MAGNESIUM ISOTOPE COMPOSITIONS OF CHONDRULES FROM THE MURCHISON AND MURRAY CARBONACEOUS CHONDRITES.

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Introduction: High-precision Mg isotope compositions of meteorites and their components can provide unique constraints on the time scales and processes involved in their formation [1]. Since the advent of multicollector inductively coupled plasma mass spectrometry (MC-ICPMS), there have been several reports of high-precision analyses of the mass-dependent fractionation of Mg isotopes in chondrules [2-5]. Most such studies have focused on chondrules from the Allende carbonaceous chondrite. As such, the purpose of this investigation is to determine high-precision Mg isotope compositions of petrographically well-characterized chondrules from other unequilibrated chondrites with the goal of understanding their formation processes and time scales. As a follow-up to an earlier report [6], we present here high-precision Mg isotope compositions of a suite of chondrules separated from the Murchison and Murray carbonaceous chondrites.

Sample Documentation and Analytical Methodology: Chondrules from the CM2 chondrites Murchison (MRC) and Murray (MRY) were hand-picked from bulk samples of these two meteorites that had been previously subjected to freeze-thaw disaggregation and density separation at the University of Chicago.
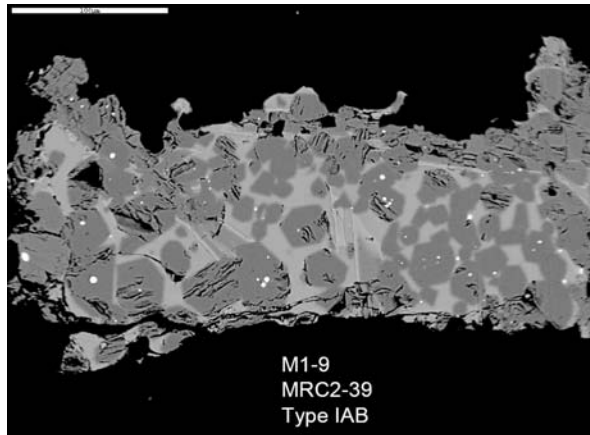

Figure 1: Backscattered electron image of a fragment of a type IAB chondrule (MRC2-39) from Murchison. Phenocrysts of enstatite, euhedral forsterite with metal inclusions, and late clinopyroxene are enclosed in an FeO-free feldspathic glass; no secondary alteration phases were found to be present. Scale bar is 100μm. This chondrule was measured to have a $^{27}Al/^{24}Mg$ ratio of 0.316, but shows no resolvable excess in $^{26}Mg^*$ (see text for details).

Samples were placed on tape and examined using the JEOL JEM-5800LV scanning electron microscope (SEM) at the University of Chicago (SEM) prior to any polishing or carbon-coating. Preliminary classifications were made based on estimated olivine/pyroxene ratios and their Mg/Fe ratios determined by energy-dispersive X-ray analysis.

Following the preliminary documentation described above, each sample identified as a chondrule was crushed between sapphire disks in a clean lab, one fragment mounted in a polished section, and the remainder reserved for bulk chemical and isotopic analyses. Mineralogical and petrological characterization of the fragments in the polished sections were then conducted using the SEM at the University of Chicago The Mg isotope compositions and Al/Mg ratios were measured in fractions taken from 19 chondrules (15 from Murchison, and 4 from Murray, which included 15 type I and 4 type II chondrules) at Arizona State University using established procedures similar to those described by [7]. The original diameters were 380-600 μm for Murchison chondrules and 200-390 μm for Murray chondrules.

Prior to dissolution and isotopic analysis, chondrule fractions were cleaned by ultrasonicating in acetone, and subsequent rinsing with ultrapure water. Samples were digested in concentrated $HF-HNO_3$ (5:1), evaporated to dryness and then refluxed with concentrated HNO_3 until completely dissolved. The sample solution was then evaporated to dryness and the residue was dissolved in 1M HNO_3; a ~1-2% aliquot was reserved for the determination of Al/Mg ratios, while Mg was separated from the remaining solution using cation chromatography. A sample size equivalent to ~1-5 μg of Mg was loaded onto a pressurized 1 ml cation exchange column. Separation of Mg (with >99% yield) from elements such as Al, Ca, Na, or Ti was achieved after 2 passes through the column in a 1M HNO_3 medium. Total procedural blank was ≤~1 ng, which was negligible compared to the amount of Mg present even in the smallest fraction (~1μg).

The purified Mg solutions were analyzed using a Thermo-Finnigan Neptune MC-ICPMS, with ^{24}Mg, ^{25}Mg, ^{26}Mg and ^{27}Al ion beams measured simultaneously on Faraday cups at medium resolution. Sample solutions were diluted to 250-300 ppb in 3% HNO_3, typically producing a ^{24}Mg signal of ~6 × 10^{-11}A using

an Apex desolvating nebulizer with a flow rate of 100 µL/min. To correct for instrumental mass bias, each sample analysis was bracketed by measurements of the DSM3 Mg isotope standard (concentration-matched to the sample to within ~10%). Mass-dependent fractionation of Mg isotopes in the chondrule samples is reported relative to the DSM3 standard in per mil (‰) units of $\delta^{25}Mg$ and $\delta^{26}Mg$. To determine the non mass-dependent anomalies in the $^{26}Mg/^{24}Mg$ ratio due to the decay of ^{26}Al (i.e., $\delta^{26}Mg*$), the measured $^{26}Mg/^{24}Mg$ ratio was normalized to $^{25}Mg/^{24}Mg = 0.12663$ using the exponential law. To assess the accuracy of our Mg isotope measurements, during each analytical session, we measured the isotopic compositions of terrestrial rock and mineral standards processed through the same chemical procedures as the chondrule samples. Therefore, along with our samples, we processed and analyzed several aliquots of the BCR-2 USGS rock standard and a homogenized powder of San Carlos olivine.

The $^{27}Al/^{24}Mg$ ratios of the chemically unprocessed aliquots of the sample solutions were determined against a calibration curve generated using gravimetrically prepared pure SPEX Claritas™ ICPMS standard solutions with a range of Al/Mg ratios. The accuracy and reproducibility of the $^{27}Al/^{24}Mg$ ratio measurements during each analytical session were assessed by the analysis of rock and mineral standard solutions such as San Carlos olivine, BCR-2, and AGV-2. Based on the reproducibility of repeated measurements of these rock standards, the error on our $^{27}Al/^{24}Mg$ analyses is estimated to be better than ±2% (2SD).
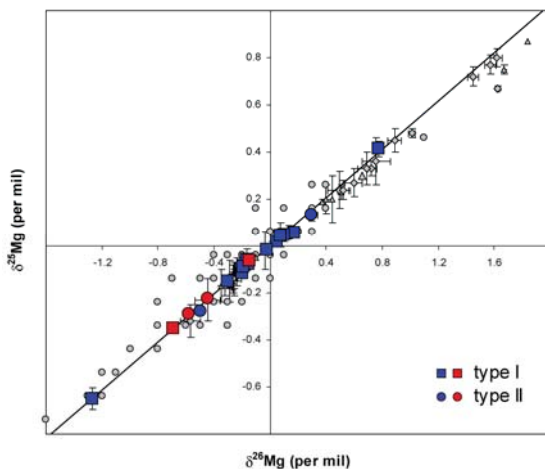

Figure 2: Mg isotopic data for chondrules of carbonaceous chondrites: Murchison (blue) and Murray (red) of this study, and Allende from the literature (grey triangles [2], circles [3], and diamonds [4], respectively). Error bars for data from [3] are not shown for clarity but are typically ±0.15‰ for $\delta^{25}Mg$ and ±0.25‰ $\delta^{26}Mg$. Errors shown for all other data are ±2SE. Solid line is the best-fit line to the Murchison and Murray chondrule data (this study) and has a slope of 0.513 ± 0.017 (2σ).

Results: The $^{27}Al/^{24}Mg$ ratios of the Murchison and Murray chondrules range from 0.004 to 0.316, with most values being sub-chondritic to near-chondritic (~0.10). The Mg isotopic compositions of these chondrules range from -0.65 to +0.41‰ for $\delta^{25}Mg$ and -1.27 to +0.77‰ for $\delta^{26}Mg$ (Fig. 2). No deviations in $^{26}Mg*$ are detectable in any of the chondrules, not even in the Murchison type I chondrule with the highest $^{27}Al/^{24}Mg$ ratio of 0.316. This chondrule has $\delta^{26}Mg*$ of -0.01 ± 0.04‰ (2SE), indicating an upper limit on the $^{26}Al/^{27}Al$ ratio of $<2 \times 10^{-5}$. As can be seen in Fig. 2, the range of Mg isotopic compositions defined by the Murchison and Murray chondrules overlaps with the range defined by Allende chondrules.

Discussion: As can be seen in Fig. 2, the range of Mg isotope compositions of Murchison and Murray chondrules extends to compositions that are heavier and lighter than the average carbonaceous chondrite (which is similar to the DSM3 standard composition; [8]). As previously suggested for Allende chondrules, the deviations towards lighter compositions from the "canonical" chondritic value could be associated with parent body alteration by aqueous fluids whereas deviations towards heavier compositions may be associated with the presence of relict refractory olivines [3]. We did not, however, observe a correlation between isotopic composition and modal abundance of alteration products in the polished chips. Alternatively, it is possible that the Mg isotope compositions of these chondrules have been fractionated due to volatilization and recondensation processes.

The absence of resolvable $^{26}Mg*$ excesses in the chondrule with the superchondritic $^{27}Al/^{24}Mg$ ratio of 0.316 may be interpreted either as indicative of formation >1 Ma after CAIs or of resetting of the Al-Mg isotope systematics by secondary alteration processes on the CM parent body. The latter is not a likely explanation in this case given that this chondrule shows no petrographic evidence for secondary alteration (Fig. 1).

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