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High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry

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Abstract

Multiple-collector inductively coupled plasma mass spectrometry has been used for the precise measurement of variations in the isotopic composition of Mg in a range of materials. The contributions of C–C, C–N, and Mg–H molecular species to the mass spectrum in the Mg mass region are minimised. Variations in sample ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg ratios are expressed as δ^{26}Mg and δ^{25}Mg units, which are deviations in parts per 10^3 from the same ratio in the SRM 980 Mg standard. The long-term repeatability of the ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg ratios of a sample Mg solution relative to the SRM 980 Mg isotope standard are 0.12‰ and 0.06‰, respectively, at 95% confidence. The addition of Na, Al, and Ca in a solution of Mg having a known isotopic composition induces 0.2‰–1‰ increase of δ^{26}Mg. This chemical bias is a result of a mass-dependent process and is observed to be greater with Ca than Na. Isobaric interference from doubly charged ^{48}Ca ions on mass 24 is observed to be significant when [Ca]/[Mg] $\geq$ 0.5. The results obtained on nine terrestrial material show a variation of Mg-isotopes of 4‰ in δ^{26}Mg. When plotted in a three-isotope diagram, all the data fall on a single mass fractionation line. The excess of ^{26}Mg has been determined by the deviation from that mass-dependent relationship, and its long-term repeatability is 0.06‰ at 95% confidence. (Int J Mass Spectrom 208 (2001) 89–98) © 2001 Elsevier Science B.V.

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1. Introduction

Magnesium has three naturally occurring isotopes, ^{24}Mg, ^{25}Mg, and ^{26}Mg, with relative abundance of 78.99%, 10.00%, and 11.01%, respectively [1]. Natural variations of the isotopic composition of Mg may arise through: (1) stellar nucleosynthesis and incorporation of presolar grains into meteorites [2–4], (2) the decay of ^{26}Al to ^{26}Mg (e.g. [2,5–9]), (3) isotopic fractionation through volatilisation/condensation reactions [9–11], (4) isotope fractionation during low temperature fluid/rock interactions, and (5) kinetic and thermodynamic isotope effects accompanying biological incorporation and rejection. The last three processes are characterised by a mass-dependent fractionation similar to any instrumental fractionation (α_{inst}). Previous investigations (thermal ionisation or secondary ionisation mass spectrometry) of Mg isotopic variations have been limited by an uncertainty of 1‰–2‰ on α_{inst} [3,5,6,12,13]. Because of this technical limitation to accurate measurement of α_{inst} of Mg, relatively few investigations have been made of

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mass-dependent fractionation in terrestrial samples. Original investigations concluded that terrestrial variations of Mg isotopic ratio are restricted to a few per mil [2,14]. The aim of this study is to use multiple collector-inductively coupled mass spectrometry (MC-ICPMS) for the measurement of precise Mg isotope ratios suitable for the study of terrestrial and extraterrestrial samples.

2. Analytical procedure

The accurate measurement of Mg isotopes using Ar-ICP source mass spectrometers is potentially hindered by the presence of molecular interferences (C_2^+, C_2H^+, $C_2H_2^+$, CN^+, and NaH^+) or doubly charged ions ($^{48}Ca^{2+}$, $^{48}Ti^{2+}$, $^{50}Ti^{2+}$, $^{50}V^{2+}$, $^{50}Cr^{2+}$, and $^{52}Cr^{2+}$). Although ^{50}V is uncommon (~ 0.24%), and V and Mg exhibit contrasting chemical behaviour, Ca and Mg have a very similar chemistry in aqueous solutions, both are present in biological materials and Mg can be associated with Cr and Ti in igneous rocks. This study describes a technique, which both reduces and corrects for these potential isobaric interference on ^{24}Mg, ^{25}Mg, and ^{26}Mg and studies the effects of the presence of interfering elements in a Mg solution.

2.1. Sample preparation

All standards and samples were prepared in 0.1 N nitric acid solution and introduced into the plasma through a modified Cetac MCN 6000 desolvating nebuliser. This device minimises the introduction of H_2O, CO_2, O_2, and N_2 into the plasma thus reducing the abundance of interfering molecular species. Memory effect from the Cetac MCN 6000 nebuliser were suppressed after ~5 min of washing with 0.1 N nitric acid solution.

High-purity Mg metal and natural samples of carbonate minerals and magnesia were dissolved in 2N HNO_3 at room temperature. The residue after dissolution was separated by centrifugation and the supernate evaporated to dryness and then re-dissolved in 0.1 N HNO_3. Samples and standards were diluted with 0.1 N HNO_3 to 0.5–1.5 ppm Mg to obtain the best counting statistics for mass spectrometric analysis. The effects of Na, Al, and Ca on the measurement of Mg isotopes have been tested by adding varying amounts of these elements in a solution of one of the Mg samples (Dead Sea Metal) studied.

Table 1
Instrumental operating conditions and signal measurement parameters

rf power	1400 W
Plasma gas flow rate	12 L/min
Interfaces cones	nickel
Acceleration voltage	4 kV
Ion lens setting	Optimised for max. intensity
Instrument resolution	~300
Mass analyser pressure	2×10^{-9} mbar
Detector	12 Faraday collectors
Nebuliser	microconcentric
Spray chamber temp	75 °C
Desolvator temp	160 °C
Swep gas (argon)	3.9 L/min (optimised daily)
Sample uptake rate	70 μL/min
Typical ^{24}Mg sensitivity	7 V/ppm
Sampling time	three repetitions of 200 s
Background time	six repetitions of 5 s

2.2. Mass spectrometry

Mg-isotope ratios were measured using a Nu Instruments MC-ICPMS. This instrument is a double focusing magnetic sector instrument with variable dispersion ion optics and a fixed array of 12 Faraday collectors [15]. The normal operating conditions adopted for the mass spectrometer are summarised in Table 1. The Nu Instruments MC-ICPMS produces Mg peaks with flat-tops at a working mass resolution of ~300, as required for high-precision isotope ratio measurement. The 3 Mg isotopes are positioned in the multiple collector for simultaneous measurement as follow: ^{26}Mg in the extreme cup on the high mass side of the multiple collector; ^{25}Mg in the axial cup; and ^{24}Mg in the extreme cup on the low mass side of the multiple collector.

3. Results

3.1. Molecular interference

Under-optimised conditions observed signal intensities for the $^{24}Mg^+$ beam are typically higher than

4×10^{-11} A. The residual noise after electronic background correction has been estimated to be $\sim 7 \times 10^{-17}$ A by the measurement of the signal on the 9 faradays cups situated on masses 24.25, 24.5, 24.75, 24.875, 25.125, 25.25, 25.375, 25.5, and 25.75. A signal as low as 10^{-15} A can be easily detected and measured with a precision of ±10%. It is, therefore, observed that a small background ($\sim 2 \times 10^{-14}$ A on mass 24) is always present which has a Mg-like isotopic composition and is likely to be a trace amount (~300 ppt) of Mg in the dilute nitric acid solution. A detailed study of this background signal suggests the contribution to mass 24 is slightly enriched (by 4 ± 7%) with respect to masses 25 and 26 for pure Mg. This is possibly a molecular interference of $^{12}C_2^+$ of 10^{-15} A or lower, which is in good agreement with the observed levels of other molecular species involving C, like $^{12}C^{16}O_2^+$, in similar conditions [16,17]. Such molecular interference on mass 24 will induce a systematic bias lower than 0.02‰ on $^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$ ratios. The use of a desolvating nebuliser acts to reduce O, N, C, and H interference to an insignificant level. In addition, the level of Mg blank is low enough that a 100% difference between the isotopic composition of the Mg in the blank and the Mg in the sample would induce a difference of only 0.05‰ in the measured ratio. The blank and molecular interference contribute an overall uncertainty of <0.07‰ on the measured $^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$ ratios.

3.2. Intensity of the instrumental fractionation

As expected for a plasma source mass spectrometer the measured isotopic composition of the international standard SRM 980 [12] is greatly enriched in heavy isotopes though the precise mechanism of the enrichment is still not fully understood [18]. Under normal conditions Mg isotopes measured in this laboratory display an enrichment of ~7.5 ± 0.5‰/amu (Fig. 1).

The instrumental mass-dependent fractionation for the $^{25}Mg/^{24}Mg$ ratio and $^{26}Mg/^{24}Mg$ ratio, respectively, are

$$\alpha^{25}_{\text{inst}} = (^{25}\text{Mg}/^{24}\text{Mg})_{\text{measured}}/(^{25}\text{Mg}/^{24}\text{Mg})_{\text{true}}$$

$$\alpha^{26}_{\text{inst}} = (^{26}\text{Mg}/^{24}\text{Mg})_{\text{measured}}/(^{26}\text{Mg}/^{24}\text{Mg})_{\text{true}}$$

whereas the theoretical relationship between these values may be expressed as (derived from [19])

$$\alpha^{25}_{\text{inst}} = (\alpha^{26}_{\text{inst}})^{\beta}$$

If this isotopic fractionation occurs under thermodynamic equilibrium, β will have a value of 0.5210, whereas a situation involving pure kinetic isotopic fractionation is described with a β of 0.5105.

The variations observed in α_{inst} on the instrument in this laboratory, obtained from a best fit of the raw data, is $\beta = 0.5180 \pm 0.0004$ (Fig. 1), which is not related to variations in the intensity of the Mg beam. Using this measured value of β, the $^{26}Mg/^{24}Mg$ ratio, normalised to the certified value for $^{25}Mg/^{24}Mg$ of 0.12663 [12], is 0.139828 ± 0.000037 (Table 2) which is slightly higher than the accepted value of 0.13932 ± 0.00026 [1]. This offset of +3.6 ± 4.2‰ on the $^{26}Mg/^{24}Mg$ would require a molecular interference on mass 24 of $\sim 2 \times 10^{-13}$ A. This offset is 2 orders of magnitude higher than the molecular interference observed and less than 2% of the observed offset can be related to blank and isobaric interferences. The normalised $^{26}Mg/^{24}Mg$ ratio of SRM 980 has been found to be identical to other terrestrial Mg [5,14,20]. The reported values are, however, highly variable (Table 2). The value obtained in this laboratory by MC-ICPMS, is very close to recent thermal ionisation mass spectrometry (TIMS) measurements (Table 2), and suggests that the accepted value for the SRM 980 should be more accurately defined.

The calculated value of 0.5180 for β is close to the theoretical value for fractionation in conditions of thermodynamic equilibrium of 0.5210 and implies a near-equilibrium process for the instrumental isotopic fractionation occurring in a MC-ICPMS. In the case of Mg, the exponential law, commonly used for correcting α_{inst} on MC-ICPMS [15,30,31], would deliver a β of 0.5110, and the normalised $^{26}Mg/^{24}Mg$ ratio of SRM 980 would be 0.139563 ± 0.000041 (2σ, $N = 2040$), which differs by −1.9‰ from the

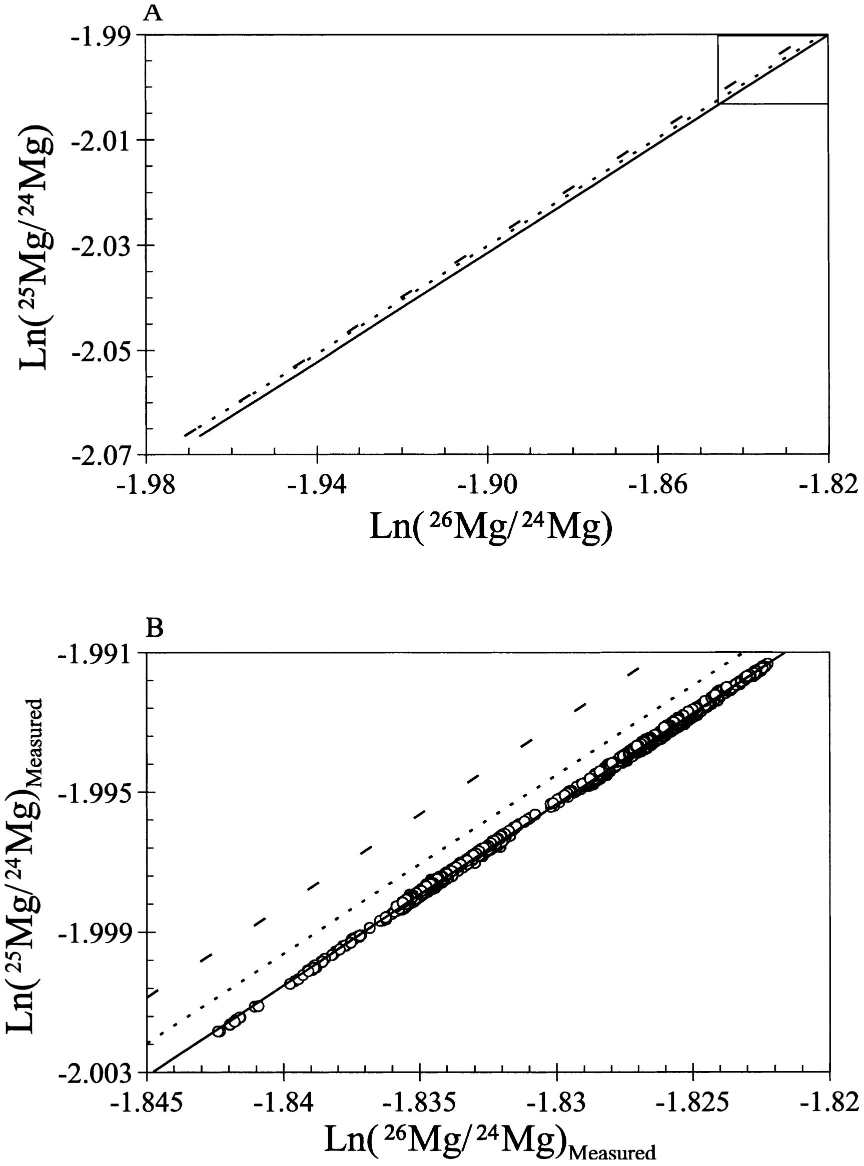

Fig. 1. Three-isotope representation of the natural logarithm of Mg isotope ratios of the SRM 980. The theoretical relationship between the instrumental mass-dependent fractionation for the $^{25}Mg/^{24}Mg$ ratio and $^{26}Mg/^{24}Mg$ (α^{25}_{inst} and α^{26}_{inst}) are straight lines. (A) All the data are in the rectangle in the upper right corner, corresponding to the enlargement shown in (B). The solid line corresponds to the best fit of 2040 measurements and is extrapolated to the $^{25}Mg/^{24}Mg$ of 0.12663 [12]. The dashed line and the dotted line correspond to the evolution of the $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ ratios from [12] along a pure thermodynamic ($\beta = 0.5210$) and a pure kinetic ($\beta = 0.5105$) mass-dependent fractionation, respectively.

observed best-fit value. This suggests the limitation of the use of the exponential law in correcting for fractionation of light elements measured with MC-ICPMS.

The α_{inst} is sensitive to instrumental conditions, including effects from the nebulizer as well as those occurring during ion formation, extraction and focusing and may vary from day to day between 1‰ and 6‰. In order to minimise the effects of this drift we use a standard-sample bracketing technique [17]. A

Table 2
Normalised magnesium isotopic composition

Year	Material	Method	$^{26}Mg/^{24}Mg_{normal}$	$\pm 2\sigma_{mean}$	Source
1966	SRM 980	TIMS	0.139 32	0.000 26	[12]
1970	Terrestrial	TIMS	0.139 805	0.000 016	[5]
1970	Terrestrial	TIMS	0.139 493	0.000 066	[20]
1974	Terrestrial	TIMS	0.139 649	0.000 019	[21]
1981	Terrestrial	TIMS	0.140 16	0.000 12	[22]
1983	Terrestrial	SIMS	0.139 9	0.000 7	[23]
1984	Terrestrial	SIMS	0.139 38	nr[a]	[3]
1985	Terrestrial	SIMS	0.139 313	0.000 056	[24]
1986	Terrestrial	SIMS	0.139 432	0.000 013	[25]
1992	Terrestrial	TIMS	0.141 410	0.000 036	[26]
1996	Terrestrial	TIMS	0.139 733	0.000 028	[27]
2000	Terrestrial	TIMS	0.139 819	0.000 009	[13]
2000	SRM 980	TIMS	0.139 60	0.000 06	[28]
2000	Terrestrial	SIMS	0.139 32	0.000 08	[29]
	SRM 980	MC-ICPMS	0.139 828	0.000 037[b]	This study

[a] nr: not reported.
[b] 2σ, $N = 2040$.

negligible cross-contamination between the sample and the standard is achieved by aspirating a 0.1 N HNO_3 wash solution for 5 min between analyses. Mg-isotopic compositions are expressed as a permil deviation from the isotopic composition of the SRM 980 as follows: $\delta^{x}Mg = \{(^{x}Mg/^{24}Mg)_{Sample}/(^{x}Mg/^{24}Mg)_{SRM980} - 1\} \times 1000$. Such normalisation reduces the contribution of Mg blank from the nitric acid and isobaric interferences since both affect the sample and standard in an identical manner. In this protocol, standard and sample isotope values are measured 4 and 3 times, respectively, for 200 s each. Each 200 s measurement consists of 5 s integration of the electronic background followed by 100 s acquisition of the signal, repeated twice. This protocol allows the calculation of five brackets, and each value corresponds to their average.

3.3. Magnesium standard measurements

In addition to SRM980, two analytical grade Mg solutions and a high purity metal (Table 2), have been used to characterise the accuracy of the measurements. Measured values for these samples show a variation of up to 4 permil in their $\delta^{26}Mg$ values relative to SRM980. The typical 2σ precision of individual measurements is 0.05‰/amu (between 0.01‰/amu and 0.37‰/amu) and includes counting statistics for the sample and the standard as well as the drift of the standard value between measurements of the sample. The precision of a measured sample using the sample-standard bracketing technique was observed to be 0.06‰/amu (2σ, $n = 167$), assessed from the external repeatability measured over a period of 15 months (Table 3 and Fig. 2).

The measured values of these materials define a mass-dependent fractionation line by the relation: $\delta^{25}Mg = (0.5132 \pm 0.0008) \times \delta^{26}Mg - (0.003 \pm 0.002)$ (Fig. 3). When the variation of mass-dependent fractionation is not greater than 1%, the slope in the above relationship corresponds to β. For each Mg solution, the individual measurements lie on that line (Fig. 3), and the external error on $\delta^{25}Mg$ and $\delta^{26}Mg$ are therefore correlated. The β value of 0.5132 obtained from these samples is close to the value of a kinetic fractionation and may be indicative of the main processes operating during chemical purification of Mg in industrial process used for the purification of these Mg solutions or metals.

3.4. Excess of $^{26}Mg(\Delta^{26}Mg)$

The long-term reproducibility of the normalised $^{26}Mg/^{24}Mg$ ratio of SRM 980 has been found to be

Table 3
Mg isotopic composition for commercial reagents and selected carbonate[a]

Sample		δ^{26}Mg (‰)	±2σ	δ^{25}Mg (‰)	±2σ	Δ^{26}Mg (‰)	±2σ	N
Commercial Mg reagent								
SRM 980	Mg metal	0.00	0.07	0.00	0.04	−0.01[b]	0.05	58
Romil	Mg solution	2.44	0.09	1.24	0.05	0.02[b]	0.05	14
Aldrich	Mg solution	2.60	0.17	1.33	0.08	0.00[b]	0.05	48
Dead Sea	Mg metal	3.96	0.15	2.03	0.08	0.01[b]	0.08	47
AG177	Magnesia	2.03	0.04	1.03	0.01	0.00	0.03	4
Natural Magnesite								
OUM 10988	magnesite, Piemont, Italy	1.22	0.04	0.60	0.03	0.03[c]	0.05	3
OUM 22450	magnesite, Transvaal, South Africa	1.90	0.14	0.98	0.08	−0.02[c]	0.01	3
Commercial chlorophyll								
AG27	chlorophyll b, spinach	1.06	0.07	0.54	0.03	−0.02[c]	0.03	4
AG28	chlorophyll a, spinach	1.96	0.10	1.00	0.06	−0.02[c]	0.05	3

[a] Errors quoted are based on the measurement repeatability based on the replicates N number of replicates.

[b] Average of each measurement. The Δ^{26}Mg has been calculated by the relationship: $\Delta^{26}\text{Mg} = \delta^{26}\text{Mg} - [(1/0.5132) \times (\delta^{25}\text{Mg} + 0.003)]$, where 0.5132 is the slope and −0.003 the Y-axis intercept (determined on the 167 measurements, Fig. 2).

[c] The Δ^{26}Mg excess has been calculated by the relationship: $\Delta^{26}\text{Mg} = \delta^{26}\text{Mg} - [(1/0.5118) \times (\delta^{25}\text{Mg} + 0.009)]$, where 0.5118 is the slope and −0.009 the Y-axis intercept (determined on the 9 samples, Fig. 6).

0.26‰. The daily 2σ precision is, however much better, typically, 0.06‰, and the poor long-term reproducibility is related to a small and low frequency (week to month) evolution of β. In order to get round the difficulty of accurately quantifying the instrumental mass fractionation law, we took advantage of the

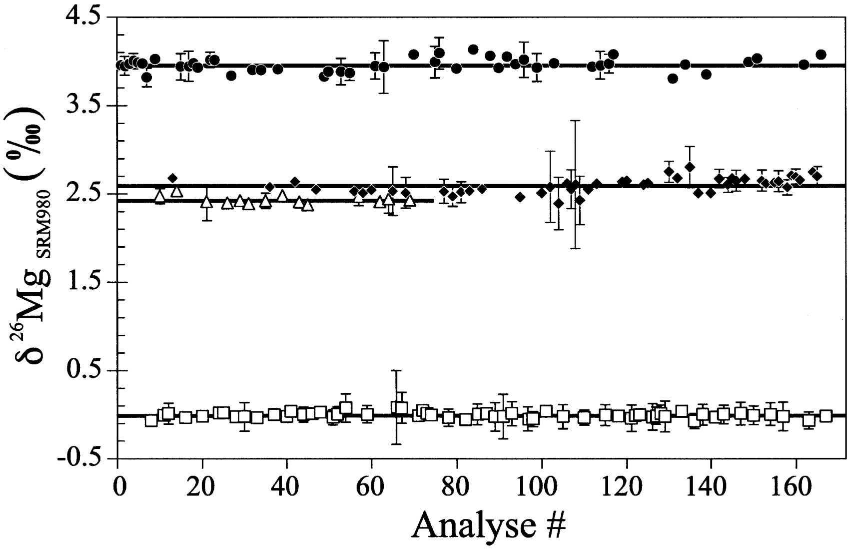

Fig. 2. Repeatability of ^{26}Mg/^{24}Mg measurements. The SRM 980 Mg (open square), the Romil Mg solution (open triangle), the Aldrich Mg solution (diamond), and the Dead Sea Mg metal (solid circles) are expressed relative to SRM 980 Mg-isotope reference standard. The error bars on individual measurements having a 2σ precision smaller than the size of the symbols have been omitted. They correspond to the 95% confidence on a measurement made up of five brackets.

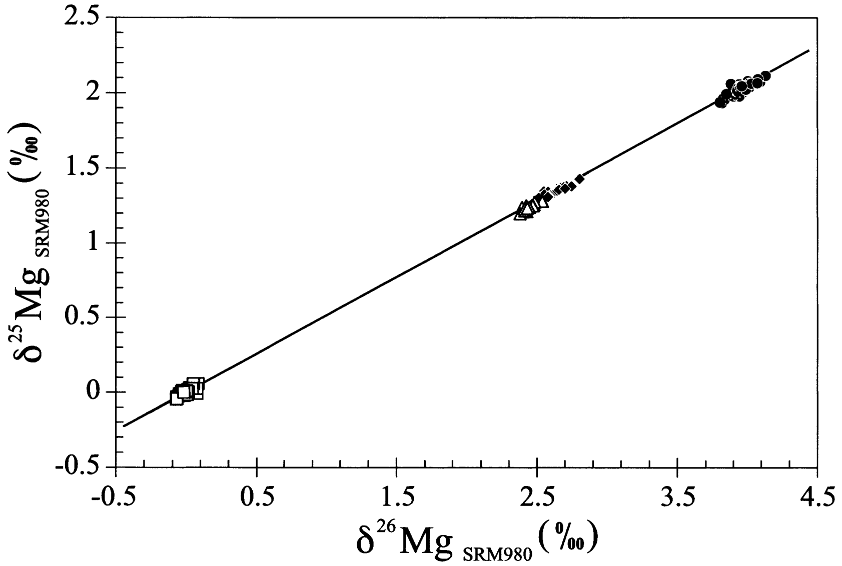

Fig. 3. Three-isotope representation of the Mg isotope ratios, expressed in δ unit. Symbols are same as those in Fig. 2. The solid line corresponds to the best fit of the 167 measurements.

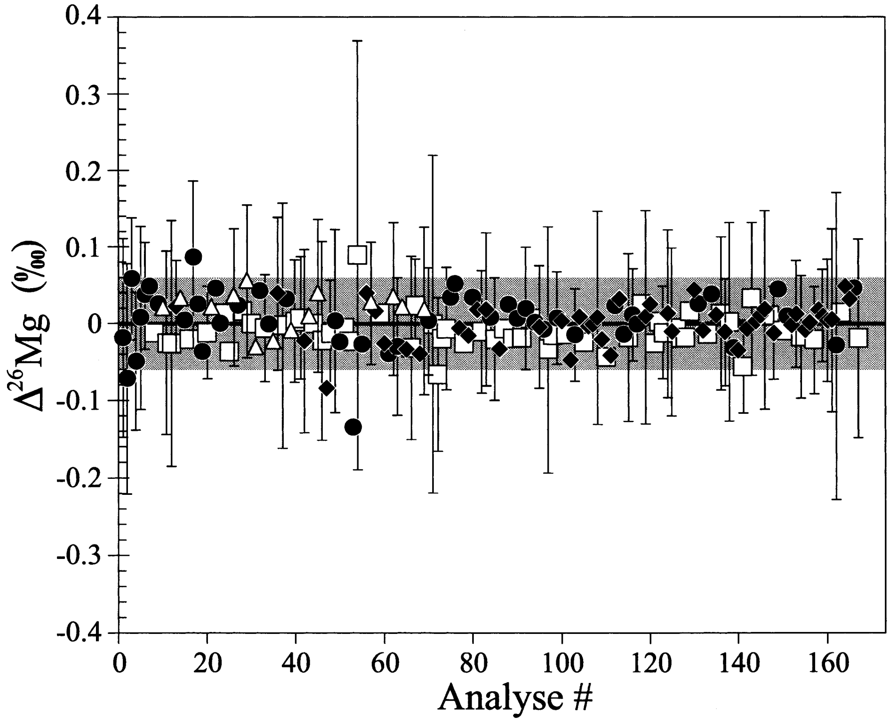

Fig. 4. Repeatability of the $^{26}Mg_{excess}$ ($\Delta^{26}Mg$) measurements. Symbols are same as those in Fig. 2. $\Delta^{26}Mg$ is calculated as the deviation from the best-fit line in Fig. 2. The gray area corresponds to the 2σ of the whole data set. The error bars on individual measurements having a 2σ precision better than 0.06‰ have been omitted.

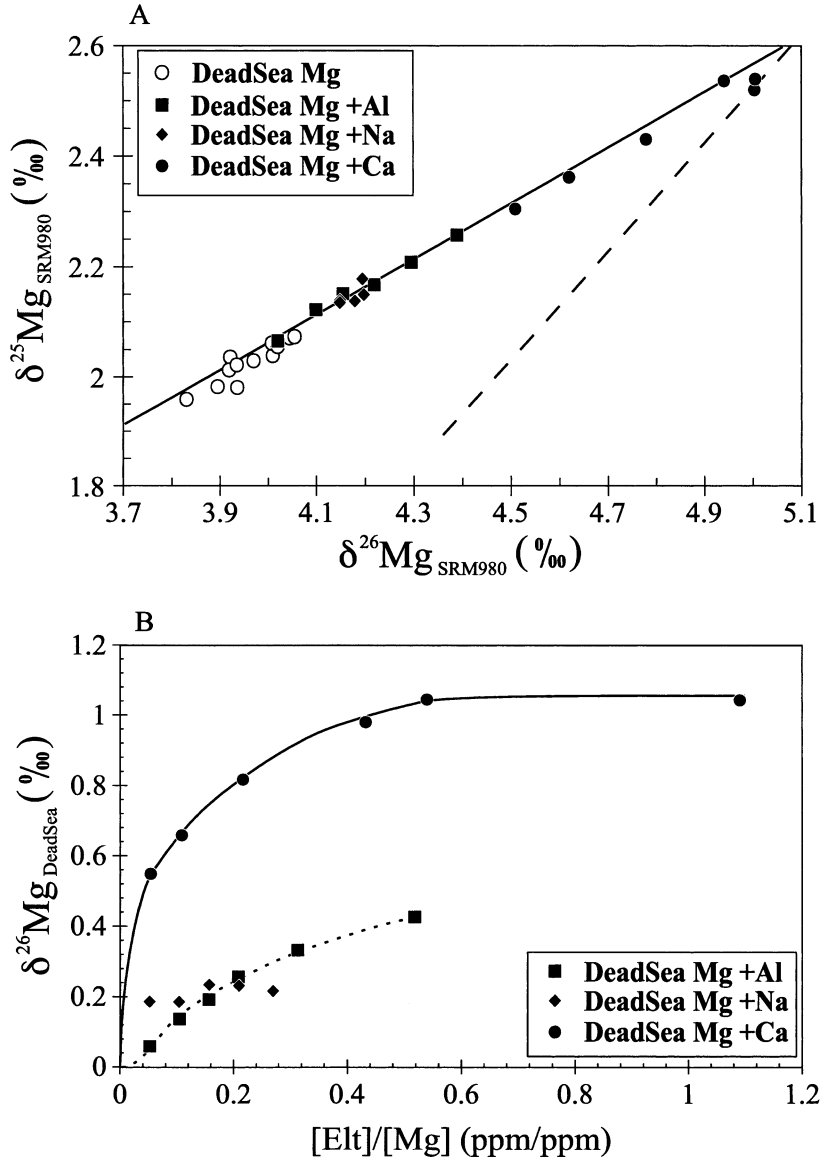

Fig. 5. Matrix effect on the Mg isotope ratios, measured against a pure solution of Mg, and expressed in δ unit. (A) Three-isotope representation of the Mg isotope ratios. The solid line corresponds to the mass-dependent fractionation curve, and the dashed line has a slope of 1, modeling an isobaric interference on mass 24. (B) Isotopic shift from the pure Mg-solution measurement, expressed in δ unit, vs. the chemical composition of the sample solution.

relative measurement against the standard SRM980. By analogy with the excess of ^{17}O (quoted Δ^{17}O) (e.g. [32]), the excess of ^{26}Mg, quoted Δ^{26}Mg, can be defined as the per million deviation from the mass-dependent fractionation line (Fig. 3). Δ^{26}Mg is calculated by the relationship: $\Delta^{26}\text{Mg} = \delta^{26}\text{Mg} - (1/\beta) \times (\delta^{25}\text{Mg} + \epsilon)$, where β is the slope and ϵ is the Y-axis intercept in the three-isotope plot (Table 3). The precision of a measured sample was observed to be 0.06‰ (2σ, $n = 167$), assessed from the external repeatability measured over a period of 15 months (Fig. 4).

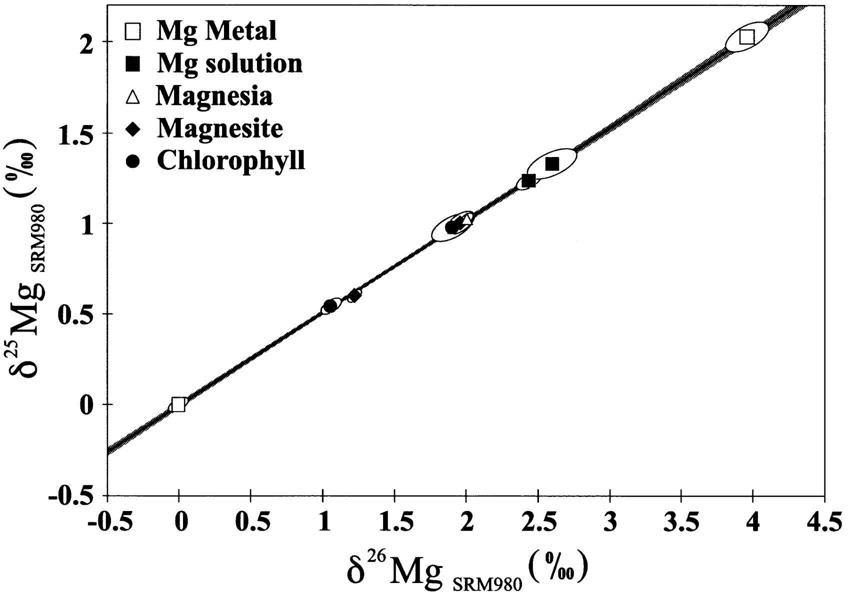

Fig. 6. Three-isotope representation of the Mg isotope ratios of terrestrial material. The solid line corresponds to the best fit of the nine measurements. The gray area corresponds to 95% confidence envelope.

3.5. Matrix effects

To assess the importance of chemical purification of Mg solutions prior to their introduction into the MC-ICPMS the affect of the addition of Na, Al, and Ca on the measured Mg isotope ratios, measured against a pure Mg solution, has been investigated. The tested concentrations ranged from zero to 120% of the Mg concentration and was observed to give rise to increased values of δ^{26}Mg ranging from 0.2 to 1‰ (Fig. 5). This chemical bias is a result of a mass-dependent process and increases with increasing concentration of the added element. The α_{inst} for Mg is, therefore, affected by the occurrence of other chemical elements entering the plasma, and is most sensitive to Ca, followed by Al and Na. In addition isobaric interference from doubly charged ^{48}Ca ions on mass 24 starts to be significant when [Ca]/[Mg] $\geq$ 0.5. These observed matrix effects determine that chemical purification of Mg should be carried out before measurement on the MC-ICPMS if high accuracies are required. In the case of magnesia, magnesite, and chlorophyll, the chemistry of those materials allowed a direct measurement without chemical separation.

3.6. Mass-dependent fractionation curve

A number of natural samples have been analysed as part of this investigation and include Mg–carbonate from metamorphic sources, together with commercial chlorophyll and magnesia (Table 3). These nine terrestrial samples exhibit a range of 3.96‰ in their δ^{26}Mg and define a single mass-dependent fractionation line in a three-isotope plot (Fig. 6). The slope (equivalent to β) of 0.5118 ± 0.0038 ($R^2 = 0.99962$, $N = 9$) is within error of the slope determined on the pure Mg materials (Fig. 3). The two extreme isotopic compositions correspond to high purity Mg metal.

4. Conclusion

The new technique reported here for Mg-isotope ratio measurement using MC-ICPMS offers more than an order of magnitude improvement in repeatability over previous techniques. The technique is both rapid, with a throughput for this method of about 12–15 samples per day, and sensitive, allowing sample sizes as small as 0.5×10^{-6} g Mg may be analysed at high precision.

The range in isotopic composition of pure magnesium obtained commercially (~4‰) suggests the use of a homogenised and well-distributed standard, such as SRM 980, for normalisation of stable isotopic composition of Mg between laboratories. The preliminary results for several materials indicate a different isotopic composition of Mg in biological and geological environments. It is necessary to investigate the systematic of the biological and geochemical control of magnesium isotope ratios in the global magnesium cycle

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