HIGH PRECISION MAGNESIUM ISOTOPIC COMPOSITION OF ALLENDE MATERIAL: A MULTIPLE COLLECTOR INDUCTIVELY COUPLED MASS SPECTROMETRY STUDY. A. Galy, E. D. Young, R. D. Ash, and R. K. O'nions, Department of Earth Sciences, University of Oxford, Parks Road, OX1 3PR, UK. albertg@earth.ox.ac.uk

Introduction: Three processes account for variations of the isotopic composition of Mg found in CAIs from Allende (CV3) [1-5]: 1) the decay of ^{26}Al to ^{26}Mg, 2) isotopic fractionation through volatilization/condensation reactions, and 3) nucleosynthetic anomalies. The occurrence of ^{26}Al in the early solar nebula has been largely discussed and is now well established e.g. [6-7].

The methods (TIMS or SIMS) applied to the search for Mg isotopic variations have an uncertainty of ≥ 1 ‰/amu because of technical limitations to accurate measurement of the instrumental fractionation (α_{inst}) for Mg [2, 5, 6]. Therefore, relatively few investigations have addressed mass-dependant fractionations and so little is known about the initial heterogeneity of Mg isotopes in the early solar system.

The aim of this study is to develop a method able to resolve sub-permil variations in $^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ and use this method to investigate the Mg isotopes in Mg-rich constituants of Allende, including chondrules and matrix.

Samples and Methods: Two size fractions (<20 μm and <48 μm, described in [8]) were dissolved in concentrated HF, HNO_3 and $HClO_4$ mixture. A large chondrule from the same Allende sample was hand-picked while seven other originate from another Allende sample. Each chondrule was split in two. One half was washed in pure water and ultrasonic bath to remove small matrix material stuck on the surface and then dissolved in the same manner as matrix. The other half was mounted and polished for petrological and oxygen isotope investigation [9]. A chemical separation of Mg was performed following a slightly modified method from [1], yielding >99% of Mg upon collection.

Mg solutions are introduced through a Cetac MCN-6000 nebulizer into the multiple collector-inductively coupled mass spectrometry (MC-ICP-MS) from Nu Instruments [10]. This instrument allows simultaneous measurement of the 3 isotopes of Mg. The α_{inst} has been determined on the international Mg isotopic standard SRM980 [11] and is 1.077 for $^{25}Mg/^{24}Mg$. The α_{inst} is sensitive to instrumental conditions, including both the nebulizer as well as ion -formation, extraction, and focussing. Results are expressed in δ units relative to SRM 980 standard :

$$\delta^{25}Mg=\{(^{25}Mg/^{24}Mg)_{Sample}/(^{25}Mg/^{24}Mg)_{SRM} - 1\}*1000.$$
$$\delta^{26}Mg=\{(^{26}Mg/^{24}Mg)_{Sample}/(^{26}Mg/^{24}Mg)_{SRM} - 1\}*1000.$$

The reproducibility of the α_{inst} over a day is variable and ranges between 3 and 6 ‰. In order to reduce the effects of drift we adopted a standard-sample bracketing technique [12]. In this protocol, standard and sample isotope values are measured 6 and 8 times, respectively, for 200s each. Using this technique, the internal reproducibility is between 0.01 and 0.14‰/amu (2σ) and includes counting statistics for the sample and the standard as well as the drift for the standard between 2 measurements of the sample. The external reproductibility of the MC-ICPMS obtained on pure Mg solutions is 0.06‰/amu (2σ, n=50). Based on duplicate chemistry and measurement of a variety of samples, including Allende matrix, sea water, and foraminifers, the overall reproductibility of our method is 0.06‰/amu (2σ, n=15).

Results: The measurements of 8 chondrules and 2 granulometric fractions of the matrix are presented in Fig. 1. All but one chondrule lies on the mass-dependant fractionation line defined by 18 terrestrial samples. The range of $\delta^{25}Mg$ is 0.9‰. One chondrule shows a ^{26}Mg excess ($^{26}Mg^*$) of 0.25‰. The 2 granulometric fractions of the matrix have similar Mg-isotopic composition within 0.05‰/amu.

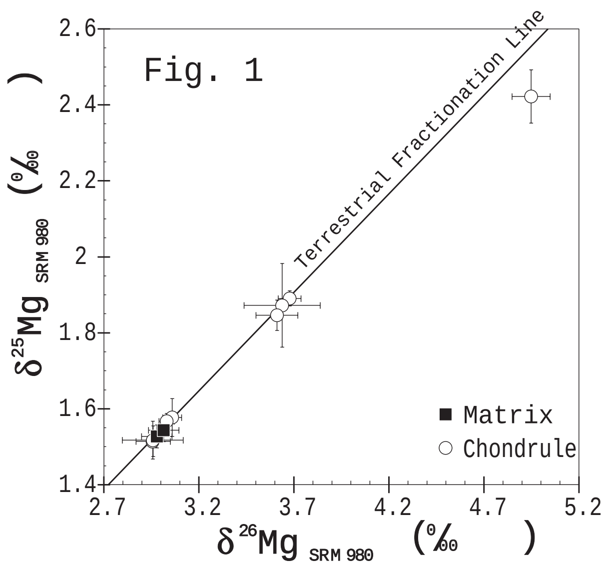
In addition, a systematic inverse relationship has been found between the size of the chondrule (estimated from their masses) and $\delta^{25}Mg$ (Fig 2), and $\delta^{25}Mg$ forms a crude positive correlation with the presence of aluminous phases.

Discussion: Allende had a complex history and several processes that affected this meteorite may have acted in concert to explain these data.

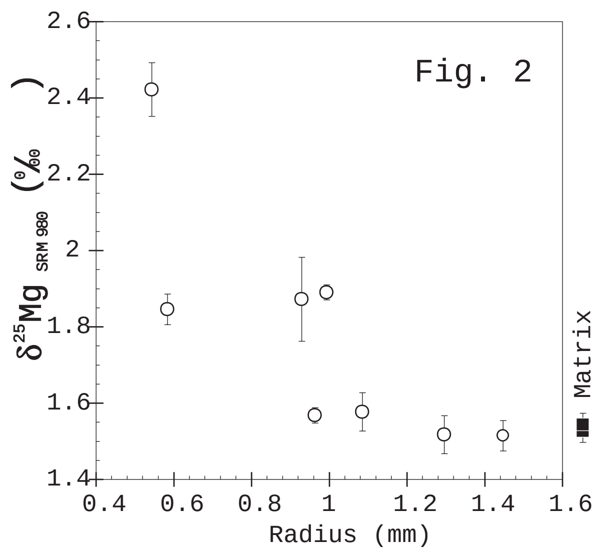
Alteration and Metamorphism. Hypothetical mass-dependent processes related to late metamorphism can not explain the $^{26}Mg^*$ observed. In addition, the $\delta^{25}Mg$ of plagioclase from different chondrule are different by up to 8‰ [13], which implies no isotopic homogenization by alteration or metamorphism.

^{26}Al decay. The chondrule showing a $^{26}Mg^*$ is Al-rich, with plagioclase >> spinel being the major aluminous phase. Since $^{26}Mg^*$ is correlated with Al/Mg in all chondrules showing $^{26}Mg^*$ [7, 13], the $^{26}Mg^*$ observed is likely the result of ^{26}Al decay.

Initial Heterogeneity. While initial Mg-isotopic heterogeneity has been proposed to explain some negative $^{26}Mg^*$ in CAIs [4] or heterogeneity within a single phase of a chondrule [13], such heterogeneity can not explain the relationship between mass fractionation in Mg isotopes and chondrule size. In addition, the correlation between δ^{25}Mg and δ^{30}Si in Allende CAIs is consistent with mass-dependant fractionation of Mg isotopes by volatilization during melting [14-15]. Our results extend this process of mass fractionation of light element isotopes in the molten phase to chondrule formation.



Volatilization and Condensation. If mass-dependant fractionation occurred during the condentation of chondrule precursor, the first condensates would be the heavier isotopically. High δ^{25}Mg in the most Al-rich chondrule could therefore be the result of early condensation of this chondrule relative to the others. Petrological arguments suggest that feldspar is not an early condensate. However, coincidence of matrix and large-aluminous-poor chondrule δ^{25}Mg is more easily explained by progresive enrichment in heavy isotope [15] by volatilisation of Mg. Numerical modeling of Mg-isotope fractionation has been performed following the approach of [16]. Assuming a kinetic isotope effect, Fig 2 can be matched with $1000>\beta>250$. These high values imply a high evaporation rate relative to the value of Mg diffusion [16], which is consistent with a high pressure environment [17]. Alternatively, if the constraint of high β is relaxed ($\beta<250$), the isotopic fractionation factor has to approach 1 (equilibrium), suggesting back reaction and recondensation. This process has already been proposed to explain Na enrichment at the edge of chondrule [18] and also implies high pressure. Therefore, the Mg-isotope variations in Allende chondrules support an high partial pressure condition during chondrule melting.



Conclusion: The MC-ICP-MS allows the measurement of small variations of Mg isotopic composition as small as 0.05‰/amu.

Small but resolvable ^{26}Mg excess has been found in an Al-rich chondrule from Allende.

δ^{25}Mg variations with chondrules and matrix are best explained by volatilization/condensation processes. Comparisons with experimental data suggest either a high total pressure or a high partial pressure of Mg during chondrule melting.

References:

[1] Lee T. and Papanastassiou D. A. (1974) *GRL*, 1, 225-228. [2] Gray C. M. and Compston W. (1974). *Nature*, 251, 495-497. [3] Lee T. et al. (1976). *GRL*, 3, 109-112. [4] Wasserburg G. J. et al. (1977) *GRL*, 4, 299-302. [5] Bradley J. G. et al. (1978) *JGR*, 83, 244-254. [6] MacPherson G. J. et al. (1995) *Meteoritics*, 30, 365-386. [7] Russel S. S. et al. (1996). *Science*, 273, 757-762. [8] Arden J. W. (1983) *EPSL*, 62, 395-406. [9] Ash R. D. et al., *this issue*. [10] Belshaw N. S. et al. (1998) *IJMS*, 181, 51-58. [11] Catanzaro E. J. et al. (1966). *J. Natl. Bur. Stand.*, 70A, 453-458. [12] Halicz L. et al. (1999) *JAAS*, 14, 1835-1838. [13] Sheng Y. J. et al. (1991) *GCA*, 55, 581-599. [14] Clayton R. N. et al. (1988) *Phil. Trans. R. Soc. Lond.*, A 325, 483-501. [15] Davis et al. (1990). *Nature*, 347, 655-658. [16] Young E. D. et al. (1998). *GCA*, 62, 3109-3116. [17] Richter F. M. et al. (1999). *LPS*, XXX. [18] Lewis R. D. et al. (1993). *Meteoritics*, 28, 622-628.