wet plasma and similar interferences (e.g., $^{12}\text{C}_2^+$, $^{12}\text{C}^{14}\text{N}^+$, and $^{25}\text{MgH}^+$) to “dry” plasma conditions (Pogge von Strandmann et al., 2011).

1.2 MC-ICP-MS Measurement

An advantage of MC-ICP-MS for stable isotope measurement relative to TIMS is that instrumental mass bias is rather constant and can be accurately corrected. The standard-sample bracketing technique was used for this drift calibration. During Mg isotope measurements, ^{24}Mg , ^{25}Mg , ^{26}Mg as well as ^{27}Al and ^{23}Na ion beams were measured in order to verify that Al and Na peak tails are negligible relative to Mg signal. The “dry” plasma conditions with the DSN increases sensitivity and minimizes introduction of H_2O , CO_2 , O_2 , and N_2 into the plasma, thus reducing the isobaric effects of interfering molecular species (Galy et al., 2001), but the DSN could add contamination to the samples. On the other hand, using “wet” plasma with a quartz cyclonic spray chamber and a micro-uptake glass concentric nebulizer can achieve higher precision but consume more samples (Li et al., 2010; Teng et al., 2010a). Therefore, we should choose the right conditions of instruments based on the amount of analyzed samples. Generally, the average long-term repeatability of Mg isotope measurements obtained on the Nu-plasma is marginally better than the precision reached by the isoprobe (Galy et al., 2001).

The in-situ laser ablation (LA)-MC-ICP-MS has been used widely in determining isotopic composition of minerals due to its high spatial resolution, low blank, speed and simplicity of analytical processes. However, conflicting result exists between LA-MC-ICP-MS Mg isotope studies of mantle olivine by

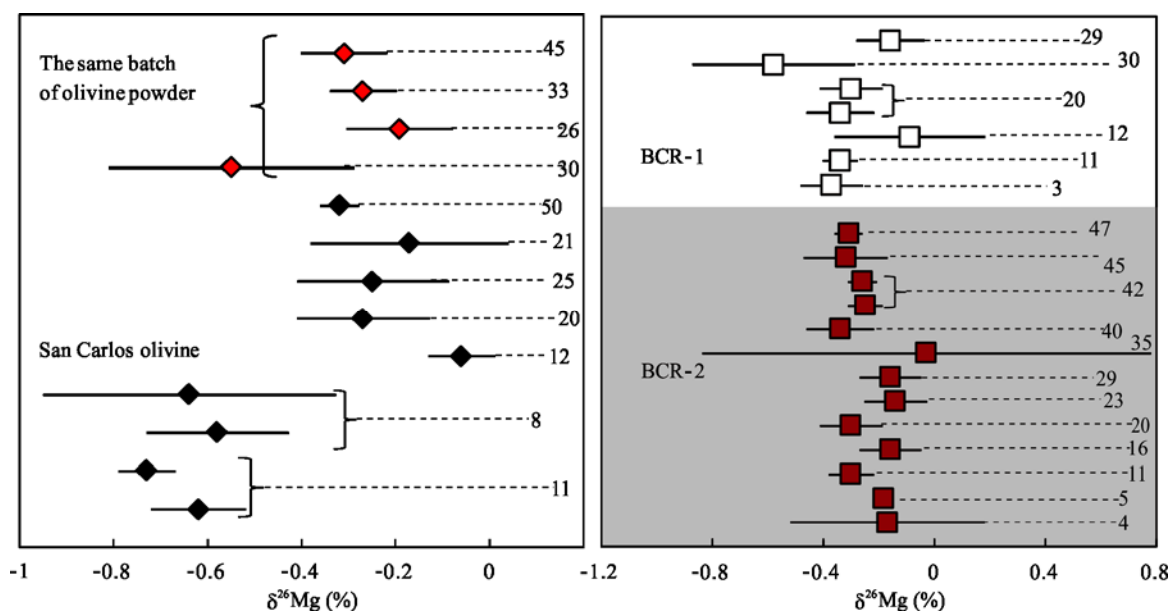


Figure 1. Comparison of Mg isotope data for reference samples (‰) San Carlos olivine, BCR-1 and BCR-2 from different laboratories. Data sources are listed in Table 1. Red diamond symbols: Measured Mg isotopic compositions of different aliquots of homogenized San Carlos olivine powder in different laboratories at Arizona State University, Oxford University and University of California at Los Angeles. Other diamond symbols represent different grains of San Carlos olivine. Error bars in this figure represent 2SD.

Pearson et al. (2006) and Norman et al. (2006). The former discovered $\sim 2\%$ amu^{-1} variations while the latter only found minimal ranges within their analytical uncertainties, respectively. Handler et al. (2009) re-analyzed the same olivine samples in Pearson et al. (2006) using solution MC-ICP-MS and did not observe heterogeneous Mg isotopic compositions in olivine within current error. Thus they pointed out that there are probably unresolved analytical issues with the LA-MC-ICP-MS analytical method employed by Pearson et al. (2006) which can result in apparent greater Mg isotope variations than the true isotopic variability. Several major technical issues must be carefully evaluated when using this method: matrix match between the standard and the sample, intrinsic signal instability, subsequent aerosol transport to the ICP torch, and isotope fractionation in ablation pits (Pearson et al., 2006).

1.3 Reference Materials

Routine measurement of reference materials is critical for normalizing instrumental mass bias, justifying data quality, and inter-lab data comparison. Widely used standards include the DSM-3 and Cambridge-1 (CAM-1), provided by Dr. Albert Galy in Cambridge University. These two standards have been well characterized in multiple laboratories. Several basalt standards such as BHVO-1 and BCR-1 were also reported to show the data quality for whole rock analyses (Pogge von Strandmann et al., 2011; Bourdon et al., 2010; Chakrabarti and Jacobsen, 2010; Huang et al., 2009b; Teng et al., 2007; Wiechert and Halliday, 2007; Baker et al., 2005; Bizzarro et al., 2004; Young and Galy, 2004). Measurements of these basalt standards over long periods were used to detect analytical biases. In the following section, we will summarize standard data reported in the literature.

NIST SRM 980 Mg: this standard consists of metal chips

weighing between 1 and 50 mg and each unit delivered by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) corresponds to a bottle of solution containing about 0.3 g Mg. Mg isotopic composition of the SRM 980 was initially measured using TIMS technique with error for $\delta^{26}\text{Mg}$ of 1.87‰ (Catanzaro and Murphy, 1966). With better precision achieved by using MC-ICP-MS, Mg isotopic heterogeneity in NIST SRM 980 Mg metal chips was revealed, and thus SRM 980 Mg are unsuitable as a reference material (Galy et al., 2003).

IRMM-3704: this standard was supplied by the European Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium. It is a homogeneous Mg solution that was prepared from NIST-980 Mg metal, containing 3 mL 1 M HNO_3 with approximately 60 ppm Mg, and was initially intended for use as a zero-delta material. However, this is not an ideal Mg standard because its $\delta^{26}\text{Mg}$ value is -3.7% , far from that of major Mg reservoirs on the Earth.

DSM-3 and CAM-1: DSM-3 (provided by Dead Sea Magnesium Ltd., Israel) is homogeneous and mono-elemental Mg solution made from pure Mg metal. Two large batches (around 10 g of pure Mg metal in each) of 10 000 ppm Mg solutions (dissolved in 0.3 M HNO_3) were prepared and well characterized by Albert Galy, Cambridge University (Galy et al., 2003). These 2 solutions were named as DSM-3 and CAM-1, which have been widely used for international reference materials. The Mg isotopic composition of DSM-3 is very similar to that of carbonaceous chondrites (such as Orgueil and Allende) and terrestrial samples. Therefore, offset of Mg isotopic ratios relative to DSM-3 are effectively close to values reported relative to “chondrites”. Galy et al. (2003) suggested using DSM-3 as the primary isotopic (zero-delta) reference material to report Mg-isotopic variations.

Table 1 Continued

$\delta^{26}\text{Mg}$	13	14	15	16	17	18	19	20	21	22	23	24
	Pogge von Strandmann et al. (2008a)	Pogge von Strandmann et al. (2008b)	Pogge von Strandmann et al. (2008c)	Tipper et al. (2008a)	Tipper et al. (2008b)	Bolou-Bi et al. (2009)	Hipper et al. (2009)	Huang et al. (2009b)	Handler et al. (2009)	Shen et al. (2009)	Wombacher et al. (2009)	Yang et al. (2009)
CAM-1	-2.64±0.08	-2.78±0.15	-2.78±0.15	-2.592±0.087	-2.592±0.087	-2.62±0.13	-2.58±0.04	-2.63±0.11		-2.61±0.18	-2.64±0.23	-2.63±0.09
BCR-1								-0.30±0.11				
BCR-2					-0.16±0.11			-0.30±0.11			-0.14±0.11	
BHVO-1								-0.30±0.08				
BHVO-2		-0.25±0.11										
BIR-1											-0.23±0.23	
DTS-1								-0.33±0.14			-0.25±0.08	-0.30±0.05
DTS-2												-0.38±0.14
												-0.32±0.07
PCC-1								-0.22±0.10				
W-2												
GA						-0.75±0.14		-0.34±0.15				
GSN-1								-0.24±0.23				
Allende												-0.28±0.1
Murchison												-0.31±0.06
Orgueil												
San								-0.27±0.14	-0.171±0.21			-0.32±0.04
Carlos ol.												
Bulk silicate earth					Chondritic			Chondritic	Chondritic			Chondritic

Although DSM-3 has provided an ideal international standard for a short term, it is not a standard certified or issued by a reference material institute (Vogl et al., 2004). Therefore, a new, certified, and homogeneous SI-traceable material is required by the community in the long run. CAM-1 has been suggested as a secondary reference solution (analytical grade atomic absorption standard Mg solution) and it has also been widely analyzed, yielding similar $\delta^{26}\text{Mg}$ values of $-2.61 \pm 0.05\%$ (Fig. 2). The difference between DSM-3 and CAM-1 covers up to 44% of the terrestrial Mg isotopic variations reported so far.

San Carlos olivine: San Carlos olivines are natural mantle olivine from San Carlos, Arizona, USA with Mg# from 90 to 91. They occur as small (<5 mm) single gem-quality grains from disaggregated spinel peridotite xenoliths. Consensus on $\delta^{26}\text{Mg}$ of San Carlos olivine has not been reached so far (Chakrabarti and Jacobsen, 2010; Liu et al., 2010; Huang et al., 2009b; Tipper et al., 2008a; Teng et al., 2007; Wiechert and Halliday, 2007). The differences among reported values could result from sampling biases, Mg isotopic heterogeneity, and analytical artifacts. To rule out the effects of sample heterogeneity, Chakrabarti and Jacobsen (2010) powdered and mixed ~50 g of hand-picked fresh San Carlos olivine. They dissolved ~100 mg of this homogeneously mixed powder from this large batch to prepare a concentrated stock solution. However, as discussed later, $\delta^{26}\text{Mg}$ of the homogenized San Carlos olivine powder measured in a few laboratories is still not consistent, suggesting that analytical artifact may be the reason for the inconsistency (Chakrabarti and Jacobsen, 2010; Liu et al., 2010; Young et al., 2009).

To assess the accuracy and long-term external precision, several rock reference standards were also widely analyzed for inter-lab comparison, such as basalts BIR-1 (USGS), BE-N (CRPG) and BHVO-1 (Halemaumau, Hawaii) rock standards, serpentinite UB-N (CRPG), dunite DTS-1 (USGS), peridotite JP-1, harzburgite PCC-1 (Cazadero ophiolite, California), diabase (W-1), andesite (AGV-1), granite (French granite standard GA and USGS granite standards G-2, GSP-1, and GSN-1), magnesite, magnesia, and commercial chlorophyll (see Table 1 for details). It is important to note that Mg isotope data can be accepted by the community only if the measured standard values are consistent and accurate.

1.4 Sample Digestion and Purification Procedures

High-precision Mg isotope data can only be obtained with extreme cautions on digestion and chemical purification. Here we summarize the procedures described in recent literatures.

1.4.1 Sample preparation

The digestion procedures are slightly different based on characteristics of samples. Ultrapure concentrated hydrochloric/nitric acids or acids prepared by sub-boiling distillation, and 18.2 M Ω Milli-Q water are used to minimize the procedural blanks. Based on the Mg contents of samples, approximately 5–10 mg of minerals or whole-rock powder were dissolved in capped teflon beakers or high pressure bomb (Bizzarro et al., 2011; Teng et al., 2010a; Young et al., 2009). Mixture of concentrated HF-HNO₃ (~3 : 1, v/v) was normally used for digestion. After samples were evaporated to dryness, they were

treated with aqua regia and dried again. Then they were re-fluxed with concentrated HNO₃ to remove residual fluorides and were finally dissolved in 1 N HNO₃ ready for column chemistry. After digestion procedure, it is important to note that no secondary precipitates or residual materials should be observed in the solution. Samples can be centrifuged to ensure complete dissolution before resin loading if no significant Mg is lost to the residue. For soil and plant samples, hydrogen peroxide (H₂O₂) can be added for complete digestion of the organic matter (Bolou-Bi et al., 2009). For loess and shale samples, a few drops of HClO₄ were added (Li et al., 2010).

1.4.2 Chemical purification

Separation of matrices is required for precise and accurate Mg isotope data. In order to reduce potential matrix effects, isobaric interferences, and isotope fractionation during the chemical separation process (Chang et al., 2003), it is necessary to achieve excellent separation of matrix elements and complete recovery of Mg. The matrices should be low enough to eliminate observable bias. For this purpose, dissolved samples were passed through chromatographic columns with cation resins to purify Mg from other elements. Commonly used resins include Bio-Rad AG[®] 50W-X12 resin (200–400 mesh, hydrogen form) (Huang et al., 2009b; Pogge von Strandmann, 2008; Black et al., 2006; Baker et al., 2005; Chang et al., 2003) and Bio-Rad 200–400 mesh AG[®] 50W-X8 resin (Liu et al., 2010; Teng et al., 2010a, b, 2007; Wombacher et al., 2009; Yang et al., 2009). The strongly cross-linked (X12) (200–400 mesh) cation exchange resin has high separation efficiency, while the medium cross-linkage type (X8) allows for faster fluid flow (by gravity) (Wombacher et al., 2009). In some works, anion exchange resin such as Bio-RadTM AG1-X8 (Teng et al., 2010a; Young et al., 2009; Wiechert and Halliday, 2007), AG1-X4 (Schiller et al., 2010a, b), Eichrom Ni-spec resin (Schiller et al., 2010a, b), and AG[®] MP-1M (Bolou-Bi et al., 2009) were also used to remove Mn, Ti, Fe, Ni, Cu, and Zn from Mg.

In order to verify that chemical procedure does not fractionate Mg isotopes, standard solutions were recommended to be processed through chemistry. Samples containing 20–100 μg of Mg (more than 10 times of the amount required for MC-ICP-MS analysis) were loaded onto the columns. Although an individual analysis can be processed with only 200 ng of Mg, it is better to work with large amount of Mg to eliminate the baseline contribution from blank (acid, column and resin) if the column is not overloaded. The Mg elution curves (Fig. 3) were carefully calibrated using different samples including pure Mg standard solutions and dissolved rocks with different compositions (such as granite, basalt, and andesite). An adequate separation of Mg (with >99% yield) from other matrix elements such as K, Fe, Al, Ca, Na, or Ti can be obtained by passing the Bio-Rad AG[®] 50W-X12 cation exchange column twice (Huang et al., 2009b). Ni cannot be effectively removed but the matrix effect of Ni for most samples is insignificant because it is a trace element in most natural samples (Handler et al., 2009; Huang et al., 2009b).

Some studies have also described quite different approaches for the separation of Mg dependent on the chemical

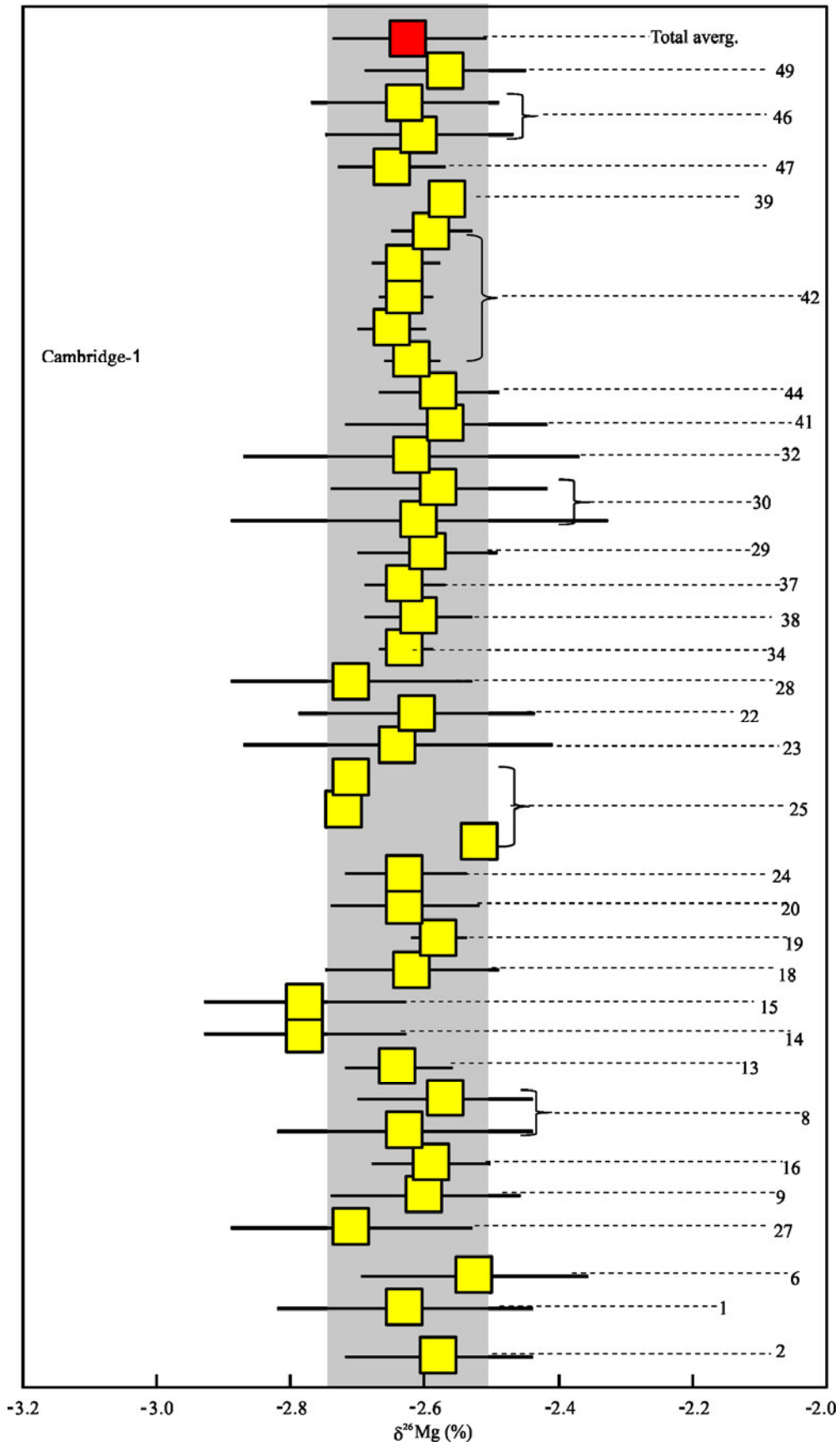


Figure 2. Comparison of Mg isotope data for reference samples (‰) Cambridge-1 from different laboratories. Error bars in this figure represent 2SD.

composition of samples, including seawater and carbonates (Chang et al., 2003), chlorophyll-a extracted from cyanobacteria (Black et al., 2006), basalts (Teng et al., 2007), and alkali-rich samples (granite, soil, plants) (Bolou-Bi et al., 2009). Despite the different details for purification procedures, there are a few general tips for successful separation: not overloading the column, checking Mg yields for each sample, and checking all matrices in the purified Mg solution. Obviously, for the latter two tips, we can only check several samples for those with similar nature and matrix compositions.

1.5 Magnesium Isotope Measurements

Two major obstacles for high precision measurements are briefly reviewed here, i.e., isobaric interferences and instrumental mass bias. The most important isobaric interferences include $^{48}\text{Ti}^{++}$, $^{48}\text{Ca}^{++}$, $^{12}\text{C}^{12}\text{C}^+$ for ^{24}Mg , $^{50}\text{Ti}^{++}$, $^{50}\text{Cr}^{++}$, $^{12}\text{C}^{13}\text{C}^+$ for ^{25}Mg , and $^{40}\text{Ar}^{12}\text{C}^{++}$, $^{52}\text{Cr}^{++}$, $^{12}\text{C}^{14}\text{N}^+$, $^{12}\text{C}^{13}\text{CH}^+$ for ^{26}Mg . Isobaric interferences can be eliminated, decreased, or effectively corrected by excellent chemical purification, applying suitable instrumental setups (e.g., high resolution, desolvation, collision cells), and calibration based on standard analyses during data reduction.

Instrumental mass bias is caused by preferential transmission of isotopes with different mass. Instrumental mass bias of Mg isotopes is normally corrected by sample-standard bracketing method because Mg has only three isotopes and thus the double-spike technique is not applicable. In this method, analyses of the sample solutions are bracketed by standard solutions, and isotope ratios of samples are simply referenced to the average values of the bracketing standard. The concentrations of sample and standard solutions should be similar with difference less than $\pm 10\%$. Cross-contamination between samples and standards can be eliminated by washing the instrument with diluted HNO_3 for enough time. Standard solutions (e.g., CAM-1 and BCR-1) should be regularly measured to monitor instrumental stability and reproducibility. It should be noted that, because samples have tiny amount of matrices different with a pure Mg bracketing standard, excellent separation of Mg from matrix elements is required for precise and accurate Mg isotope measurement.

2 RESULTS: INTER-LABORATORY COMPARISON FOR MG ISOTOPE DATA OF STANDARDS

We summarized $\delta^{26}\text{Mg}$ data for reference materials reported in literature in Table 1. Generally, there is excellent agreement of the offset between pure Mg solution standards such as DSM-3 and CAM-1 (Fig. 2), and non-silicate samples like seawater (Fig. 4). However, data for whole rock and mineral standards show larger variations, such as BCR-1/-2, San Carlos olivine, and the granite standard GA (Li et al., 2010, -0.26 ± 0.07 ; Huang et al., 2009a, -0.34 ± 0.15 ; Bolou-Bi et al., 2009, -0.75 ± 0.14) (Fig. 5). Figure 5 shows a relatively comprehensive comparison for Mg isotopic compositions of terrestrial rocks, minerals, and chondrites measured in different laboratories. $\delta^{26}\text{Mg}$ values reported in most studies are consistent within the uncertainties with the exception of one investigation (Chakrabarti and Jacobsen, 2010) which reported systematically lighter Mg isotope compositions by 0.2% – 0.7% .

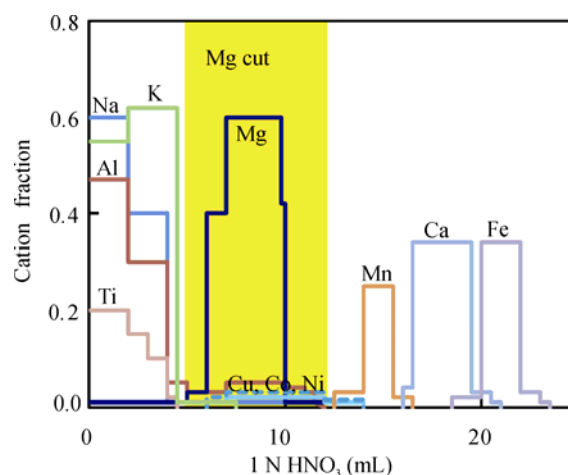


Figure 3. Elution curves of Mg and matrix elements for natural samples. Generally, alkaline metal elements and Ti-Al are eluted before Mg cut. Mn, Fe, and Ca are eluted after Mg cut. Cu, Co, and Ni cannot be removed effectively but the matrix effect of them is insignificant. Modified from Wang et al. (2011); Huang et al. (2009b); Wombacher et al. (2009); Teng et al. (2007).

Although Mg isotopic compositions of standards were measured under great scrutiny, the reported Mg isotope data still showed significant inconsistency greater than the claimed error of 0.1% (2σ), hindering direct comparison of results obtained in different laboratories and application of Mg isotope geochemistry in many fundamental problems.

$\delta^{26}\text{Mg}$ values of one of the most commonly analyzed USGS basaltic rock standards, BCR-1 and its second generation equivalent BCR-2, vary from $-0.09\% \pm 0.27\%$ (Wiechert and Halliday, 2007) to $-0.58\% \pm 0.29\%$ (Chakrabarti and Jacobsen, 2010) (Fig. 1). The $\delta^{26}\text{Mg}$ value of BCR-2 determined by standard addition method (Tipper et al., 2008b) is consistent with that of Bizzarro et al. (2004), Baker et al. (2005) and Wombacher et al. (2006) within an error of 0.03% , but it is different from the data in Teng et al. (2007) and Huang et al. (2009b) ($-0.30 \pm 0.11\%$, 2SD) by an offset of 0.15% . Similarly, the average $\delta^{26}\text{Mg}$ value of BCR-1 reported in Huang et al. (2009b) ($-0.34\% \pm 0.12\%$) is consistent with that obtained by Teng et al. (2007) ($-0.34\% \pm 0.06\%$), Young and Galy (2004) ($-0.37\% \pm 0.11\%$), but lighter than other reported values (Bourdon et al., 2010; Wiechert and Halliday, 2007; Baker et al., 2005; Bizzarro et al., 2004).

Although it is still not clear what is the reason for the different $\delta^{26}\text{Mg}$ values of standards reported in the literature, it is most likely due to analytical procedures as indicated by the measurement of San Carlos olivine. The $\delta^{26}\text{Mg}$ values of San Carlos olivine showed considerable variations from -0.06% to -0.73% larger than the claimed precision (-0.05% amu^{-1}) (Pearson et al., 2006, -0.58% and -0.64% ; Wiechert and Halliday, 2007, $-0.06\% \pm 0.03\%$; Teng et al., 2007, average $-0.68\% \pm 0.10\%$; Handler et al., 2009, $-0.17\% \pm 0.07\%$; Huang et al., 2009b, $-0.27\% \pm 0.14\%$). This variation could reflect Mg isotopic heterogeneity of the olivines (Pearson et al., 2006) or analytical artifacts. In order to answer this question, a batch of homogenized San Carlos olivine powder were made and meas-

ured in a few labs using Thermo Neptune MC-ICP-MS, GVI IsoProbe-P MC-ICPMS, and Nu Plasma MC-ICP-MS and the reported $\delta^{26}\text{Mg}$ values still have a significant range from -0.19‰ to -0.55‰ (Fig. 1) (Young et al., 2009, -0.19‰ ; Chakrabarti and Jacobsen, 2010, -0.55‰ ; Liu et al., 2010, -0.27‰ ; Bouvier et al., 2013, -0.31‰). This indicates that the inter-laboratory discrepancies for standards may not be due to Mg isotopic heterogeneity but inter-laboratory offsets.

Uncertainties of Mg isotope compositions of chondrites also exist in different laboratories. There are clear systematic differences in the Mg isotopic compositions between different types of carbonaceous chondrites (such as CI chondrite Orgueil, CM2 chondrite Murchison, and CV3 chondrite Allende). Notably, the observed ^{26}Mg range in Orgueil is from 0.0 (Young and Galy, 2004; Galy et al., 2003) to -0.365‰ (Young et al., 2009) (Fig. 5). However, Teng et al. (2010a) have analyzed different types of chondrites and showed that they have relatively homogeneous Mg isotopic composition. Consequently, these dis-

crepancies in different labs should reflect analytical artifacts rather than sample heterogeneity in primitive meteorites. Additionally, researchers have also reported that Mg isotopes can be fractionated in carbonaceous chondrites (CM2) (Bouvier et al., 2013) and thus we should clarify the true reason for Mg isotopic variations before the comparison of data from different labs. All above factors can cause additional uncertainty of comparison of $\delta^{26}\text{Mg}$ values of the Earth with planetary materials.

3 DISCUSSION

3.1 How to Get Perfect Purification for Mg?

Because Mg isotopes can be significantly fractionated during ion exchange reactions (Chang et al., 2003), it is vital to obtain $\sim 100\%$ Mg yield from the purification process. In the elution process, solutions before and after the Mg cut are collected and analyzed for Mg content to check the yield. Potential matrix species (e.g., Na, Fe, Ca, Cr, Ti, and Ni) of the purified

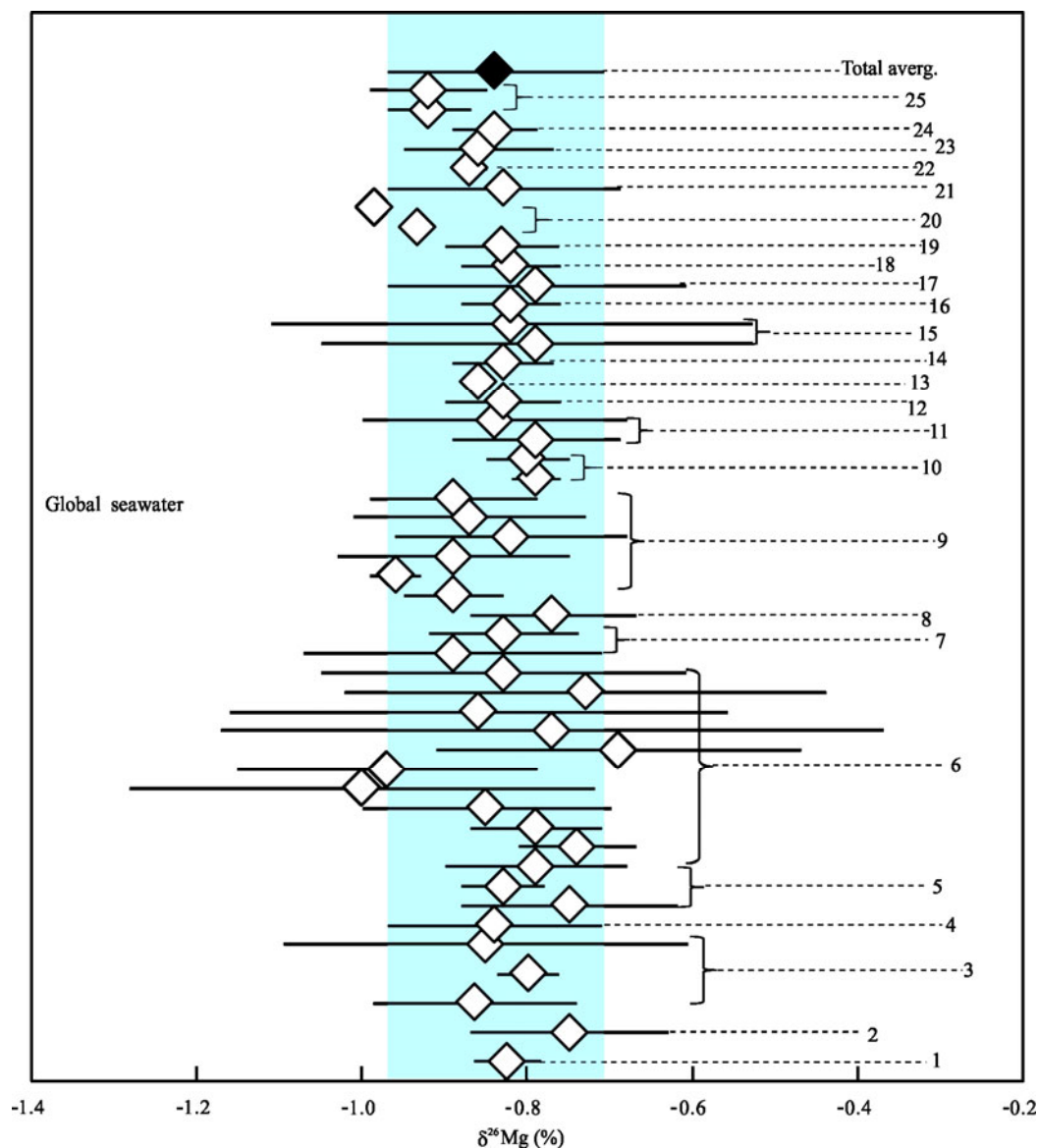


Figure 4. Compilation of published estimates of the Mg isotopic compositions of seawater. Data sources are listed in Table 2. Error bars in this figure represent 2SD. The grey band represents the average $\delta^{26}\text{Mg}$ of all the seawater samples.

Mg solution should be checked before Mg isotope analysis.

The total procedural Mg blank should be negligible relative to the amount of Mg in samples. For instance, some authors report the procedural blank as low as <10 ng, which is insignificant relative to the amount of Mg loaded to the column for most samples (>10 µg) (Bourdon et al., 2010; Teng et al., 2010a; Tipper et al., 2006a). However, the blank contribution could become a problem if the amount of Mg is only a few µg or less (e.g., corals and planktonic foraminifera). And thus double-distilled acids, clean column and resin should be used to reduce this effect.

3.2 Reproducibility and Accuracy

Precision and accuracy of Mg isotope data are evaluated by replicated measurements of samples and standards including pure Mg solution standards, seawater, synthetic multi-element standards, and mineral and rock reference materials over a long period of time. These standards provide direct assessment of accuracy and precision which can be compared among different labs. The errors reported in most studies are normally denoted by two standard deviation of repeat measurements (2SD), representing the maximum, long-term external precision for Mg isotope measurements. This is more conservative than the standard error 2SE values ($2SE=2SD/\sqrt{n}$, where n is the number of replicate analyses) unless student's T is considered. These analyses include independent digestions of the same rock powder (or standard materials) processed in different chemical separation batches, duplicate column chemistry using aliquots of the same bulk raw solution, and re-measurements of purified Mg solution on different days.

3.3 Pitfalls for Mg Isotope Measurement

Many pitfalls may cause significant artifact for Mg isotope measurement, including storage of Mg standard solution, effects of invisible matrices, Mg blank, and organics leached from resin during chemical purification, and influences of concentration mismatch and isobaric interference ($^{12}\text{C}^{14}\text{N}^+$). In the following sections, we will review the effects of these factors.

3.3.1 Fractionation in purification

Chemical purification process can cause significant Mg isotope fractionation if yield of Mg is not high enough (Teng et al., 2007; Chang et al., 2003). Overloading the cation resin column may result in low Mg yield because the Mg peak may be eluted earlier than the normal position (Huang et al., 2009b). The amount of sample loaded to the column can also affect the efficiency of Mg separation because the capacity of the column depends on the amount of resin and the length of the column. Low sample loads may improve Mg separation from the matrix but the effect of acid and column blanks could be amplified. Therefore, to monitor whether there is Mg isotope fractionation or other analytical artifacts occurred during the Mg purification process, aliquots of Mg standard solutions should be processed with similar procedure of the samples. We can also test the column effect by loading the same sample solution through chemistry for multiple times.

3.3.2 The matrix effects

Although most matrix elements (Na, Al, K, Ti, Mn, Zn, Ca, and Fe) in samples can be well separated by chemical procedures, a few percent residual elements may still lead to mass-dependent fractionations and artifacts of Mg isotopic measurements. Mg purity required for accurate isotope analyses varies depending on running conditions for different MC-ICP-MS instruments. Therefore, it is critical to know to what level the matrix starts causing significant effect. Notably, the effect of some specific matrix elements can be dramatic for certain samples such as Ni for Ni-rich samples (e.g., chondrites), Ca for low-Mg carbonate samples, Ti, Mn and Fe for silicate samples and sediments, and Fe for mafic minerals and chondrites (Wiechert and Halliday, 2007).

The most important way to decrease the matrix effect is decreasing the amount of matrix materials introduced to the MC-ICP-MS. Although chemical separation procedures vary in different laboratories, the final goal is always to obtain sufficiently pure Mg solutions for analysis. Different types of resin and eluent medium can be used to decrease the matrix effects. For example, the Eichrom DGA resin column quantitatively removes Ca, and thus interference from Ca is avoided. Using HCl as an eluent medium can have smaller $^{12}\text{C}^{14}\text{N}$ interference on ^{26}Mg observed than the case of using HNO_3 (Black et al., 2006). Pogge von Strandmann (2008) used HNO_3 as an eluent (rather than HCl) to purify carbonates, leading to Mg complete separation from Ca^{2+} and a low total procedural blank (0.17 ng). Trace amounts of HF can also be added in the eluting acid with two advantages: (1) Fe is eluted prior to Mg and (2) the separation of Al and Ti from Mg is more rapid and quantitative (100%) (Schiller et al., 2010a; Handler et al., 2009).

3.3.3 Invisible matrix effects

Besides the observed matrices by MC-ICP-MS, there are some organic materials impurities and blank coming from the resin or the samples (Pietruszka and Reznik, 2008). Although the organic matrices may be invisible to the detectors of the MC-ICP-MS, they may also cause significant fractionation especially for samples with small amounts of Mg (i.e., <3 µg) (Huang et al., 2009b; Chang et al., 2003; Galy et al., 2002). Such effects of "invisible matrix" have been observed in systematic tests on igneous rocks with very low MgO content (<0.5 wt.%). These results showed a systematic change to significantly lighter isotopic composition (up to 1‰ lighter) (Fig. 6).

To avoid such "invisible matrix" effect, a large amount of Mg is preferred to pass through the chemical purification procedure. Because the total amount of sample was limited to avoid overloading the resin column, this may cause a problem for low Mg samples analysis. It is still not exactly clear how the blank and organic matrices cause biases in Mg isotope measurements. More work need to be done in the future with appropriate chemical purification for low Mg samples.

3.3.4 Concentration mismatch

For light stable isotope measurements, the mass bias factor is sensitive to the concentration of running solutions. Concentration mismatch may also amplify the effects of isobaric

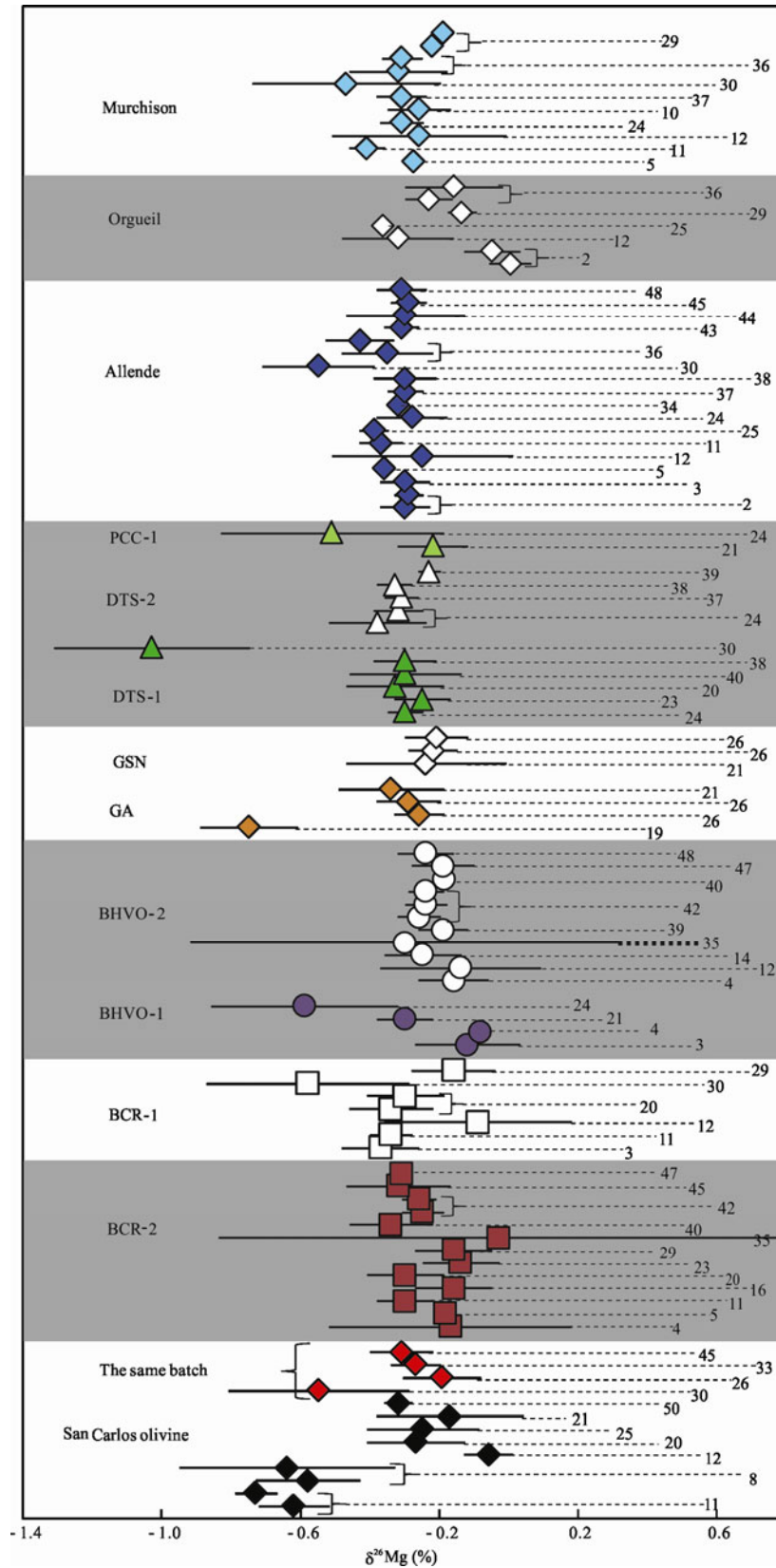


Figure 5. Summary of $\delta^{26}\text{Mg}_{\text{DSM-3}}$ values of the terrestrial mantle-rocks, minerals and whole-rock chondrites standards analyzed by different research groups for the terrestrial BCR-1 or BCR-2, the San Carlos olivine, and the whole-rock samples of the carbonaceous chondrites Allende, Murchison and Orgueil. Data sources are listed in Table 1. Error bars in this figure represent 2SD.

Table 2 Compilations of published estimates of the Mg isotopic composition of seawater

		$\delta^{25}\text{Mg}(\text{‰})$	2SD	$\delta^{26}\text{Mg}(\text{‰})$	2SD
1	Chang et al. (2003)	-0.42	0.08	-0.82	0.04
2	Chang et al. (2004)	-0.40	0.04	-0.75	0.12
3	Young and Galy (2004)	-0.43	0.11	-0.86	0.12
	Young and Galy (2004)	-0.41	0.01	-0.80	0.04
	Young and Galy (2004)	-0.42	0.12	-0.85	0.24
4	Tipper et al. (2006a)	-0.43	0.15	-0.84	0.13
5	Pearson et al. (2006)	-0.39	0.07	-0.75	0.13
	Pearson et al. (2006)	-0.40	0.04	-0.83	0.05
	Pearson et al. (2006)	-0.40	0.01	-0.79	0.11
6	Ra and Kitagawa (2007)	-0.37	0.04	-0.74	0.07
	Ra and Kitagawa (2007)	-0.37	0.05	-0.79	0.08
	Ra and Kitagawa (2007)	-0.47	0.09	-0.85	0.15
	Ra and Kitagawa (2007)	-0.51	0.01	-1.00	0.28
	Ra and Kitagawa (2007)	-0.49	0.12	-0.97	0.18
	Ra and Kitagawa (2007)	-0.38	0.13	-0.69	0.22
	Ra and Kitagawa (2007)	-0.39	0.16	-0.77	0.40
	Ra and Kitagawa (2007)	-0.34	0.12	-0.86	0.30
	Ra and Kitagawa (2007)	-0.40	0.14	-0.73	0.29
	Averg.	-0.42	0.12	-0.83	0.22
7	Pogge von Strandmann et al. (2008b)	-0.46	0.14	-0.89	0.18
	Pogge von Strandmann et al. (2008b)	-0.44	0.08	-0.83	0.09
8	Tipper et al. (2008a)	-0.39	0.04	-0.77	0.10
9	Bolou-Bi et al. (2009)	-0.47	0.11	-0.89	0.06
	Bolou-Bi et al. (2009)	-0.46	0.03	-0.96	0.03
	Bolou-Bi et al. (2009)	-0.51	0.08	-0.89	0.14
	Bolou-Bi et al. (2009)	-0.42	0.08	-0.82	0.14
	Bolou-Bi et al. (2009)	-0.47	0.08	-0.87	0.14
	Averag.	-0.47	0.06	-0.89	0.10
10	Hippler et al. (2009)	-0.42	0.02	-0.79	0.03
	Hippler et al. (2009)	-0.42	0.02	-0.80	0.05
11	Wombacher et al. (2009)	-0.41	0.06	-0.79	0.10
	Wombacher et al. (2009)	-0.43	0.07	-0.84	0.16
12	Yang et al. (2009)	-0.42	0.05	-0.83	0.07
13	Li et al. (2010)	-0.45	0.02	-0.86	0.02
14	Teng et al. (2010a)	-0.43	0.03	-0.83	0.06
15	Chakrabarti and Jacobsen (2010)	-0.40	0.15	-0.79	0.26
	Chakrabarti and Jacobsen (2010)	-0.41	0.18	-0.82	0.29
16	Tipper et al. (2010)	-0.42	0.03	-0.82	0.06
17	Higgins and Schrag (2010)	-0.41	0.09	-0.79	0.18
18	Foster et al. (2010)	-0.43	0.06	-0.82	0.06
19	Ling et al. (2011)	-0.43	0.05	-0.83	0.07
20	Bizzarro et al. (2011)	-0.48	0.01	-0.93	0.02
		-0.51	0.01	-1.00	0.02
21	Bolou-Bi et al. (2012)	-0.43	0.06	-0.83	0.14
22	Li et al. (2012)	-0.45	0.02	-0.87	0.02
23	Choi et al. (2012)			-0.86	0.09
24	Huang et al. (2012)	-0.43	0.03	-0.84	0.05
	Huang et al. (2013)	-0.46	0.06	-0.92	0.05
		-0.48	0.03	-0.92	0.07
	Total averg.	-0.43	0.08	-0.83	0.15

2SD stands for 2 standard deviations of repeated measurements of in-house standards.

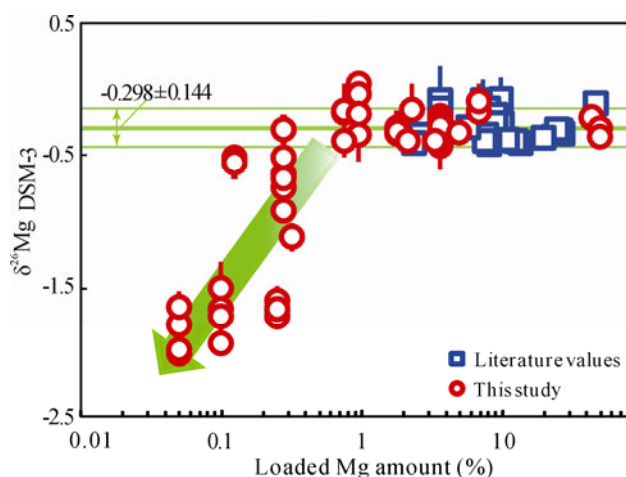


Figure 6. Tests of analytical error induced by chemical purification, so-called “invisible” matrix effect. When the amount of Mg loaded to the column is small (i.e., <0.5 wt.% MgO), chemical purification can cause significant negative bias of Mg isotopes which could be due to organic matrix effects invisible to the MC-ICP-MS. Red circle: unpublished data.

interferences, producing heavier values for $\delta^{26}\text{Mg}$ in low sample/standard concentration ratios with high Mg concentration (Huang et al., 2009b). Therefore, it is important to match the concentrations of sample and standard solutions in order to obtain a similar instrumental mass bias.

3.3.5 Mg solution storage

It is critical to ensure that no isotopic changes occur to the bracketing standard. Long-term storage of weak Mg solution in plastic bottles could cause significant deviations. Storage of a concentrated Mg standard (40 ppm–500 ppm) in clean Teflon[®] bottles or polypropylene/high density polyethylene (HDPE) bottles has not caused any deviations in isotope ratios for a period of a few years (Young et al., 2009). However, it was also observed that weak Mg standard solutions (0.2 ppm) stored in 500 mL fluorinated plastic (PTFE or Teflon[®]) bottles would deviate to lighter values with time of a few weeks (Huang et al., 2009b). Similarly, solutions with Mg concentration ≥ 40 ppm or aliquots of the 5 ppm diluted CAM-1 solution stored in non-Teflon containers could also result in drift over a period of a few months (Young et al., 2009). The reason for the isotopic drift in the dilute standard solutions is unknown but most likely related to absorption of heavy isotopes by the container or organic matrix extracted from the container. Therefore, the use of fresh bracketing solution standards is encouraged. It is essential to prepare standards and samples from the same acid stock solutions at the same time immediately before mass spectrometric analyses.

3.4 Guidelines for High-Precision Mg Isotope Measurement

In order to obtain high precision Mg isotope data, a few guidelines are summarized here.

(1) The diluted purified Mg solution can probably change its compositions and has a limited stored life. And

thus all running solutions of samples and standards should be newly diluted from concentrated bulk stocks before measurements.

(2) High-quality Mg isotope data requires excellent chemical separation of Mg from matrices and no artificial mass fractionation of Mg isotopes introduced by the separation procedures.

(3) Duplicated analyses should be performed for mono-elemental pure Mg solution standards such as DSM-3 and CAM-1, synthetic solutions like DSM-3 mixed with silicate matrices, mineral and rock reference materials including BCR-1 and homogeneous San Carlos olivine, and a certain proportion of natural samples.

4 APPLICATIONS

4.1 Mg Isotope Fractionation in High and Low Temperature

Mg isotope geochemistry provides a useful tool to study a variety of fundamental geological processes at both high and low temperatures. Although theoretical studies suggest that the magnitude of equilibrium fractionation decreases as the temperature increases and it is likely to be negligible during high- T processes (Chacko et al., 2001), recent studies on eclogites and peridotites reveal significant inter-mineral Mg isotope fractionations, reflecting different coordination environment (Li et al., 2011; Liu et al., 2011; Young et al., 2009). The large high-temperature equilibrium inter-mineral Mg isotope fractionation (such as spinel-olivine and omphacite-garnet) can potentially be used as geothermometers. In the future, more high temperature experiments and theoretical work are needed to decipher the temperature dependence of the inter-mineral $\Delta^{26}\text{Mg}$.

Significant kinetic Mg isotope fractionations have been observed in recent literature. Mg isotope fractionation associated with evaporation-condensation processes (Galy et al., 2000) was used for the interpretation of various Mg isotope compositions for the CAIs in chondritic meteorites (Richter et al., 2009b; Young et al., 2005; Grossman et al., 2000; Clayton et al., 1988). Mg isotopes may also be used to identify the effect of chemical and thermal diffusion (i.e., Soret diffusion) in the thermal boundary layers of molten silicate systems in laboratory conditions (Huang et al., 2009a; Richter et al., 2009a). Recent studies have also found that Mg-Fe inter-diffusion in zoned olivines during magmatic differentiation can produce large kinetic isotope fractionation (Teng et al., 2011; Dauphas et al., 2010).

Comparison of Mg isotope composition between the terrestrial and extra-terrestrial materials provides constraints on the origin and evolution of the Earth. Studies of Mg isotopic compositions in high-temperature magmatic processes mainly focused on the chondritic origin of terrestrial Mg based on terrestrial basalts (Chakrabarti and Jacobsen, 2010; Teng et al., 2010a, 2007), mantle peridotites and olivines (Handler et al., 2009; Yang et al., 2009; Wiechert and Halliday, 2007) and Archean komatiites (Dauphas et al., 2010). There is still uncertainty in the magnitude of Mg isotope fractionation at mantle temperatures and whether the BSE has a chondritic or non-chondritic Mg isotopic composition.

Magnesium is a fluid-mobile, major element in both the mantle and the crust, and the relative mass difference of ~8% between ^{24}Mg and ^{26}Mg can potentially lead to large mass-dependent Mg isotope fractionation. Therefore the Mg isotopes can be used to study low temperature process such as silicate weathering and biological processes. Previous studies have demonstrated that continental weathering could significantly fractionate Mg isotopes by retaining heavy ^{26}Mg in solid residues while waters were enriched in light Mg isotopes (Teng et al., 2010b; Pogge von Strandmann et al., 2008b; Brenot et al., 2008; Tipper et al., 2008a, 2006a, b). Mg isotopes could also be used to trace recycled sedimentary materials in granite sources (Shen et al., 2009). Additionally, chemical weathering of silicate rocks might involve removal of Mg by primary mineral dissolution and incorporation of Mg into secondary minerals, both coupled with large Mg isotope fractionation (Huang et al., 2012). Finally, Mg isotopic compositions of biogenic and inorganic carbonates bear on paleoclimate and paleoceanography studies because Mg isotope fractionation could be related to many factors such as abiotic and enzymatic processes, and transporting in organisms (Li et al., 2012; Bolou-Bi et al., 2010; Black et al., 2007, 2006).

5 CONCLUSIONS AND FUTURE WORK

High-quality Mg isotope data obtained by MC-ICP-MS require excellent chemical separation of Mg from matrices. The precision and accuracy should be proved by enough amounts of replicate measurements of standard materials and unknown samples. We should avoid the pitfalls for analytical artifacts, including non-perfect chemical procedure, standard solution storage, contamination, and matrix effects.

Although Mg isotopes have provided a plethora of information in a number of fundamental geological processes, more Mg isotope work is needed to be done in the future such as measurement of low-Mg reference materials and isotope fractionation mechanisms. Additionally, with the increasing precision of measurements, Mg isotope geochemistry will have promising future in the studies of high and low temperature as well as biological and non-biological processes. We can also combine experimental studies work with theoretical calculations for bettering application of a multi-proxy approach including non-conventional isotope systems.

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