

DEVELOPMENT OF PRECISE AND ACCURATE MAGNESIUM ISOTOPE MEASUREMENTS BY MULTIPLE-COLLECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Introduction: Magnesium has three isotopes (24, 25 & 26), one of which can be produced by the short-lived decay of ²⁶Al ($t_{1/2} = 0.73$ Myr). Since the demonstration of the former presence of ²⁶Al in calcium-aluminium-rich inclusions (CAIs) [1], the ²⁶Al-to-²⁶Mg chronometer has been used to date the relative timing of CAIs and chondrules as well as the formation of some basaltic meteorites [e.g., 2,3]. Recent application of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) to Mg isotope analysis has potentially opened up a new range of dating opportunities. In particular, small excesses or deficits in meteorites and their constituents should now be resolvable that might allow isochron or model age dating of material that was previously impossible to date. For example, the presence of small ²⁶Mg excesses in bulk basaltic meteorites might be used to date the increase in Al/Mg ratio associated with the formation of basaltic magmas. Conversely, Al/Mg ratios of essentially zero in some types of differentiated meteorites and their minerals should allow ²⁶Mg deficits to place age constraints on their formation if this took place within 2 million years of CAI formation.

The $\delta^{26}\text{Mg}^*$ excesses and deficits expected from such processes will be ca. $\leq \pm 0.050\%$ and require both the precision and accuracy of Mg isotope measurements to be ca. $\pm 0.005\%$ if the full potential of the ²⁶Al-to-²⁶Mg dating system is to be utilised. Here, we describe analytical developments intended to assess whether MC-ICPMS techniques can really produce Mg isotope data at these levels of precision and accuracy.

Analytical Methods:

Chemical separation of Mg. We explored Mg separation from silicate meteoritic material using a number of methods, primarily based around the elution of Mg on cation exchange resins in dilute HNO₃ media. While this method can satisfactorily remove most Na, Cr, Al, Ti, and Ca from Mg, several percent of other elements may remain in the Mg solution even after several column passes (e.g., [4,5]). These contaminants could potentially preclude the acquisition of very accurate $\delta^{26}\text{Mg}^*$ excess and deficit data. We have developed procedures designed to achieve Mg yields of > 99.5% with > 99.5% purity. For most samples we now routinely apply a 4-step column separation procedure to produce high purity Mg separates.

Samples are taken fully into solution after normal HF-HNO₃ digestion techniques. An aliquot of this solution containing 2 mg of dissolved sample is then processed as follows:

- (1) Fe is removed by eluting Mg in conc. HCl through a 0.5 ml AG-1 X8 anion exchange resin bed.
- (2) Ca is removed by eluting Mg in 3M HNO₃ through a 0.25 ml DGA (Eichrom) resin bed. This step is repeated at least twice for high Ca samples (e.g., CAIs).
- (3) Na, Al, Ti and Cr are eluted in 6 ml of 1M HNO₃-0.1M HF on a AG50W-X8 cation exchange resin (200-400 mesh). Mg is then collected by eluting >10 ml of 1M HNO₃-0.1M HF. This step is repeated for high Al samples.
- (4) Mn is removed from Mg by elution in dilute HCl-acetone through AG50W-X8 cation exchange resin.

Mg isotope measurements by MC-ICPMS. Mg isotope ratios are measured on a Nu Plasma MC-ICPMS at Victoria University of Wellington. The Faraday collector used to measure ²⁴Mg is equipped with a 10¹⁰ Ohm resistor that allows larger 25 and 26 ion beams (3-9 V) to be measured during analysis. Mg is introduced into the plasma via a desolvating nebuliser as dilute HCl solutions. Each measurement typically comprises 8 min of baseline and 26.67 min of data acquisition acquired in four blocks. Sample analyses are bracketed by analyses of standards and data are reported in the per mil (‰) notation as the difference from the average value of the two bracketing standards. Uncertainties on each analysis are calculated by rigorously incorporating that on the sample run with those from the bracketing standards. $\delta^{26}\text{Mg}^*$ is calculated from the offset of a sample's mass-bias corrected ²⁶Mg/²⁴Mg (using the exponential mass fractionation law and ²⁵Mg/²⁴Mg = 0.12663) compared to the average value obtained from bracketing standards. Implicit in this approach is the assumption that any natural stable isotope differences between the sample and standard are the result of kinetic processes. Using this approach, single Mg isotope analyses have uncertainties (2 se) on mass-bias-corrected $\delta^{26}\text{Mg}^*$ that are $\leq \pm 0.016\%$ and as low as $\pm 0.012\%$. Multiple analysis of samples routinely results in weighted means with uncertainties that are $\leq \pm 0.005\%$. Analyses are carried out in pseudo-medium resolution mode at a resolution of 2000, which permits complete resolution of all interferences with the exception of hydrides and Cr⁺⁺, Ti⁺⁺ and Ca⁺⁺.

Results: A number of tests were conducted to examine the veracity of Mg isotope data obtainable by MC-ICPMS (Table 1). Analyses were made of:

- an ICPMS Mg standard (Aristar) gravimetrically spiked with pure ^{26}Mg to produce solutions with 10, 20 and 30 ppm excesses
- an ICPMS Mg standard (Aristar) doped with 2 mol % of a range of contaminant elements
- a range of Mg standard solutions against a Bulk Earth Mg composition as represented by Mg separated from mantle olivine (J11)
- aliquots of Mg collected during the elution of Mg through AG50W-X8 cation exchange resin
- a Mg standard solution processed through both anion and cation exchange chemistry
- mantle olivine (J11) subjected to differing levels of chemical separation i.e., just anion exchange removal of Fe and the complete separation procedure through anion, DGA and cation exchange chemistry

Table 1 $\delta^{26}\text{Mg}^*$ - $\delta^{25}\text{Mg}$ data of analytical experiments.

Sample	$\delta^{26}\text{Mg}^*$ (‰)	$\delta^{25}\text{Mg}$ (‰)	n
Aristar $\delta^{26}\text{Mg}^*$ 0.01‰ ¹	+0.0107±0.0052	-0.04±0.10	8
Aristar $\delta^{26}\text{Mg}^*$ 0.03‰ ¹	+0.0311±0.0069	-0.05±0.15	5
Aristar Ca/Mg = 2.0 ¹	+0.2425±0.0240	+0.76±0.18	1
Aristar Ca/Mg = 0.2 ¹	+0.0294±0.0142	+0.80±0.13	1
Aristar Ca/Mg = 0.02 ¹	+0.0102±0.0080	+0.67±0.15	4
Aristar Mn/Mg = 0.02 ¹	-0.0022±0.0089	+0.64±0.05	3
Aristar Ti/Mg = 0.02 ¹	+0.0074±0.0094	+0.30±0.01	3
Aristar Ni/Mg = 0.02 ¹	-0.0008±0.0074	+0.16±0.03	5
Aristar Fe/Mg = 0.02 ¹	+0.0095±0.0081	+0.24±0.05	4
Aristar Cr/Mg = 0.02 ¹	-0.0036±0.0096	+0.35±0.20	3
Aristar Al/Mg = 0.02 ¹	-0.0072±0.0083	+0.27±0.01	3
Aristar Na/Mg = 0.02 ¹	-0.0002 ± 0.012	+0.05±0.01	2
Aristar Mg ²	+0.0161±0.058	-0.81±0.12	5
Alfa Aesar Mg ²	+0.0153±0.0071	-1.72±0.10	5
DSM-3 Mg ²	-0.0014±0.0065	+0.14±0.10	9
SRM-980 Mg ²	+0.0030±0.0063	-2.33±0.09	7
Column cut 60-70 ml ³	-0.0149±0.0084	+0.51±0.17	3
Column cut 70-80 ml ³	+0.0010±0.0220	+0.16±0.07	3
Column cut 80-90 ml ³	+0.0145±0.0078	-0.44±0.09	3
Column cut 90-100 ml ³	+0.0260±0.0210	-0.67±0.11	3
Aristar Mg anion-processed ¹	-0.0002±0.0062	-0.03±0.17	6
Aristar Mg cation-processed ¹	-0.0019±0.0049	-0.03±0.04	10
J11 anion-processed ⁴	+0.0022±0.0040	-0.11±0.06	24
J11 cation-processed ⁴	+0.0007±0.0053	-0.16±0.05	9

¹measured vs pure Aristar Mg, ²measured vs J11 olivine (anion-processed), ³measured vs bulk Mg standard, ⁴measured vs DSM-3

Discussion: The results presented in Table 1 illustrate a number of important points. Repeated analyses of Mg standards with gravimetrically prepared ^{26}Mg anomalies can be reproduced with an accuracy and precision of $\leq \pm 0.005\%$. Similarly, replicate analyses of Mg standard (Aristar) and mantle olivine (J11) subjected to anion and cation chemistry show no

significant deviation from the expected $\delta^{26}\text{Mg}^*$ (i.e., 0.000‰).

Our data also illustrate some potential difficulties in attempting to obtain highly precise and accurate Mg isotope data by MC-ICPMS. Some ICPMS Mg standards with fractionated stable isotope compositions have experienced some part of this fractionation by equilibrium processes that produces apparent $\delta^{26}\text{Mg}^*$ excesses in isotopically light standards. In contrast, despite the fact that SRM980 is the lightest isotopically standard we have analysed, most of this fractionation was induced by a kinetic process. Given that DSM-3 is slightly isotopically heavier than mantle olivine and terrestrial basalts, we prefer to use matrix-matched olivine and basalt standards as bracketing standards for analyses of unknowns.

Small amounts of contaminant elements remaining after chemistry can be seen to variably bias sample stable Mg isotope data to heavier values, suggesting that discussions regarding small stable isotopic variations amongst planetary materials are premature [4,5], given the levels of contaminants reported by these studies to be present in their analysed Mg cuts. However, the presence of most elements appear to have little effect on $\delta^{26}\text{Mg}^*$ if the Mg cut is $>99\%$ pure. Care must be taken that recovery of Mg is high as the stable isotopic fractionation associated with incomplete recovery on ion exchange resins is controlled by an equilibrium process that introduces analytical artefacts on the $\delta^{26}\text{Mg}^*$ when this is calculated using the approach adopted here.

In summary, our results indicate that it is possible to resolve $\delta^{26}\text{Mg}^*$ anomalies to high precision and accuracy ($\leq \pm 0.005\%$) in meteorites, which should allow extension of ^{26}Al -to- ^{26}Mg dating to meteorite materials with small anomalies. We will present new high-precision Mg isotope data for meteorites where small $\delta^{26}\text{Mg}^*$ excesses (anrites, eucrites) and deficits (pallasite olivines, ureilites, aubrites) have previously been reported [e.g., 6], and used to constrain rapid timescales of planetesimal melting, differentiation and accretion in the young Solar System. For example, 66 new analyses of olivine from four main group pallasites have a weighted mean $\delta^{26}\text{Mg}^* = -0.0155 \pm 0.0017\%$, that can be used to calculate a model age for olivine crystallization and diffusive isolation on the pallasite parent body of 1.05 ± 0.12 Myr ($^{26}\text{Al}/^{27}\text{Al}_0 = [2.16 \pm 0.24] \times 10^{-5}$) after formation of calcium-aluminium-rich inclusions.

References:

- [1] Lee T. et al. (1976) *GRL* 3, 109-112. [2] Kita N.T. et al. (2000) *GCA* 64, 3913-3922. [3] Srinivasan G. et al. (1999) *Science* 284, 1348-1350. [4] Wiechert U. & Halliday A. N. (2007) *EPSL* 256, 360-371. [5] Teng F. et al. (2007) *EPSL*, in press. [6] Bizzarro. M. et al. (2005) *ApJ* 632, L41-44.