Mg ISOTOPIC HETEROGENEITY, Al-Mg ISOCHRONS, AND CANONICAL $^{26}Al/^{27}Al$ IN THE EARLY SOLAR SYSTEM.

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Introduction: It is well known that the isotopic composition of Mg in CAIs is variable [1]. Subsequent work by many groups showed that a vast number of "heavy" elements have variable isotopic compositions, typically at a level of less than in a few parts in 10^4 in some CAIs to much smaller variations in other meteoritic materials. These variations are the result of somewhat incomplete mixing of the diverse stellar debris that made up the bulk solar system. These effects are distinct from the large oxygen isotopic effects (~5%) [2], which do not appear to be due to stellar nucleosynthetic processes. The nature of isotopic variations in Mg has attracted little attention due to the fact that as ^{26}Al was present in the early solar system (ESS) this results in variable increases in $^{26}Mg/^{24}Mg$ due to ^{26}Al decay [3]. As Mg has only three isotopes, the ratio $^{25}Mg/^{24}Mg$ is used to determine mass fractionation effects. It is not possible to actually assign the anomaly to a particular Mg isotope data due to the "normalization" processes used. However, extrapolating a linear array of data in the ($^{27}Al/^{24}Mg$, $^{26}Mg/^{24}Mg$) space to $^{27}Al/^{24}Mg$ = 0 provides a measure of shifts in the initial $(^{26}Mg/^{24}Mg)_0$ value in a sample assumed to originally have had a uniform isotopic composition [4]. This approach was first used by [5] in a study of the type B CAI called "Egg-3", which is a FUN CAI with known anomalies in Ti [6]. These workers found what appeared to be a clear indication of a deficit in $(^{26}Mg/^{24}Mg)_0$ of ~1‰ [4, 5]. If this deficit reflected the bulk initial value, it would require an enormously high $^{26}Al/^{27}Al$ for the bulk solar system, as the canonical value of $^{26}Al/^{27}Al = 5.23 \times 10^{-5}$ would only give a shift of 38 ppm in ^{26}Mg with a bulk solar $^{27}Al/^{24}Mg = 0.101$. Since these data were reported several decades ago on very small samples, we felt it is important to establish the validity of this claim. Our first efforts to check this using ion probe techniques [7] did not provide evidence for a deficiency in ^{26}Mg as large as reported by [5]. However, a hint of very low intercept $(\delta^{26}Mg)_o = -0.089\pm0.058$‰ barely resolvable from the solar initial of -0.038‰ was seen in [7]. The precision of the data with SIMS was not adequate to settle the matter. In this report, we present new measurements on Egg-3 using with modern high precision MC-ICP-MS technique.

Methods: The CAI Egg-3 was separated into 3 fractions based on density and grain size. These are < 60µm (sinks in 3.3 g/cc heavy liquid), <100µm (no heavy liquid), and 60-200µm (floats in 3.3 g/cc heavy liquid). In addition, we also analyzed a bulk fragment from Egg-3, and a bulk fragment of the Allende CAI WA. Sample sizes averaged 0.5mg and were dissolved using the standard HF:HNO_3 dissolution technique. After dissolution, ~1% of this material was saved for $^{27}Al/^{24}Mg$ analyses. The remainder was centrifuged, before processing using cation exchange resin. This ensures separation of Mg from any potential interferences in order to accurately measure the Mg isotope ratio. Both Mg isotopes and Al/Mg ratios were measured on a Thermo *Neptune Plus* HR-MC-ICP-MS in the Geology Department at UC Davis.

$^{27}Al/^{24}Mg$ ratios of CAI samples were obtained by calibrating to five reference materials with a range of well-known $^{27}Al/^{24}Mg$ ratios (BCR-2, BHVO-2, AGV-2, Peace River Chondrite, San Carlos Olivine). Magnesium isotope ratios were bracketed against the DSM-3 standard, with each sample measured a minimum of nine times. We used an exponential law to correct instrumental mass fractionation with $^{25}Mg/^{24}Mg = 0.12663$, with a fractionation factor $\beta = 0.511$. The choice of "laws" to correct the CAI data with relatively large natural mass fractionation in Mg isotopes and low Al/Mg is critically reviewed in [9]. The $\delta^{26}Mg$ is reported relative to the international DSM-3 Mg standard. Typical reproducibility of Mg isotope ratio is better than 0.015‰ (2 s.e.). Accuracy was assessed by repeat measurements of BCR-2, giving a $\delta^{26}Mg$ value of 0.002 +/- 0.013 (n = 6).

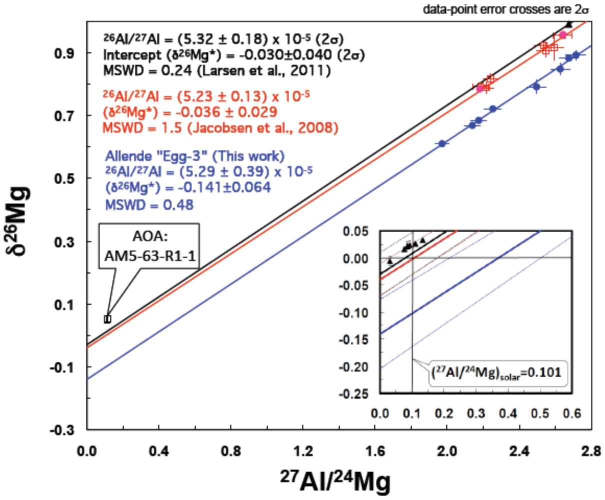

Fig. 1. Allende "Egg-3" CAI internal ^{26}Al-^{24}Mg isochron (blue solid circle) from this study. Whole rock CAI isochrons of Larsen et al [8] and Jacobsen et al [9] are shown as black and red regression lines, respectively, for comparison. Mineral separates of A43 CAI from [9] are rerun in this study (pink solid circles). AOAs from both [9] (main figure) and [8] (inset) are excluded from the individual regressions. Inset shows close up of regression lines in the main figure with their respectively error envelops (dotted lines) near intercept region

Results and Discussion: Our results are shown in Fig. 1. We repeated four mineral separates analyses of A43 CAI of [9] in this study, shown as pink solid circles in Fig. 1 (two seen in this scale). It can be seen that we fully confirm the results by [9] with our new repeat measurements. In addition, we show that Allende WA-1 whole rock fragment from the original discovery paper by [10] also plot on the red line of [9] in Fig. 1 (outside the scale). The new high precision data on Egg-3 define an excellent linear array and yield $^{26}Al/^{27}Al = (5.29 \pm 0.39) \times 10^{-5}$ from samples with $1.97 < ^{27}Al/^{24}Mg < 2.71$. This result is in agreement with the ion probe value of 4.9×10^{-5} found for Egg-3 using phases with very high $^{27}Al/^{24}Mg$ up to 400 [see Fig. 15 in ref. 11]. However, the initial $(^{26}Mg/^{24}Mg)_0$ that we have found for Egg-3 is clearly negative with $(\delta^{26}Mg)_o = -0.141 \pm 0.064$ ‰ and lie well below the whole rock CAI isochron intercept with $(\delta^{26}Mg)_o = -0.036 \pm 0.029$ ‰ from [9]. The negative $(\delta^{26}Mg)_o$ value for Egg-3 CAI is qualitatively consistent with the initial finding of [5], although the magnitude is far smaller, likely resulting from difficult measurements on microsamples in earlier years.

We have also plotted the very recent results by [8] which lie far above the results found here for Egg-3. The data by [8] again yield the canonical value for $^{26}Al/^{27}Al = (5.252 \pm 0.019) \times 10^{-5}$ but demonstrate a very small deficiency in $(\delta^{26}Mg)_o$ of -0.0159 ± 0.0014 ‰. This is contradictory to the $(\delta^{26}Mg)_o$ of -0.0317 ± 0.0038 ‰ reported by the same group [12]. We must note, however, that the elevated $\delta^{26}Mg$ of [8] above the expected average solar system initial value of -38 ppm is accomplished by pooling amoeboid olivine aggregates (AOAs) with very low Al/Mg together with CAIs. As seen in Fig. 1, AOAs are clearly above the bulk CAI regression line. If we regress the *bona fide* CAIs only from the Efremovka sample in [8] without AOAs, the intercept is $(\delta^{26}Mg)_o = -0.030 \pm 0.040$ ‰, entirely consistent with whole rock CAI intercept of $(\delta^{26}Mg)_o = -0.036 \pm 0.029$ ‰ [9] (Fig. 1). Regression of AOAs of [8] alone gives an intercept $(\delta^{26}Mg)_o = -0.014 \pm 0.002$‰. Radiogenic ingrowths in $\delta^{26}Mg$ from solar initial value of -0.038‰ to -0.014‰ (AOA initial) with canonical $^{26}Al/^{27}Al$ would take anytime between 24 Kyr to 1 Myr depending on the choice of $(^{27}Al/^{24}Mg)_{reservoir}$ between 2.8 to 0.101. Temporal sequence of AOAs formation after CAIs from an isotopically evolved reservoir is consistent with isotopic data of [13, 14].

However, difference in $(\delta^{26}Mg)_o$ could very well be due to primordial heterogeneity rather than radiogenic ingrowths in the solar nebula. As can be seen in Fig. 1, the offset of the three nearly parallel lines correspond to the same $(^{26}Al/^{27}Al)_0$ but require different initial values of $(^{26}Mg/^{24}Mg)_0$. The offset of Egg-3 is most noteworthy and lies outside of analytical error. *This is a direct reflection of a small isotopic heterogeneity in Mg in different ESS lithic units but a uniform value for the different phases within each individual CAI.* However, the data by [8-9, 12] are from several different objects. As will be shown below, if there is any isotopic heterogeneity in Mg, then the only "refined" correlation that attempts to define a $(^{26}Mg/^{24}Mg)_0$ must come from a single, initially equilibrated CAI object.

In considering the role of isotopic heterogeneity of Mg, we take the initial state of an individual CAI to be uniform for all phases. Then the relations between the different phases (p) in the same inclusion (X) after ^{26}Al decay with an initial; $^{26}Al/^{27}Al$ inventory of $(^{26}Al/^{27}Al)_0$ is assuming no subsequent metamorphism:

$$(^{26}Mg/^{24}Mg)_p = (^{26}Mg/^{24}Mg)_{X0} + (^{26}Al/^{27}Al)_0 (^{27}Al/^{24}Mg)_p$$

where the ratios of $(^{24}Mg{:}^{25}Mg{:}^{26}Mg)_p$ are determined from the measured values by normalization to some standard reference value. The choice of the reference value will control the values of $(^{26}Mg/^{24}Mg)_{X0}$ for different samples but not the difference $(^{26}Mg/^{24}Mg)_{X0} - (^{26}Mg/^{24}Mg)_{Y0}$ for samples X & Y if $(^{26}Al/^{27}Al)_0$ is the same for both. Thus isotopic anomalies (at a relatively low level) will not affect the determination of $^{26}Al/^{27}Al$ and as such are not directly connected to the degree of homogeneity of $^{26}Al/^{27}Al$ in the ESS, except insofar as significant variations of $(^{26}Al/^{27}Al)_0$ are demonstrated. Lower values of $^{26}Al/^{27}Al$ are easily explained by the passage of time and have been the usual explanation. It is not certain that this is correct. The absence of ^{26}Al in ultra-refractory samples has been known since the discovery of HAL [15]. The issue is whether refractory/ultra-refractory samples were formed at different times over solar system evolution. Recent reports show that Al_2O_3 grains show a wide range in $(^{26}Al/^{27}Al)_0$ from around canonical to near zero [16]. These workers propose that they were formed nearly simultaneously, thus concluding that there were gross heterogeneities in ^{26}Al. However, we find no basis for accepting such a scenario. The demonstration of initial $(^{26}Al/^{27}Al)$ heterogeneity requires knowledge of near simultaneity of different objects whose detailed source and formation are not yet known.

Additional notable feature of Egg-3 is that Mg isotopes are fractionated towards heavy isotope composition by ~6‰ in $\delta^{25}Mg$. The mass fractionation in bulk Egg-3 suggests that its precursor material may have evolved by evaporative loss of some 40 wt% Mg [17]. This might be responsible for the inconsistency between earlier study [5] and this work.

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