




Originally published as:

Shalev, N., Farkaš, J., Fietzke, J., Novák, M., Schuessler, J. A., Pogge von Strandmann, P. A. E., Törber, P. B. (2018): Mg Isotope Interlaboratory Comparison of Reference Materials from Earth-Surface Low-Temperature Environments. - *Geostandards and Geoanalytical Research*, 42, 2, pp. 205—221.

DOI: <http://doi.org/10.1111/ggr.12208>

# Mg Isotope Interlaboratory Comparison of Reference Materials from Earth-Surface Low-Temperature Environments

Netta Shalev (1, 2, 3)\* , Juraj Farkaš (4, 5, 6), Jan Fietzke (7), Martin Novák (5), Jan A. Schuessler (8), Philip A.E. Pogge von Strandmann (9, 10) and Philip B. Törber (4, 5, 6)

(1) Institute of Earth Science, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Jerusalem, 91904, Israel

(2) Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel

(3) Department of Earth Sciences, Institute of Geochemistry and Petrology, ETH Zürich, Clausiusstrasse 25, Zürich, 8092, Switzerland

(4) Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, Prague 6, 165 21, Czech Republic

(5) Department of Geochemistry, Czech Geological Survey, Geologická 6, Prague 5, 152 00, Czech Republic

(6) Department of Earth Sciences, University of Adelaide, North Terrace, Adelaide, SA, 5005, Australia

(7) GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstr. 1-3, Kiel, 24148, Germany

(8) GFZ German Research Centre for Geosciences, Telegrafenberg, Potsdam, 14473, Germany

(9) London Geochemistry and Isotope Centre (LOGIC), University College London, and Birkbeck, University of London, Gower Street, London, WC1E 6BT, UK

(10) Bristol Isotope Group (BIG), Bristol University, Wills Memorial Building, Queen's Road, Bristol, BS8 1RJ, UK

\* Corresponding author. e-mail: netta.shalev@erdw.ethz.ch

To enable quality control of measurement procedures for determinations of Mg isotope amount ratios, expressed as  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values, in Earth-surface studies, the  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of eight reference materials (RMs) were determined by interlaboratory comparison between five laboratories and considering published data, if available. These matrix RMs, including river water SLRS-5, spring water NIST SRM 1640a, Dead Sea brine DSW-1, dolomites JDo-1 and BCS-CRM 512, limestone BCS-CRM 513, soil NIST SRM 2709a and vegetation NIST SRM 1515, are representative of a wide range of Earth-surface materials from low-temperature environments. The interlaboratory variability,  $2s$  (twice the standard deviation), of all eight RMs ranges from 0.05 to 0.17‰ in  $\delta^{26}\text{Mg}$ . Thus, it is suggested that all these materials are suitable for validation of  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  determinations in Earth-surface geochemical studies.

Keywords: Earth-surface, interlaboratory comparison, low-temperature, Mg isotopes, reference materials.

Received 24 Jul 17 – Accepted 29 Jan 18

Magnesium is a major element of the silicate Earth and vital in biogeochemical cycling. It has three stable isotopes:  $^{24}\text{Mg}$  (78.99%),  $^{25}\text{Mg}$  (10.00%) and  $^{26}\text{Mg}$  (11.01%). Analytical improvements over the past decades have made the differentiation between the Mg isotope amount ratios (expressed as  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  relative to the international  $\delta$ -zero reference material DSM3; Equation (1); Galy *et al.* 2003, IUPAC, see Brand *et al.* 2014) of terrestrial materials possible and enable today's rapid increase in the use of Mg isotopes as a powerful tool in investigations of Earth's biogeochemistry (e.g., Young and Galy 2004, Teng 2017). Yet, determinations of  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of natural samples are challenging, due to the significant risk of bias introduced during Mg purification, the large instrumental mass bias and the sensitivity of the

calibrator-sample bracketing (standard-sample-bracketing, SSB) measurements to matrix effects (e.g., Young and Galy 2004, An and Huang 2014, Teng 2017). Hence, processing well-characterised reference materials (RMs), similar in matrix to the samples, is required to validate the results. While  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of silicate rock RMs are available for high-temperature systems (Teng *et al.* 2015), Mg isotope data of RMs representative of samples with complex matrices from Earth-surface low-temperature environments are scarce (Bolou-Bi *et al.* 2009, Foster *et al.* 2010, An and Huang 2014, Teng 2017). To assess systematic errors and achieve comparability of Mg isotope data between different laboratories concerning Earth-surface low-temperature systems, well-characterised matrix RMs need to be established.

doi: 10.1111/ggr.12208

© 2018 The Authors. *Geostandards and Geoanalytical Research* published by John Wiley & Sons Ltd on behalf of International Association of Geoanalysts.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

$\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values are being used as a biogeochemical tool to study many different processes in low-temperature environments, for example in marine environments and marine sediments and rocks (e.g., Ling *et al.* 2011, Wombacher *et al.* 2011, Pogge von Strandmann *et al.* 2014, Higgins and Schrag 2015), evaporitic environments (e.g., Geske *et al.* 2015, Shalev *et al.* 2017), soils and vegetation (e.g., Tipper *et al.* 2010, Opfergelt *et al.* 2012, Pogge von Strandmann *et al.* 2012, Ma *et al.* 2015, Uhlig *et al.* 2017) and groundwater, spring water and rivers (e.g., Tipper *et al.* 2006a, b, Brenot *et al.* 2008, Pogge von Strandmann *et al.* 2008, Chapela Lara *et al.* 2017). The most fractionated materials on Earth are found in low-temperature environments, with the lowest  $\delta^{26}\text{Mg}$  values found in carbonates ( $\delta^{26}\text{Mg}$  of  $-5.6\%$ , Wombacher *et al.* 2011) and the highest in weathered residual silicates ( $\delta^{26}\text{Mg}$  of  $+1.8\%$ , Liu *et al.* 2014) and evaporites ( $\delta^{26}\text{Mg} = +1.4\%$ , Permian camallite, Shalev *et al.* 2017). However, the only natural Earth-surface RM which is well characterised to date is seawater ( $\delta^{26}\text{Mg}$  of  $-0.83 \pm 0.09\%$ ; 2s;  $N = 90$ ; Foster *et al.* 2010, Ling *et al.* 2011 and references therein). Published  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  data of Earth-surface materials from more than two laboratories ( $N > 2$ ) are also available for limestone Cal-S ( $-4.38 \pm 0.09\%$ , 2s,  $N = 3$ ; Wombacher *et al.* 2006, Bolou-Bi *et al.* 2009), shale SCo-1 ( $-0.89 \pm 0.08\%$ , 2s,  $N = 3$ ), aragonite JCp-1 ( $-1.96 \pm 0.05\%$ , 2s,  $N = 4$ ) and dolomite JDo-1 ( $-2.37 \pm 0.04\%$ , 2s,  $N = 5$ ; Teng 2017 and references therein). Here,  $N$  is used to denote the number of full-procedure replicates, that is independent sample dissolution and Mg purification, while  $n$  is used to denote the number of repeated measurements of the purified Mg sample solutions by MC-ICP-MS. 2s is twice the standard deviation on  $N$  or  $n$  values.

In this study, the  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of eight RMs (Table 1), representative for their respective Earth-surface environments, were estimated by interlaboratory comparison, conducted in five laboratories. The participating laboratories utilised different sample preparation methods, that is different analyte-matrix separation procedures, and MC-ICP-mass spectrometers from various manufacturers with different sample introduction systems (Table 2). This approach is suitable to test the applicability of these different measurement methods with respect to the varying chemical and physical material properties and to identify potential bias originating from differences in sample preparation and instrument set-up. Whereas measurement results from a single laboratory might produce very precise  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values for any material never analysed before, there is still the potential risk that the data are affected by undetected bias. We suggest that our interlaboratory

comparison study provides a robust and practicable approach to provide the geo-analytical community with fit-for-purpose  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values for matrix RMs with confidence intervals constrained by the currently attainable level of measurement precision. Materials of this study included solids (carbonates, soil and organic material) and liquids (river water, spring water and brine) thereby representing most of the material types from Earth-surface low-temperature environments studied to date. Most selected RMs are provided by reference material producers and are widely available to the community. Also, certified mass fractions data are available for most materials studied in this work (Table 1). Based on the results of this study and published values, where available, recommended  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values are proposed. These can be used as quality control RMs in laboratories analysing Earth-surface materials to verify their measurement methods.

## Methods

### Investigated materials

The investigated materials include dolomites JDo-1 and BCS-CRM 512, limestone BCS-CRM 513, NIST SRM 2709a soil, NIST SRM 1515 apple leaves, IAPSO Atlantic seawater, SLRS-5 river water, NIST SRM 1640a spring water and DSW-1 Dead Sea brine. Solid samples are powdered and require complete dissolution prior to the column chemistry. The published chemical compositions of the investigated materials are described in Table 1.  $\sum c(\text{Matrix cations})/c(\text{Mg})$  molar ratios (i.e., the molar ratios of the sum of Na, K, Ca, Si, Al, Ti, Fe and Mn relative to Mg) of the RMs vary significantly: Na/Mg ratios range between 0.0 (carbonates) and 8.8 (seawater), Ca/Mg ratios range between 0.2 (seawater) and 220 (BCS-CRM 513 limestone) and K/Mg ratios range between 0.0 (JDo-1 and BCS-CRM 512 dolomites) and 3.7 (NIST SRM 1515 apple leaves). The soil (NIST SRM 2709a), spring water (NIST SRM 1640a) and limestone (BCS-CRM 513) have the most complex matrices with significant Si/Mg ratios (18, 3.3 and 0.8, respectively), Al/Mg ratios (4.6, 0.04 and 0.45, respectively), Fe/Mg ratios (1.0, 0.02 and 0.08, respectively) and Ti/Mg ratio (0.12 in the soil NIST SRM 2709a).

### Measurement procedures

The eight RMs, IAPSO Atlantic seawater and Cambridge-1 were analysed for  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values in the laboratories of the University of Bristol (BIG) and University of London (UCL), UK (BIG LOGIC); The Geological Survey of Israel (GSI), Jerusalem, Israel; the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) at GFZ

**Table 1.**  
Reference materials studied and their chemical composition

RM	Producer	Data source	g/100 g													mol mol <sup>-1</sup> Σ c(matrix-cations)/c(Mg) <sup>a</sup>
			SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> (total)	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>	BaO	S	
<b>Solids</b>																
JDo-1 (dolomite)	GSI	b	0.216	0.001	0.017	0.0208	0.007	18.47	33.96	0.013	0.002	0.034	46.5		1.3	
BCS-CRM 512 (dolomite)	BAS	b	0.379	0.002	0.055	0.03	0.004	21.59	30.61	<0.15	<0.01	<0.001	46.66	<0.02	<0.0085	
BCS-CRM 513 (limestone)	BAS	b	0.228	<0.007	0.108	0.0275	0.01	0.182	55.59	<0.05	0.015	<0.01	43.71	<0.02	0.01	
SRM 2709a (soil)	NIST	b	64.81	0.56	13.92	4.80	0.068	2.42	2.67	1.6	2.54	0.16			26	
<b>µg g<sup>-1</sup></b>																
SRM 1515 (apple leaves)	NIST	b	286	83	54	2710	15260	2.44	16100	1590	22500	49	1800	579	7.2	
<b>Liquids</b>																
<b>µg ml<sup>-1</sup></b>																
Cambridge-1 (Mg solution)	Univ. of Cambridge															0
IAPSO (Atlantic seawater)	OSIL	c	2.8	5E-04	5.5E-5	1E-05	1290	412	10770	399	27.6	0.014	904	19354	9.2	
SIRS-5 (river water)	CANMET (CCRMF)	b	0.002	0.05	0.0912	0.004	2.54	10.5	5.38	0.839	0.014				5.0	
SRM 1640a (spring water)	NIST	b	5.169	0.053	0.0365	0.04	1.05	5.57	3.112	0.575	0.151				1.0	
<b>mmol kg<sup>-1</sup></b>																
DSW-1 <sup>f</sup> (Dead Sea brine)	GSI	d,e				1663	391	1081	169	0.86					5294	0.9

<sup>a</sup> Refers to the molar ratio of the sum of Na, K, Ca, Sr, Al, Ti, Fe and Mn relative to Mg. <sup>b</sup> Producer's certificate of analysis. <sup>c</sup> Summerhayes and Thorpe (1996). <sup>d</sup> Golan et al. (2016). <sup>e</sup> Concentrations refer to average Dead Sea composition (in 2013) and may be slightly different from DSW-1, although elemental mass ratios are similar. <sup>f</sup> DSW-1 can be freely obtained from the Geological Survey of Israel (GSI).

Potsdam, Germany; the Czech Geological Survey (CGS) in Prague (Czech Republic); and the GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany. The powdered or liquid RMs were split and spread among the different laboratories. Each laboratory conducted measurements, using its own previously established measurement procedure, to get completely independent results and potentially identify any method-specific bias. The different procedures for material digestion, Mg purification and instrumentation, conducted in each laboratory, are described below and summarised in Table 2. All Mg isotope ratio measurements were conducted by MC-ICP-MS using calibrator-sample bracketing (with DSM3 as the calibrator), and the calculated isotope amount ratios are reported as per mil deviation from the delta-zero reference material DSM3 in the delta notation according to Coplen (2011):

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

where x denotes either 26 or 25 and DSM3 is the mean value of the two bracketing calibrators measured before and after the sample, respectively. Multiplication of Equation (1) by a factor 1000 gives the per mil (‰) deviation relative to DSM3.

To validate the different measurement procedures used by the participating laboratories and to test for any potential interlaboratory bias, we adapted the following approach. During this study, Cambridge-1 and IAPSO Atlantic seawater were analysed by all participating laboratories. These results are compared with literature values (e.g., compilations in Teng 2017, An and Huang 2014, and the in GeoReM database, Jochum *et al.* 2005) in order to validate the measurement procedure of each laboratory. Thereby, the pure Mg-solution Cambridge-1 was used to evaluate the repeatability precision of the MC-ICP-MS measurements (solution not processed through columns) for each laboratory. Then, seawater was used to evaluate the intermediate precision of the entire measurement procedure for each laboratory, including sample pre-treatment, matrix separation by column chemistry and MC-ICP-MS analysis. In addition, a typical intermediate precision was estimated by each laboratory (Table 2), based on long-term (more than 1 year) repeated measurements of one or more matrix materials as detailed below (following subsections). The only case where this long-term experience with matrix material is missing is at GEOMAR, and therefore only Cambridge-1 repeatability precision was considered. These estimates are considered as a benchmark against which we can evaluate the precision obtained on the matrix

RMs investigated in this interlaboratory comparison study. Then, to provide consensus  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values for each Earth-surface reference material, the arithmetic mean of  $N \geq 3$  full-procedure replicates was calculated. These comprised all data produced by the participating laboratories and – where available – literature data and are reported together with 95% confidence intervals.

**Sample preparation and Mg isotope ratio measurements at UCL and Bristol (BIG LOGIC):** Procedures for sample analyses are similar to those described in previous studies (Pogge von Strandmann 2008, Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011, 2012). A brief description is given below.

Carbonate powders (ca. 20 mg) were dissolved in 2 mol l<sup>-1</sup> HCl. Apple leaves (NIST SRM 1515, ca 50 mg) were dissolved in repeated steps of concentrated HNO<sub>3</sub>, heated at 130 °C and evaporated to dryness. Soil powders (ca. 10 mg) were dissolved in stages of concentrated HF-HNO<sub>3</sub>, followed by HNO<sub>3</sub>, and finally 6 mol l<sup>-1</sup> HCl. Water samples (ca. 0.01–0.2 ml) were simply dried down. Subsequently, the samples were dissolved in 2 mol l<sup>-1</sup> HNO<sub>3</sub>, and a small aliquot (around 0.2–3 µg Mg) was taken for column chemistry.

Magnesium analyte-matrix separation was performed by a two-stage cation exchange chemistry, using Bio-Rad AG® 50W-X12 (200–400 mesh) resin in 2 mol l<sup>-1</sup> HNO<sub>3</sub>, as described by Pogge von Strandmann *et al.* (2011). Soil samples were subjected to an additional column to quantitatively remove Ti (because <sup>48</sup>Ti<sup>2+</sup> and <sup>50</sup>Ti<sup>2+</sup> are direct interferences on <sup>24</sup>Mg<sup>+</sup> and <sup>25</sup>Mg<sup>+</sup>). This column contained 0.25 ml of TRU-Spec™ resin, and Mg was eluted in 7 mol l<sup>-1</sup> HNO<sub>3</sub> (Pogge von Strandmann *et al.* 2012). The total procedural blank for Mg isotope ratio measurements by this method is ca. 0.4 ng Mg, which is insignificant compared to the amount of Mg put through chemistry (< 0.2%). Splits of the elution were collected before and after the Mg collection bracket, to ensure close to 100% Mg yield was achieved, that is < 0.1% of the processed Mg was detected in these splits.

Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS with a high-sensitivity 'X' Ni skimmer cone and conventional Ni sample cone interface. A purified sample solution of ca. 100 ng ml<sup>-1</sup> Mg was introduced via an Elemental Scientific Inc. Apex-Q, with a ca. 50 µl min<sup>-1</sup> uptake rate nebuliser tip, in 2% v/v HNO<sub>3</sub>. Mg isotope ratios were measured in low mass resolution mode (see footnote in Table 2), with all intensities at *m/z* 24, 25 and 26 measured simultaneously in separate Faraday cups (H3, Centre, L3). Each individual

**Table 2.**  
Summary of analytical techniques used by each laboratory

Laboratory	Test portion <sup>a</sup>	Dissolution method	Mg column purification	Typical column procedure blank	Instrument <sup>b</sup> , sample introduction system, uptake rate, acid matrix	Integration time / bracket <sup>c</sup> , number of brackets <sup>d</sup> , <sup>24</sup> Mg signal intensity / analyte concentration Typical Mg consumption per single analysis ( $n = 1$ ) <sup>e</sup>	Typical intermediate precision on $\delta^{26}\text{Mg}$ ; $\delta^{25}\text{Mg}$ (2s)
UCL/Bristol	10–50 mg (0.2–3 µg Mg)	Carbonates: HCl Leaves: HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> Soil: HF/ HNO <sub>3</sub> + HCl liquids: evaporation	2 steps: Bio-Rad AG50W-X12 resin in 2 mol l <sup>-1</sup> HNO <sub>3</sub> + TRUSpec in 7 mol l <sup>-1</sup> HNO <sub>3</sub>	< 0.4 ng Mg	Neptune (LR), Apex-Q desolvator, 50 µl min <sup>-1</sup> , 2% HNO <sub>3</sub>	20 × 4.2 s, 1 18–20 V / 100 ng ml <sup>-1</sup> Mg 7 ng Mg	±0.06‰; ±0.04‰
GSI	100–150 mg (200–500 µg Mg)	Carbonates: HNO <sub>3</sub> Liquids: evaporation	1 step: Bio-Rad AG50W-X12 resin in 1.3/2.3 mol l <sup>-1</sup> HCl	< 100 ng Mg	NU plasma II (MR), DSN-100 desolvator, 100 µl min <sup>-1</sup> , 0.1 mol l <sup>-1</sup> HNO <sub>3</sub>	20 × 10 s, 1 25–35 V / 2000 ng ml <sup>-1</sup> Mg 670 ng Mg	±0.11‰; ±0.05‰
GFZ	30–100 mg / in addition 1 g for NIST SRM 1515 (2.5–1.5 µg Mg)	Carbonates: HCl Leaves: HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> Soil: HF/ HNO <sub>3</sub> + HCl + H <sub>2</sub> O <sub>2</sub> liquids: HF + evaporation + H <sub>2</sub> O <sub>2</sub>	2 steps: Bio-Rad AG50W-X12 resin in 1 & 2 mol l <sup>-1</sup> HNO <sub>3</sub> (repeated twice)	< 12 ng Mg	Neptune (MR), double pass cyclone-Scott quartz-glass spray chamber (SS), 100 µl min <sup>-1</sup> , 0.3 mol l <sup>-1</sup> HNO <sub>3</sub>	20 × 4.2 s, 1 10–15 V / 500 ng ml <sup>-1</sup> Mg 70 ng Mg	±0.10‰; ±0.06‰
CGS	50–100 mg (20–50 µg Mg)	Carbonates: HCl Leaves: HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> Soil: HF/ HNO <sub>3</sub> liquids: evaporation	3 steps: Bio-Rad AG50W-X12 resin in 2.5 mol l <sup>-1</sup> HCl (twice) + 0.4 mol l <sup>-1</sup> HNO <sub>3</sub>	< 2 ng Mg	Neptune (MR), cyclonic quartz-glass spray chamber, 100 µl min <sup>-1</sup> , 3% v/v HNO <sub>3</sub>	30 × 8.4 s, 3 4–8 V / 500 ng ml <sup>-1</sup> Mg 630 ng Mg	±0.13‰; ±0.09‰
GEOMAR	Same as CGS	Same as CGS	Same as CGS	Same as CGS	AXIOM (LR), Airdus desolvator, 50 µl min <sup>-1</sup> , 5% HNO <sub>3</sub>	50 × 2 s, 9 3.5 V / 200 ng ml <sup>-1</sup> Mg 150 ng Mg	±0.08‰; ±0.06‰

<sup>a</sup> The test portion refers to the aliquot amount of the original sample taken for analysis. Amount of Mg processed through column purification is given in parenthesis.

<sup>b</sup> LR and MR refers to the mass resolving power  $R_p$ , defined as  $m/\Delta m = m/(m(5\%) - m(95\%))$ , where  $m(5\%)$  and  $m(95\%)$  are the masses at 5% and 95% peak intensity, respectively, and  $m$  is the mass of the peak. LR = low  $R_p$  (ca. > 1000), MR = medium  $R_p$  (< 6000).

<sup>c</sup> Integration time/bracket refers to the measurement time of a sample or each one of the bracketing calibrators in a single bracket.

<sup>d</sup> The number of brackets that were used to calculate a single  $\delta$  result ( $n = 1$  in Table 3).

<sup>e</sup> Including the data acquisition time only, without take-up time, etc.

measurement consisted of twenty ratios (84 s total integration time). These conditions gave typical signals of 18–20 V per 100 ng ml<sup>-1</sup> on <sup>24</sup>Mg. The on-peak background in 2% v/v HNO<sub>3</sub> was repeatedly recorded during the sequence and subtracted from all calibrator and sample intensities. Each sample was analysed three or four times ( $n = 3$  or  $n = 4$  in Table 3) during the same session (336 s per sample), each time separated by several hours. The difference in the measured <sup>26</sup>Mg/<sup>24</sup>Mg intensities ratio between bracketing DSM3 calibrators was  $\leq 0.06\%$  in all analyses performed for this study.

USGS (United States Geological Survey) and GSI (Geological Survey of Japan) silicate rock reference material measurement results by this procedure are documented by Pogge von Strandmann *et al.* (2011), other silicate rocks by Teng *et al.* (2015), IAPSO Atlantic seawater results by Foster *et al.* 2010 and carbonates by Pogge von Strandmann 2008, Kasemann *et al.* (2014) and Pogge von Strandmann *et al.* (2014). For example, measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave  $-2.63 \pm 0.07\%$  for  $\delta^{26}\text{Mg}$  and  $-1.36 \pm 0.06\%$  for  $\delta^{25}\text{Mg}$  (2s,  $n = 126$ ) and IAPSO Atlantic seawater results were  $-0.82 \pm 0.06\%$  for  $\delta^{26}\text{Mg}$  and  $-0.43 \pm 0.04\%$  for  $\delta^{25}\text{Mg}$  (2s,  $n = 26$ , Foster *et al.* 2010). Hence, the typical intermediate precision of this method, based on several years of repeated measurements, is estimated at  $\pm 0.06\%$  (2s) on  $\delta^{26}\text{Mg}$ , and  $\pm 0.04\%$  (2s) on  $\delta^{25}\text{Mg}$ . The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

**Sample preparation and Mg isotope ratio measurements at GSI:** Carbonate powders (ca. 100–150 mg) were dissolved in HNO<sub>3</sub> and evaporated to dryness. Water samples (ca. 10  $\mu\text{l}$  DSW-1 and 2 ml IAPSO) were simply dried down. All samples were then redissolved in 10 ml 1.3 mol l<sup>-1</sup> HCl, and an aliquot (200–500  $\mu\text{g}$  Mg) was taken for column chemistry.

Magnesium purification was performed by liquid chromatography (Galy *et al.* 2002) using Bio-Rad Econo-Pac Chromatography Columns 732-1010 with an extended reservoir, filled with ca. 18 ml of Bio-Rad AG® 50W-X12 100-200 mesh resin. The matrix was rinsed with 25 ml of 1.3 mol l<sup>-1</sup> HCl, and 20 ml of 2.3 mol l<sup>-1</sup> HCl. Mg<sup>2+</sup> was then eluted with 24 ml of 2.3 mol l<sup>-1</sup> HCl. Total procedural blanks contained  $< 0.5\%$  Mg of the amount of Mg processed through column chemistry. The first and the last 2 ml before and after the Mg elution were collected separately in order to verify close to 100% Mg recovery. In addition, the Mg amount in the Mg cut (Mg-COL) was compared to the amount originally loaded to the column

(Mg-ORIG). Only samples with Mg-COL/Mg-ORIG  $> 95\%$  (taking into account the uncertainties of both measurements), no detectable Mg in the first and the last 2 ml before and after the Mg fraction, and molar ratio of  $\sum c(\text{matrix cations})/c(\text{Mg})$  in the final Mg fraction of  $< 5\%$  (after Galy *et al.* 2001 and others) were used for isotope ratio measurements. These parameters were verified for each sample separation using ICP-AES (Optima 3300, Perkin-Elmer). Once Mg was purified, the solution was fully evaporated and the chloride salts were redissolved in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>.

Magnesium isotope ratio measurements were conducted using a Nu instruments Plasma II HR-MC-ICP-MS. The 2  $\mu\text{g ml}^{-1}$  Mg solutions (in 0.1 mol l<sup>-1</sup> HNO<sub>3</sub>) were introduced into the mass spectrometer via a DSN-100 desolvation system (self-aspirating PFA nebuliser, uptake rate of ca. 100  $\mu\text{l min}^{-1}$ ) and standard Ni cones interface. The measurements were conducted using pseudo-high resolution, with a 50  $\mu\text{m}$  source slit at a mass resolving power  $R_p(5,95\%) = 7000$  (see footnote in Table 2). Three Faraday cup collectors were used to measure the ion beam intensities at  $m/z$  24, 25 and 26 simultaneously. Each measurement run comprises twenty integrations of 10 s data acquisition, that is a total 200 s of data acquisition per measurement. These conditions gave sample signal intensities of 25–35 V on  $m/z$  24. The zero reference points were reset simultaneously for all measured masses by deflecting the potential of the electrostatic analyser before measuring each block. A blank solution measured in the beginning of each measurements day produced  $< 5$  mV on  $m/z$  24, and therefore, the difference from the off-peak zero is considered insignificant. Each sample solution was measured by several brackets of calibrator-sample-calibrator, which were used for statistical analysis, where  $n$  is the number of brackets of each sample. Outliers were eliminated as long as their elimination reduced the 95% confidence interval ( $= t \cdot \frac{s}{\sqrt{n}}$ ), despite the reduction of  $n$  that rises both  $\frac{1}{\sqrt{n}}$  and the  $t$  distribution value.

The  $\delta^{26}\text{Mg}$  mean of pure Mg Cambridge-1 solution measured in this study is  $-2.62 \pm 0.14\%$  (2s,  $n = 36$ , Table 3), identical within stated precisions to results reported by other laboratories (e.g., compilations by Teng 2017, An and Huang 2014,  $-2.61 \pm 0.05\%$ , 2s). The  $\delta^{26}\text{Mg}$  value of IAPSO Atlantic seawater reference material measured in this study ( $-0.84 \pm 0.09\%$ , 2s,  $n = 12$ , Table 3) is also identical to the previously reported seawater value ( $-0.83 \pm 0.09\%$ , 2s,  $N = 90$ ; Foster *et al.* 2010, Ling *et al.* 2011 and references therein). In order to further test the measurement procedure, a sample of modern Dead Sea brine (DSW-1) was purified through Mg column chemistry and this single solution was repeatedly measured over 2 years

**Table 3.**  
 $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of the low-temperature RMs determined in the current and previous studies

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	2s	n <sup>b</sup>
<b>Internationally established RMs</b>							
<b>Cambridge-1 (pure Mg solution)</b>							
Bristol/UCL <sup>d</sup>	-2.63	0.01	0.07	-1.36	0.00	0.05	126
CGS	-2.59	0.04	0.16	-1.34	0.03	0.11	18
GSI	-2.62	0.02	0.14	-1.35	0.01	0.07	36
GFZ	-2.61	0.01	0.07	-1.35	0.01	0.05	62
GEOMAR <sup>e</sup>	-2.63	0.15	0.12	-1.31	0.04	0.03	3
<b>Arithmetic mean</b>	<b>-2.62</b>	<b>0.02</b>	<b>0.03</b>	<b>-1.34</b>	<b>0.02</b>	<b>0.04</b>	<b>N<sup>c</sup> = 5</b>
<b>An and Huang (2014) (compilation)</b>	<b>-2.61</b>		<b>0.05</b>				
<b>IAPSO Atlantic seawater (OSIL)</b>							
Bristol/UCL <sup>f</sup>	-0.82	0.01	0.06	-0.43	0.01	0.04	26
CGS	-0.87	0.03	0.10	-0.45	0.02	0.06	14
GSI	-0.84	0.03	0.09	-0.44	0.02	0.05	12
GFZ A	-0.81	0.03	0.12	-0.41	0.02	0.06	13
GFZ B <sup>g,h</sup>	-0.85	0.06	0.07	-0.43	0.05	0.07	4
GEOMAR	-0.81	0.05	0.04	-0.40	0.05	0.04	3
<b>Arithmetic mean</b>	<b>-0.83</b>	<b>0.02</b>	<b>0.05</b>	<b>-0.43</b>	<b>0.02</b>	<b>0.04</b>	<b>N<sup>c</sup> = 6</b>
<b>Ling <i>et al.</i> (2011) (compilation)</b>	<b>-0.83</b>		<b>0.09</b>	<b>-0.43</b>		<b>0.06</b>	<b>90</b>
<b>Surface water RMs</b>							
<b>DSW-1 (Dead Sea brine)</b>							
CGS	-0.68	0.09	0.17	-0.34	0.05	0.10	6
GSI A	-0.67	0.02	0.11	-0.35	0.01	0.05	35
GSI B <sup>g,i</sup>	-0.51	0.03	0.07	-0.28	0.01	0.03	8
GFZ A	-0.59	0.31	0.07	-0.30	0.17	0.04	2
GFZ B <sup>g</sup>	-0.57	0.05	0.10	-0.30	0.03	0.06	7
GFZ C <sup>g</sup>	-0.53	0.05	0.12	-0.26	0.03	0.07	7
GFZ D <sup>g</sup>	-0.54	0.06	0.08	-0.26	0.05	0.06	4
Karasinski <i>et al.</i> (2017) <sup>j</sup>	-0.57	0.06	0.18				10
<b>Arithmetic mean</b>	<b>-0.58</b>	<b>0.05</b>	<b>0.12</b>	<b>-0.30</b>	<b>0.03</b>	<b>0.07</b>	<b>N<sup>c</sup> = 8</b>
<b>SLRS-5 (river water)</b>							
Bristol/UCL	-1.14	0.05	0.06	-0.59	0.04	0.05	4
CGS	-1.11	0.10	0.20	-0.60	0.06	0.12	6
GFZ A <sup>g</sup>	-1.30	0.43	0.10	-0.72	0.31	0.07	2
GFZ B <sup>g</sup>	-1.31	0.05	0.09	-0.67	0.02	0.04	6
GFZ C <sup>g</sup>	-1.25	0.03	0.06	-0.65	0.02	0.05	6
GFZ D <sup>g</sup>	-1.24	0.05	0.12	-0.64	0.03	0.07	8
GFZ E <sup>g,h</sup>	-1.28	0.04	0.10	-0.67	0.03	0.07	10
GEOMAR	-1.17	0.05	0.04	-0.57	0.03	0.03	3
<b>Arithmetic mean</b>	<b>-1.22</b>	<b>0.06</b>	<b>0.15</b>	<b>-0.64</b>	<b>0.04</b>	<b>0.10</b>	<b>N<sup>c</sup> = 8</b>
<b>NIST SRM 1640a (spring water)</b>							
Bristol/UCL A <sup>g</sup>	-0.76	0.06	0.05	-0.42	0.06	0.05	3
Bristol/UCL B <sup>g</sup>	-0.81	0.07	0.05	-0.44	0.05	0.04	3
CGS	-0.72	0.10	0.16	-0.35	0.04	0.07	5
GFZ A <sup>g</sup>	-0.75	0.14	0.03	-0.39	0.46	0.10	2
GFZ B <sup>g</sup>	-0.73			-0.37			1
GFZ C <sup>g</sup>	-0.72	0.07	0.06	-0.39	0.07	0.05	3
GFZ D <sup>g</sup>	-0.68	0.02	0.07	-0.35	0.01	0.03	13
GFZ E <sup>g,h</sup>	-0.73	0.05	0.03	-0.39	0.06	0.03	6
GEOMAR	-0.68	0.07	0.06	-0.31	0.04	0.03	3
<b>Arithmetic mean</b>	<b>-0.73</b>	<b>0.03</b>	<b>0.08</b>	<b>-0.38</b>	<b>0.03</b>	<b>0.08</b>	<b>N<sup>c</sup> = 9</b>
<b>Organic-rich solids</b>							
<b>NIST SRM 2709a (soil)</b>							
Bristol/UCL	-0.20	0.02	0.02	-0.11	0.04	0.03	3
CGS	-0.11	0.07	0.17	-0.07	0.04	0.08	8
GFZ A (MW) <sup>g</sup>	-0.14	0.02	0.09	-0.07	0.01	0.05	19
GFZ B <sup>g</sup>	-0.17	0.04	0.10	-0.09	0.02	0.05	8
GFZ C <sup>g</sup>	-0.15	0.06	0.08	-0.08	0.04	0.05	4



Table 3 (continued).

$\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of the low-temperature RMs determined in the current and previous studies

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	2s	n <sup>b</sup>
GFZ D <sup>g,h</sup>	-0.14	0.10	0.02	-0.08	0.06	0.01	6
<b>Arithmetic mean</b>	<b>-0.15</b>	<b>0.03</b>	<b>0.06</b>	<b>-0.08</b>	<b>0.02</b>	<b>0.03</b>	<b>N<sup>c</sup> = 6</b>
<b>NIST SRM 1515 (apple leaves)</b>							
Bristol/UCL	-1.24	0.01	0.01	-0.64	0.08	0.06	3
CGS	-1.24	0.08	0.13	-0.65	0.08	0.13	5
GFZ A (MW) <sup>g,h</sup>	-1.24	0.04	0.01	-0.64	0.04	0.01	2
GFZ B <sup>g,h</sup>	-1.20	0.04	0.12	-0.61	0.02	0.07	12
GFZ C <sup>g,h</sup>	-1.20	0.02	0.02	-0.60	0.08	0.07	3
GEOMAR	-1.19	0.05	0.04	-0.58	0.03	0.03	3
<b>Arithmetic mean</b>	<b>-1.22</b>	<b>0.03</b>	<b>0.05</b>	<b>-0.62</b>	<b>0.03</b>	<b>0.05</b>	<b>N<sup>c</sup> = 6</b>
<b>Carbonates</b>							
<b>JDo-1 (dolomite)</b>							
Bristol/UCL	-2.25	0.06	0.05	-1.16	0.05	0.04	3
CGS	-2.49	0.03	0.05	-1.30	0.06	0.12	6
GSI	-2.19	0.04	0.07	-1.14	0.04	0.07	5
GFZ A <sup>g</sup>	-2.36	0.25	0.06	-1.24	0.03	0.01	2
GFZ B <sup>g</sup>	-2.32	0.05	0.10	-1.20	0.03	0.05	6
Wombacher <i>et al.</i> (2009)	-2.38	0.06	0.18	-1.22	0.02	0.07	12
Pearce <i>et al.</i> (2012)	-2.33	0.04	0.09	-1.22	0.025	0.06	7
Mavromatis <i>et al.</i> (2013)	-2.37	0.03	0.08	-1.25	0.02	0.06	9
Mavromatis <i>et al.</i> (2014)	-2.36	0.03	0.06	-1.25	0.03	0.06	6
Beinlich <i>et al.</i> (2014)	-2.38	0.04	0.08	-1.23	0.03	0.05	6
Lavoie <i>et al.</i> (2014)	-2.38	0.29	0.36	-1.27	0.07	0.09	4
<b>Arithmetic mean</b>	<b>-2.35</b>	<b>0.05</b>	<b>0.15</b>	<b>-1.23</b>	<b>0.03</b>	<b>0.09</b>	<b>N<sup>c</sup> = 11</b>
<b>BCS-CRM 512 (dolomite)</b>							
Bristol/UCL A <sup>g</sup>	-1.92	0.03	0.02	-1.00	0.02	0.02	3
Bristol/UCL B <sup>g</sup>	-2.01	0.06	0.05	-1.06	0.004	0.003	3
CGS	-2.16	0.11	0.09	-1.13	0.04	0.03	3
GSI	-2.00	0.21	0.27	-1.03	0.09	0.12	4
GFZ A <sup>g</sup>	-2.09	0.29	0.07	-1.08	0.06	0.01	2
GFZ B <sup>g</sup>	-1.97	0.02	0.03	-1.03	0.01	0.02	7
<b>Arithmetic mean</b>	<b>-2.03</b>	<b>0.09</b>	<b>0.17</b>	<b>-1.05</b>	<b>0.05</b>	<b>0.09</b>	<b>N<sup>c</sup> = 6</b>
<b>BCS-CRM 513a (limestone)</b>							
Bristol/UCL A <sup>g</sup>	-4.48	0.10	0.08	-2.33	0.07	0.06	3
Bristol/UCL B <sup>g</sup>	-4.50	0.11	0.09	-2.33	0.07	0.06	3
GFZ	-4.41	0.08	0.07	-2.29	0.07	0.06	3
<b>Arithmetic mean</b>	<b>-4.46</b>	<b>0.12</b>	<b>0.10</b>	<b>-2.32</b>	<b>0.05</b>	<b>0.04</b>	<b>N<sup>c</sup> = 3</b>

<sup>a</sup> 95% confidence intervals calculated as  $2SE_i$  (95% conf) =  $t \cdot s / \sqrt{n}$ , with  $s$  = standard deviation of  $n$  (or  $N$ ) repeated measurements or replicates,  $t$  = correction factor for low  $n$  (or  $N$ ) from Student's  $t$ -distribution at 95% probability.

<sup>b</sup>  $n$  is the number of  $\delta$  values used for the calculation of the result given by each laboratory. As mentioned in Table 2,  $n = 1$  refers to one bracket measured at Bristol/UCL, GSI and GFZ, an average of three brackets measured at CGS or an average of nine brackets measured at GEOMAR.

<sup>c</sup>  $N$  refers to the number of average  $\delta$  values used for the calculations of the inter-laboratory arithmetic mean.

<sup>d</sup> From Pogge von Strandmann *et al.* (2011).

<sup>e</sup> Processed through columns.

<sup>f</sup> From Foster *et al.* (2010).

<sup>g</sup> A, B, C, D and E are replicates of the full procedure including sample dissolution (solids) or evaporation (liquids), Mg column purification and MC-ICP-MS measurements. MW indicates solid sample dissolution using a microwave system.

<sup>h</sup> From Uhlig *et al.* (2017).

<sup>i</sup> Different samples of the Dead Sea brine.

( $\delta^{26}\text{Mg} = -0.67 \pm 0.11\%$ ,  $\delta^{25}\text{Mg} = -0.35 \pm 0.05\%$ , 2s,  $n = 35$ , Table 3). Accordingly, our long-term estimate of the typical intermediate precision is  $\pm 0.11\%$  (2s) on  $\delta^{26}\text{Mg}$ , and  $\pm 0.05\%$  (2s) on  $\delta^{25}\text{Mg}$ . The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

**Sample preparation and Mg isotope ratio measurements at GFZ:** Solid powders (30–100 mg) were digested in HF/HNO<sub>3</sub> mixture at 110 °C, followed by 6 mol l<sup>-1</sup> HCl, and 14 mol l<sup>-1</sup> HNO<sub>3</sub>. For all samples, H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub> treatment in closed PFA vials on a hot plate at 150 °C for 24 h was used to remove organics. In addition, a separate

batch of the organic-rich soil (NIST SRM 2709a) and vegetation (NIST SRM 1515) (ca. 1 g) were also acid-digested ( $\text{H}_2\text{O}_2/\text{HNO}_3$ ) using a microwave system (MLS Start) at 160 °C (for 20 min) and elevated pressure. Both the PFA vial-hot plate and the microwave method achieved complete sample dissolution. Water RMs were evaporated on a hot plate (10 to 20 ml for SLRS-5 and NIST SRM 1640a; 0.1 to 0.5 ml for the others), then treated with HF and  $\text{H}_2\text{O}_2/\text{HNO}_3$  and evaporated again to remove Si and dissolved organic carbon, respectively. All samples were finally redissolved in 1 mol l<sup>-1</sup>  $\text{HNO}_3$ , and aliquots containing between 2.5 and 15 µg Mg were taken for Mg purification.

Procedures for Mg purification and isotope ratio measurements are similar to those described previously (Uhlig *et al.* 2017). A brief description of the method applied during this study is given below. Magnesium purification was performed using chromatography columns (Spectrum PP 104704, ID 8 mm) filled with 2.8 ml Bio-Rad AG® 50W-X12 resin. After matrix elution with 32 ml 1 mol l<sup>-1</sup>  $\text{HNO}_3$ , Mg was quantitatively eluted with 10 ml 2 mol l<sup>-1</sup>  $\text{HNO}_3$ . The Mg fraction was treated again with  $\text{H}_2\text{O}_2/\text{HNO}_3$ , evaporated and redissolved in 0.3 mol l<sup>-1</sup>  $\text{HNO}_3$ . Each material was processed twice through the column procedure. Each column batch was accompanied by at least one commonly used reference material (IAPSO Atlantic seawater, basalts BCR-2, BHVO-2 or granite GS-N) and a blank. Total procedural blanks of the column chemistry and the  $\text{H}_2\text{O}_2/\text{HNO}_3$  treatment contained < 12 ng Mg, which is < 0.5% Mg compared with the amount of Mg processed through column chemistry and is therefore considered insignificant (potential bias in  $\delta^{26}\text{Mg}$  is estimated < 0.03‰). Magnesium recovery (quantitative column yield), purity of the Mg solutions (> 90% Mg was found to produce no bias using our measurement instrumental set-up; see Pokharel *et al.* 2017) and the Mg content in total procedural blanks were checked by ICP-OES (Varian 720ES) and quadrupole ICP-MS (Thermo Scientific iCAP-Qc), respectively.

Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS equipped with a Neptune Plus Jet Interface (using a Pfeiffer OnToolBooster interface pump; standard sample cone and X skimmer cone). The 500 ng ml<sup>-1</sup> Mg solutions were introduced into the mass spectrometer via a quartz-glass spray chamber (double pass cyclone-Scott type, Thermo SIS) equipped with a self-aspirating PFA nebuliser with an uptake rate of ca. 100 µl min<sup>-1</sup>. The ion beam intensities at *m/z* 24, 25 and 26 were measured simultaneously in medium mass resolution mode (see footnote Table 2) on Faraday detectors (L2, C, H2, all 10<sup>11</sup> Ω amplifiers). The H2 cup was slightly

moved towards higher masses so that <sup>26</sup>Mg<sup>+</sup> was measured on the interference-free low mass side of the flat-top peak (to avoid potential interference from <sup>12</sup>C<sup>14</sup>N<sup>+</sup>). <sup>27</sup>Al<sup>+</sup> and <sup>23</sup>Na<sup>+</sup> were simultaneously monitored on Faraday detectors H4 and L4, respectively. Each measurement run comprises twenty cycles, with an integration time of 4.2 s for each cycle. These conditions gave sample signal intensities > 10 V for <sup>24</sup>Mg. Background intensities (typically < 8 mV <sup>24</sup>Mg) were measured on-peak in 0.3 mol l<sup>-1</sup>  $\text{HNO}_3$  before and after each calibrator-sample bracketing block and were subtracted from the sample and the calibrator signal intensities. Measurement results were accepted only if the instrumental mass bias was stable, that is linear drift < 0.2‰, which is the deviation in <sup>26</sup>Mg/<sup>24</sup>Mg between two bracketing DSM3 calibrators.

The intermediate precision of this measurement procedure (including dissolution, Mg column separation, dilution and MC-ICP-MS analyses) was evaluated by repeat analyses of reference materials (silicate rocks, IAPSO Atlantic seawater) over the course of about 3 years (e.g., Pokharel *et al.* 2017, Uhlig *et al.* 2017). For example, for BHVO-2 basalt we obtained a mean  $\delta^{26}\text{Mg}$  of  $-0.24 \pm 0.10\text{‰}$  and a mean  $\delta^{25}\text{Mg}$  of  $-0.13 \pm 0.06\text{‰}$  (2s, *n* = 24 measurements on *N* = 6 full dissolution and column chemistry replicates), which is identical within stated precisions to results produced independently in other laboratories ( $\delta^{26}\text{Mg} = -0.24 \pm 0.08\text{‰}$ ,  $\delta^{25}\text{Mg} = -0.12 \pm 0.05\text{‰}$ , Teng 2017 and references therein). Measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave a mean of  $-2.61 \pm 0.07\text{‰}$  for  $\delta^{26}\text{Mg}$  and  $-1.35 \pm 0.05\text{‰}$  for  $\delta^{25}\text{Mg}$  (2s, *n* = 62) and IAPSO Atlantic seawater results were  $-0.81 \pm 0.12\text{‰}$  for  $\delta^{26}\text{Mg}$  and  $-0.41 \pm 0.06\text{‰}$  for  $\delta^{25}\text{Mg}$  (2s, *n* = 13). Hence, our long-term estimate of the typical intermediate precision (based on repeated analyses on different materials over ca. 3 years) is  $\pm 0.10\text{‰}$  (2s) for  $\delta^{25}\text{Mg}$  and  $\pm 0.06\text{‰}$  (2s) for  $\delta^{26}\text{Mg}$ , respectively. The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

**Sample preparation and Mg isotope ratio measurements at CGS and GEOMAR:** Sample preparation for the measurements conducted at CGS and GEOMAR was done in the CGS laboratory according to the following procedure. Carbonate powders were digested in 6 mol l<sup>-1</sup> HCl. Powders of the soil NIST SRM 2709a and apple leaves NIST SRM 1515a were successively dissolved in concentrated 1:1 HF:HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>:HNO<sub>3</sub>, respectively, to breakdown the silicate fractions and organic matter. Aliquots of water RMs (equivalent to ca. 20 µg of Mg) were evaporated to dryness and treated with concentrated

HNO<sub>3</sub>. Solutions with visible solid residues were once again redissolved in concentrated 1:1 HNO<sub>3</sub>:H<sub>2</sub>O<sub>2</sub>. All sample solutions were then evaporated to dryness and redissolved in 3% v/v HNO<sub>3</sub>. Prior to loading samples onto micro-columns, at least 20 µg Mg aliquots were taken, evaporated to dryness and redissolved in 100 µl of 2.5 mol l<sup>-1</sup> HCl.

Purification of Mg was accomplished by a three-step chromatographic separation, using 1.25 ml resin (Bio-Rad AG® 50W-X12, 200–400 mesh) in Savillex PFA 3.2 mm × 20 cm (inner diameter × length) microcolumns, for the first and third steps, and 0.12 ml resin in 2.4 mm × 1.5 cm microcolumns for the second step. In the first step, the Mg fraction, which still contains Na and Fe, was separated from other matrix elements by elution with 4.90 ml 2.5 mol l<sup>-1</sup> HCl and collected subsequently. In the second step, the Mg fraction (with Fe) was separated from Na by elution with 4.96 ml 0.4 mol l<sup>-1</sup> HCl and subsequently collected with 1.5 ml 6 mol l<sup>-1</sup> HCl. In the third step, the Mg fraction was separated from Fe by rinsing with 5.2 ml 2 mol l<sup>-1</sup> HNO<sub>3</sub> prior to the elution of the purified Mg solution with 5.5 ml 2 mol l<sup>-1</sup> HNO<sub>3</sub>. The purified Mg fractions were then evaporated to dryness, redissolved in 200 µl concentrated 1:1 HF:HNO<sub>3</sub>, evaporated to dryness, redissolved in 200 µl concentrated 1:1 H<sub>2</sub>O<sub>2</sub>:HNO<sub>3</sub>, evaporated to dryness again and finally dissolved in ca. 3% v/v HNO<sub>3</sub> for Mg isotope amount ratios analyses. Total procedural blank was < 2 ng Mg. Mg yields of close to 100% and molar ratios of Σc(matrix cations)/c(Mg) in the final Mg fractions of < 5% were verified by a Thermo Scientific iCAP-Q ICP-MS, as well as a Varian 720 series ICP-OES for each sample.

**- Mg isotope ratio measurements at CGS.** Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-MS, equipped with Ni sampler and X-Version Ni skimmer cones. The 500 ng ml<sup>-1</sup> Mg solutions were introduced into the plasma via a 100 µl min<sup>-1</sup> PFA nebuliser and a cyclonic quartz-glass spray chamber. All measurements were carried out with the guard electrode tuned on and in medium mass resolution mode (see footnote Table 2). The following cup configuration was used: the ion beam intensities at *m/z* 24, 25 and 26 were measured simultaneously using Faraday cups L1, C and H2, respectively. Measurements were carried out on the low mass side of the peak to avoid <sup>12</sup>C<sup>14</sup>N<sup>+</sup> interference signals on *m/z* 26. Each individual measurement comprised thirty cycles with 8.4 s acquisition time per cycle. Each single delta value (equivalent to *n* = 1, as reported in Table 3) was calculated by at least three

repeated measurements of the same sample solution, each bracketed by DSM3. Thus, each single delta value reported in Table 3 (*n* = 1) represents an average of three measurements of a sample and four measurements of DSM3. Typical signals on *m/z* 24 were about 4 to 8 V (i.e., ion beam of <sup>24</sup>Mg<sup>+</sup>). Procedural blank contributions, including background, were consistently below 0.1% of sample signals. Due to these very low blank contributions to the analyte signals, no on-peak blank corrections were applied. Only an electronic background was collected at half mass unit before each block and subtracted from the measured signals.

Isotope fractionation during column chemistry was not detected with δ<sup>26</sup>Mg values of -0.01 ± 0.05‰ (2s, *n* = 3, based on a comparison of column processed and unprocessed DSM3), which further substantiates high Mg yields after column chemistry of close to 100%. Measurements of the pure Mg solution Cambridge-1 (without processing through columns) gave a mean of -2.59 ± 0.16‰ for δ<sup>26</sup>Mg and -1.34 ± 0.11‰ for δ<sup>25</sup>Mg (2s, *n* = 18). The intermediate precision of the sample preparation procedure and MC-ICP-MS measurement was estimated based on repeat column purifications and measurements of IAPSO Atlantic seawater and was -0.87 ± 0.10‰ for δ<sup>26</sup>Mg and -0.45 ± 0.06‰ for δ<sup>25</sup>Mg (2s, *n* = 14) during the period between the years 2012 and 2016. Hence, based on these long-term observations we estimate our typical intermediate precision at ±0.13‰ for δ<sup>26</sup>Mg and ±0.09‰ for δ<sup>25</sup>Mg (2s). The results on reference materials agree with data obtained in other laboratories, indicating no bias outside the stated precision.

**- Mg isotope ratio measurements at GEOMAR.** The magnesium isotope ratio measurements were carried out in August 2012 using a Thermo Scientific AXIOM MC-ICP-MS. RA. Chilton cones (RAC19 and RAC705) were used to achieve the best sensitivity. Samples, prepared as 200 ng ml<sup>-1</sup> Mg solutions in 5% v/v HNO<sub>3</sub>, were introduced via an ESI MicroFlow PFA-50 nebuliser (50 µl min<sup>-1</sup>) coupled to a CETAC ARIDUS desolvator (sweep Ar gas: ca. 2 l/min, N<sub>2</sub>: ca. 20 ml min<sup>-1</sup>). Three Faraday cups were utilised (L4: *m/z* 24, AX: *m/z* 25, H4: *m/z* 26) for simultaneous data acquisition. The instrumentation was allowed to stabilise by running for ca. 1 day for preliminary tuning before final fine tuning began. Tuning focused on hot and stable plasma conditions, not primarily on maximum intensity. Typically, 200 ng ml<sup>-1</sup> Mg solutions yielded ca. 3.5 V <sup>24</sup>Mg<sup>+</sup> intensity. Each individual measurement result consisted of ten DSM3 calibrator runs bracketing nine runs of the

unknown sample. A single run started with a 15 s on-peak-zero baseline measurement, while clean 5% v/v HNO<sub>3</sub> was introduced, followed by 50 × 2 s data collection (on either reference material or unknown). Finally, sample washout was performed introducing clean 5% v/v HNO<sub>3</sub> for 60 s. Within each run, the collected fifty individual ratios of <sup>25</sup>Mg/<sup>24</sup>Mg and <sup>26</sup>Mg/<sup>24</sup>Mg, respectively, were calculated based on the on-peak baseline-corrected *m/z* 24, 25 and 26 signal intensities. Results were calculated using the mean of the individual ratios after removing statistical outliers (1s). Each run of the unknown was used to calculate the  $\delta$ -value relative to the preceding and following runs of DSM3. The resulting nine  $\delta$ -values were combined to an average for the measurement. Each measurement consumed about 200 ng of total Mg.

The repeatability precision is estimated by repeated measurements of Cambridge-1 during this study (without processing through columns), which gave  $-2.58 \pm 0.08\text{‰}$  for  $\delta^{26}\text{Mg}$  and  $-1.33 \pm 0.06\text{‰}$  for  $\delta^{25}\text{Mg}$  (2s, *n* = 11). Measurements of Cambridge-1 processed through columns gave  $-2.63 \pm 0.12\text{‰}$  for  $\delta^{26}\text{Mg}$  and  $-1.31 \pm 0.03\text{‰}$  for  $\delta^{25}\text{Mg}$  (2s, *n* = 3; Table 3). The results agree with data obtained in other laboratories, indicating no bias outside the stated precision. Because no long-term data on repeated measurements on materials with different matrices are available to estimate the typical intermediate precision of the GEOMAR laboratory, as was done for the other laboratories, the typical precision was estimated by the long-term repeatability of the MC-ICP-MS to be  $\pm 0.08\text{‰}$  (2s) for  $\delta^{26}\text{Mg}$  and  $\pm 0.06\text{‰}$  (2s) for  $\delta^{25}\text{Mg}$ , based on the unprocessed Cambridge-1 results.

## Results and discussion

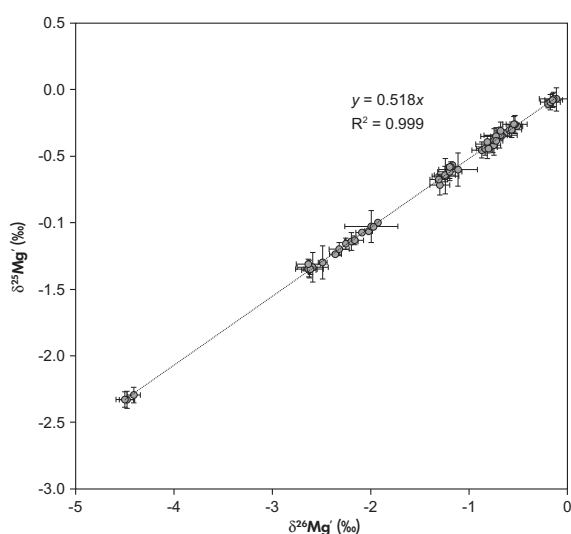
### Individual results validation of the participating laboratories

All the  $\delta^{26}\text{Mg}$ ' versus  $\delta^{25}\text{Mg}$ ' results determined in different laboratories during this study plot on a single line with a slope of  $0.518 \pm 0.004$  (Figure 1; linear fit was obtained using the *Isoplot* software), suggesting no major influence of isobaric interferences on the measured Mg isotope ratios. In addition, the  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of Cambridge-1 and seawater, on which large data sets are available in the literature (e.g., compilations in Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011, Ling *et al.* 2011, An and Huang 2014, Teng 2017, and references therein and in the GeoReM database, Jochum *et al.* 2005), were used to validate the individual measurement procedures

and measurement results performed by each laboratory. First, to validate each mass spectrometric measurement procedure, the pure Mg solution Cambridge-1 was analysed without processing through Mg column chemistry. Second, to include the various sample preparation methods for Mg purification in the interlaboratory comparison, IAPSO Atlantic seawater, which contains a complex element matrix ( $\sum c(\text{matrix cations})/c(\text{Mg}) = 9.2$ ; Table 1), was processed and analysed repeatedly in each laboratory. For both RMs, the  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values agree well between all laboratories. The absolute differences (bias) between the values measured in this study and published consensus values are less than 0.04‰ and 0.03‰ for  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$ , respectively (Table 3, Figure 2), which are well within the precisions reported by each laboratory. These observations indicate that the various measurement procedures (including sample preparation and MC-ICP-MS measurements) do not induce any significant bias outside the reported measurement precision. However, due to the fact that all measurements in this and previous studies were conducted by MC-ICP-MS instruments, an independent validation using a different method cannot be made to exclude any potential systematic MC-ICP-MS bias. However, to date no other technique is able to measure  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  at the level of precision obtainable by MC-ICP-MS.

The MC-ICP-MS repeatability precision for Cambridge-1 determined by each laboratory ranges from 0.07 to 0.16‰ (2s) for  $\delta^{26}\text{Mg}$  and 0.03 to 0.11‰ (2s) for  $\delta^{25}\text{Mg}$  (Table 3). The intermediate precision of the entire measurement procedure based on multiple IAPSO Atlantic seawater sample preparations and MC-ICP-MS analyses ranges from 0.04 to 0.12‰ (2s) for  $\delta^{26}\text{Mg}$  and 0.04 to 0.09‰ (2s) for  $\delta^{25}\text{Mg}$  (Table 3). Because the 2s of IAPSO Atlantic seawater results is not systematically larger than the precision (2s) of Cambridge-1 results, we conclude that the different sample preparation methods do not introduce any additional significant sources of uncertainty that are not already included in the intermediate measurement precision (2s) reported for each RM result by the different laboratories.

These findings are also consistent with the 'typical' intermediate precision reported by each laboratory, based on  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values measurements of various RMs and natural samples over the long term (between 0.06‰ and 0.13‰, 2s, in  $\delta^{26}\text{Mg}$ , and 0.04‰ and 0.09‰, 2s, in  $\delta^{25}\text{Mg}$ , Table 2, Figure 2). Thus, the individual results from the different laboratories can be used to evaluate the consensus  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of the 'new' Earth-surface RMs analysed in this study. This means that the consensus mean  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values of the full-procedure replicates measured by the different laboratories



**Figure 1.**  $\delta^{25}\text{Mg}'$  versus  $\delta^{26}\text{Mg}'$  values determined in this study. Error bars are 2s of each result. The data are in accordance with a regression line (dotted) that crosses the origin and has a slope of 0.52, typical of mass-dependent fractionation of terrestrial material.

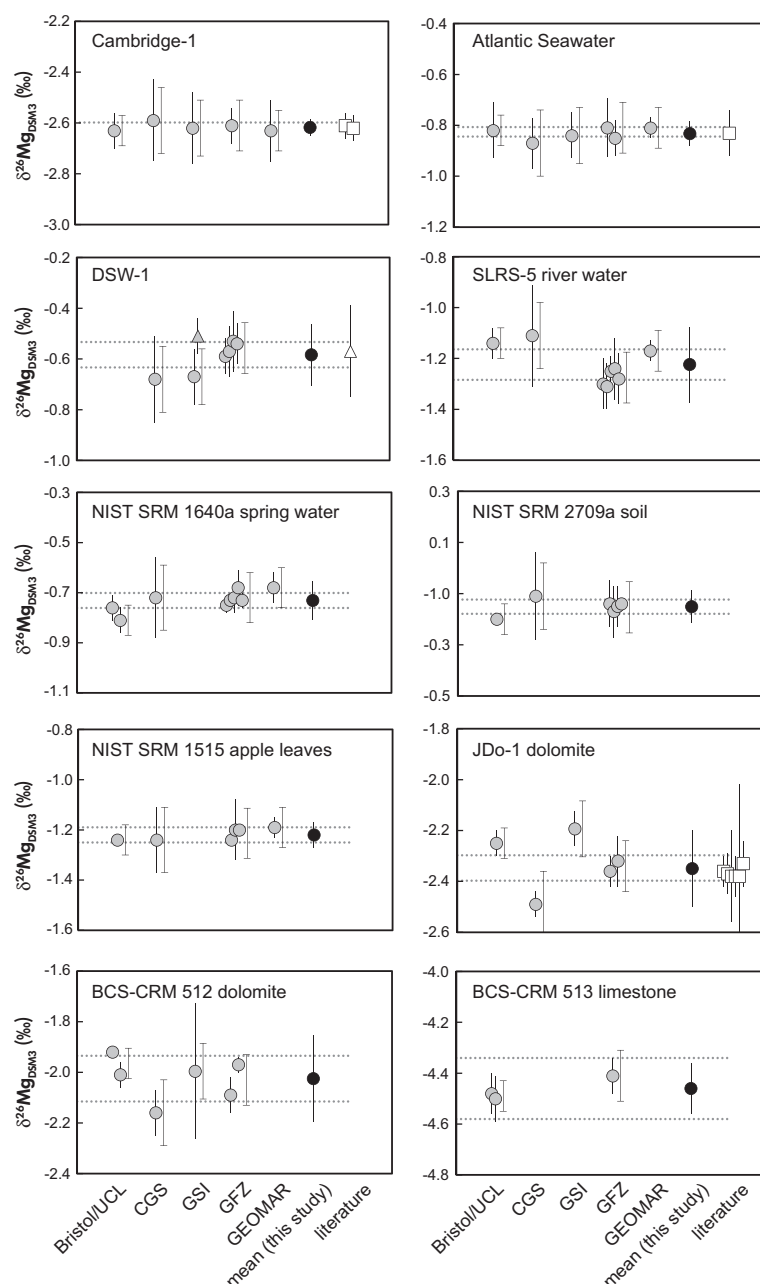
and their variance (reported both as 2s and 95% confidence interval in Tables 3 and 4) include random errors that stem from all influencing factors (sample preparation, matrix separation, instrumental conditions, etc.). Hence, following a 'top-down' approach of uncertainty evaluation (e.g., Potts 2012a, b), we report consensus mean values for each Earth-surface RM characterised in this study together with an uncertainty statement (95% confidence interval, based on the  $\delta^{25}\text{Mg}$  and  $\delta^{26}\text{Mg}$  values reported by each laboratory, as discussed in the next section.

### Assigning consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values to the reference materials

The results of the eight RMs, from the laboratories participating in this study, as well as the available literature data, are shown in Table 3 and Figure 2. The range of  $\delta^{26}\text{Mg}$  values of the studied RMs covers almost the entire range of terrestrial materials (e.g., Teng 2017). As expected, the lowest  $\delta^{26}\text{Mg}$  values were found in carbonates: limestone BCS-CRM 513a ( $-4.46 \pm 0.12\text{‰}$ , 95% conf.,  $n = 3$ ), which represents the lower part of the global  $\delta^{26}\text{Mg}$  range of limestones, and dolomites JDo-1 and BCS-CRM 512 ( $-2.35 \pm 0.05\text{‰}$ , 95% conf.,  $n = 11$  and  $-2.03 \pm 0.09\text{‰}$ , 95% conf.,  $n = 6$ , respectively), which are within the typical range for dolomites (Teng 2017 and references therein). The most positive  $\delta^{26}\text{Mg}$  value was found in the soil NIST SRM 2709a ( $-0.15 \pm 0.03\text{‰}$ , 95% conf.,  $n = 6$ ), typical for silicate soils (Teng 2017 and references therein).

NIST SRM 1515 (apple leaves) has  $\delta^{26}\text{Mg}$  value of  $-1.22 \pm 0.03\text{‰}$  (95% conf.,  $n = 6$ ), consistent with previous findings.  $\delta^{26}\text{Mg}$  values in plants depend on the sources of Mg and on complex isotope fractionation processes during the uptake of Mg and transport within the plant (e.g., Black *et al.* 2008, Bolou-Bi *et al.* 2010, 2012, Tipper *et al.* 2010). In general, Mg in rivers and groundwater yield a large range of  $\delta^{26}\text{Mg}$  values with a flux-weighted  $\delta^{26}\text{Mg}$  of global run-off of  $-1.09\text{‰}$  (Tipper *et al.* 2006b). SLRS-5 river water ( $-1.22 \pm 0.06\text{‰}$ , 95% conf.,  $n = 8$ ) has lower  $\delta^{26}\text{Mg}$  value, and spring water NIST SRM 1640a ( $-0.73 \pm 0.03\text{‰}$ , 95% conf.,  $n = 9$ ) has higher  $\delta^{26}\text{Mg}$  value, relative to this average. The higher  $\delta^{26}\text{Mg}$  value of the Dead Sea brine (DSW-1;  $-0.58 \pm 0.05\text{‰}$ , 95% conf.,  $n = 8$ ) relative to its precursor seawater may represent a contribution of  $^{24}\text{Mg}$ -depleted dolomitising brines (Gavrieli *et al.* 2009, Shalev *et al.* 2014).

To obtain mean  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values for the RMs, we evaluate the interlaboratory reproducibility (indicated as 2s on the consensus value derived from the results of all laboratories and literature data; Table 3). All eight RMs have an interlaboratory reproducibility (2s) of 0.05 to 0.17‰ in  $\delta^{26}\text{Mg}$ . For most RMs (DSW-1, NIST SRM 1640a, NIST SRM 2709a, NIST SRM 1515 and BCS-CRM 513), the interlaboratory reproducibility (0.05–0.12‰) is within or below the range of the 'typical' intermediate precision of the laboratories estimated from repeat analysis of different materials over the long term (0.06–0.13‰ in  $\delta^{26}\text{Mg}$ ), indicating that the measurement procedures used in all laboratories do not induce any additional uncertainty contributions when samples with such matrices are processed and measured. For these RMs, the individual results from all laboratories also agree within the reported measurement precision of each sample (Table 3 and Figure 2). However, the interlaboratory reproducibilities of three RMs, river water SLRS-5, dolomites JDo-1 and BCS-CRM 512 (2s of 0.15‰, 0.15‰ and 0.17‰, respectively), are slightly higher than the 'typical' intermediate precisions reported by the participating laboratories. While all the individual SLRS-5 results agree within 2s measurement precision of the repeat measurements of each RM, this is not the case for all individual results of JDo-1 and BCS-CRM 512 (Figure 2). Averaged data of JDo-1 reported in the literature seem to be more uniform, but in some cases, the reported 2s is larger, covering the whole range obtained in current research (Wombacher *et al.* 2009, Pearce *et al.* 2012, Mavromatis *et al.* 2013, 2014, Beinlich *et al.* 2014, Lavoie *et al.* 2014, Figure 2). Similar to the results of this study, Wombacher *et al.* (2009) reported a precision of 0.18‰ (2s) on the mean of twelve measurement results of JDo-1 from four different Mg separations (test portions of 2.5–40 mg). Note that most of these values (Pearce *et al.* 2012,



**Figure 2.**  $\delta^{26}\text{Mg}$  values of the studied Earth-surface low-temperature materials. Individual results from each laboratory (grey circles) are presented with their repeatability precision ( $2s$ , twice the standard deviation of  $n$  repeated measurements). Multiple results from individual laboratories represent full-procedure replicates (including dissolution, Mg columns and MC-ICP-MS measurements). Capped error bars next to each individual results indicate the typical intermediate precision ( $2s$ ) for each laboratory (based on repeat analyses of samples with different matrices over the long-term) for comparison with the measurement precision of the matrix RMs. Available literature data (specified in Table 3) are also presented (white squares). Triangles, in the DSW-1 plot, refer to different samples of the Dead Sea brine. The interlaboratory arithmetic mean of these individual results is also shown (black circle) with  $2s$  error bars and 95% confidence interval (presented by grey dotted lines). The vertical axis in all plots ranges 0.8‰.

Mavromatis *et al.* 2013, 2014, Beinlich *et al.* 2014) were obtained using a similar chemical sample preparation procedure.

The reasons for the slightly higher interlaboratory variance in the dolomite RMs are unknown. Interlaboratory variance can arise from many factors, including material

**Table 4.**  
Interlaboratory consensus  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values from this study and literature, if available, of low-temperature, Earth-surface reference materials

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf <sup>a</sup>	N <sup>b</sup>
DSW-1 (Dead Sea brine)	-0.58	0.05	-0.30	0.03	8
SLRS-5 (river water)	-1.22	0.06	-0.64	0.04	8
NIST SRM 1640a (spring water)	-0.73	0.03	-0.38	0.03	9
NIST SRM 2709a (soil)	-0.15	0.03	-0.08	0.02	6
NIST SRM 1515 (apple leaves)	-1.22	0.03	-0.62	0.03	6
JDo-1 (dolomite)	-2.35	0.05	-1.23	0.03	11
BCS-CRM 512 (dolomite)	-2.03	0.09	-1.05	0.05	6
BCS-CRM 513a (limestone)	-4.46	0.12	-2.32	0.05	3

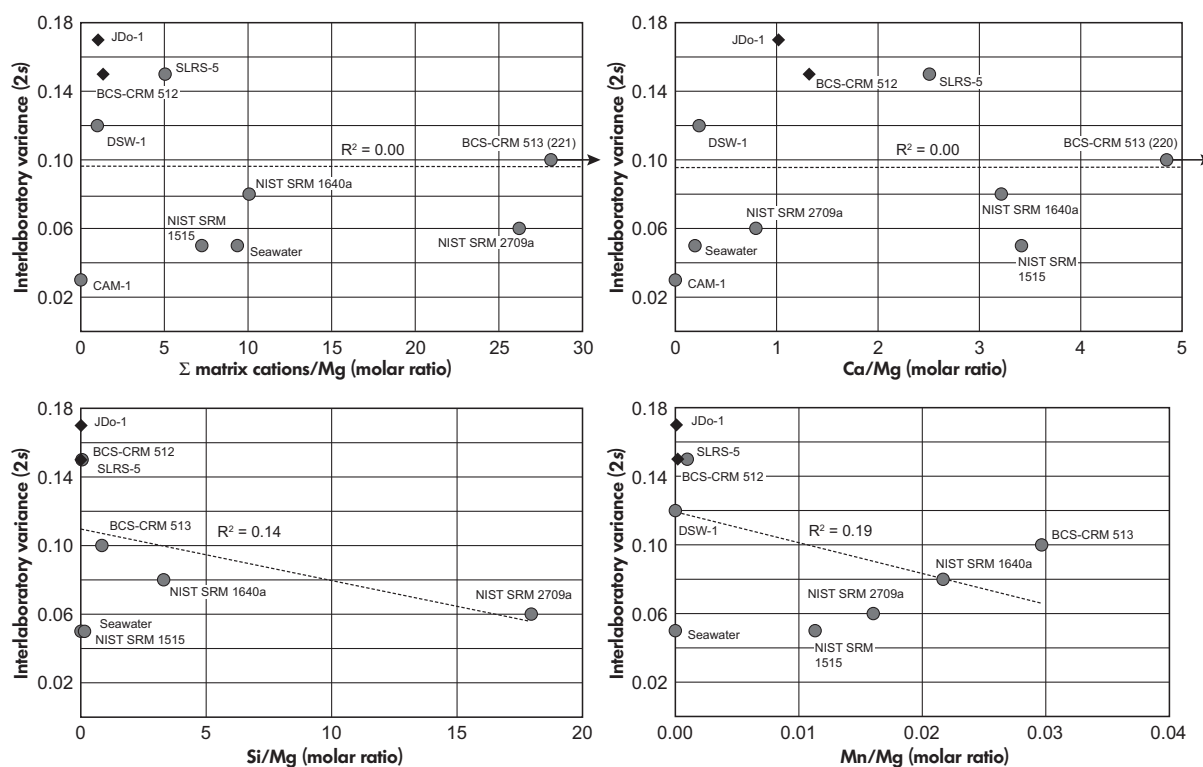
<sup>a</sup> 95% confidence intervals calculated as  $2SE$ , (95% conf) =  $t \cdot s / \sqrt{N}$ , with  $s$  = standard deviation of  $N$  full-procedure replicates,  $t$  = correction factor for low  $N$  from Student's  $t$ -distribution at 95% probability.

<sup>b</sup>  $N$  is the number of results used for the calculation of the consensus values and the 95% confidence interval. These are detailed in Table 3.

properties (e.g., homogeneity at the level of the test portion, or stability over time), sample preparation procedure (e.g., incomplete dissolution, column yield, analyte purity and blank) and the procedures used in the mass spectrometric measurements and data reduction (e.g., mass bias stability and mass bias correction, matrix effects). No correlation was found between molar matrix elements/Mg ratios and the interlaboratory variance (examples in Figure 3). Moreover,

we checked for any correlations between individual  $\delta^{26}\text{Mg}$  values and test portions, blank/Mg, column capacity, but did not find any systematic relations. Thus, further investigation on these RMs is required to determine the sources of the observed variance.

The consensus  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  mean values for the studied RMs are provided in Table 4 together with an



**Figure 3.** Interlaboratory variance ( $2s$  reproducibilities) of the studied materials versus selected matrix element molar ratios (before Mg purification by column chemistry). Dolomite RMs (JDo-1, BCS-CRM 512), are shown as diamonds. Low  $R^2$  of the linear regression lines (dashed lines) demonstrates absence of any correlation.

associated uncertainty for each value. This uncertainty was estimated by the 95% confidence interval on the mean of  $N$  laboratory results, including literature data, if available.

## Summary and conclusions

In this study, the  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  values of eight Earth-surface reference materials (RMs), representative of different low-temperature environments and material types were determined by interlaboratory comparison. Despite the differences in sample preparation procedures, different test portions, instrumentation and isotope ratio measurement procedures, good agreement of the  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  data from the different laboratories was found. This encouraging result suggests that all methods described in this study are suitable for geochemical studies on these types of materials given they are strictly monitored and calibrated (recovery, blanks, matrix removal, etc.). Moreover, the investigated RMs are suitable to be used by other laboratories for routine quality control of Mg isotope ratio measurement procedures during environmental and Earth-surface geochemical studies. The wide range of matrices, including river water, spring water, brine, dolomites, limestone, soil and plant leaves, allow analysts to identify potential issues (and facilitate modifications) with sample preparation methods previously developed for silicate rocks, for example, which are then applied to different sample types, such as Ca-rich carbonates, organic-rich soils or vegetation.

## Acknowledgements

PvS acknowledges ERC Consolidator Grant 682760 – CONTROLPASTCO2. J. Bartel and J. Buhk are acknowledged for laboratory support at GFZ. F. von Blanckenburg and the Helmholtz Association are thanked for infrastructure support at GFZ. The analytical work done at CGS, GEOMAR and CULS was supported via the European Union's Horizon 2020 research and innovation programme, under Grant Agreement No. 643084 (*Base-LiNE Earth* project), and the Czech Science Foundation (GACR) Grant nos. 17-18120S and P210/12/P631. Technical and laboratory assistance of T. Magna, M. Francová, M. Šimeček and J. Míková at CGS is acknowledged. The research done at the University of Adelaide was supported via *Base-LiNE Earth*, and the ARC linkage project LP160101353 to JF. NS acknowledges L. Halicz, I. Gavrieli, B. Lazar and D. Vance for their advices and support and N. Teplyakov, Y. Zakun and K. Weiss for laboratory support at GSI. The work at GSI was funded by the DFG-trilateral project TRION (Ei272/30-1), the Israeli Ministry of Science, Technology and Space (Eshkol scholarship), the Israeli Ministry of National Infrastructures, Energy and Water resources and Dalia and Dan Maydan

Fellowship. The research done at ETH Zürich was funded by an ETH postdoctoral fellowship (FEL-14 16-1). The authors would also like to thank the editor, T. Meisel and two anonymous reviewers whose comments helped to significantly improve this manuscript.

## References

- An Y. and Huang F. (2014)**  
A review of Mg isotope analytical methods by MC-ICP-MS. *Journal of Earth Science*, **25**, 822–840.
- Beinlich A., Mavromatis V., Austrheim H. and Oelkers E.H. (2014)**  
Inter-mineral Mg isotope fractionation during hydrothermal ultramafic rock alteration – Implications for the global Mg-cycle. *Earth and Planetary Science Letters*, **392**, 166–176.
- Black J.R., Epstein E., Rains W.D., Yin Q.Z. and Casey W.H. (2008)**  
Magnesium-isotope fractionation during plant growth. *Environmental Science and Technology*, **42**, 7831–7836.
- Bolou-Bi E.B., Vigier N., Brenot A. and Poszwa A. (2009)**  
Magnesium isotope compositions of natural reference materials. *Geostandards and Geoanalytical Research*, **33**, 95–109.
- Bolou-Bi E.B., Poszwa A., Leyval C. and Vigier N. (2010)**  
Experimental determination of magnesium isotope fractionation during higher plant growth. *Geochimica et Cosmochimica Acta*, **74**, 2523–2537.
- Bolou-Bi E.B., Vigier N., Poszwa A., Boudot J.P. and Dambrine E. (2012)**  
Effects of biogeochemical processes on magnesium isotope variations in a forested catchment in the Vosges Mountains (France). *Geochimica et Cosmochimica Acta*, **87**, 341–355.
- Brand W.A., Coplen T.B., Vogl J., Rosner M. and Prohaska T. (2014)**  
Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report). *Pure and Applied Chemistry*, **86**, 425–467.
- Brenot A., Cloquet C., Vigier N., Carignan J. and France-Lanord C. (2008)**  
Magnesium isotope systematics of the lithologically varied Moselle river basin, France. *Geochimica et Cosmochimica Acta*, **72**, 5070–5089.
- Chapela Lara M., Buss H.L., Pogge von Strandmann P.A.E., Schuessler J.A. and Moore O.W. (2017)**  
The influence of critical zone processes on the Mg isotope budget in a tropical, highly weathered andesitic catchment. *Geochimica et Cosmochimica Acta*, **202**, 77–100.





## references

- Coplen T.B. (2011)**  
Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. *Rapid Communications in Mass Spectrometry*, 25, 2538–2560.
- Foster G.L., Pogge von Strandmann P.A.E. and Rae J.W.B. (2010)**  
Boron and magnesium isotopic composition of seawater. *Geochemistry Geophysics Geosystems*, 11, 1–10.
- Galy A., Belshaw N.S., Halicz L. and O’Nions R.K. (2001)**  
High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry. *International Journal of Mass Spectrometry*, 208, 89–98.
- Galy A., Bar-Matthews M., Halicz L. and O’Nions R.K. (2002)**  
Mg isotopic composition of carbonate: Insight from speleothem formation. *Earth and Planetary Science Letters*, 201, 105–115.
- Galy A., Yoffe O., Janney P.E., Williams R.W., Cloquet C., Alard O., Halicz L., Wadhwa M., Hutcheon I.D., Ramon E. and Carignan J. (2003)**  
Magnesium isotope heterogeneity of the isotopic standard SRM 980 and new reference materials for magnesium-isotope-ratio measurements. *Journal of Analytical Atomic Spectrometry*, 18, 1352–1356.
- Gavrieli I., Yoffe O., Burg A. and Halicz L. (2009)**  
Mg isotope fractionation in the Ca-chloride Dead Sea brine system. *Geochimica et Cosmochimica Acta Supplement*, 73, A419.
- Geske A., Lokier S., Dietzel M., Richter D.K., Buhl D. and Immenhauser A. (2015)**  
Magnesium isotope composition of sabkha porewater and related (Sub-)Recent stoichiometric dolomites, Abu Dhabi (UAE). *Chemical Geology*, 393–394, 112–124.
- Golan R., Gavrieli I., Ganor J. and Lazar B. (2016)**  
Controls on the pH of hyper-saline lakes—A lesson from the Dead Sea. *Earth and Planetary Science Letters*, 434, 289–297.
- Higgins J.A. and Schrag D.P. (2015)**  
The Mg isotopic composition of Cenozoic seawater – evidence for a link between Mg-clays, seawater Mg/Ca, and climate. *Earth and Planetary Science Letters*, 416, 73–81.
- Jochum K.P., Nohl U., Herwig K., Lammel E., Stoll B. and Hofmann A.W. (2005)**  
GeoReM: A new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research*, 29, 333–338.
- Karasinski J., Bulska E., Wojciechowski M., Halicz L. and Krata A.A. (2017)**  
High precision direct analysis of magnesium isotope ratio by ion chromatography/multicollector-ICP-MS using wet and dry plasma conditions. *Talanta*, 165, 64–68.
- Kasemann S.A., Pogge von Strandmann P.A.E., Prave A.R., Fallick A.E., Elliott T. and Hoffmann K.H. (2014)**  
Continental weathering following a Cryogenian glaciation: Evidence from calcium and magnesium isotopes. *Earth and Planetary Science Letters*, 396, 66–77.
- Lavoie D., Jackson S. and Girard I. (2014)**  
Magnesium isotopes in high-temperature saddle dolomite cements in the lower Paleozoic of Canada. *Sedimentary Geology*, 305, 58–68.
- Ling M.-X., Sedaghatpour F., Teng F.-Z., Hays P.D., Strauss J. and Sun W. (2011)**  
Homogeneous magnesium isotopic composition of seawater: An excellent geostandard for Mg isotope analysis. *Rapid Communications in Mass Spectrometry*, 25, 2828–2836.
- Liu X.M., Teng F.Z., Rudnick R.L., McDonough W.F. and Cummings M.L. (2014)**  
Massive magnesium depletion and isotope fractionation in weathered basalts. *Geochimica et Cosmochimica Acta*, 135, 336–349.
- Ma L., Teng F.-Z., Jin L., Ke S., Yang W., Gu H.-O. and Brantley S.L. (2015)**  
Magnesium isotope fractionation during shale weathering in the Shale Hills Critical Zone Observatory: Accumulation of light Mg isotopes in soils by clay mineral transformation. *Chemical Geology*, 397, 37–50.
- Mavromatis V., Gautier Q., Bosc O. and Schott J. (2013)**  
Kinetics of Mg partition and Mg stable isotope fractionation during its incorporation in calcite. *Geochimica et Cosmochimica Acta*, 114, 188–203.
- Mavromatis V., Meister P. and Oelkers E.H. (2014)**  
Using stable Mg isotopes to distinguish dolomite formation mechanisms: A case study from the Peru Margin. *Chemical Geology*, 385, 84–91.
- Opfergelt S., Georg R.B., Delvaux B., Cabidoche Y.-M., Burton K.W. and Halliday A.N. (2012)**  
Mechanisms of magnesium isotope fractionation in volcanic soil weathering sequences, Guadeloupe. *Earth and Planetary Science Letters*, 341–344, 176–185.
- Pearce C.R., Saldi G.D., Schott J. and Oelkers E.H. (2012)**  
Isotopic fractionation during congruent dissolution, precipitation and at equilibrium: Evidence from Mg isotopes. *Geochimica et Cosmochimica Acta*, 92, 170–183.
- Pogge von Strandmann P.A.E. (2008)**  
Precise magnesium isotope measurements in core top planktic and benthic foraminifera. *Geochemistry, Geophysics, Geosystems*, 9, 1–13.
- Pogge von Strandmann P.A.E., Burton K.W., James R.H., van Calsteren P., Gislason S.R. and Sigfússon B. (2008)**  
The influence of weathering processes on riverine magnesium isotopes in a basaltic terrain. *Earth and Planetary Science Letters*, 276, 187–197.
- Pogge von Strandmann P.A.E., Elliott T., Marschall H.R., Coath C., Lai Y.J., Jeffcoate A.B. and Ionov D.A. (2011)**  
Variations of Li and Mg isotope ratios in bulk chondrites and mantle xenoliths. *Geochimica et Cosmochimica Acta*, 75, 5247–5268.

## references

---

- Pogge von Strandmann P.A.E., Opfergelt S., Lai Y.-J., Sigfússon B., Gislason S.R. and Burton K.W. (2012)**  
Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. *Earth and Planetary Science Letters*, 339–340, 11–23.
- Pogge von Strandmann P.A.E., Forshaw J. and Schmidt D.N. (2014)**  
Modern and Cenozoic records of magnesium behaviour from foraminiferal Mg isotopes. *Biogeosciences Discussions*, 11, 7451–7484.
- Pokharel R., Gerrits R., Schuessler J.A., Floor G., Gorbushina A.A. and von Blanckenburg F. (2017)**  
Mg isotope fractionation during uptake by a rock-inhabiting, model microcolonial fungus *Knufia petricola* at acidic and neutral pH. *Environmental Science and Technology*, 51, 9691–9699.
- Potts P.J. (2012a)**  
A proposal for the publication of geochemical data in the scientific literature. *Geostandards and Geoanalytical Research*, 36, 225–230.
- Potts P.J. (2012b)**  
Glossary of analytical and metrological terms from the International Vocabulary of Metrology (2008). *Geostandards and Geoanalytical Research*, 36, 231–246.
- Shalev N., Lazar B., Halicz L. and Gavrieli I. (2014)**  
Magnesium isotope fractionation during epigenetic dolomitization of carbonate rocks. *Goldschmidt Abstracts*, 2014, 2257.
- Shalev N., Lazar B., Halicz L. and Gavrieli I. (2017)**  
Mg isotope fractionation during precipitation of marine Mg-evaporites. *Goldschmidt Abstracts*, 2017, 3606.
- Summerhayes C.P. and Thorpe S.A. (1996)**  
*Oceanography – An illustrated guide*: Chapter 11. CRC Press (Boca Raton, FL), 165–181.
- Teng F.-Z. (2017)**  
Magnesium isotope geochemistry. *Reviews in Mineralogy and Geochemistry*, 82, 219–287.
- Teng F.-Z., Yin Q.-Z., Ullmann C.V., Chakrabarti R., Pogge von Strandmann P.A.E., Yang W., Li W.-Y., Ke S., Wimpenny F.S.J., Meixner A., Romer R.L., Wiechert U. and Jacobsen S.B. (2015)**  
Interlaboratory comparison of magnesium isotopic compositions of twelve felsic to ultramafic igneous rock standards analyzed by MC-ICP-MS. *Geochemistry Geophysics Geosystems*, 16, 3197–3209.
- Tipper E.T., Galy A. and Bickle M.J. (2006a)**  
Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle. *Earth and Planetary Science Letters*, 247, 267–279.
- Tipper E.T., Galy A., Gaillardet J., Bickle M.J., Elderfield H. and Carder E.A. (2006b)**  
The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science Letters*, 250, 241–253.
- Tipper E., Gaillardet J., Louvat P., Capmas F. and White A.F. (2010)**  
Mg isotope constraints on soil pore-fluid chemistry: Evidence from Santa Cruz, California. *Geochimica et Cosmochimica Acta*, 74, 3883–3896.
- Uhlir D., Schuessler J.A., Bouchez J., Dixon J.L. and von Blanckenburg F. (2017)**  
Quantifying nutrient uptake as driver of rock weathering in forest ecosystems by magnesium stable isotopes. *Biogeosciences*, 14, 3111–3128.
- Wombacher F., Eisenhauer A., Heuser A. and Weyer S. (2006)**  
Combined chemical separation of Mg, Ca and Fe from geological reference samples for stable isotope determination by MC-ICP-MS and double-spike TIMS. *Geophysical Research Abstracts*, 8, A06219.
- Wombacher F., Eisenhauer A., Heuser A. and Weyer S. (2009)**  
Separation of Mg, Ca and Fe from geological reference materials for stable isotope ratio analyses by MC-ICP-MS and double-spike TIMS. *Journal of Analytical Atomic Spectrometry*, 24, 627.
- Wombacher F., Eisenhauer A., Böhm F., Gussone N., Regenberg M., Dullo W.-C. and Rüggeberg A. (2011)**  
Magnesium stable isotope fractionation in marine biogenic calcite and aragonite. *Geochimica et Cosmochimica Acta*, 75, 5797–5818.
- Young E.D. and Galy A. (2004)**  
The isotope geochemistry and cosmochemistry of magnesium. *Reviews in Mineralogy and Geochemistry*, 55, 197–230.

