MG ISOTOPE STUDY OF CAI's BY UV LASER ABLATION AND SOLUTION MC-ICPMS: IMPLICATIONS FOR CANONICAL AND SUPRA-CANONICAL EVOLUTION. E.K. Tonui[1], H.H. Connolly[2], T. McCoy[3], and E.D. Young[1,4], [1]Department of Earth and Space Sciences, University of California, Los Angeles, 595 Charles E. Young Drive East, Los Angeles, CA, 90095 (etonui@ess.ucla.edu), [2]City University of New York, Department of Earth and Environmental Sciences, 365 Fifth Avenue New York, NY 10016, [3]Smithsonian Institution, P.O. Box 37012, MRC 119 Washington, DC 20013-7012, [4]Institute of Geophysics and Planetary Physics, University of California, Los Angeles, 595 Charles E. Young Drive East, Los Angeles, CA, 90095.

Introduction: The canonical $(^{26}Al/^{27}Al)_o$ of 4.5 x 10^{-5} has for a long time been regarded as the marker for the beginning of the early solar system. This view was challenged by recent high-precision Laser Ablation Multi-Collector ICPMS (LA-MC-ICPMS) and SIMS data from studies of mineral phases in CAI's. These data suggest that there was more ^{26}Al in the early solar system than previously thought [1-3]. These supra-canonical values were also found by solution MC-ICPMS studies of "whole-rock" CAI's and fragments of CAI's [4,5]. However, the most recent solution studies of similar specimens suggest canonical values of between 4.4 and 5 x 10^{-5} [6,7]. The discrepancies in data presented by high-precision studies of similar specimens raises fundamental questions as to what the true $(^{26}Al/^{27}Al)_o$ value of the solar system is. An urgent resolution of these differences is crucial if the scientific community is to continue to use CAI's as the 'time zero' for solar system formation. In this study, we attempt to address these problems through comparative studies of CAI's by LA-MC-ICPMS and MC-ICPMS analysis of acid digested samples.

Samples: A total of 7 inclusions from Allende USNM 3509 (HC samples) and Hoering sample (HB1) were investigated. Areas of the inclusions were carefully dug out after coring out of cut slabs and ground to a fine powder [8]. Of the 7, three (HC1, HC7 and HC15) are fluffy type A's that experienced varying levels of alteration, HC1 being the least altered and HC 15 being the most extensively altered. Sample HB1 is a type A CAI composed almost entirely of melilite with a thin Wark-Lovering (W-L) rim. Two type B inclusions, HC13 and 16, both contain evidence for only minor alteration and both have a W-L rim. One type B2 inclusion, HC17 exhibits no obvious evidence for alteration. This sample does not have a W-L rim, suggesting that it may be a fragment of a larger object. HC16 and HC17 are unusual in that they contain mm-sized anorthite grains. Finally, one amoeboid olivine aggregate (AOA) was also analyzed. Like other AOAs from Allende, the margins of olivine grains are enriched in FeO, suggesting some degree of alteration.

Methods: The laser ablation Mg isotopes were obtained using a Neptune MC-ICPMS and 213 and 193 UV solid lasers following the approach of [1]. In-situ analyses were performed as spots or line scans. Sample standard bracketing affords precision of +/–0.2 ‰ (2σ) for $\delta^{25}Mg$ and +/–0.3 ‰ (2σ) for $\delta^{26}Mg$. The CAI fragment samples were dissolved in HF-HNO_3 mixture and Mg was separated by cation exchange procedures using AG50W×12 resin. Reference samples of San Carlos olivine (USNM) yield an average of –0.010±0.003‰ and 0.009±0.007‰ (2σ) providing an estimate of the reproducibility of $\delta^{25}Mg$ and $\delta^{26}Mg$, respectively. Values for $^{27}Al/^{24}Mg$ are obtained by MC-ICPMS using matrix-matched standards. The precision of our solution data for both $^{27}Al/^{24}Mg$ and $\delta^{26}Mg^*$ compares favorably with recent Mg isotope data from other laboratories [5-8]. All Mg isotope data have been normalized to the DSM3 standard.

Results: The best fit to the data for five unaltered CAI fragments yields an initial $^{26}Al/^{27}Al$ value of 4.36 (±0.08 1σ) x 10^{-5} and $\delta^{26}Mg^*$ intercept of 0.019 ±0.08 1σ (Fig. 1). Two fluffy type A's are displaced to the right; their Fe/Mg ratios of 0.28 and 0.56 indicate that these CAI's are appreciably altered and hence we haven't included them in our slope calculations. The AOA exhibits a clearly resolvable $\delta^{26}Mg^*$ intercept of -0.011 ±0.007 1σ with a $^{27}Al/^{24}Mg$ value of 0.091 +/– 0.009.

Weighted linear regression of all the data for Allende HB1 (Fig. 2) defines an $(^{26}Al/^{27}Al)_o$ value of 7.10 ±0.033 1σ x 10^{-5} with an intercept of -0.53 (±0.15 2σ) per mil. However, an MSWD of 3.75 indicates that the pooled data represent several populations marked by isotopic discordance.

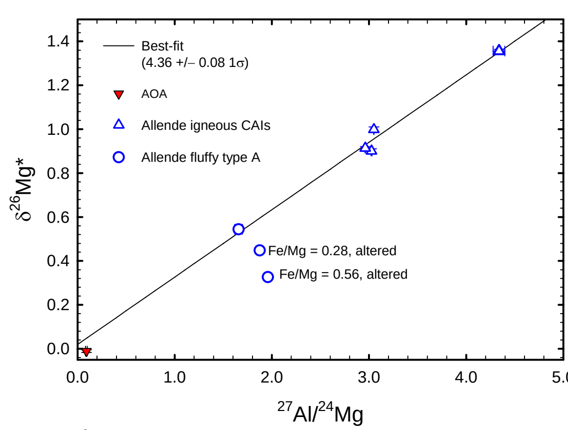

Fig. 1. ^{26}Al-$^{26}Mg^*$ evolution diagram for fragments of 7 CAI's from Allende analysed using solution MC-ICPMS.

Discussion: Our solution data yield a slightly different ($^{26}Al/^{27}Al)_o$ value from the 4.9 (±0.28) x 10^{-5} of [6] but very similar to that for one of two igneous CAI's analyzed by [7] that yields a ($^{26}Al/^{27}Al)_o$ value of 4.4 (±0.3) x 10^{-5}. Assuming that these differences are not due to interlaboratory analytical bias, this raises the critical question of whether the true representative canonical value is 4.5 x 10^{-5} or closer to 5 x 10^{-5}. Nevertheless, we interpret these latest sets of whole rock Mg isotope data as manifestations of conventional canonical values.

The dilemma posed by acid digestion data is how to reconcile the most recent solution analyses of CAI fragments with prior supra-canonical values of 5.83 and 6.68 x 10^{-5} suggested by [2] and [5], respectively. For the purposes of this study, we will assume that the most recent data provides further proof for resetting of CAIs to canonical ($^{26}Al/^{27}Al)_o$ as suggested by [1] pending further revelations to the contrary.

The LA-MC-ICPMS and solution data for Allende HB1 (Fig. 2) are critical to the debate over canonical vs. supra-canonical evolution. The fact that we have observed canonical values using both techniques [9] and that supra-canonical values are corroborated by MC-SIMS studies [2,3] demonstrates convincingly that CAI's record supra-canonical values in some mineral phases. This raises the fundamental question as to why we are not observing these values in whole rock CAI's.

If relative ages defined by "whole-rock" CAI's represents closure of a CAI reservoir with respect to Al-Mg isotopes, then the canonical ($^{26}Al/^{27}Al)_o$ determined by analysis of CAI fragments represents a record of the youngest resetting of the Al-Mg clock by a series of melting events [10]. Nonzero intercepts, like those for HB1 are manifestations of intermineral exchange [1]. The data for the AOA is also relevant in explaining the relationship between a proposed supra-canonical solar reference and average earth/solar; the AOA datum is consistent with the intercept for a sample from a solar system with uniform and supra-canonical ($^{26}Al/^{27}Al)_o$ not subjected to resetting. Thus, the 0.019 intercept suggested by digested fragment data presented here represents a significant increase of $\delta^{26}Mg^*$ relative to the non-radiogenic intercept (as low as -0.04 ‰).

Allende HB1 is composed almost entirely of melilite with no anorthite and yet anorthite is the only other CAI phase with high Al/Mg that melilite could have exchanged with. This exchange would only happen if the bulk $^{27}Al/^{24}Mg$ of the exchange couple was >10. This hardly seems possible given the tiny amount of anorthite present.

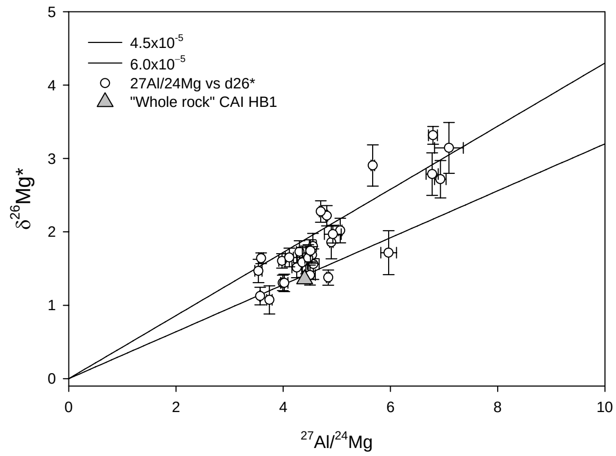

Fig. 2. ^{26}Al-$^{26}Mg^*$ evolution diagram for Allende HB1 showing in-situ analyses and a single acid digestion analysis of a fragment of the object obtained by MC-ICPMS.

We agree with [6] that interlaboratory bias and ^{26}Al heterogeneity in the solar nebula do not appear to explain the apparent discrepancies in all analytical results to date. Another logical explanation for the differences in mineral and digested fragment data may be biases in sampling of the CAI's themselves. To the best of our knowledge, most of the samples that have so far been utilized for "whole-rock" solution analysis are fragments rather than whole objects. This is a consequence in part of the difficulty in separation of whole CAI's from their host rocks.

This argument posits that because of evaporation, CAI's do not meet the criterion for simple radiogenic ingrowth since they were not closed systems. Minerals in CAI's that escaped resetting would record supra-canonical ($^{26}Al/^{27}Al)_o$ > 6×10^{-5} that reflect the true solar system value. A key consequence of this protracted open system evolution is that actual whole-rock isochrons (not fragments) record minimum ($^{26}Al/^{27}Al)_o$, and that the true ($^{26}Al/^{27}Al)_o$ must have been greater than that recorded by whole rock CAI's. Hence in-situ analyses often, but not always exhibit vestiges of supra-canonical ($^{26}Al/^{27}Al)_o$. Studies of properly sampled whole rock CAI's and interlaboratiry comparison of results using all the techniques menioned here are clearly warranted. LA-MC-ICPMS studies of aliquots of the 7 whole rock CAI's are currently in progress.

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