BACK TO THE CANONICAL $^{26}Al/^{27}Al$ RATIO IN THE EARLY SOLAR SYSTEM: NEW HIGH PRECISION MC-ICP-MS ANALYSES OF THE ALLENDE CAIs. Benjamin Jacobsen[1], Qing-zhu Yin[1], Frederic Moynier[1], Ian D. Hutcheon[2] and Alexander N. Krot[3]. [1]Department of Geology, University of California, Davis, CA 95616 (jacobsen@geology.ucdavis.edu, yin@geology.ucdavis.edu), [2]Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, CA 94551, [3]HIGP, University of Hawai'i at Manoa, HI 96822.

Introduction: Ca,Al-rich inclusions (CAIs) play a pivotal role in the early Solar System chronology, since they mark the beginning of the Solar System evolution [1,2]. Over three decades of scrutiny aided by the high resolution ^{26}Al-^{26}Mg chronometry ($t_{1/2}$ = 0.73Myr) reveal that most CAIs define the initial $^{26}Al/^{27}Al$ ratio of $\sim5\times10^{-5}$ referred as the solar "canonical" value; some CAIs subsequently experienced a complex thermal history in the solar nebula extending over 1-2 Myr [3-7]. The "canonical" $^{26}Al/^{27}Al$ value has been recently revised upwards to "supra-canonical" value of $\sim6\text{-}7\times10^{-5}$ using high precision MC-SIMS and MC-ICP-MS measurements of Mg isotopic compositions of individual CAI minerals [4-6] and bulk CAIs [8-10]. However, the tight spread of "supra-canonical" $^{26}Al/^{27}Al=(5.85\pm0.05)\times10^{-5}$ obtained for bulk CAIs from four CV chondrites using high precision MC-ICP-MS measurements implies that the initial formation of the CV CAIs occurred within 20 Kyr [10]. An important question to resolve is what is the duration of CAI formation in the early solar nebula? To gain further insight into the earliest history of the solar system, we have investigated six bulk CAIs using techniques similar to those used previously [8-10].

Samples: Six CAI fragments (A33, A39, A43, A44A, A60, and AJEF) from Allende weighting between 11-24 mg were dissolved and ~1% aliquots were processed through wet chemistry for Al-Mg analyses. Fragments of each sample were also mounted and polished for petrographic characterization by JEOL 5900LV SEM equipped with an EDS system. A39, A43, A44A and AJEF are coarse-grained, igneous objects (Type B). A33 is a compact Type A. They are composed of melilite, fassaite, and anorthite; all poikilitically enclosing euhedral spinel grains; perovskite is minor. These CAIs experienced alteration to a relatively *small* degree. Melilite grains are pseudomorphed or crosscut by veins of grossular+monticellite±forsterite±wollastonite; other secondary minerals (anorthite, nepheline, sodalite, anorthite, and andradite) are minor. A60 is a fluffy Type A CAI composed of melilite with minor spinel and hibonite; melilite is *extensively* replaced by secondary nepheline, sodalite, and Al-rich phyllosilicates(?).

Experimental: Mg isotopic measurements were performed under medium resolution mode on the UC Davis Nu Plasma MC-ICP-MS to resolve interfering isobaric species such as $^{12}C^{14}N$ from ^{26}Mg. Standard-sample-standard bracketing and time extrapolation was applied for drift corrections. Replicate measurements confirm the precision of the data. The precision of our individual data for both $^{27}Al/^{24}Mg$ and $\delta^{26}Mg^*$ (*denotes the radiogenic ^{26}Mg component) is comparable to or slightly better than that of [8,9] (Fig. 2). The exponential law (β=0.511) was used to correct for mass fractionation. $\delta^{26}Mg^*$ is relative to DSM-3 as in [8].

Results: All coarse-grained Type B and compact Type A CAIs yield data lying along an isochron with slope corresponding to $(^{26}Al/^{27}Al)_o = (4.90\pm0.28)\times10^{-5}$ and intercept $\delta^{26}Mg = 0.039\pm0.055$ (Fig. 1). A sixth CAI, A60 (extensively altered, fluffy Type A), is displaced ~3σ to the right; including these data increases the isochron slope to $(4.96\pm0.57)\times10^{-5}$. The larger relative uncertainty in our slope, 5.7%, compared to the 1.9% value in [8,9], reflects the more limited spread in the $^{27}Al/^{24}Mg$ ratios among our samples.

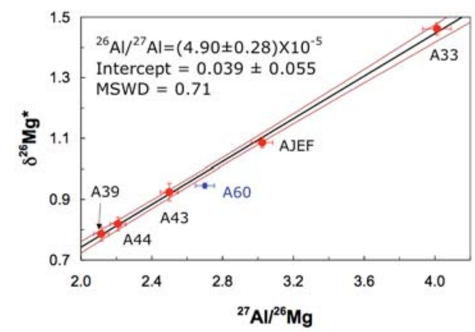

Fig. 1. ^{26}Al-^{26}Mg isochron diagram for six bulk CAIs samples from Allende obtained with MC-ICP-MS at UC Davis.

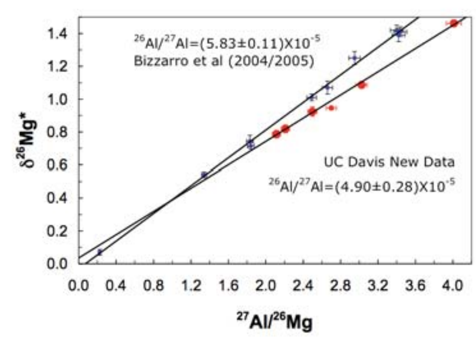

Fig. 2. The red data points are UC Davis new results. The blue dots are from [8,9]. The difference in slope corresponds to $181^{+65}/_{-61}$Kyr at 4567 Myr ago.

Note on $^{27}Al/^{24}Mg$ Determination: It is critical to determine the $^{27}Al/^{24}Mg$ atomic ratio accurately in deriving the solar initial $^{26}Al/^{27}Al$ ratio (Fig. 2). We used MC-ICP-MS to measure atomic $^{27}Al/^{25}Mg$ ratios directly from an aliquot of very dilute sample solution without chemistry; ^{26}Mg is avoided because of radiogenic effects, while ^{24}Mg is too distant from ^{27}Al for the *Nu Plasma* collector array. The measured ratio is normalized to a gravimetrically prepared standard Al-Mg mixture using the relation (Eq. 1):

$$\left(\frac{^{27}Al}{^{25}Mg}\right)_{sample}^{corr} = \left(\frac{^{27}Al}{^{25}Mg}\right)_{sample}^{measured} \times \frac{\left(\frac{Al}{Mg}\right)_{std}^{gravimetric} \times \frac{1}{Ab^{25}Mg} \times \frac{At_{Mg}}{At_{Al}}}{\left(\frac{^{27}Al}{^{25}Mg}\right)_{std}^{measured}}$$

where $Ab^{25}Mg$ refers to isotopic abundance of ^{25}Mg, and At_{Al} and At_{Mg} refer to atomic weight of Al and Mg, respectively. Standard-sample-standard bracketing and time extrapolation techniques are used throughout the analysis. The corrected ^{27}Al/^{25}Mg ratio is then converted to the ^{27}Al/^{24}Mg ratio using the nominal ^{25}Mg/^{24}Mg ratio. Measurements based on ^{26}Mg instead of ^{25}Mg as the denominator in Eq. 1 show very little difference (<0.3%, partly due to the radiogenic effect on ^{26}Mg for CAI samples). Fig. 3 demonstrates that our technique reproduces the ^{27}Al/^{24}Mg ratio of USGS standard values to within 1.3%, comparable to or slightly better than <±2% reported by [8] using similar technique. All CAI sample analyses are repeated multiple times and in multiple sessions to ensure there is no systematic error associated with our technique beyond ±1.3%.

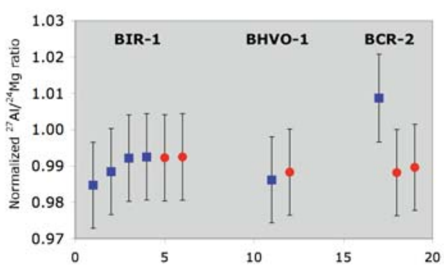

Fig. 3. Measured atomic ^{27}Al/^{24}Mg ratio normalized to nominal ^{27}Al/^{24}Mg ratios of USGS standards. Blue squares and red circles are repeat mass spectrometry measurements of the same sample solution in two different analytical sessions (three weeks apart).

Discussions: The current results suggest several possible interpretations.

(a) *Inter-laboratory bias*. The ^{26}Al/^{24}Mg ratios in [8] appears to have omitted the factor of At_{Mg}/At_{Al}= 0.9008 = 1/1.11 shown in Eq. (1), resulting in the systematic downward revision of ^{27}Al/^{24}Mg by the constant factor of 0.9008 in a corrigendum [9]. Without this correction, the difference in slope in Fig. 2 would disappear within error. With the corrigendum [9], the difference in slope in Fig. 2 appears to be real. We do not discern any mistakes in our procedures nor in [8-10] that could result in a 10% uncertainty.

(b) *Sampling bias.* Sampling of coarse-grained CAIs by microdrilling [8-10] or LA MC-ICP-MS [4] *vs.* isolated fragments [5, this study] may produce some systematic differences. The former techniques could preferentially sample minerals, which experienced some isotopic redistribution [3], rather than bulk CAIs. The preferential sampling of individual minerals by microdrilling may also explain samples with very low (non-CAI like) Al/Mg ratios in [8-10]. The latter techniques, on the other hand, may not have avoided completely, by visual inspection alone, contamination by matrix or Wark-Lovering rim material; both could have different Mg isotopic compositions than host CAIs.

(c) *^{26}Al heterogeneity in the solar nebula.* Although recent work [11] suggests that up to 10% of spatial heterogeneity of ^{26}Al is expected in the early solar nebula and is not inconsistent with data reported by [10] and Fig. 2, it seems to be the unlikely explanation for the observed differences in slopes of model isochrons of bulk CAIs from a single carbonaceous chondrite group.

(d) *Chronological.* The difference in the slopes shown in Fig. 2 could reflect two major thermal events in the solar nebula separated by $181^{+65}/_{-61}$Kyr, recording two set of CAIs formation at the birth of solar system.

Our new CAI data differ in several important aspects from earlier studies [8,9]. (*i*) All CAIs studied by [8,9] lie within 2σ of a single line of $(5.83\pm0.11)\times10^{-5}$, whereas five out six CAIs studied by us define a slope of $(4.90\pm0.28)\times10^{-5}$. One of our CAIs, A60, deviates significantly from the best-fit isochron, possibly reflecting open-system behavior of Mg during alteration. The data by [5] also show spread in slope; (*ii*) The slope of our isochron (Fig. 1) closely reflects the general distributions of Mg isotopic compositions for ~1500 data points of individual minerals for "normal" CAIs [3]; (*iii*) The intercept value for δ^{26}Mg = +0.039±0.055 (Fig. 1) significantly higher than those obtained for the Allende CAIs by [8,9] (δ^{26}Mg = -0.0264 ± 0.016, Fig. 2) or δ^{26}Mg = -0.0317±0.0038 by [10]. It is tempting to interpret, based on the slope and intercept differences, the bulk CAI samples studied here to represent a population formed from an evolved reservoir, where the entire CAI populations reservoir composition is represented by the cross point in Fig. 2 at ^{27}Al/^{24}Mg = ~1 and δ^{26}Mg* = ~0.4. We note, however, that clean sampling of two populations of coarse-grained CAIs from Allende seems highly unlikely.

Conclusion: Our new MC-ICP-MS data for bulk CAIs returns the solar initial ^{26}Al/^{27}Al ratio back to the "canonical" value.

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