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Mg isotope inter-laboratory comparison of reference materials from earth-surface low-temperature environments

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1 **Mg isotope inter-laboratory comparison of reference materials from earth-**
2 **surface low-temperature environments**

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25 **Abstract**

26 To enable quality control of measurement procedures for determinations of Mg isotope amount
27 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
28 eight reference materials (RMs) were determined by inter-laboratory comparison between five
29 laboratories and considering published data, if available. These matrix RMs, including river water
30 SLRS-5, spring water SRM 1640a, Dead Sea brine DSW-1, dolomites JDo-1 and CRM 512, limestone
31 CRM 513, soil SRM 2709a and vegetation SRM 1515 apple leaves, are representative for a wide
32 range of earth-surface materials from low-temperature environments. The inter-laboratory
33 variability, $2s$ (twice the standard deviation), of all eight RMs ranges from 0.05 to 0.17 ‰ in $\delta^{26}\text{Mg}$.
34 Thus, it is suggested that all these materials are suitable for validation of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$
35 determinations of earth-surface geochemical studies.

36 **Keywords:** Mg isotopes, Reference materials, Low-temperature, Earth-surface, Inter-laboratory
37 comparison

39 **1. Introduction**

40 Magnesium is a major element of the silicate Earth and vital in biogeochemical cycling. It has three
41 stable isotopes: ^{24}Mg (78.99%), ^{25}Mg (10.00%), and ^{26}Mg (11.01%). Analytical improvements over the
42 past decades have made the differentiation between the Mg isotope amount ratios (expressed as
43 $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ relative to the international δ -zero standard, DSM3; equation 1; Galy *et al.* 2003,
44 IUPAC, see Brand *et al.*, 2014) of terrestrial materials possible and enable today's rapid increase in
45 the use of Mg isotopes as a powerful tool in investigations of Earth's biogeochemistry (e.g., Young
46 and Galy 2004, Teng 2017). Yet, determinations of $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of natural samples are
47 challenging, due to the significant risk of bias introduced during Mg purification, the large
48 instrumental mass bias and the sensitivity of the sample-standards-bracketing measurements to
49 matrix effects (e.g., Young and Galy 2004, An and Huang 2014, Teng 2017). Hence, processing well-

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3 50 characterised reference materials (RMs), similar in matrix to the samples, is required to validate the
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5 51 results. While $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of silicate rock RMs are available for high-temperature
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7 52 systems (Teng *et al.* 2015), Mg isotope data of RMs representative of samples with complex matrices
8
9 53 from earth-surface low-temperature environments are scarce (Bolou-Bi *et al.* 2009, Foster *et al.*
10
11 54 2010, An and Huang 2014, Teng 2017). To assess systematic errors and achieve comparability of Mg
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13 55 isotope data between different laboratories concerning earth-surface low-temperature systems,
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15 56 well-characterised matrix RMs need to be established.
16
17 57 $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values are being used as a biogeochemical tool to study many different processes
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19 58 in low-temperature environments, e.g., in marine environments and marine sediments and rocks
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21 59 (e.g., Ling *et al.* 2011, Wombacher *et al.* 2011, Pogge von Strandmann *et al.* 2014, Higgins and Schrag
22
23 60 2015), evaporitic environments (e.g., Geske *et al.* 2015b, Shalev *et al.* 2017), soils and vegetation
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25 61 (e.g., Tipper *et al.* 2010, Opfergelt *et al.* 2012, Pogge von Strandmann *et al.* 2012, Ma *et al.* 2015,
26
27 62 Uhlig *et al.* 2017) and ground water, spring water and rivers (e.g., Tipper *et al.* 2006b, Pogge von
28
29 63 Strandmann *et al.* 2008, Brenot *et al.* 2008, Chapela Lara *et al.* 2017). The most fractionated
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31 64 materials on earth are found in low-temperature environments, with the lowest $\delta^{26}\text{Mg}$ values found
32
33 65 in carbonates ($\delta^{26}\text{Mg}$ of -5.6 ‰, Wombacher *et al.* 2011) and the highest in weathered residual
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35 66 silicates ($\delta^{26}\text{Mg}$ of +1.8 ‰, Liu *et al.* 2014b) and evaporites ($\delta^{26}\text{Mg}$ = +1.4 ‰, Permian carnallite,
36
37 67 Shalev *et al.* 2017). However, the only natural earth surface RM which is well-characterised to date is
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39 68 seawater ($\delta^{26}\text{Mg}$ of -0.83 ± 0.09 ‰; 2s; N=90; Foster *et al.* 2010, Ling *et al.* 2011 and references
40
41 69 therein). Published $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ data of earth surface materials from more than two
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43 70 laboratories (N >2) are also available for Cal-S limestone (-4.38 ± 0.09 ‰, 2s, N=3; Wombacher *et al.*
44
45 71 2006; Bolou-Bi *et al.* 2009), SCo-1 shale (-0.89 ± 0.08 ‰, 2s, N=3), JCo-1 aragonite (-1.96 ± 0.05 ‰, 2s,
46
47 72 N=4) and JDo-1 dolomite (-2.37 ± 0.04 ‰, 2s, N=5; Teng 2017 and references therein). Here, N is
48
49 73 used to denote the number of full-procedure replicates, i.e. independent sample dissolution and Mg
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51 74 purification, while n is used to denote the number of repeated measurements of the purified Mg
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53 75 sample solutions by MC-ICP-MS. 2s is twice the standard deviation on N or n values.
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77 In this study, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of eight RMs (Table 1), representative for their respective
78 earth surface environments, were estimated by inter-laboratory comparison, conducted in five
79 laboratories. The participating laboratories utilised different sample preparation methods, i.e.,
80 different analyte-matrix separation procedures, and MC-ICP-mass spectrometers from various
81 manufacturers with different sample introduction systems (Table 2). This approach is suitable to test
82 the applicability of these different measurement methods with respect to the varying chemical and
83 physical material properties and to identify potential bias originating from differences in sample
84 preparation and instrument setup. Whereas measurement results from a single laboratory might
85 produce very precise $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for any material never analysed before, there is still
86 the potential risk that the data is affected by undetected bias. We suggest that our inter-laboratory
87 comparison study provides a robust and practicable approach to provide the geo-analytical
88 community with fit-for-purpose $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for matrix-RMs with confidence intervals
89 constrained by the currently attainable level of measurement precision. Materials of this study
90 included solids: carbonates, soil and organic material (leaves), and liquids: river water, spring water
91 and brine, thereby represent most of the material types from earth surface low-temperature
92 environments studied to date. Most selected RMs are provided by reference material producers and
93 are widely available to the community. Also, certified mass fractions data are available for most
94 materials studied in this work (Table 1). Based on the results of this study and published values,
95 where available, recommended $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values are proposed. These can be used as quality
96 control RMs in laboratories analysing earth surface materials to verify their measurement methods.

97 [Table 1]

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99 **2. Methods**100 **2.1. Investigated materials**

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3 101 The investigated materials include: JDo-1 and BCS-CRM 512 dolomites, BCS-CRM 513 limestone,
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5 102 SRM 2709a soil, SRM 1515 apple leaves, IAPSO Atlantic seawater, SLRS-5 river water, SRM 1640a
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7 103 spring water and DSW-1 Dead Sea brine. Solid samples are powdered and require complete
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9 104 dissolution prior to the column chemistry. The published chemical compositions of the investigated
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11 105 materials are described in Table 1. $\sum c(\text{Matrix-cations})/c(\text{Mg})$ molar ratios (i.e., the molar ratios of the
12
13 106 sum of Na, K, Ca, Si, Al, Ti, Fe and Mn relative to Mg) of the RMs vary significantly: Na/Mg ratios
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15 107 range between 0.0 (carbonates) and 8.8 (seawater), Ca/Mg ratios range between 0.2 (seawater) and
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17 108 220 (BCS-CRM 513 limestone) and K/Mg ratios range between 0.0 (JDo-1 and BCS-CRM 512
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19 109 dolomites) and 3.7 (SRM 1515 apple leaves). The soil (SRM 2709a), spring water (SRM 1640a) and
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21 110 limestone (BCS-CRM 513) have the most complex matrices with significant Si/Mg ratios (18, 3.3 and
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23 111 0.8, respectively), Al/Mg ratios (4.6, 0.04 and 0.45, respectively), Fe/Mg ratios (1.0, 0.02 and 0.08,
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25 112 respectively) and Ti/Mg ratio (0.12 in the soil SRM 2709a).
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30 114 **2.2. Measurement procedures**

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32 115 The eight RMs, IAPSO Atlantic seawater and Cambridge-1 were analysed for $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values
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34 116 in the laboratories of the University of Bristol (BIG) and University of London (UCL), UK (BIG LOGIC);
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36 117 The Geological Survey of Israel (GSI), Jerusalem, Israel; the Helmholtz Laboratory for the
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38 118 Geochemistry of the Earth Surface (HELGES) at GFZ Potsdam, Germany; the Czech Geological Survey
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40 119 (CGS) in Prague (Czech Republic); and the GEOMAR Helmholtz Center for Ocean Research, Kiel,
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42 120 Germany. The powdered or liquid RMs were split and spread among the different laboratories. Each
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44 121 laboratory conducted measurements, using its own previously established measurement procedure,
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46 122 to get completely independent results, and potentially identify any method-specific bias. The
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48 123 different procedures for material digestion, Mg purification and instrumentation, conducted in each
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50 124 laboratory, are described below and summarized in Table 2. All Mg isotope ratio measurements
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53 125 were conducted by MC-ICP-MS using standard-sample bracketing and the calculated isotope amount
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126 ratios are reported as per mil deviation from the delta-zero measurement standard DSM3 in the
 127 delta notation according to Coplen (2011):

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

129 where x denotes either 26 or 25 and DSM3 is the mean value of the two bracketing standards
 130 measured before and after the sample, respectively. Multiplication of equation (1) with a factor
 131 1000 gives the per mil (‰) deviation relative to DSM3.

132 To validate the different measurement procedures used by the participating laboratories and to test
 133 for any potential inter-laboratory bias, we adapted the following approach. During this study,
 134 Cambridge-1 and IAPSO Atlantic seawater were analysed by all participating laboratories. These
 135 results are compared to literature values (e.g., compilations in Teng 2017; An and Huang 2014; and
 136 the in GeoReM database, Jochum *et al.* 2005) in order to validate the measurement procedure of
 137 each laboratory. Thereby, the pure Mg-solution Cambridge-1 was used to evaluate the repeatability
 138 precision of the MC-ICP-MS measurements (solution not processed through columns) for each
 139 laboratory. Then, seawater was used to evaluate the intermediate precision of the entire
 140 measurement procedure for each laboratory, including sample pre-treatment, matrix separation by
 141 column chemistry, and MC-ICP-MS analysis. In addition, a typical intermediate precision was
 142 estimated by each laboratory (Table 2), based on long-term (more than one year) repeated
 143 measurements of one or more matrix materials as detailed below (sections 2.2.1-2.2.4). The only
 144 case where this long-term experience with matrix material is missing is at GEOMAR and therefore
 145 only Cambridge-1 repeatability precision was considered. These estimates are considered as a
 146 benchmark against which we can evaluate the precision obtained on the matrix RMs investigated in
 147 this inter-laboratory comparison study. Then, to provide consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for each
 148 earth-surface reference material, the arithmetic mean of $N \geq 3$ full-procedure-replicates was
 149 calculated. These comprised all data produced by the participating laboratories and – where
 150 available – literature data and are reported together with 95% confidence intervals.

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3 151 [Table 2]
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7 153 *2.2.1. Sample preparation and Mg isotope ratio measurements at UCL and Bristol (BIG*

8
9 154 *LOGIC)*
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11 155 Procedures for sample analyses are similar to those described in previous studies (Pogge von
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13 156 Strandmann 2008, Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011, 2012). A brief description is
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15 157 given below.

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17 158 Carbonate powders (ca. 20 mg) were dissolved in 2 mol/l HCl. Apple leaves (SRM 1515, ca 50 mg)
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19 159 were dissolved in repeated steps of concentrated HNO₃, heated at 130 °C and evaporated to
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21 160 dryness. Soil powders (ca. 10 mg) were dissolved in stages of concentrated HF-HNO₃, followed by
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23 161 HNO₃, and finally 6 mol/l HCl. Water samples (ca. 0.01–0.2 ml) were simply dried down.

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26 162 Subsequently, the samples were dissolved in 2 mol/l HNO₃, and a small aliquot (around 0.2 - 3 µg
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28 163 Mg) was taken for column chemistry.

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30 164 Magnesium analyte-matrix separation was performed by a two-stage cation exchange chemistry,
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32 165 using Bio-Rad AG® 50W-X12 (200-400 mesh) resin in 2 mol/l HNO₃, as described by Pogge von
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34 166 Strandmann *et al.* (2011). Soil samples were subjected to an additional column to quantitatively
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36 167 remove Ti (because ⁴⁸Ti²⁺ and ⁵⁰Ti²⁺ are direct interferences on ²⁴Mg⁺ and ²⁵Mg⁺). This column
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38 168 contained 0.25 ml of TRU-Spec™ resin, and Mg was eluted in 7 mol/l HNO₃ (Pogge von Strandmann
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40 169 *et al.* 2012). The total procedural blank for Mg isotope ratio measurements by this method is ca. 0.4
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42 170 ng Mg, which is insignificant compared to the amount of Mg put through chemistry (<0.2 %). Splits
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44 171 of the elution were collected before and after the Mg collection bracket, to ensure close to 100 %
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46 172 Mg yield was achieved, i.e., <0.1 % of the processed Mg was detected in these splits.

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49 173 Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-
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51 174 MS with a high-sensitivity “X” Ni skimmer cone and standard Ni sample cone interface. A purified
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53 175 sample solution of ca. 100 ng/ml Mg was introduced via an Elemental Scientific Inc. Apex-Q, with a
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55 176 ca. 50 µl/min uptake rate nebuliser tip, in 2 % HNO₃ (v/v). Mg isotope ratios were measured in low
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3 177 mass resolution mode (see footnote in table 2), with all intensities at m/z 24, 25 and 26 measured
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5 178 simultaneously in separate Faraday cups (H3, Centre, L3). Each individual measurement consisted of
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7 179 20 ratios (84 seconds total integration time). These conditions gave typical signals of 18 - 20 V/100
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9 180 ng/ml on ^{24}Mg . The on-peak background in 2 % HNO_3 (v/v) was repeatedly recorded during the
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11 181 sequence and subtracted from all standard and sample intensities. Each sample was analysed 3 or 4
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13 182 times ($n = 3$ or $n = 4$ in Table 3) during the same session (336 seconds/sample), each time separated
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15 183 by several hours. The difference in the measured $^{26}\text{Mg}/^{24}\text{Mg}$ intensities ratio between bracketing
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17 184 DSM3 standards was ≤ 0.06 ‰ in all analyses performed for this study.
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19 185 USGS (United States Geological Survey) and GSJ (Geological Survey of Japan) silicate rock reference
20
21 186 material measurement results by this procedure are documented by Pogge von Strandmann *et al.*
22
23 187 (2011), other silicate rocks by Teng *et al.* (2015), IAPSO Atlantic seawater results by Foster *et al.*
24
25 188 2010, and carbonates by Pogge von Strandmann 2008, Kasemann *et al.* (2014) and Pogge von
26
27 189 Strandmann *et al.* (2014). For example, measurements of the pure Mg solution Cambridge-1
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29 190 (without processing through columns) gave -2.63 ± 0.07 ‰ for $\delta^{26}\text{Mg}$ and -1.36 ± 0.06 ‰ for $\delta^{25}\text{Mg}$
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31 191 (2s, $n=126$) and IAPSO Atlantic seawater results were -0.82 ± 0.06 ‰ for $\delta^{26}\text{Mg}$ and -0.43 ± 0.04 ‰ for
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33 192 $\delta^{25}\text{Mg}$ (2s, $n=26$, Foster *et al.* 2010). Hence, the typical intermediate precision of this method, based
34
35 193 on several years of repeated measurements, is estimated at ± 0.06 ‰ (2s) on $\delta^{26}\text{Mg}$, and ± 0.04 ‰
36
37 194 (2s) on $\delta^{25}\text{Mg}$. The results on reference materials agree with data obtained in other laboratories,
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39 195 indicating no bias outside the stated precision.
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197 2.2.2. Sample preparation and Mg isotope ratio measurements at GSI

46 198 Carbonate powders (ca. 100-150 mg) were dissolved in HNO_3 and evaporated to dryness. Water
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48 199 samples (ca. 10 μl DSW-1 and 2 ml IAPSO) were simply dried down. All samples were then re-
49
50 200 dissolved in 10 ml 1.3 mol/l HCl and an aliquot (200-500 μg Mg) was taken for column chemistry.
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52 201 Magnesium purification was performed by liquid chromatography (Galy *et al.* 2002) using Bio-Rad
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54 202 Econo-Pac Chromatography Columns 732-1010 with an extended reservoir, filled with ca. 18 ml of
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3 203 Bio-Rad AG® 50W-X12 100-200 mesh resin. The matrix was rinsed with 25 ml of 1.3 mol/l HCl and 20
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5 204 ml of 2.3 mol/l HCl. Mg²⁺ was then eluted with 24 ml of 2.3 mol/l HCl. Total procedural blanks
6
7 205 contained <0.5 % Mg of the amount of Mg processed through column chemistry. The first and the
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9 206 last 2 ml before and after the Mg elution were collected separately in order to verify close to 100%
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11 207 Mg recovery. In addition, the Mg amount in the Mg cut (Mg-COL) was compared to the amount
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13 208 originally loaded to the column (Mg-ORIG). Only samples with Mg-COL/Mg-ORIG >95 % (taking into
14
15 209 account the uncertainties of both measurements), no detectable Mg in the first and the last 2 ml
16
17 210 before and after the Mg fraction, and molar ratio of $\sum c(\text{matrix-cations})/c(\text{Mg})$ in the final Mg fraction
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19 211 of <5 % (after Galy *et al.* 2001 and others) were used for isotope ratio measurements. These
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21 212 parameters were verified for each sample separation using ICP-AES (Optima 3300, Perkin–Elmer).
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23 213 Once Mg was purified, the solution was fully evaporated and the chloride salts were re-dissolved in
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25 214 0.1 mol/l HNO₃.
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27 215 Magnesium isotope ratio measurements were conducted using a Nu instruments Plasma II HR-MC-
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29 216 ICP-MS. The 2 µg/ml Mg solutions (in 0.1 mol/l HNO₃) were introduced into the mass spectrometer
30
31 217 via a DSN-100 desolvation system (self-aspirating PFA nebuliser, uptake rate of ca. 100 µl/min) and
32
33 218 standard Ni cones interface. The measurements were conducted using pseudo-high resolution, with
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35 219 a 50 µm source slit at a mass resolving power $R_p(5,95\%) = 7000$ (see footnote in table 2). Three
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37 220 Faraday cup collectors were used to measure the ion beam intensities at m/z 24, 25 and 26
38
39 221 simultaneously. Each measurement run comprises 20 integrations of 10 s data acquisition, i.e. a total
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41 222 200 seconds of data acquisition per measurement. These conditions gave sample signal intensities of
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43 223 25-35 V on m/z 24. The zero reference points were reset simultaneously for all measured masses by
44
45 224 deflecting the potential of the electrostatic analyser before measuring each block. A blank solution
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47 225 measured in the beginning of each measurements day, produced <5 mV on m/z 24 and therefore
48
49 226 the difference from the off-peak zero is considered insignificant. Each sample solution was measured
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51 227 by several brackets of standard-sample-standard, which were used for statistical analysis, where n is
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53 228 the number of brackets of each sample. Outliers were eliminated as long as their elimination
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3 229 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
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5 230 t-distribution value.
6
7 231 The $\delta^{26}\text{Mg}$ mean of pure Mg Cambridge-1 solution measured in this study is $-2.62 \pm 0.14 \text{ ‰}$ (2s, n=36,
8
9 232 Table 3), identical within stated precisions to results reported by other laboratories (e.g.,
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11 233 compilations by Teng 2017, An and Huang 2014; $-2.61 \pm 0.05 \text{ ‰}$, 2s). The $\delta^{26}\text{Mg}$ value of IAPSO
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13 234 Atlantic seawater reference material measured in this study ($-0.84 \pm 0.09 \text{ ‰}$, 2s, n=12, Table 3) is also
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15 235 identical to the previously reported seawater value ($-0.83 \pm 0.09 \text{ ‰}$, 2s, N=90; Foster *et al.* 2010, Ling
16
17 236 *et al.* 2011 and references therein). In order to further test the measurement procedure, a sample of
18
19 237 modern Dead Sea brine (DSW-1) was purified through Mg column chemistry and this single solution
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21 238 was repeatedly measured over two years ($\delta^{26}\text{Mg} = -0.67 \pm 0.11 \text{ ‰}$, $\delta^{25}\text{Mg} = -0.35 \pm 0.05 \text{ ‰}$, 2s, n=35,
22
23 239 Table 3). Accordingly, our long-term estimate of the typical intermediate precision is $\pm 0.11 \text{ ‰}$ (2s) on
24
25 240 $\delta^{26}\text{Mg}$, and $\pm 0.05 \text{ ‰}$ (2s) on $\delta^{25}\text{Mg}$. The results on reference materials agree with data obtained in
26
27 241 other laboratories, indicating no bias outside the stated precision.
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243 2.2.3. Sample preparation and Mg isotope ratio measurements at GFZ

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35 244 Solid powders (30 - 100 mg) were digested in HF/HNO₃ mixture at 110 °C, followed by 6 mol/l HCl,
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37 245 and 14 mol/l HNO₃. For all samples, H₂O₂/HNO₃ treatment in closed PFA-vials on a hotplate at 150
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39 246 °C/ 24 h was used to remove organics. In addition, a separate batch of the organic-rich soil (SRM
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41 247 2709a) and vegetation (SRM 1515) (ca. 1 g) were also acid-digested (H₂O₂/HNO₃) using a microwave
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43 248 system (MLS Start) at 160 °C/ 20 min and elevated pressure. Both, the PFA-vial-hotplate and the
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45 249 microwave method achieved complete sample dissolution. Water RMs were evaporated on a hot
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47 250 plate (10 to 20 ml for SLRS-5 and SRM 1640a; 0.1 to 0.5 ml for the others), then treated with HF and
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49 251 H₂O₂/HNO₃ and evaporated again to remove Si and dissolved organic carbon, respectively. All
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51 252 samples were finally re-dissolved in 1 mol/l HNO₃ and aliquots containing between 2.5 and 15 µg Mg
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53 253 were taken for Mg purification.
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3 254 Procedures for Mg purification and isotope ratio measurements are similar to those described
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5 255 previously (Uhlig *et al.* 2017). A brief description of the method applied during this study is given
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7 256 below. Magnesium purification was performed using chromatography columns (Spectrum PP
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9 257 104704, ID 8 mm) filled with 2.8 ml Biorad AG® 50W-X12 resin. After matrix elution with 32 ml 1
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11 258 mol/l HNO₃, Mg was quantitatively eluted with 10 ml 2 mol/l HNO₃. The Mg fraction was treated
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13 259 again with H₂O₂/HNO₃, evaporated and re-dissolved in 0.3 mol/l HNO₃. Each material was processed
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15 260 twice through the column procedure. Each column batch was accompanied by at least one
16
17 261 commonly used reference material (IAPSO Atlantic Seawater, basalts BCR-2, BHVO-2 or granite GS-
18
19 262 N) and a blank. Total procedural blanks of the column chemistry and the H₂O₂/HNO₃ treatment
20
21 263 contained <12 ng Mg, which is <0.5 % Mg compared to the amount of Mg processed through column
22
23 264 chemistry and is therefore considered insignificant (potential bias in δ²⁶Mg is estimated <0.03 ‰).
24
25 265 Magnesium recovery (quantitative column yield), purity of the Mg solutions (>90 % Mg was found to
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27 266 produce no bias using our measurement instrumental setup; see Pokharel *et al.* 2017), and the Mg
28
29 267 content in total procedural blanks were checked by ICP-OES (Varian 720ES) and quadrupole ICP-MS
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31 268 (Thermo Scientific iCAP-Qc), respectively.
32
33 269 Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-
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35 270 MS equipped with a Neptune Plus Jet Interface (using a Pfeiffer OnToolBooster interface pump;
36
37 271 standard sample cone and X skimmer cone). The 500 ng/ml Mg solutions were introduced into the
38
39 272 mass spectrometer via a quartz-glass spraychamber (double pass cyclon-Scott type, Thermo SIS)
40
41 273 equipped with a self-aspirating PFA nebuliser with an uptake rate of ca. 100 µl/min. The ion beam
42
43 274 intensities at m/z 24, 25 and 26 were measured simultaneously in medium mass resolution mode
44
45 275 (see footnote table 2) on Faraday detectors (L2, C, H2, all 10¹¹ Ω amplifiers). The H2 cup was slightly
46
47 276 moved toward higher masses so that ²⁶Mg⁺ was measured on the interference-free low mass side of
48
49 277 the flat-top peak (to avoid potential interference from ¹²C¹⁴N⁺). ²⁷Al⁺ and ²³Na⁺ were simultaneously
50
51 278 monitored on Faraday detectors H4 and L4, respectively. Each measurement run comprises 20
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53 279 cycles, with an integration time of 4.2 seconds for each cycle. These conditions gave sample signal
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3 280 intensities >10 V for ^{24}Mg . Background intensities (typically <8 mV ^{24}Mg) were measured on-peak in
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5 281 0.3 mol/l HNO_3 before and after each standard-sample bracketing block and were subtracted from
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7 282 the sample and the standard signal intensities. Measurement results were accepted only if the
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9 283 instrumental mass bias was stable, i.e. linear drift <0.2 ‰, which is the deviation in $^{26}\text{Mg}/^{24}\text{Mg}$
10
11 284 between two bracketing DSM3 standards.
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13 285 The intermediate precision of this measurement procedure (including dissolution, Mg column
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15 286 separation, dilution, and MC-ICP-MS analyses) was evaluated by repeat analyses of reference
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17 287 materials (silicate rocks and IAPSO Atlantic Seawater) over the course of about 3 years (e.g., Uhlig et
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19 288 al. 2017, Pokharel *et al.* 2017). For example, for BHVO-2 basalt we obtained a mean $\delta^{26}\text{Mg}$ of -0.24
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21 289 ± 0.10 ‰ and a mean $\delta^{25}\text{Mg}$ of -0.13 ± 0.06 ‰ (2s, n=24 measurements on N = 6 full dissolution and
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23 290 column chemistry replicates), which is identical within stated precisions to results produced
24
25 291 independently in other laboratories ($\delta^{26}\text{Mg} = -0.24 \pm 0.08$ ‰, $\delta^{25}\text{Mg} = -0.12 \pm 0.05$ ‰, Teng 2017 and
26
27 292 references therein). Measurements of the pure Mg solution Cambridge-1 (without processing
28
29 293 through columns) gave a mean of -2.61 ± 0.07 ‰ for $\delta^{26}\text{Mg}$ and -1.35 ± 0.05 ‰ for $\delta^{25}\text{Mg}$ (2s, n=62)
30
31 294 and IAPSO Atlantic seawater results were -0.81 ± 0.12 ‰ for $\delta^{26}\text{Mg}$ and -0.41 ± 0.06 ‰ for $\delta^{25}\text{Mg}$ (2s,
32
33 295 n=13). Hence, our long-term estimate of the typical intermediate precision (based on repeated
34
35 296 analyses on different materials over ca. 3 years) is ± 0.10 ‰ (2s) for $\delta^{25}\text{Mg}$ and ± 0.06 ‰ (2s) for
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37 297 $\delta^{26}\text{Mg}$, respectively. The results on reference materials agree with data obtained in other
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39 298 laboratories, indicating no bias outside the stated precision.
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300 2.2.4. Sample preparation and Mg isotope ratio measurements at CGS and GEOMAR

301 Sample preparation for the measurements conducted at CGS and GEOMAR was done in the CGS
302 laboratory according to the following procedure. Carbonate powders were digested in 6 mol/l HCl.
303 Powders of the soil NIST SRM 2709a and apple leaves NIST SRM 1515a were successively dissolved in
304 concentrated 1:1 HF:HNO₃ and H₂O₂:HNO₃, respectively, to breakdown the silicate fractions and
305 organic matter. Aliquots of water RMs (equivalent to ca. 20 µg of Mg) were evaporated to dryness

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3 306 and treated with concentrated HNO₃. Solutions with visible solid residues were once again re-
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5 307 dissolved in concentrated 1:1 HNO₃:H₂O₂. All sample solutions were then evaporated to dryness and
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7 308 re-dissolved in 3 % HNO₃ (v/v). Prior to loading samples onto microcolumns, at least 20 µg Mg
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9 309 aliquots were taken, evaporated to dryness and re-dissolved in 100 µl of 2.5 mol/l HCl.
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11 310 Purification of Mg was accomplished by a three-step chromatographic separation, using 1.25 ml
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13 311 resin (BioRad AG® 50W-X12, 200-400 mesh) in Savillex PFA 3.2 mm x 20 cm (inner diameter x length)
14
15 312 microcolumns, for the first and third steps, and 0.12 ml resin in 2.4 mm × 15 cm microcolumns for
16
17 313 the second step. In the first step, the Mg fraction, which still contains Na and Fe, was separated from
18
19 314 other matrix elements by elution with 4.90 ml 2.5 mol/l HCl and collected subsequently. In the
20
21 315 second step, the Mg fraction (with Fe) was separated from Na by elution with 4.96 ml 0.4 mol/l HCl
22
23 316 and subsequently collected with 1.5 ml 6 mol/l HCl. In the third step, the Mg fraction was separated
24
25 317 from Fe by rinsing with 5.2 ml 2 mol/l HNO₃ prior to the elution of the purified Mg solution with 5.5
26
27 318 ml 2 mol/l HNO₃. The purified Mg fractions were then evaporated to dryness, re-dissolved in 200 µl
28
29 319 concentrated 1:1 HF:HNO₃, evaporated to dryness, re-dissolved in 200 µl concentrated 1:1
30
31 320 H₂O₂:HNO₃, evaporated to dryness again and finally dissolved in ca. 3 % HNO₃ (v/v) for Mg isotope
32
33 321 amount ratios analyses. Total procedural blank was <2 ng Mg. Mg yields of close to 100 % and molar
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35 322 ratios of $\sum c(\text{matrix-cations})/c(\text{Mg})$ in the final Mg fractions of <5 % were verified by a Thermo
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37 323 Scientific iCAP-Q ICP-MS, as well as a Varian 720 series ICP-OES for each sample.
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42 325 2.2.4.1. Mg isotope ratio measurements at CGS

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45 326 Magnesium isotope ratio measurements were conducted using a Thermo Scientific Neptune MC-ICP-
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47 327 MS, equipped with Ni sampler and X-Version Ni skimmer cones. The 500 ng/ml Mg solutions were
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49 328 introduced into the plasma via a 100 µl min⁻¹ PFA nebuliser and a cyclonic quartz-glass spray
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51 329 chamber. All measurements were carried out with the guard electrode turned on and in medium
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53 330 mass resolution mode (see footnote table 2). The following cup configuration was used: the ion
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55 331 beam intensities at m/z 24, 25 and 26 were measured simultaneously using Faraday cups L1, C, and
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3 332 H2, respectively. Measurements were carried out on the low mass side of the peak to avoid $^{12}\text{C}^{14}\text{N}^+$
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5 333 interference signals on m/z 26. Each individual measurement comprised 30 cycles with 8.4 seconds
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7 334 acquisition time per cycle. Each single delta value (equivalent to $n = 1$, as reported in Table 3) was
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9 335 calculated by at least 3 repeated measurements of the same sample solution, each bracketed by
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11 336 DSM3. Thus, each single delta value reported in Table 3 ($n = 1$) represents an average of 3
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13 337 measurements of a sample and 4 measurements of DSM3. Typical signals on m/z 24 were about 4 to
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15 338 8 V (i.e., ion beam of $^{24}\text{Mg}^+$). Procedural blank contributions, including background, were
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17 339 consistently below 0.1 % of sample signals. Due to these very low blank contributions to the analyte
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19 340 signals, no on-peak blank corrections were applied. Only an electronic background was collected at
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21 341 half mass unit before each block and subtracted from the measured signals.
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23 342 Isotope fractionation during column chemistry was not detected with $\delta^{26}\text{Mg}$ values of -0.01 ± 0.05 ‰
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25 343 (2s, $n=3$, based on a comparison of column processed and unprocessed DSM3) which further
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27 344 substantiates high Mg yields after column chemistry of close to 100 %. Measurements of the pure
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29 345 Mg solution Cambridge-1 (without processing through columns) gave a mean of -2.59 ± 0.16 ‰ for
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31 346 $\delta^{26}\text{Mg}$ and -1.34 ± 0.11 ‰ for $\delta^{25}\text{Mg}$ (2s, $n=18$). The intermediate precision of the sample preparation
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33 347 procedure and MC-ICP-MS measurement was estimated based on repeat column purifications and
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35 348 measurements of IAPSO Atlantic seawater and was -0.87 ± 0.10 ‰ for $\delta^{26}\text{Mg}$ and -0.45 ± 0.06 ‰ for
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37 349 $\delta^{25}\text{Mg}$ (2s, $n = 14$) during the period between the years 2012 and 2016. Hence, based on these long-
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39 350 term observations we estimate our typical intermediate precision at ± 0.13 ‰ for $\delta^{26}\text{Mg}$ and ± 0.09
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41 351 ‰ for $\delta^{25}\text{Mg}$ (2s). The results on reference materials agree with data obtained in other laboratories,
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43 352 indicating no bias outside the stated precision.
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354 2.2.4.2. Mg isotope ratio measurements at GEOMAR

355 The magnesium isotope ratio measurements were carried out in August 2012 using a Thermo
356 Scientific AXIOM MC-ICP-MS. R.A. Chilton cones (RAC19 & RAC705) have been used for best
357 sensitivity. Samples, prepared as 200 ng/ml Mg solutions in 5 % HNO_3 (v/v), were introduced via an

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3 358 ESI *MicroFlow PFA-50* nebuliser (50 $\mu\text{l}/\text{min}$) coupled to a CETAC *ARIDUS* desolvator (sweep Ar gas:
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5 359 ca. 2 l/min, N_2 : ca. 20 ml/min). Three Faraday cups have been utilized (L4: m/z 24, AX: m/z 25, H4:
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7 360 m/z 26) for simultaneous data acquisition. The instrumentation had been allowed for stabilization
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9 361 running ca. 1 day preliminarily tuned before actual fine tuning started. Tuning focused on hot and
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11 362 stable plasma conditions, not primarily on maximum intensity. Typically, 200 ng/ml Mg solutions
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13 363 yielded ca. 3.5 V $^{24}\text{Mg}^+$ intensity. Each individual measurement result consisted of 10 DSM3 standard
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15 364 runs bracketing 9 runs of the unknown sample. A single run started with a 15 seconds on-peak-zero
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17 365 baseline measurement, while clean 5 % HNO_3 (v/v) was introduced, followed by 50 x 2 s data
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19 366 collection (on either standard or unknown). Finally, sample washout was performed introducing
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21 367 clean 5 % HNO_3 (v/v) for 60 seconds. Within each run, the collected 50 individual ratios of $^{25}\text{Mg}/^{24}\text{Mg}$
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23 368 and $^{26}\text{Mg}/^{24}\text{Mg}$, respectively, were calculated based on the on-peak baseline-corrected m/z 24, 25
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25 369 and 26 signal intensities. Results were calculated using the mean of the individual ratios after
26
27 370 removing statistical outliers (1s). Each run of the unknown was used to calculate the δ -value relative
28
29 371 to the preceding and following runs of DSM3. The resulting 9 δ -values were combined to an average
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31 372 for the measurement. Each measurement consumed about 200 ng of total Mg.
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33 373 The repeatability precision is estimated based on repeated measurements of Cambridge-1 during
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35 374 this study (without processing through columns) which gave $-2.58 \pm 0.08 \text{‰}$ for $\delta^{26}\text{Mg}$ and -1.33
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37 375 $\pm 0.06 \text{‰}$ for $\delta^{25}\text{Mg}$ (2s, n =11). Measurements of Cambridge-1 processed through columns gave -
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39 376 $2.63 \pm 0.12 \text{‰}$ 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
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41 377 obtained in other laboratories, indicating no bias outside the stated precision. Because no long-term
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43 378 data on repeated measurements on materials with different matrices is available to estimate the
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45 379 typical intermediate precision of the GEOMAR laboratory, as was done for the other laboratories,
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47 380 the typical precision was estimated by the long-term repeatability of the MC-ICP-MS to be $\pm 0.08 \text{‰}$
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49 381 (2s) for $\delta^{26}\text{Mg}$ and $\pm 0.06 \text{‰}$ (2s) for $\delta^{25}\text{Mg}$, based on the unprocessed Cambridge-1 results.
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51 382 [Table 3]
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384 3. Results and Discussion

385 3.1 Individual results validation of the participating laboratories

386 All the $\delta^{26}\text{Mg}'$ versus $\delta^{25}\text{Mg}'$ results determined in different laboratories during this study plot on a
387 single line with a slope of 0.518 ± 0.004 (Fig. 1; linear fit was obtained using the *Isoplot* software),
388 suggesting no major influence of isobaric interferences on the measured Mg isotope ratios. In
389 addition, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of Cambridge-1 and Seawater, on which large datasets are
390 available in the literature (e.g., compilations in Foster *et al.* 2010, Pogge von Strandmann *et al.* 2011,
391 Ling *et al.* 2011, An and Huang 2014, Teng 2017, and references therein and in the GeoReM
392 database, Jochum *et al.* 2005), were used to validate the individual measurement procedures and
393 measurement results performed by each laboratory. First, to validate each mass spectrometric
394 measurement procedure, the pure Mg solution Cambridge-1 was analysed without processing
395 through Mg column chemistry. Second, to include the various sample preparation methods for Mg
396 purification in the inter-laboratory comparison, IAPSO Atlantic seawater, which contains a complex
397 element matrix ($\sum c(\text{matrix-cations})/c(\text{Mg}) = 9.2$; Table 1), was processed and analysed repeatedly in
398 each laboratory. For both RMs, the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values agree well between all laboratories. The
399 absolute differences (bias) between the values measured in this study and published consensus
400 values are less than 0.04 ‰ and 0.03 ‰ for $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$, respectively (Table 3, Fig. 2), which
401 are well within the precisions reported by each laboratory. These observations indicate that the
402 various measurement procedures (including sample preparation and MC-ICP-MS measurements) do
403 not induce any significant bias outside the reported measurement precision. However, due to the
404 fact that all measurements in this and previous studies were conducted by MC-ICP-MS instruments,
405 an independent validation using a different method cannot be made to exclude any potential
406 systematic MC-ICP-MS bias. However, to date no other technique is able to measure $\delta^{26}\text{Mg}$ and
407 $\delta^{25}\text{Mg}$ at the level of precision obtainable by MC-ICP-MS.

408 The MC-ICP-MS repeatability precision for Cambridge-1 determined by each laboratory ranges from
409 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

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3 410 precision of the entire measurement procedure based on multiple IAPSO Atlantic seawater sample
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5 411 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 ‰
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7 412 (2s) for $\delta^{25}\text{Mg}$ (Table 3). Because the 2s of IAPSO Atlantic seawater results is not systematically larger
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9 413 than the precision (2s) of Cambridge-1 results, we conclude that the different sample preparation
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11 414 methods do not introduce any additional significant sources of uncertainty that are not already
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13 415 included in the intermediate measurement precision (2s) reported for each RM result by the
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15 416 different laboratories.

17 417 These findings are also consistent with the 'typical' intermediate precision reported by each
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19 418 laboratory, based on $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values measurements of various RMs and natural samples
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21 419 over the long-term (between 0.06 ‰ and 0.13 ‰, 2s, in $\delta^{26}\text{Mg}$, and 0.04 ‰ and 0.09 ‰, 2s, in
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23 420 $\delta^{25}\text{Mg}$, Table 2, Fig. 2). Thus, the individual results from the different laboratories can be used to
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25 421 evaluate the consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of the 'new' earth-surface RMs analysed in this
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27 422 study. This means that the consensus mean $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of the full-procedure-replicates
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29 423 measured by the different laboratories and their variance (reported both as 2s and 95 % confidence
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31 424 interval in tables 3 and 4) include random errors that stem from all influencing factors (sample
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33 425 preparation, matrix separation, instrumental conditions, etc.). Hence, following a "top-down"
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35 426 approach of uncertainty evaluation (e.g., Potts 2012a,b), we report consensus mean values for each
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37 427 earth-surface RM characterised in this study together with an uncertainty statement (95 %
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39 428 confidence interval- 95 % conf.), based on the $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values reported by each laboratory,
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41 429 as discussed in the next section.

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45 430 [Figure 1]

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47 431 [Figure 2]

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50 51 433 **3.2 Assigning consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values to the reference materials**

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53 434 The results of the eight RMs, from the laboratories participating in this study, as well as the available
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55 435 literature data, are shown in table 3 and figure 2. The range of $\delta^{26}\text{Mg}$ values of the studied RMs

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3 436 covers almost the entire range of terrestrial materials (e.g., Teng 2017). As expected, the lowest
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5 437 $\delta^{26}\text{Mg}$ values were found in carbonates: limestone BCS-CRM 513a ($-4.46 \pm 0.12 \text{ ‰}$, 95 % conf., n=3),
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7 438 which represents the lower part of the global $\delta^{26}\text{Mg}$ range of limestones, and the dolomites, JDo-1
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9 439 and CRM 512 ($-2.35 \pm 0.05 \text{ ‰}$, 95 % conf., n=11 and $-2.03 \pm 0.09 \text{ ‰}$, 95 % conf., n=6, respectively),
10
11 440 which are within a typical range of dolomites (Teng 2017 and references therein). The most positive
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13 441 $\delta^{26}\text{Mg}$ value was found in the soil SRM 2709a ($-0.15 \pm 0.03 \text{ ‰}$, 95 % conf., n=6), typical for silicate
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15 442 soils (Teng 2017 and references therein). The apple leaves SRM 1515 has $\delta^{26}\text{Mg}$ value of -1.22 ± 0.03
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17 443 ‰ (95 % conf., n=6), consistent with previous findings. $\delta^{26}\text{Mg}$ values in plants depend on the sources
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19 444 of Mg and on complex isotope fractionation processes during the uptake of Mg and transport within
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21 445 the plant (e.g., Black *et al.* 2008, Bolou-Bi *et al.* 2010, 2012, Tipper *et al.* 2010). In general, Mg in
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23 446 rivers and groundwaters yield a large range of $\delta^{26}\text{Mg}$ values with a flux-weighted $\delta^{26}\text{Mg}$ of global
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25 447 runoff of -1.09 ‰ (Tipper *et al.* 2006b). SLRS-5 river water ($-1.22 \pm 0.06 \text{ ‰}$, 95 % conf., n=8) has
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27 448 lower $\delta^{26}\text{Mg}$ value and spring water SRM 1640a ($-0.73 \pm 0.03 \text{ ‰}$, 95 % conf., n=9) has higher $\delta^{26}\text{Mg}$
28
29 449 value, relative to this average. The higher $\delta^{26}\text{Mg}$ value of the Dead Sea brine (DSW-1; $-0.58 \pm 0.05 \text{ ‰}$,
30
31 450 95 % conf., n=8) relative to its precursor seawater may represent a contribution of ^{24}Mg -depleted
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33 451 dolomitizing brines (Gavrieli *et al.* 2009, Shalev *et al.* 2014).
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35
36 452 To obtain mean $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values for the RMs, we evaluate the inter-laboratory
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38 453 reproducibility (indicated as 2s on the consensus value derived from the results of all laboratories
39
40 454 and literature data; Table 3). All eight RMs have an inter-laboratory reproducibility (2s) of 0.05 to
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42 455 0.17 ‰ in $\delta^{26}\text{Mg}$. For most RMs (DSW-1, SRM 1640a, SRM 2709a, SRM 1515 and CRM 513), the
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44 456 inter-laboratory reproducibility (0.05 ‰ – 0.12 ‰) is within or below the range of the ‘typical’
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46 457 intermediate precision of the laboratories estimated from repeat analysis of different materials over
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48 458 the long-term (0.06 ‰ – 0.13 ‰ in $\delta^{26}\text{Mg}$), indicating that the measurement procedures used in all
49
50 459 laboratories do not induce any additional uncertainty contributions when samples with such
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52 460 matrices are processed and measured. For these RMs, the individual results from all laboratories
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54 461 also agree within the reported measurement precision of each sample (Table 3 and Fig. 2). However,
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3 462 the inter-laboratory reproducibilities of three RMs, i.e., SLRS-5 river water, JDo-1 dolomite and CRM
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5 463 512 dolomite (2s of 0.15 ‰, 0.15 ‰ and 0.17 ‰, respectively), are slightly higher than the ‘typical’
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7 464 intermediate precisions reported by the participating laboratories. While all the individual SLRS-5
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9 465 results agree within 2s measurement precision of the repeat measurements of each RM, this is not
10
11 466 the case for all individual results of the two dolomite RMs, JDo-1 and CRM 512 (Fig. 2). Averaged
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13 467 data of JDo-1 reported in the literature seem to be more uniform, but in some cases the reported 2s
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15 468 is larger, covering the whole range obtained in current research (Wombacher *et al.* 2009, Pearce *et*
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17 469 *al.* 2012, Mavromatis *et al.* 2013, Beinlich *et al.* 2014, Mavromatis *et al.* 2014, Lavoie *et al.* 2014; Fig.
18
19 470 2). Similar to the results of this study, Wombacher *et al.* (2009) reported a precision of 0.18 ‰ (2s)
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21 471 on the mean of twelve measurement results of JDo-1 from four different Mg separations (test
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23 472 portions of 2.5 – 40 mg). Note that most of these values (Pearce *et al.* 2012, Mavromatis *et al.* 2013,
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25 473 Beinlich *et al.* 2014, Mavromatis *et al.* 2014) were obtained using a similar chemical sample
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27 474 preparation procedure.

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29
30 475 The reasons for the slightly higher inter-laboratory variance in the dolomite RMs are unknown. Inter-
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32 476 laboratory variance can arise from many factors, including material properties (e.g., homogeneity at
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34 477 the level of the test portion, or stability over time), sample preparation procedure (e.g., incomplete
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36 478 dissolution, column yield, analyte purity and blank) and the procedures used in the mass
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38 479 spectrometric measurements and data reduction (e.g., mass bias stability and mass bias correction,
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40 480 matrix effects). No correlation was found between molar matrix elements/Mg ratios and the inter-
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42 481 laboratory variance (examples in Fig. 3). Moreover, we checked for any correlations between
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44 482 individual $\delta^{26}\text{Mg}$ values and test portions, blank/Mg, column capacity, but did not find any
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46 483 systematic relations. Thus, further investigation on these RMs is required to determine the sources
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48 484 of the observed variance.

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51 485 The consensus $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ mean values for the studied RMs are provided in Table 4 together
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53 486 with an associated uncertainty for each value. This uncertainty was estimated by the 95 %
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55 487 confidence interval on the mean of N laboratory results, including literature data, if available.
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3 488 [Table 4]
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4. Summary and conclusions

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10 491 In this study, the $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values of eight earth surface reference materials (RMs),
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12 492 representative of different low-temperature environments and material types, were determined by
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14 493 inter-laboratory comparison. Despite the differences in sample preparation procedures, different
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16 494 test portions, instrumentation, and isotope ratio measurement procedures, good agreement of the
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18 495 $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ data from the different laboratories was found. This encouraging result suggests
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20 496 that all methods described in this study are suitable for geochemical studies on these type of
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22 497 materials given they are strictly monitored and calibrated (recovery, blanks, matrix-removal, etc.).
23
24 498 Moreover, the investigated RMs are suitable to be used by other laboratories for routine quality
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26 499 control of Mg isotope ratio measurement procedures during environmental and earth surface
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28 500 geochemical studies. The wide range of matrices, including river water, spring water, brine,
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30 501 dolomites, limestone, soil and plant leaves, allow analysts to identify potential issues (and facilitate
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32 502 modifications) with sample preparation methods previously developed for silicate rocks, for
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34 503 example, which are then applied to different sample types, such as Ca-rich carbonates, organic-rich
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36 504 soils or vegetation.
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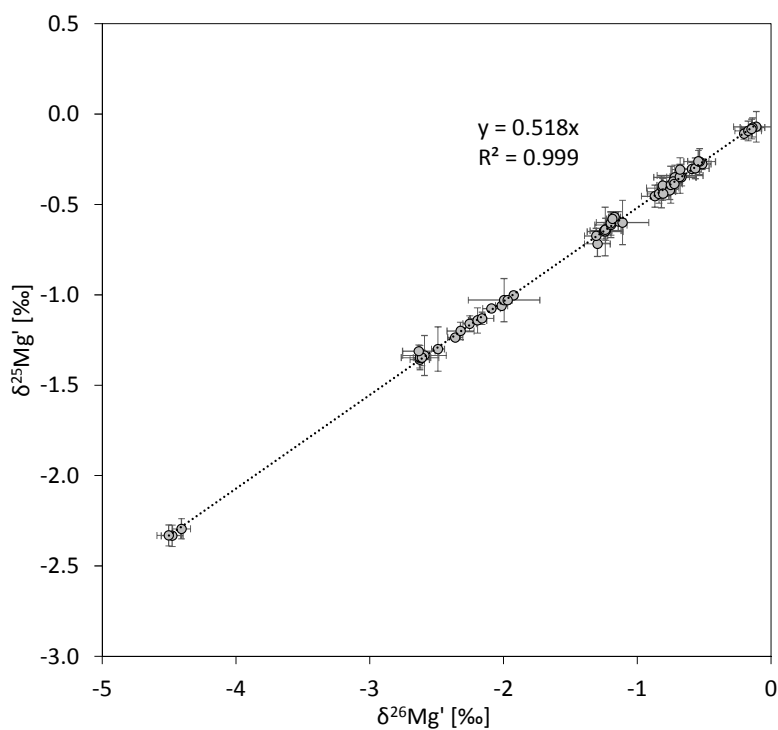
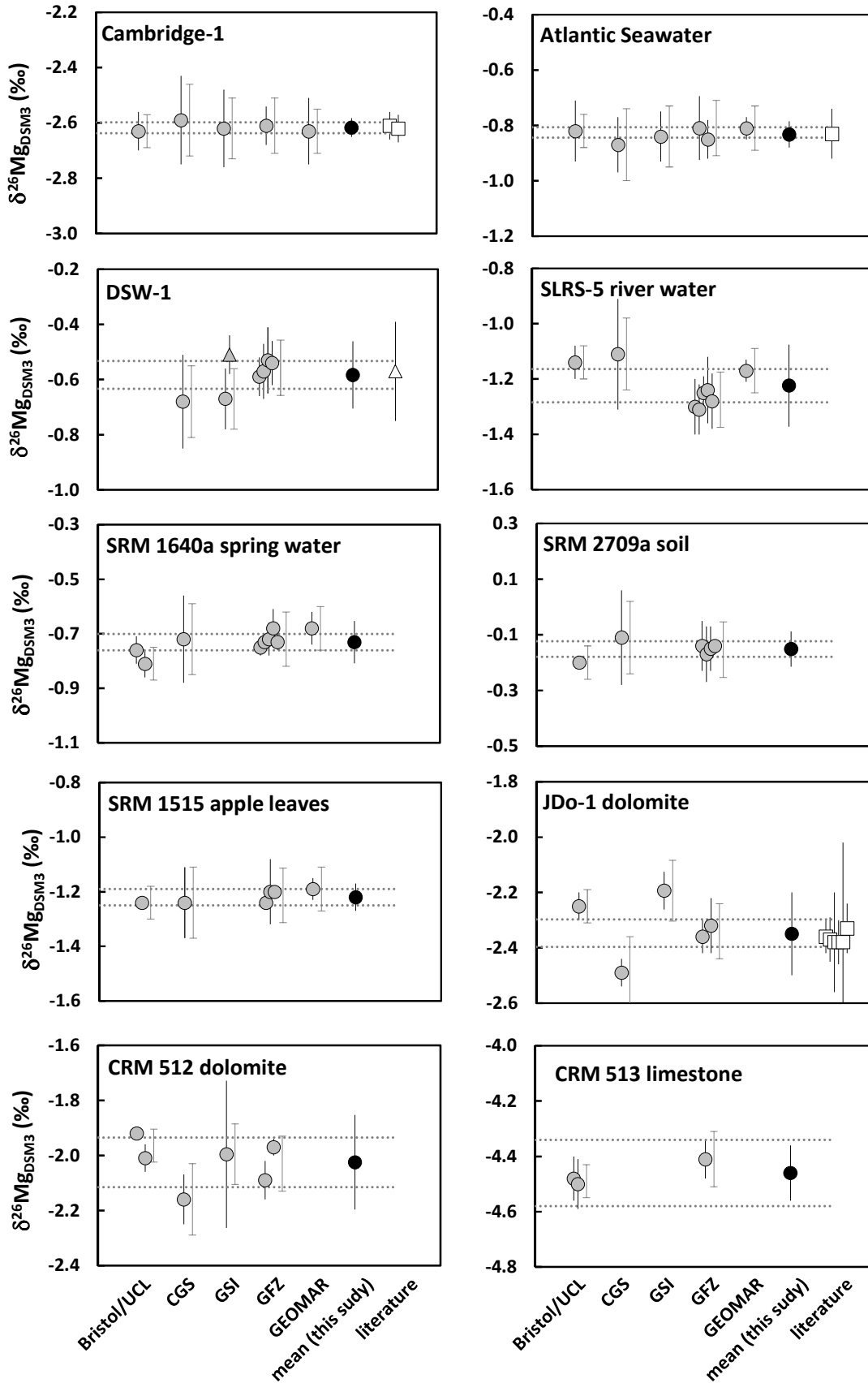


Figure 1: $\delta^{25}\text{Mg}'$ versus $\delta^{26}\text{Mg}'$ values determined in this study. Error bars are 2s of each result. All the data is in accordance with a regression line that crosses the origin (dotted line) and has a slope of 0.52, typical to mass-dependant fractionation of terrestrial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



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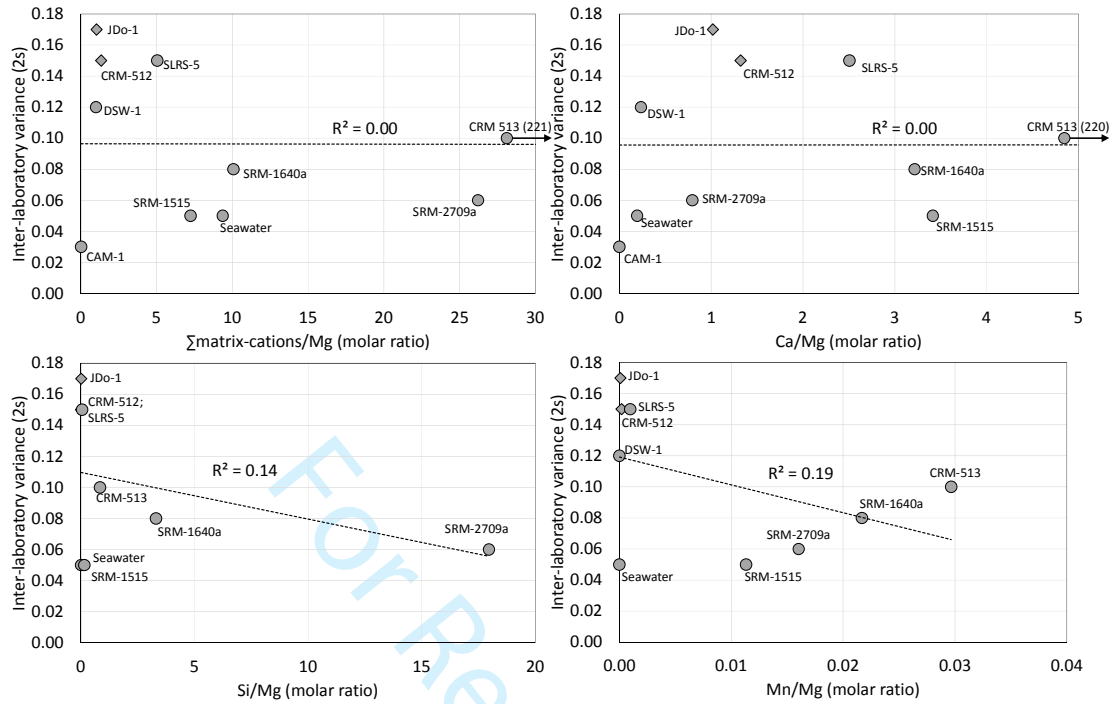


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Table 1: Materials descriptions and chemical compositions. GSJ: Geological Survey of Japan, BAS: Bureau of Analysed Samples Ltd., NIST: National Institute for Science and Technology, CCRMP: Canadian Certified Reference Material Programme, GSI: Geological Survey of Israel.

Material	Producer	Data source	g/100g										mol/mol					
			SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ (total)	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	BaO	S	$\Sigma c(\text{matrix-cations})/c(\text{Mg})^1$		
solids																		
JDo-1 dolomite	GSJ	suppliers certificate	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	suppliers certificate	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		1.0	
BCS - CRM 513 limestone	BAS	suppliers certificate	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		220	
SRM 2709a soil	NIST	suppliers certificate	64.81	0.56	13.92	4.80	0.068	2.42	2.67	1.6	2.54	0.16					26	
SRM 1515 apple leaves																		
			µg/g															
			Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	N _(total)	C _(total)	Ba	S	Cl	
					286	83	54	2710	15260	24.4	16100	1590	22500		49	1800	579	7.2
liquids																		
			µg/ml															
			Si	Al	Fe	Mn	Mg	Ca	Na	K			C _(total)	Ba	S	Cl		
Cambridge-1 (pure Mg solution)	U. of Cambridge						10000										0	
IAPSO Atlantic seawater	OSIL	Summerhayes and Thorpe 1996	2.8		5E-04	5.5E-5	1E-05	1290	412	10770	399			27.6	0.014	904	193 54	9.2
SLRS-5 river water	CANMET (CCRMP)	suppliers certificate	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	suppliers certificate	5.169		0.053	0.0365	0.04	1.05	5.57	3.112	0.575				0.151			10
DSW-1 Dead Sea brine																		
			mmol/kg solution															
			Si	Al	Fe	Mn	Mg	Ca	Na	K			C _(total)	Ba	S	Cl		
DSW-1 Dead Sea brine	GSI ²	Golan <i>et al.</i> 2016 ³					1663	391	1081	169				0.86			529 4	0.9

¹ $\Sigma c(\text{matrix cations})/c(\text{Mg})$ refers to the molar ratio of the sum of Na, K, Ca, Si, Al, Ti, Fe and Mn relative to Mg.

² DSW-1 can be obtained for free from the GSI (I. Gavrieli).

³ Concentrations refer to average Dead Sea (2013) and may be slightly different from DSW-1. However, the elemental ratios are similar.

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Table 2: Summary of analytical techniques used by each laboratory

Laboratory	Sample test portion ¹	Dissolution method	Mg column purification	Typical column procedure blank	Instrument ² , sample introduction system, uptake rate, acid matrix	Integration time/bracket ³ , number of brackets ⁴ ²⁴ Mg signal intensity / analyte concentration Typical Mg consumption per single analysis (n = 1) ⁵	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: $\text{HNO}_3 + \text{H}_2\text{O}_2$ soil: HF/ $\text{HNO}_3 + \text{HCl}$ liquids: evaporation	2 steps: Bio-Rad AG50W-X12 resin in 2 N $\text{HNO}_3 + \text{TRUSpec}$ in 7 N HNO_3	<0.4 ng Mg	Neptune (LR), Apex-Q desolvator, 50 $\mu\text{l}/\text{min}$, 2 % HNO_3	20x4.2 sec, 1 18 - 20 V / 100 ng/ml Mg 7 ng Mg	$\pm 0.06 \text{‰}$; $\pm 0.04 \text{‰}$
GSI	100-150 mg (200-500 μg Mg)	carbonates: HNO_3 liquids: evaporation	1 step: Bio-Rad AG50W-X12 resin in 1.3/2.3 N HCl	<100 ng Mg	nu plasma II (MR), DSN-100 desolvator, 100 $\mu\text{l}/\text{min}$, 0.1 N HNO_3	20x10 sec, 1 25 - 35 V / 2000 ng/ml Mg 670 ng Mg	$\pm 0.11 \text{‰}$; $\pm 0.05 \text{‰}$
GFZ	30 - 100 mg / in addition 1 g for SRM 1515 (2.5 - 15 μg Mg)	carbonates: HCl leaves: $\text{HNO}_3 + \text{H}_2\text{O}_2$ soil: HF/ $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2$ liquids: HF + evaporation + H_2O_2	2 steps: Bio-Rad AG50W-X12 resin in 1 N/2 N HNO_3 (repeated twice)	<12 ng Mg	Neptune (MR), double pass cyclon- Scott quartz-glass spray chamber (SIS), 100 $\mu\text{l}/\text{min}$, 0.3 N HNO_3	20x4.2 sec, 1 10 - 15 V / 500 ng/ml Mg 70 ng Mg	$\pm 0.10 \text{‰}$; $\pm 0.06 \text{‰}$
CGS	50-100 mg (20 - 50 μg Mg)	carbonates: HCl leaves: $\text{HNO}_3 + \text{H}_2\text{O}_2$ soil: HF/ HNO_3 liquids: evaporation	3 steps: Bio-Rad AG50W-X12 resin in 2.5 N HCl (twice) + 0.4 N HNO_3	<2 ng Mg	Neptune (MR), cyclonic quartz- glass spray chamber, 100 $\mu\text{l}/\text{min}$, 3 % (v/v) HNO_3	30x8.4 sec, 3 4 - 8 V / 500 ng/ml Mg 630 ng Mg	$\pm 0.13 \text{‰}$; $\pm 0.09 \text{‰}$
GEOMAR	same as CGS	same as CGS	same as CGS	same as CGS	AXIOM (LR), Aridus desolvator, 50 $\mu\text{l}/\text{min}$, 5 % HNO_3	50x2 sec, 9 3.5 V / 200 ng/ml Mg 150 ng Mg	$\pm 0.08 \text{‰}$; $\pm 0.06 \text{‰}$

¹ 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.

² 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)

³ Integration time/bracket refers to the measurement time of a sample or each one of the bracketing standards in a single bracket.

⁴ The number of brackets that were used to calculate a single δ result (n = 1 in Table 3)

⁵ Including the data acquisition time only, without take-up time, etc.

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

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	n ²
Internationally established RMs							
Cambridge-1 (pure Mg solution)							
Bristol/UCL ⁴	-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 ⁵	-2.63	0.15	0.12	-1.31	0.04	0.03	3
Arithmetic mean	-2.62	0.02	0.03	-1.34	0.02	0.04	N³ = 5
An and Huang 2014 (compilation)	-2.61		0.05				
IAPSO Atlantic seawater (OSIL)							
Bristol/UCL ⁶	-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 ^{7,8}	-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
Arithmetic mean	-0.83	0.02	0.05	-0.43	0.02	0.04	N³ = 6
Ling et al. 2011 (compilation)	-0.83		0.09	-0.43		0.06	90
Surface water RMs							
DSW-1 (Dead Sea brine)							
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 ^{7,9}	-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 ⁷	-0.57	0.05	0.10	-0.30	0.03	0.06	7
GFZ C ⁷	-0.53	0.05	0.12	-0.26	0.03	0.07	7
GFZ D ⁷	-0.54	0.06	0.08	-0.26	0.05	0.06	4
Karasinski et al. 2017 ⁹	-0.57	0.06	0.18				10
Arithmetic mean	-0.58	0.05	0.12	-0.30	0.03	0.07	N³ = 8
SLRS-5 (river water)							
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 ⁷	-1.30	0.43	0.10	-0.72	0.31	0.07	2
GFZ B ⁷	-1.31	0.05	0.09	-0.67	0.02	0.04	6
GFZ C ⁷	-1.25	0.03	0.06	-0.65	0.02	0.05	6
GFZ D ⁷	-1.24	0.05	0.12	-0.64	0.03	0.07	8
GFZ E ^{7,8}	-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
Arithmetic mean	-1.22	0.06	0.15	-0.64	0.04	0.10	N³ = 8
NIST SRM 1640a (spring water)							
Bristol/UCL A ⁷	-0.76	0.06	0.05	-0.42	0.06	0.05	3
Bristol/UCL B ⁷	-0.81	0.07	0.05	-0.44	0.05	0.04	3
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	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	n ²
CGS	-0.72	0.10	0.16	-0.35	0.04	0.07	5
GFZ A ⁷	-0.75	0.14	0.03	-0.39	0.46	0.10	2
GFZ B ⁷	-0.73			-0.37			1
GFZ C ⁷	-0.72	0.07	0.06	-0.39	0.07	0.05	3
GFZ D ⁷	-0.68	0.02	0.07	-0.35	0.01	0.03	13
GFZ E ^{7,8}	-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
Arithmetic mean	-0.73	0.03	0.08	-0.38	0.03	0.08	N³ = 9
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Organic-rich solids							
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NIST SRM 2709a (soil)							
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) ⁷	-0.14	0.02	0.09	-0.07	0.01	0.05	19
GFZ B ⁷	-0.17	0.04	0.10	-0.09	0.02	0.05	8
GFZ C ⁷	-0.15	0.06	0.08	-0.08	0.04	0.05	4
GFZ D ^{7,8}	-0.14	0.10	0.02	-0.08	0.06	0.01	6
Arithmetic mean	-0.15	0.03	0.06	-0.08	0.02	0.03	N³ = 6
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NIST SRM 1515 (apple leaves)							
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) ^{7,8}	-1.24	0.04	0.01	-0.64	0.04	0.01	2
GFZ B ^{7,8}	-1.20	0.04	0.12	-0.61	0.02	0.07	12
GFZ C ^{7,8}	-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
Arithmetic mean	-1.22	0.03	0.05	-0.62	0.03	0.05	N³ = 6
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Carbonates							
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JDo-1 (dolomite)							
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 ⁷	-2.36	0.25	0.06	-1.24	0.03	0.01	2
GFZ B ⁷	-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
Arithmetic mean	-2.35	0.05	0.15	-1.23	0.03	0.09	N³ = 11
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BCS - CRM 512 (dolomite)							
Bristol/UCL A ⁷	-1.92	0.03	0.02	-1.00	0.02	0.02	3
Bristol/UCL B ⁷	-2.01	0.06	0.05	-1.06	0.004	0.003	3
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Shalev <i>et al.</i>							

	$\delta^{26}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ¹	2s	n ²
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 ⁷	-2.09	0.29	0.07	-1.08	0.06	0.01	2
GFZ B ⁷	-1.97	0.02	0.03	-1.03	0.01	0.02	7
Arithmetic mean	-2.03	0.09	0.17	-1.05	0.05	0.09	N³ = 6
BCS - CRM 513a (limestone)							
Bristol/UCL A ⁷	-4.48	0.10	0.08	-2.33	0.07	0.06	3
Bristol/UCL B ⁷	-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
Arithmetic mean	-4.46	0.12	0.10	-2.32	0.05	0.04	3
Weighted mean	-4.45		0.06	-2.32		0.03	N³ = 3

¹ 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.

² n is the number of δ 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.

³ N refers to the number of average δ values used for the calculations of the inter-laboratory arithmetic mean.

⁴ from: Pogge von Strandmann *et al.* 2011.

⁵ Processed through columns.

⁶ from: Foster *et al.* 2010.

⁷ 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.

⁸ from Uhlig *et al.* 2017.

⁹ Different samples of the Dead Sea brine.

Table 4: Inter-laboratory 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 ¹	$\delta^{25}\text{Mg}_{\text{DSM3}}$	95% conf ¹	N ²
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

¹ 95 % confidence intervals calculated as $2SE_t$ (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.

² 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.