SUPRA-CANONICAL ^{26}Al DETECTED BY IN SITU LA-MC-ICPMS AND SIMS TECHNIQUES: BUT WHAT DOES IT MEAN?

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Introduction: A key isotopic marker for the chronology of the earliest events in the Protoplanetary Disk is the short-lived radionuclide ^{26}Al (mean life = 1.05 My; [1-3]). Many studies [2] have inferred an initial ^{26}Al/^{27}Al ratio for the Solar System of $(4.5\text{-}5.0)\times10^{-5}$, which is referred to as the canonical ratio. Canonical initial ^{26}Al/^{27}Al values are common in CAIs and are obtained by a variety of different analytical techniques including acid digestion of mineral separates and whole-rock fragments and by *in situ* SIMS and LA-MC-ICPMS [2-7]. Recently, initial ^{26}Al/^{27}Al values greater than canonical, termed "supra-canonical" have been inferred from *in situ* analyses of CAIs using LA-MC-ICPMS [8,9], SIMS [10,11], and by high-precision analysis of whole fragments of refractory inclusions [9,12,13]. Issues surrounding the significance of these inferred supra-canonical ^{26}Al/^{27}Al in the early Solar System include: 1) the potential for analytical artifacts; 2) the timing of isotopic closure of the Mg isotope system in CAIs; 3) later open-system evolution of CAIs with respect to Mg.

Here we report a comprehensive study of CAI HC-13 from the Allende chondrite to address the role of analytical artifacts and test interpretations of supra-canonical ^{26}Al/^{27}Al data. Agreement between LA-MC-ICPMS and SIMS techniques for the ^{26}Al-^{26}Mg system is demonstrated for spinels, melilites, anorthites, and fassaites.

Experimental Techniques: HC-13 was one of several inclusions recovered from the CV3 chondrite Allende, Smithsonian Museum specimen 3509. A thin section was produced, two fragments removed for bulk analysis, and reference material retained in the collection. *Petrography:* HC-13 was characterized through backscattered electron imaging on the SEM at KCC and FE-SEM at the AMNH. Analyses of major and minor elements along with x-ray maps were obtained at the LPL on a CAMECA SX 50. *Trace elements:* Analysis was performed with the LA-ICPMS Finnigan Element 2 at the University of Maryland following the techniques of [14]. *Isotopes:* ^{26}Al-^{26}Mg systematics were analyzed by two different *in situ* techniques. LA-MC-ICPMS analyses were performed with a ThermoFinnian Neptune at UCLA and followed the methods of [9]. SIMS analyses were performed Cameca ims 1280 at the University of Hawai'i at Manoa following the techniques of [15]. The same data reduction techniques were employed and agreed upon by the three lead authors. Mg-isotope and Al/Mg values for a large fragment were obtained by acid digestion, ion exchange chromatography purification, and MC-ICPMS analysis at UCLA [6].

Overall Petrology: HC-13 is a type B1 CAI (Fig. 1), with ~ 36% melilite, 38% anorthite, 13% fassaite, and 14% spinel (all vol%). Unlike most type B inclusions it contains abundant anorthite (An$_{99}$), up to 2 mm in section that cross cut most of the core and parts of the mantle. Mantle melilite grains range from ~Ak$_{10\text{-}40}$ and are normally zoned. Core melilites are also normally zoned but range up to ~Ak$_{89}$. Fassaite TiO$_2$ contents range from ~4.70 wt% (cores) to ~8.00 wt% (rims). Spinel Ti (1500 – 2500 ppmw) and V (1200-2500 ppmw) are positively correlated; Cr is 1300-1800 ppmw, Fe is bd. Alteration is minor. *In situ* trace element analyses of REE abundances in melilite and anorthite show positive Eu anomalies with overall abundances ranging from 8 to ~ 12x CI. Fassaite is HREE-enriched with REE abundances range from ~10 to 100x CI, with negative Eu anomalies.

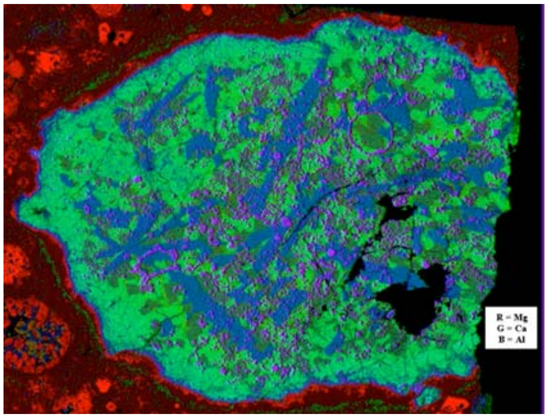

Figure 1. RGB image of HC-13, scale is 2000 μm; R = Al, G = Ca, B = Mg. Blue-colored phase is anorthite.

Isotope Results: The model initial ^{26}Al/^{27}Al value for an analysis of a large fragment of this inclusion was reported by [6] to be 4.5 x10^{-5}. *In situ* analyses from both LA-MC-ICPMS and SIMS show a wide range from sub-canonical to supra-canonical values (Figs 2, 3). Most importantly, the two data sets compare well, with spinels, fassaites, and melilites yielding ranges in values from sub-canonical to supra-canonical by both techniques and anorthites yielding sub-canonical to canonical values by both methods. The data clearly show significant Mg isotopic disturbance.

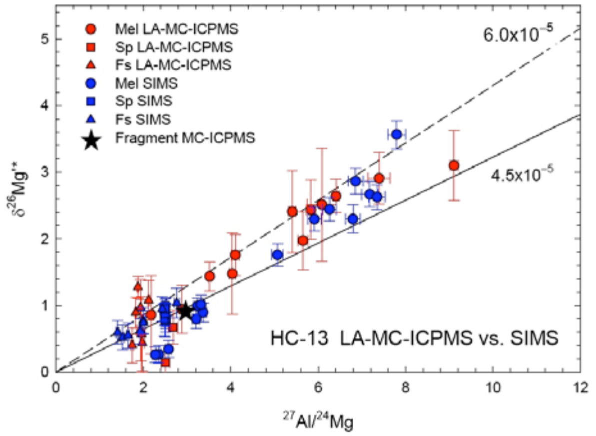

Figure 2. Comparison of UCLA LA-MC-ICPMS and Univ. of Hawai'i SIMS data for Sp (spinel), Fs (fassaite), and Me (Melilite). Excesses of ^{26}Mg* are plotted in Figs. 2 and 3 as δ^{26}Mg'*, the logarithmic definition of delta [9].

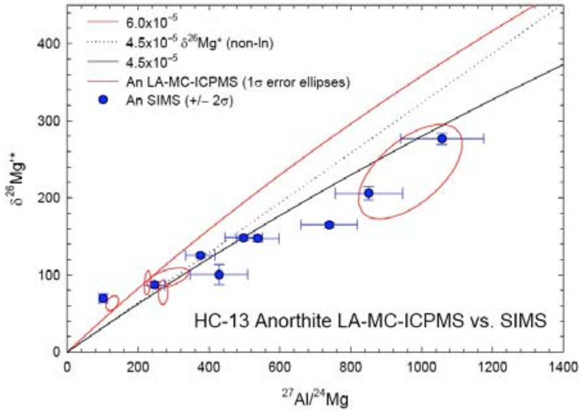

Figure 3. Comparison of UCLA LA-MC-ICPMS vs. Univ. of Hawai'i SIMS for anorthite in HC-13. The initial ^{26}Al/^{27}Al reference lines are curved at high ^{27}Al/^{24}Mg as an artifact of using logarithmic delta values for excess ^{26}Mg.

Discussion: The abnormally high abundance and size of the anorthite combined with the high Ak content of core melilites makes HC-13 atypical but not unique. Our data exhibiting δ^{26}Mg* values above the canonical line are confirmed through two different *in situ* techniques and show a range of initial ^{26}Al/^{27}Al ratios. The major question is: *What do our data mean?*

HC-13 clearly has been isotopically disturbed, however, the processes that produced this disturbance did not completely re-set the inferred initial ^{26}Al as the fragment retains a canonical values overall [6]. Two hypotheses are offered to explain the disturbance of the Mg isotope system: (1) The resetting reflects diffusive exchange of Mg (±Al) among minerals in the CAI long after the decay of ^{26}Al, potentially in a parent body, or (2) The resetting occurred prior to the complete decay of ^{26}Al, potentially in a pre-accretion environment.

Hypothesis (1) and (2) would require isotopic exchange of Mg and chemical diffusion of Mg (±Al) among phases, particularly anorthite and melilite. Isotopic exchange could both raise δ^{26}Mg* in melilite slightly and decrease δ^{26}Mg* in anorthite significantly. In the case of hypothesis (1) loss of Mg from anorthite during mild metamorphism would result in higher measured Al/Mg ratios and lower the inferred isochron.

Hypothesis (2) requires either partial melting or subsolidus heating of HC-13. The abundance, size, and location of the anorthite grains (crosscutting the core and protruding into the mantle) require that anorthite began crystallizing early, soon after melilite. It is highly unlikely that this object experienced significant partial remelting, thus it would have to be totally remelted. If the latter, then the ^{26}Al system would be reset and a new internal isochron produced, which is not observed.

If HC-13 experienced subsolidus heating prior to accretion, perhaps soon after formation (e.g., potentially within 300,000 years after t=0 [9]), then it is possible that it experience diffusive redistribution of radiogenic Mg and Mg (±Al), resetting the system.

Conclusions: Our investigations shows: (1) Agreement of data from one inclusion generated by two different *in situ* analytical techniques from two different laboratories, eliminating analytical artifacts as the cause of supra-canonical data in this inclusion, (2) Not all the minerals fall on a isochron from the *in situ* analyses and thus HC-13 is disturbed, (3) A fragment of this inclusion has a bulk inferred initial ^{26}Al of 4.5 x10^{-5}, suggesting that this object was likely isotopically a closed system, and (4) The presence of abundant anorthite in HC-13 provides an explanation for the disturbances in the Mg isotopic system, but other inclusions with similar Mg isotope systematics that lack anorthite require a different explanation.

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