HIGH PRECISION MAGNESIUM ISOTOPIC MEASUREMENTS OF CAI EVAPORATION RESIDUES.

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Introduction. Type B Ca-Al-rich inclusions have textures that have been interpreted as indicative of re-heating to temperatures of about 1400°C, sufficient to produce a high degree of partial melting, and subsequent cooling at rates of the order of degrees per hour [1]. They are often found to be enriched in the heavy isotopes of the moderately volatile elements silicon and magnesium, which also suggests a high temperature episode resulting in the partial evaporation of the more volatile components. This enrichment is typically interpreted as following the Rayleigh fractionation equation $R/R_o = f^{(\alpha-1)}$, where R is the isotopic ratio, initially R_o, f is the fraction of the evaporating species remaining in the residue, and α is the kinetic gas-melt isotopic fractionation factor. Quantitative constraints on the duration of the high temperature event can be obtained given data for the evaporation kinetics and proportion of an element that has to be evaporated in order to produce a given amount of isotopic fractionation [2]. Here we report new high precision magnesium isotope measurements on laboratory-produced evaporation residues of molten Type B CAI-like compositions to reexamine the relationship between the amount of magnesium removed by evaporation and the isotopic composition of the residue.

Experimental procedures and analytical methods: Molten droplets of a Type B CAI-like composition (~12% MgO, ~45% SiO_2, ~20% Al_2O_3, and ~23% CaO) were suspended in a vacuum furnace (P<10^{-6} Torr) at 1800°C for periods of time up to several hours. The chemical composition of the starting materials and the recovered residues was measured using a JEOL JSM-5800LV scanning electron microscope equipped with an Oxford Link ISIS-300 energy dispersive microanalysis system.

The magnesium isotopic analysis of the starting materials and the evaporation residues was carried out on a Micromass IsoProbe multi-collector magnetic sector ICP-MS instrument in the Isotope Geochemistry Laboratory of The Field Museum. Chips of glass were crushed and dissolved by standard HF-HNO_3 acid treatment at ≈100°C and eventually brought into a solution of dilute HNO_3. Magnesium was separated from the sample matrix via a single cation exchange column in a nitric acid medium. Recovery of magnesium is estimated to be better than 98% and the concentrations of most matrix elements are reduced by more than 99%; concentrations of Al are reduced by ≈90%. Sample magnesium aliquots were diluted with double-distilled ultrapure 3 wt% HNO_3 to Mg concentrations of ≈1 ppm for isotopic measurement. Through the use of ultrapure reagents and acid-cleaned cation exchange resins Mg procedural blanks are less than 10 ng, which are negligible compared the amounts of Mg separated (1–100 μg).

$^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$ measurements were performed by static multi-collection, with each measurement consisting of twenty cycles of ten second integrations. Isotopic compositions of samples are determined by sample-standard bracketing. Isotopic data for each sample are reported relative to the NIST SRM 980 magnesium isotope standard and are the mean of at least three sample-standard brackets. A CETAC Aridus desolvating nebulizer was used, resulting in dry plasma conditions and minimizing hydride formation.

Replicate analysis of unknowns yielded reproducibilities in $\delta^{25}Mg$ and $\delta^{26}Mg$ of or better than 0.09‰ and 0.14‰. The reproducibilities for analyses replicated on different days were indistinguishable from those measured in a single analysis session. Replicate analysis of SRM 980 over 9 months give reproducibilities of 0.06‰ and 0.12‰ for $\delta^{25}Mg$ and $\delta^{26}Mg$, respectively. Further analytical details can be found in [3].

Results and discussion: Our new high-precision magnesium isotope measurements of the evaporation residues are plotted as a function of the amount of Mg removed by evaporation in Fig. 1. Fig. 2 is a log-log plot of the fraction of Mg remaining in the evaporation residue, versus R/R_0, the relative Mg isotopic fractionation per amu. Rayleigh fractionation lies along a straight line on such a plot and the slope is $\alpha-1$. Also shown are older ion microprobe magnesium isotope data from [2,4] on laboratory-produced CAI evaporation residues. The ICPMS data can be fit with a single Rayleigh fractionation curve with a high precision. The small departures are more likely to be due to uncertainties in the actual amount of magnesium lost by each residue rather than lack of precision of the isotopic measurements. The ion microprobe data tend to lie below the curve defined by the ICPMS data. The reason for this is not known, but could be related to matrix effects in the ion probe data. The Mg isotopic fractionation factor derived from the ICPMS data (α=0.98611±0.00002) is not very different from that derived from the ion microprobe data (α=0.98869±0.00011). Both values are significantly different from the value one would expect from kinetic

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theory when the dominant gas species is Mg ($\alpha=(24/25)^{1/2}=0.9798$). In the past we have used experimental data to argue that this difference between the experimental value and the theoretical expectation is not the result of finite diffusion in the molten sample, nor is it due to recondensation [2]. The new isotopic analyses reported here are evidence that the difference is also not an artifact due to systematic errors with the previous isotope measurements.

On a plot of $\delta^{26}Mg-\delta^{25}Mg/2$ vs. $\delta^{25}Mg$ different isotopic fractionation laws plot as curves [5]. Rayleigh fractionation plots as a curve that drops below zero and then increases above zero at high $\delta^{25}Mg$. Two such curves are shown in Fig. 3, under the assumptions that magnesium evaporates as Mg atoms and as MgO molecules. Equilibrium thermodynamic calculations predict that Mg is the dominant gas phase species. The new

high precision ICPMS data lie between the two Rayleigh curves consistent with the data in Figs. 1 and 2. With the high precision magnesium isotopic data now becoming available on CAIs, the exact fractionation law used to correct for mass fractionation in ^{26}Al-^{26}Mg studies becomes important. Our data suggest that the Rayleigh law is appropriate, but that α cannot simply be calculated from the square root of the thermodynamically calculated evaporating species, but must be measured.

References: [1] E. Stolper & J. M. Paque (1986) *GCA, 50*, 1785. [2] F. M. Richter, A. M. Davis, D. S. Ebel & A. Hashimoto. (2002) *GCA, 66*, 521. [3] M. Wadhwa et al. (2003) *LPS XXXIV*, this volume. [4] R. A. Mendybaev et al. (2002) *LPS XXXIII*, #2040. [5] MacPherson et al. (1995) *Meteoritics, 30*, 365.

Fig. 1

Fig. 2

Fig. 3