RESETTING, ERRORCHRONS AND THE MEANING OF CANONICAL CAI INITIAL ^{26}Al/^{27}Al VALUES.

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Introduction: The difference between the precise MC-ICPMS analyses of bulk CAI fragments, e.g., [1], and supra-canonical values obtained by micro-analytical techniques (e.g., laser ablation MC-ICPMS [2] and SIMS [3]) at face value seems to be problematic and therefore leads many to dismiss claims of solar system (^{26}Al/^{27}Al)$_0$ greater than ~5x10^{-5} as spurious. Here we use simple mass balance calculations to quantify the importance of open system isotopic exchange during CAI evolution and show that *in situ* supra-canonical and canonical and bulk canonical measurements can all exist for an individual CAI. The modeling investigates mechanisms of isotopic exchange that may have occurred early (100's ka) and late (~1 Ma) in the solar nebulae and much later (>10's Ma) on planetary bodies. A range of possible modal mineralogies are modeled in order to populate the compositional range defined by *in situ* and bulk CAI measurements.

A central assumption is that the canonical (^{26}Al/^{27}Al)$_0$ value corresponds to an absolute age of ~4567 Ma and represents the initial abundance of ^{26}Al of our solar system as recorded by the condensation of early formed nebular solids. Based on many studies of CAIs this canonical value is 4.5x10^{-5} (e.g., [4]), although more recently some high precision bulk analyses support a slightly higher value [1] (cf. [5]). Claims of supra-canonical (^{26}Al/^{27}Al)$_0$ values discovered by micro-analytical techniques (i.e., laser ablation MC-ICPMS [2]) instead suggest that CAIs condensed prior to canonical time and that objects yielding canonical ^{26}Al represent resetting due to high-temperature events incurred by CAIs during their residence time in the protoplanetary disk. It should be noted that the vast majority of micro-analytical (^{26}Al/^{27}Al)$_0$ measurements made are found to be canonical [4], including those by [2]. The importance of this observation is two-fold:

(1) There is no question about the ubiquity and therefore the importance of a canonical ^{26}Al/^{27}Al value, just its significance.

(2) Therefore, an explanation for how some *in situ* measurements can be supra-canonical within a bulk CAI that is canonical appears to be required. Analytical tests of the latter have been relatively successful (e.g., [2, 5, 6]), but only through high costs in labor, sample destruction, and analytical time. A more effective and far simpler approach (this study) is to test numerically whether all of the existing data can be explained by a process similar to that suggested by [2] (early closed system resetting), [7] (early open system resetting) and/or [8] (late resetting).

Theoretical and experimental studies provide a basis for our understanding of the stable Mg isotope composition of planetary materials, in particular with respect to isotope effects related to evaporation at low nebular pressures [9-11]. Compositional variations due to open system isotopic exchange likely occur at higher nebular pressures as well. As such CAIs act as the sink, as well as the source of Mg transfer by mechanisms of diffusion. An example of this behavior in CAIs is presented by [12] where it is suggested that low δ^{25}Mg margins defining the outer portion of core-to-rim isotopic zoning profiles represent isotopic exchange with a chondritic gas. At issue is whether a similar process might also affect the ^{26}Mg* chronologies of CAIs.

In order to test this possibility we present a simple isotope exchange model that accounts for mineral specific isotopic exchange with an external reservoir (e.g., nebular gas or chondrite matrix). Given the modal mineralogy of CAIs mass balance calculations can then be used to model bulk CAI measurements. In turn, the modeling provides some insight into the significance of results obtained by different analytical methods and therefore can inform our interpretation of the differences found among *in situ* and bulk Mg isotope measurements.

Modeling: Our calculations show that most "bulk" analyses should exhibit canonical values despite containing some residual intra-CAI supra-canonical material (Figure 1). Minerals used in calculations include anorthite (^{27}Al/^{24}Mg ~250), åkermanitic melilite (^{27}Al/^{24}Mg ~3.5), gehlenitic melilite (^{27}Al/^{24}Mg ~9.0), spinel (^{27}Al/^{24}Mg =2.5), and fassiate (^{27}Al/^{24}Mg ~2.0). Representative ^{27}Al/^{24}Mg compositions for minerals that exhibit solid solution were used, but the results of our calculations are robust to reasonable changes in selected mineral chemistries. Equation (1) shows the general form of the model:

$$ {}^{x}R_{\text{bulk CAI}} = \sum_{i}\left[\left(\frac{C_{Mg,i}M_{i}}{\sum_{i} C_{Mg,i}M_{i}}\right)\left({}^{x}R_{Mg,i}\left(1-F_{i}\right)+{}^{x}R_{Mg,ext}F_{i}\right)\right] \tag{1} $$

where $^{x}R_{\text{bulk CAI}}$ is the isotope ratio of interest for the bulk object, $C_{Mg,i}$ is the number of atoms of Mg per atoms of O in phase *i*, M_i is the O fraction of phase *i* (defining the modal abundance of *i*), $^{x}R_{Mg,i}$ is the pre-exchange Mg isotope ratio of phase *i*, $^{x}R_{Mg,ext}$ is the Mg isotope ratio of the external reservoir, and F_i is the fraction of Mg exchanged for each mineral, respectively. Time dependent excess ^{26}Mg (i.e., ^{26}Mg*) that affects the $^{x}R_{Mg}$ value for each mineral phase *i* comes from radioactive decay of ^{26}Al and can be obtained using the standard decay equation (2):

$$^{26}R_{Mg,i} = \left(\frac{^{26}Mg}{^{24}Mg}\right)_i = \left(\frac{^{27}Al}{^{24}Mg}\right)_i \left(\frac{^{26}Al}{^{27}Al}\right)_t \tag{2a}$$

and

$$\left(\frac{^{26}Al}{^{27}Al}\right)_t = \left(\frac{^{26}Al}{^{27}Al}\right)_0 \left(1 - \exp^{(-\lambda t)}\right) \tag{2b}$$

where $\lambda = 9.52\text{x}10^{-7}$ and *t* is time. Isotopic exchange (F_i) used in equation (1) based on diffusional transport of Mg entering or leaving a sphere is given by [13]:

$$F_i = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\Gamma_i n^2 \pi^2\right) \tag{3}$$

where $\Gamma = D_i t/a_i^2$ is a dimensionless parameter that is a function of the diffusivity of Mg in each mineral phase D_i, the initial radius of each mineral a_i, and time *t*. Self diffusion coefficients for Mg for anorthite, melilite, spinel, and fassiate come from [14-16]. With all else constant (e.g., relative location to edge of object, diffusional shielding from surrounding nearest neighbors, etc.) spinel should experience the greatest degree of isotopic exchange based on both its higher Mg diffusivity and its smaller size (shorter length scale).

As a check of the veracity of the parameter space used to investigate ^{26}Mg* model results we use an analogous model to track the mineral-specific simulated bulk δ^{25}Mg. Acceptable models include ≤1.5 ‰ δ^{25}Mg isotopic variability due to differential resetting among average mineral compositions. Calculated trials for isotope exchange occurring in the early solar system in which simulated model times are less than the time required for all ^{26}Al to have decayed to ^{26}Mg* are continued until all of the parent ^{26}Al nuclide is extinct .

Conclusions: The modeling demonstrates that melilites above the "canonical" errorchron defined by simulated bulk mixtures of the phases (i.e., consistent with the compositions of fragments of CAIs obtained by analysis of acid digested samples) likely record evidence for residual supra-canonical evolution while the canonical values of the bulk objects themselves are a product of open-system exchange of Mg isotopes. Isotopic exchange could have occurred early (100's ka) and late (~1 Ma) in the solar nebulae or much later (>10's Ma) on chondrite parent bodies. The Mg isotope composition of Wark-Lovering rims surrounding CAIs [12, 17] indicate that open system exchange likely occurred prior to and/or during rim formation. Likewise the rim data indicate that nebular conditions characterized by relative high pressures and temperatures, in which open system isotopic exchange is likely to occur, existed at canonical time [11]. Although the modeling here is consistent with a range of supra-canonical values, corresponding to condensation and/or the final supersolidus event undergone by individual CAIs, the elapsed time between formation of CAIs and canonical-aged subsolidus isotopic exchange (<100's ka) indicates that the average initial ^{26}Al abundance in the solar system was ~6 x 10^{-5}.

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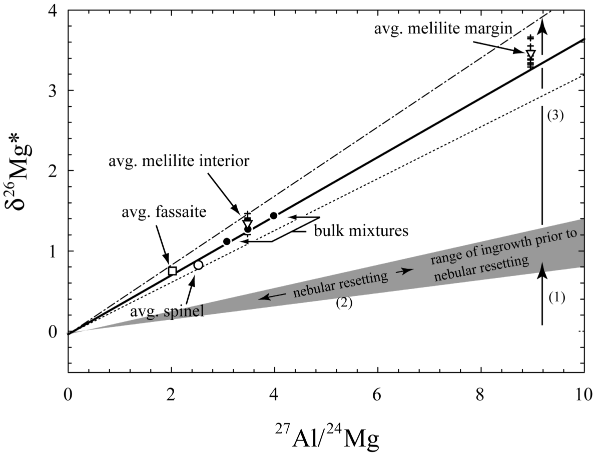

Figure 1. Simulated open system resetting of supra-canonical initial ^{26}Al/^{27}Al of CAIs match measured bulk and *in situ* data (see text). Model bulk CAIs will define a canonical line equivalent to measured bulk CAIs (e.g., [1]), whereas model *in situ* analyses show a range of values depending on mineral size, diffusivity, and location within CAIs. Upper curve is supra-canonical (6x10^{-5}), solid curve is equivalent to value of [1], and lower dashed curve has a slope equivalent to 4.5x10^{-5}. Steps: (1) shows shift due to decay and ingrowth prior to canonical time (Δt≤700 ka), (2) trend of open system isotopic exchange at canonical time, and (3) slope after all ^{26}Al decays. Symbols shown after decay has completed, i.e., as would be measured.