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Magnesium isotope heterogeneity of the isotopic standard SRM980 and new reference materials for magnesium-isotope-ratio measurements

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Multicollector ICP-MS has been used for the precise measurement of variations in the isotopic composition of the isotopic standard of magnesium (SRM980) provided by the National Institute of Standards and Technology (Gaithersburg, MD, USA). The SRM980 consists of metal chips weighing between 1 and 50 mg and each unit delivered by the National Institute of Standards and Technology corresponds to a bottle containing about 0.3 g. Height units were analysed. Variations in sample ^{25}Mg/^{24}Mg, and ^{26}Mg/^{24}Mg ratios are expressed as δ^{25}Mg and δ^{26}Mg units, respectively, which are deviations in parts per 10^3 from the same ratio in a standard solution. The differences in δ^{25}Mg and δ^{26}Mg of the SRM980 are up to 4.20 and 8.19‰, respectively, while the long-term repeatability of δ^{25}Mg and δ^{26}Mg are 0.09 and 0.16‰, respectively, at 95% confidence. However, when plotted in a three-isotope diagram, all the data fall on a single mass fractionation line. Overall limits of error of the SRM980 reported here fall within the previously reported overall limits of error. The isotopic heterogeneity not only corresponds to differences among units but has been found at the chip-size level. This result, due to the precision of the MC-ICP-MS technique, makes the SRM980 inappropriate for the international isotopic standard of magnesium. The SRM980 can still be used to report the excess of ^{26}Mg, which is defined by the deviation from the mass-dependent relationship between ^{25}Mg/^{24}Mg, and ^{26}Mg/^{24}Mg ratios. Two large batches (around 10 g of Mg in each) of pure Mg solutions (in 0.3 M HNO_3) have been prepared and characterised. These 2 solutions (DSM3 and Cambridge 1) are suitable reference material because they are immune to heterogeneity. DSM3 and Cambridge 1 are isotopically different (by 1.3‰ per u) and are available upon request from the first author. In addition, DSM3 has an isotopic composition very similar to the Mg-isotopic composition of carbonaceous chondrites (Orgueil and Allende). Because of the lack of heterogeneity and the cosmochemical and geochemical significance of DSM3, we urge the use of DSM3 as the primary isotopic reference material to report Mg-isotopic variations.

Introduction

Multiple collector inductively coupled mass spectrometry (MC-ICP-MS) has experienced a large increase in technique and application development over the past decade.[1–4] Using this technique, isotopic variations have now been described on terrestrial material for a large number of elements and most of them are mass-dependent. Because a mass-dependent isotopic variation is indistinguishable from any isotopic fractionation related to the measurement, the instrumental fractionation has to be precisely and accurately monitored. In the case of MC-ICP-MS, it is greater than a percent per u, but fairly independent of time. This led to the development of a method called the sample–standard bracketing technique.[5–14] This protocol is based on the accurate and precise acquisition of isotopic variations by gas-source mass spectrometry, in which standard and sample isotope values are alternately measured several times. For the ICP-source, a negligible cross-contamination between the sample and the standard is achieved by washing the inlet system between analyses. Isotopic compositions are expressed as a deviation from the isotopic composition of the standard solution.

The data obtained by this approach can only be meaningful when a common standard is used by the entire community, and a standard has to be available and homogeneous. In the case of Mg-isotopes, an isotopic standard has been developed by the

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National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and this SRM980 can still be purchased. The determination of its isotopic heterogeneity has been carried out by TIMS,[15] and the overall limits of error are up to 16 times greater than the external reproducibility achieved by the use of MC-ICP-MS for the study of Mg-isotopic variations.[7,16–18] In this study, potential isotopic heterogeneity within a unit or between units of the SRM980 has been investigated at the 0.06‰ per u level.

Experimental

Mass spectrometry

Magnesium isotope ratios were measured using 2 types of MC-ICP-MS: the Nu Plasma MC-ICP-MS (Nu Instruments, Wrexham, Wales) and the Isoprobe (GV Instruments, Wythenshawe, Manchester, UK). The Nu-Plasma is a double focussing MC-ICP-MS,[19] and the 3 instruments used are installed in the Department of Earth Sciences, University of Cambridge (DES UC), in the Geological Survey of Israel (GSI) and in the Department of Earth Sciences, The Open University (DES OU). The Isoprobe is a single focussing magnetic sector ICP-MS equipped with a hexapole collision cell.[20] The collision cell was flushed with helium gas at a flow rate around 135 μl s^{-1}. The instruments were installed at the Field Museum of Natural History (FMNH), the Chemical Biology & Nuclear Science Division, Lawrence Livermore National Laboratory (LLNL) and the Centre de Recherche Pétrologique et Géochimique (CRPG).

In the case of the Nu Plasma, the method applied has been previously described.[16] Briefly, all samples and standards were prepared in 0.1 M HNO_3 solution and introduced into the plasma torch through an Aridus desolvating nebuliser (Cetac, Omaha, NE, USA). The use of a desolvating nebuliser acts to reduce O, N, C and H interference to an insignificant level.[16] At CRPG, the measurements were performed under wet plasma conditions and the sample introduced through a PFA nebuliser and a cyclonic spray chamber. The potential molecular interferences (*e.g.* C_2^+, C_2H^+, $C_2H_2^+$, CN^+ and MgH^+) were suppressed by the collision cell. The two other Isoprobes used in this study (at FMNH and LLNL) were equipped with a desolvating nebuliser.

The Nu Plasma and the Isoprobe produce Mg-peaks with flat-tops at a working mass resolution of ~300, as required for high-precision isotope ratio measurement and measurement of Mg is accomplished using three Faraday collectors over a mass range of 24–26, allowing direct measurement of ^{24}Mg, ^{25}Mg and ^{26}Mg. Standard and sample isotope values were measured alternately for 200 s each. A negligible cross-contamination between the sample and the standard is achieved by washing the analytical instrumentation system and the cones with 0.1 M HNO_3 for 5 min between analyses. Results are expressed as a permil deviation from the isotopic composition of the standard:

$\delta^{x}Mg = \{(^{x}Mg/^{24}Mg)_{Sample}/(^{x}Mg/^{24}Mg)_{Standard} - 1\} \times 1000$ (where $x = 25$ or 26). The excess of ^{26}Mg is quoted $\Delta^{26}Mg$ and calculated by the relationship: $\Delta^{26}Mg = \delta^{26}Mg - ((1/0.5163) \times (\delta^{25}Mg + 0.015))$.[7]

Sample preparation

An aliquot of the SRM980 standard solution used in a previous study[7,16–18] (and labelled SRM980_O in this study) has been used and 7 other units of the SRM980 (labelled SRM980_C, SRM980_CH, SRM980_J, SRM980_M, SRM980_LL-A, SRM980_LL-B and SRM980_N) were investigated. Each unit of the SRM980 delivered by NIST consists of ~0.3 g of metal chips, and each chip weighs between 2 and 50 mg. The metal was dissolved in ~1 M HNO_3 at room temperature. When the dissolution was complete (*i.e.* no solid residue remaining by optical observation), the solutions were further diluted to 0.1–0.3 M HNO_3 by the addition of deionised water (18.2 MΩ cm^{-1}). The measured magnesium concentrations of several of the SRM980 chips investigated in this study correspond to a recovery of about 80% of expected values if the sample were 100% metal. Based on the visual aspect, the chips seem to be partly altered to hydroxide, which would explain the low recovery during the dissolution. Prior to dissolution, 6 units were split into several aliquots to test the internal heterogeneity of units. In addition, individual chips from SRM980_M weighing from 2.32 to 12.67 mg have been fully dissolved and measured. A chip from the SRM980_C (labelled SRM980_C-c and weighing 13.7 mg) has been used for either the assessment of the dissolution technique or the potential effect of the oxidation of the chip or both on the isotopic composition. The amount of HNO_3 used for the dissolution of SRM980_C-c was smaller than the required quantity by the stoichiometry for a complete reaction of dissolution. The reaction stopped when 2/3 of the chip was already dissolved and an aliquot of that solution had been withheld (labelled SRM980_C-cl) before the addition of nitric acid and the completion of the reaction. The amount of SRM980_C-cl represented less than 0.03% of the SRM980_C-c, and its removal is insignificant to the isotopic composition of SRM980_C-c. A total of 27 solutions made from the dissolution of SRM980 material were analysed.

In addition to the SRM980 material, 2 large batches of pure magnesium solution have been studied. DSM3 corresponds to dissolution of ~10 g of pure magnesium metal (provided by Dead Sea Magnesium Ltd., Israel) into 1 l of ~0.3 M HNO_3. The other large batch is called Cambridge 1 and corresponds to the batch number T432399 of the PrimAg®-xtra certified reference material (Romil Ltd., Waterbeach, Cambridge, UK). These two solutions (DSM3 and Cambridge 1) are suitable for reference material because they are immune to heterogeneity. The sum of the impurities in these two solutions is less than 1%.

Two aliquots of the Orgueil carbonaceous chondrite meteorite were analysed. This meteorite has the closest chemical composition to the bulk solar system.[21] The samples were powdered and digested in pressurised threaded PFA Teflon® vials at temperatures of about 140 °C with a mixture of concentrated distilled reagents, composed of 0.5 ml HNO_3 and 0.5 ml HF. After the removal of silicon by evaporation and the conversion of nitride salts into chloride salts, a chemical separation of Mg has been accomplished by liquid chromatographic methods using Bio-Rad AG50W-X12 resin (Bio-Rad, Hercules, CA, USA) on which >99% recovery of Mg is achieved.[17,18]

Results and discussion

Results obtained on SRM980 are listed in Tables 1 and 2. The overall variation is 11.67 and 5.93‰ in $\delta^{26}Mg$ and $\delta^{25}Mg$, respectively. A direct comparison of all the data obtained on SRM980 material is, however, not straightforward because of the use of different solutions as the standard solutions in the different laboratories. Nevertheless, this clearly demonstrates that the SRM980 material is heterogeneous for its isotopic composition at the precision reached by MC-ICP-MS.

Variations in $\delta^{25}Mg$ are roughly half those observed for $\delta^{26}Mg$ and, within the uncertainties, all the SRM980 values fall along the same curve defined by other terrestrial samples[7,16–18] (Fig. 1). The weighted average of the $\Delta^{26}Mg$ of the SRM980 material in this study is 0.00 ± 0.12‰. The single correlation between $\delta^{26}Mg$ and $\delta^{25}Mg$ strongly supports a mass-dependent process responsible for the heterogeneity of the SRM980 material.

Table 1 Magnesium isotopic composition for selected solutions measured on a Nu-Plasma (*N*—number of replicates)

Sample	Unit	Chemical treatment	Standard[a]	Laboratory	δ^{26}Mg (‰)	$\pm 2\sigma$	δ^{25}Mg (‰)	$\pm 2\sigma$	Δ^{26}Mg (‰)	$\pm 2\sigma$	*N*
SRM980_O[b]	Oxford	HNO_3 dissolution	SRM980_O	DES UC	0.01	0.07	0.02	0.05	−0.04	0.06	4
SRM980_O[b]	Oxford	HNO_3 dissolution	DSM3[c]	DES UC	−3.40	0.13	−1.74	0.07	−0.06	0.02	10
SRM980_C	Cambridge	HNO_3 dissolution	SRM980_O	DES UC	−1.02	0.11	−0.50	0.09	−0.06	0.14	2
SRM980_C-c	Cambridge	HNO_3 dissolution	SRM980_O	DES UC	1.12	0.14	0.59	0.08	−0.04	0.01	1
SRM980_C-cl	Cambridge	HNO_3 leaching	SRM980_O	DES UC	1.24	0.37	0.59	0.09	0.09	0.40	3
SRM980_CH#1	Chicago	HNO_3 dissolution	SRM980_O	DES UC	−1.25	0.03	−0.64	0.04	−0.01	0.11	4
SRM980_J-1	Jerusalem	HNO_3 dissolution	SRM980_O	DES UC	−2.64	0.36	−1.38	0.08	0.03	0.41	2
SRM980_J-2	Jerusalem	HNO_3 dissolution	SRM980_O	DES UC	0.13	0.04	0.10	0.03	−0.06	0.04	2
SRM980_J-3	Jerusalem	HNO_3 dissolution	SRM980_O	DES UC	−1.08	0.16	−0.58	0.04	0.04	0.17	5
Aldrich[b]		None	SRM980_O	DES UC	2.53	0.04	1.32	0.03	−0.03	0.05	4
DSM2[c]		HNO_3 dissolution	SRM980_O	DES UC	3.41	0.07	1.76	0.04	−0.01	0.01	5
SRM980_J-3	Jerusalem	HNO_3 dissolution	SRM980_J-2	GSI	−1.25	0.18	−0.65	0.07	0.01	0.09	3
SRM980_M-a	Milton Keynes	HNO_3 dissolution	SRM980_M-b	DES OU	0.98	0.13	0.50	0.06	0.01	0.03	14
SRM980_M-c	Milton Keynes	HNO_3 dissolution	SRM980_M-b	DES OU	−1.50	0.05	−0.78	0.02	0.00	0.02	6
SRM980_M-d	Milton Keynes	HNO_3 dissolution	SRM980_M-b	DES OU	−0.64	0.05	−0.33	0.05	−0.01	0.09	9
SRM980_M-e	Milton Keynes	HNO_3 dissolution	SRM980_M-b	DES OU	−1.66	0.14	−0.85	0.07	−0.03	0.03	3
Aldrich[b]		None	SRM980_M-b	DES OU	2.30	0.14	1.18	0.07	0.02	0.01	7

[a] Standard solution used for the measurement of the magnesium isotopic compositions of the sample using the sample-standard bracketing technique. [b] Samples already studied.[16] [c] This solution corresponds to the dissolution with ~1 M HNO_3 of another batch of the Mg metal produced from Dead Sea brines and previously studied.[16]

Table 2 Magnesium isotopic composition for selected solutions measured on an Isoprobe (*N*—number of replicates)

Sample	Unit	Chemical treatment	Standard[a]	Laboratory	δ^{26}Mg (‰)	$\pm 2\sigma$	δ^{25}Mg (‰)	$\pm 2\sigma$	Δ^{26}Mg ‰	$\pm 2\sigma$	*N*
SRM980_CH#2	Chicago	HNO_3 dissolution	SRM980_CH#1	FMNH	−0.02	0.12	−0.01	0.07	0.00	0.02	4
SRM980_CH#3	Chicago	HNO_3 dissolution	SRM980_CH#1	FMNH	1.32	0.17	0.65	0.08	0.06	0.03	5
SRM980_CH#4	Chicago	HNO_3 dissolution	SRM980_CH#1	FMNH	−0.30	0.03	−0.15	0.02	−0.01	0.01	3
SRM980_CH#5	Chicago	HNO_3 dissolution	SRM980_CH#1	FMNH	−0.02	0.13	−0.02	0.11	0.01	0.15	4
SRM980_LL-A0	Livermore-A	HNO_3 dissolution	SRM980_CH#1	FMNH	6.81	0.19	3.46	0.11	0.11	0.05	5
SRM980_O		HNO_3 dissolution	SRM980_CH#1	FMNH	1.20	0.10	0.62	0.07	0.00	0.07	6
DSM2		None	SRM980_CH#1	FMNH	4.83	0.09	2.50	0.05	−0.01	0.00	7
SRM980_LL-A0	Livermore-A	HNO_3 dissolution	SRM980_LL-B0	LLNL	5.73	0.25	2.93	0.09	0.05	0.15	11
SRM980_LL-A1	Livermore-A	HNO_3 dissolution	SRM980_LL-B0	LLNL	0.85	0.43	0.48	0.09	−0.08	0.51	3
SRM980_LL-A2	Livermore-A	HNO_3 dissolution	SRM980_LL-B0	LLNL	0.95	0.30	0.42	0.18	0.13	0.10	7
SRM980_LL-A3	Livermore-A	HNO_3 dissolution	SRM980_LL-B0	LLNL	−1.12	0.16	−0.57	0.09	−0.02	0.03	14
SRM980_LL-A4	Livermore-A	HNO_3 dissolution	SRM980_LL-B0	LLNL	0.91	0.25	0.49	0.15	−0.04	0.08	3
SRM980_LL-B0	Livermore-B	HNO_3 dissolution	SRM980_LL-B0	LLNL	−0.07	0.09	−0.03	0.05	−0.02	0.01	20
SRM980_CH#1	Chicago	HNO_3 dissolution	SRM980_LL-B0	LLNL	−1.01	0.20	−0.53	0.11	0.01	0.03	20
SRM980_N-0	Nancy	HNO_3 dissolution	Prolabo[b]	CRPG	−3.75	0.28	−1.93	0.16	−0.02	0.07	30
SRM980_N-1	Nancy	HNO_3 dissolution	Prolabo[b]	CRPG	−4.25	0.21	−2.25	0.09	0.10	0.07	4
SRM980_N-2	Nancy	HNO_3 dissolution	Prolabo[b]	CRPG	−4.86	0.34	−2.47	0.29	−0.08	0.44	4
SRM980_N-3	Nancy	HNO_3 dissolution	Prolabo[b]	CRPG	0.39	0.12	0.24	0.27	−0.08	0.81	2

[a] Standard solution used for the measurement of the magnesium isotopic compositions of the sample using the sample-standard bracketing technique. [b] Magnesium mono-elemental solution from Prolabo (VWRI, Fontenay sous Bois, France).

Internal isotopic heterogeneity of SRM980 units

Each of the 6 units investigated for internal isotopic heterogeneity has been measured with a single solution as the reference material. Isotopic differences will, therefore, traduce isotopic heterogeneity within a unit. The variations in δ^{26}Mg are 1.62‰ for SRM980_CH and up to 6.85‰ for SRM980_LLA (Tables 1 and 2). Given that the long-term reproducibility of δ^{26}Mg is 0.16‰, the observed heterogeneities are at least 10 times the uncertainty of the measurements and represent up to 118% of the reported terrestrial variation of δ^{26}Mg.[7,16–18]

An incomplete dissolution of the metal chips could induce some mass-dependent isotopic heterogeneity, but this assumption is not supported by the lack of difference between the δ^{26}Mg of the partial leaching of a single metal chip (SRM980_C-cl) and its overall δ^{26}Mg (SRM980_C-c). However, the >2‰ difference between the δ^{26}Mg of that chip and the rest of the unit clearly demonstrate that the isotopic heterogeneities of the SRM980 are at the chip level. Similar differences among chips have been found in the unit SRM980_M (Table 1). The causes of this heterogeneity remain unknown, but are likely to be related to mass-dependent isotopic fractionation occurring either during the production or the purification, or both, of the Mg metal.

Comparison of variations measured using MC-ICP-MS equipped with double focusing and hexapole collision cell

The isotopic differences between solutions measured by a single laboratory are unlikely to be related to any instrumental bias. The measurement of different solutions by different laboratories, especially when they are equipped with a different types of MC-ICP-MS, could, however, induce a bias. The average long-term repeatability of δ^{25}Mg and δ^{26}Mg obtained on the Nu-plasma (0.13 and 0.06‰, respectively) are marginally better than the precision reached by the Isoprobe (0.19 and 0.11‰, respectively). The accuracy between the laboratories has, however, to be investigated.

When a single solution has been measured in two different laboratories using different standard solutions, variations in the δ^{25}Mg and δ^{26}Mg values have been expressed relative to SRM 980_O standard by the relationship:

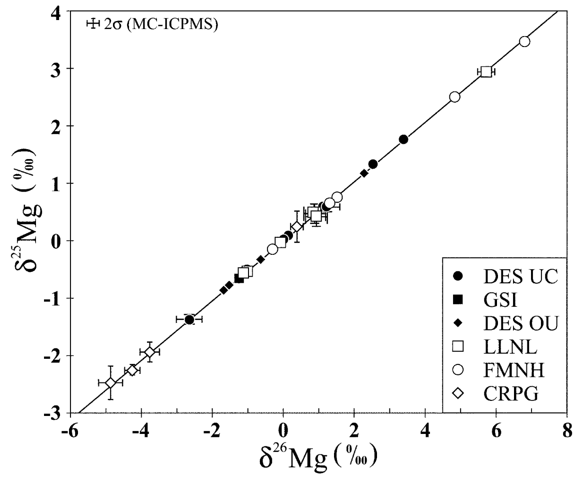

Fig. 1 Three-isotope representation of the Mg isotope ratios of SRM980 material, expressed in δ-unit. The results obtained by the six different laboratories (see text for acronym) are expressed relative to six different standards. The solid line corresponds to the terrestrial fractionation curve.[7] The individual error bars have been represented when they are larger than the average of the 2σ error bars obtained by this study.

$\delta^{x}\text{Mg}_{\text{Sample-SRM980}} = \delta^{x}\text{Mg}_{\text{Sample-Std}} + \delta^{x}\text{Mg}_{\text{Std-SRM980}} + 10^{-3} \times \delta^{x}\text{Mg}_{\text{Sample-Std}} \times \delta^{x}\text{Mg}_{\text{Std-SRM980}}$

In the case of SRM980_M, the measured (Table 1) and published[16] values from Aldrich have been used. In the case of SRM980_CH, the measured value of SRM980_CH#1 against the SRM980_O (Table 1) has been used. The SRM980_LLA and SRM980_LLB were recalculated using the measured isotopic differences between SRM980_LLA0, SRM980_CH#1 and SRM980_O. When more than one solution has been measured by two laboratories, the results can be expressed against the standard SRM980_O and directly compared (Table 3 and Fig. 2). The solutions SRM980_O, SRM980_CH#1 and DSM2 were measured on a Nu-Plasma and on an Isoprobe. The differences of the δ^{26}Mg and δ^{25}Mg are less than 0.16 and 0.09‰, respectively (Table 3 and Fig. 2), and within the long-term repeatability. This clearly implies no systematic bias between the data obtained by a Nu-Plasma (Table 1) and those from an Isoprobe (Table 2). Given the similar precisions and that the accuracy is also correct, the two sets of data obtained by these different types of MC-ICP-MS are, therefore, amalgamated.

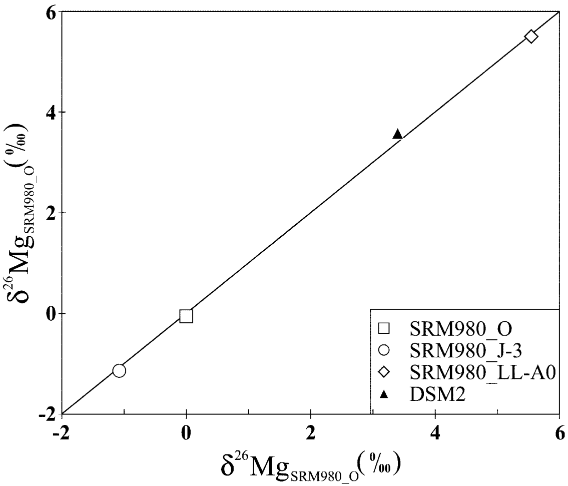

Fig. 2 Comparison of the Mg-isotopic compositions expressed in δ-unit relative to the SRM 980_O standard and measured in two different laboratories. The solid line corresponds to the equa-line.

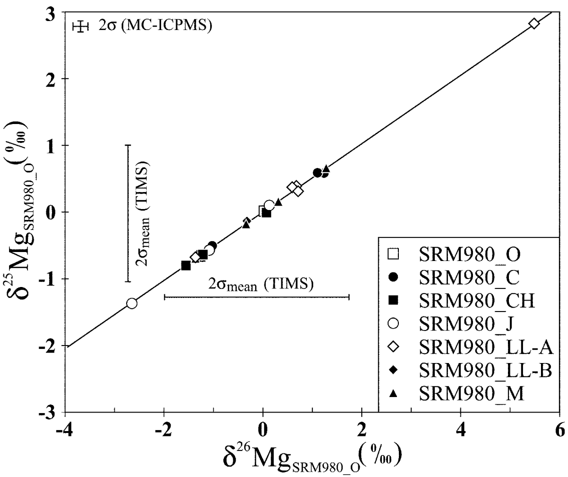

Fig. 3 Three-isotope representation of the Mg isotope ratios, expressed in δ-unit. The seven different units of SRM 980 are expressed relative to SRM 980_O standard. The solid line corresponds to the terrestrial fractionation curve.[7] The 2σ$_{\text{mean}}$ error bars obtained by TIMS are from Catanzaro *et al.*[15]

Overall SRM980 heterogeneity

The overall variation is 8.19 and 4.20‰ in δ^{26}Mg and δ^{25}Mg, respectively (Fig. 3). Expressed against the SRM980_O, the average δ^{26}Mg and δ^{25}Mg of these 23 solutions made from 7 units is −0.13 ± 3.23‰ and −0.07 ± 1.66‰, respectively. This corresponds to an overall limit of error (2σ$_{\text{mean}}$) of 0.69 and 0.35‰. The initial study of the SRM980 has been carried out using TIMS technique, and the overall limit of error for δ^{26}Mg and δ^{25}Mg was 1.87 and 1.03‰, respectively.[15] Therefore, this study does not contradict previous reports. In addition, the comparison of the uncertainty of magnesium isotopic measurement by TIMS and MC-ICP-MS of the SRM980 and the range of natural magnesium isotopic variations found by MC-ICP-MS clearly explain why terrestrial heterogeneity,[21] and SRM980 heterogeneity[15] would not be observed from TIMS measurements.

Standardisation of magnesium-isotope-ratio measurements

These results imply that the SRM980 can still be used to report the excess of ^{26}Mg. However, the heterogeneity found in this

Table 3 Magnesium isotopic composition relative to SRM980_O of solutions measured in different laboratories

Sample	Laboratory[a]	ICP-MS	δ^{26}Mg (‰)	±2σ	δ^{25}Mg (‰)	±2σ	Δ^{26}Mg (‰)	±2σ
DSM2	FMNH	Isoprobe	3.57	0.09	1.85	0.05	−0.02	0.00
DSM2	DES UC	Nu[b]	3.41	0.07	1.76	0.04	−0.01	0.01
SRM980_O	FMNH	Isoprobe	−0.05	0.10	−0.02	0.07	−0.01	0.07
SRM980_O	DES UC	Nu[b]	0.01	0.07	0.02	0.05	−0.04	0.06
SRM980_J-3	GSI	Nu[b]	−1.12	0.18	−0.55	0.07	−0.05	0.09
SRM980_J-3	DES UC	Nu[b]	−1.08	0.16	−0.58	0.04	0.04	0.17
SRM980_LLA0	LLNL	Isoprobe	5.49	0.25	2.82	0.09	0.02	0.15
SRM980_LLA0	FMNH	Isoprobe	5.55	0.19	2.81	0.11	0.09	0.05

[a] Laboratory, see text. [b] Nu Plasma.

Table 4 Magnesium isotopic composition of new reference materials and selected carbonaceous chondrite (*N*-number of replicates)

Sample	$\delta^{26}Mg^{a}$ (‰)	$\pm 2\sigma$	$\delta^{25}Mg^{a}$ (‰)	$\pm 2\sigma$	$\Delta^{26}Mg$ (‰)	$\pm 2\sigma$	*N*
DSM3	0.02	0.12	0.01	0.07	−0.02	0.02	31
Cambridge1	−2.58	0.14	−1.33	0.07	−0.03	0.01	35
Allende (AG22)[b]	−0.30	0.07	−0.16	0.03	−0.02	0.03	3
Allende (AG23)[b]	−0.29	0.04	−0.15	0.01	−0.02	0.05	2
Orgueil[c]	0.00	0.06	0.00	0.05	−0.03	0.07	6
Orgueil[c]	−0.05	0.08	−0.02	0.05	−0.05	0.02	6

[a] Mg-isotopic compositions are expressed as a permil deviation from the isotopic composition of the standard DSM3 as follows: $\delta^{x}Mg = \{(^{x}Mg/^{24}Mg)_{Sample}/(^{x}Mg/^{24}Mg)_{SRM980} - 1\} \times 1000$. Aliquots of DSM3 and Cambridge1 solutions can be obtained from the first author. [b] Sample of the bulk and matrix fraction of Allende carbonaceous chondrite meteorite (CV3) previously reported[7] against SRM980_O. [c] Two different aliquot of the sample BM 3673, Orgueil carbonaceous chondrite meteorite (CI1).

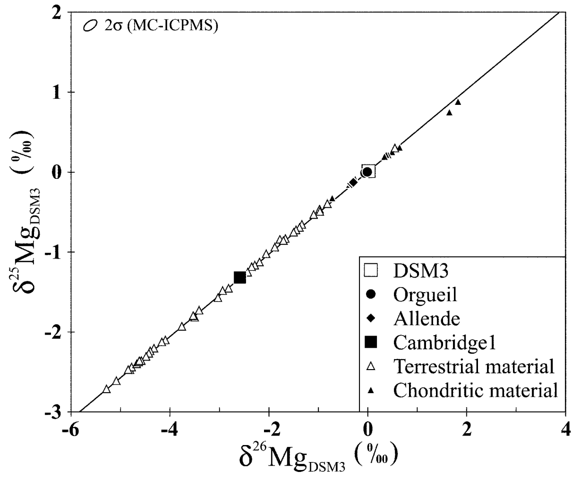

Fig. 4 Three-isotope representation of the Mg isotope ratios of terrestrial material[16–18] or chondrule[7] from Allende previously studied and expressed in δ-unit in the DSM3 scale. The solid line corresponds to the terrestrial fractionation curve.[7] The difference in the Mg-isotopic composition of the two standard solutions DSM3 and Cambridge 1 represents 44% of the reported terrestrial range. In addition, The Mg-isotopic composition of DSM3 standard is very close to the bulk composition of undifferentiated meteorite such as Allende or Orgueil, giving geochemical and cosmochemical significance to the DSM3 scale.

study means that the SRM980 is inappropriate for reporting mass-dependent isotopic variations of magnesium at the sub-permil level.

The isotopic heterogeneity is no longer an issue when the standard is kept in solution. The two large batches of pure Mg solutions (DSM3 and Cambridge 1) are perfectly suitable as a standard material and an aliquot can be obtained upon request from the first author. In addition, their isotopic compositions differ by 1.3‰ per u (Table 4), which corresponds to 44% of the terrestrial magnesium-isotopic variations reported so far (Fig. 4). Similarly to SMOW and SLAP for hydrogen,[23] the DSM3 and Cambridge 1 solutions can be used for the definition of a normalised scale if needed. DSM3 has an isotopic composition very similar to the Mg-isotopic composition of carbonaceous chondrites (Orgueil and Allende). Because of the lack of heterogeneity and the cosmochemical and geochemical significance of DSM3, we suggest using DSM3 as the primary isotopic reference material to report Mg-isotopic variations.

Conclusion

The Mg-isotopic compositions of the SRM980 are heterogeneous, and define a single mass fractionation line in the $^{25}Mg/^{24}Mg$–$^{26}Mg/^{24}Mg$ space. The isotopic heterogeneity not only corresponds to differences among units but has been found at the chip-size (few mg) level. Therefore, the SRM980 cannot be used as the international isotopic standard of magnesium, except to report the excess of ^{26}Mg which is defined by the deviation from the mass-dependent relationship between $^{25}Mg/^{24}Mg$, and $^{26}Mg/^{24}Mg$ ratios. A large batch of a mono-elemental nitric solution of magnesium called DSM3 has been produced and appears to have an isotopic composition indistinguishable from carbonaceous chondrite at the 95% confidence level, reached by the measurement of magnesium isotopic variations by MC-ICP-MS. We recommend usage of the DSM3 as the primary isotopic reference material for magnesium-bearing materials.

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