

URANIUM ISOTOPE VARIATIONS IN GROUP II REFRACTORY INCLUSIONS. F. L. H Tissot¹, N. Dauphas¹, L. Grossman², ¹Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, IL (ftissot@uchicago.edu), ²Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, IL.

Introduction:

The $^{235}\text{U}/^{238}\text{U}$ ratio shows little variability in most terrestrial and meteoritic bodies ($\leq 1\%$) [1-3]. In contrast, large excesses of ^{235}U , up to 3.5 %, have been found in a few Calcium-Aluminum rich inclusions (CAIs) and have been interpreted as evidence of live ^{247}Cm ($t_{1/2} = 15.6$ My) in the early solar system (SS) [4]. Though this is a plausible explanation, it relies on four points with high Nd/U ratio that define a “pseudo-chron”, so more work is needed to determine the cause of U isotope variations in CAIs. Here, we report some preliminary results on the identification, characterization and U isotopic analysis of 12 fine-grained, group II, CAIs from the Allende meteorite.

Background: CAIs are thought to be the first solids to condense in the early SS and are usually classified based on (1) their mineralogic and petrographic features [5], and (2) their Rare Earth Element (REE) patterns [6]. The so called group II pattern, displays strong fractionation of REEs from one another whereby the most refractory (heavy REEs except Tm) and most volatile elements (Eu and Yb) are depleted relative to the light REEs (Fig. 1). This pattern, very common in fine-grained CAIs, is thought to represent a snapshot in the sequence of condensation [7, 8]. So far, only fine-grained, group II CAIs have shown excess of ^{235}U . Because the abundance of ^{247}Cm at the time of SS formation was low, excess of ^{235}U due to ^{247}Cm decay is only resolvable in phases which preferentially incorporated Cm over U. Phases with high Nd/U (Cm has no stable isotope and Nd is usually used as a proxy), such as group II CAIs, are thus more likely to show a resolvable ^{235}U excess than other phases, had live ^{247}Cm been present in the early SS.

A complication arises, however, with group II CAIs. Since they represent a snapshot in the condensation sequence and little U was incorporated compared to Nd (Cm), the ^{235}U excess observed could also be due to fractionation during condensation of the U isotopes. The kinetic theory of gases indeed predicts that the lighter isotope (^{235}U) will condense faster than the heavier isotope (^{238}U). Because the “pseudo-chron” ($\delta^{235}\text{U}$ vs $^{144}\text{Nd}/^{238}\text{U}$) defined by [4] only uses four fine-grained group II CAIs, and because the data show some scatter, we decided to conduct a more systematic study on fine-grained CAIs in an effort to assess which processes (^{247}Cm decay and/or fractionation during condensation) were at play in the early SS.

Sample identification and characterization:

Though the sensitivity of the MC-ICPMS is excellent for U isotopes (1.4 V/ppb), the concentration of U in fine-grained CAIs is extremely low (~20 ppb) and large samples are needed. Numerous slabs of Allende were thus examined and fourteen CAIs were selected (12 fine-grained and 2 coarse-grained) based on their size. A small chip of each CAI was extracted using cleaned dental tools, under a stereoscopic zoom microscope, and mounted in epoxy for characterization. All samples were mapped using a JEOL JSM-5800LV SEM. Typical grain size was about 10 micron for the fine-grained CAIs. In good agreement with [9], the samples are mostly composed of spinels, pyroxenes, sodalite, nepheline, with small and varying amount of grossular and melilite, and some rare olivine (Fig. 2). The samples were then analyzed by LA-ICPMS. All twelve fine-grained CAIs were found to present a group II REE pattern (Fig. 1).

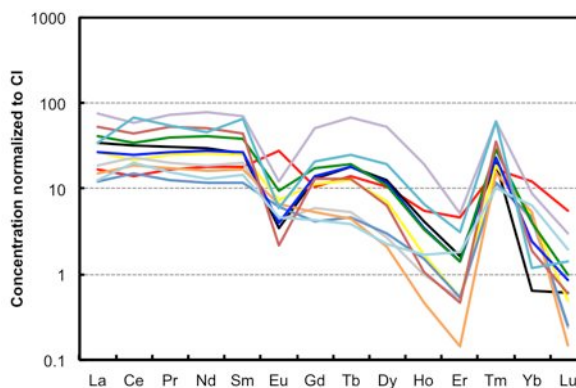


Fig. 1. Group II REE patterns in twelve fine-grained CAIs from the Allende meteorite measured by LA-ICPMS.

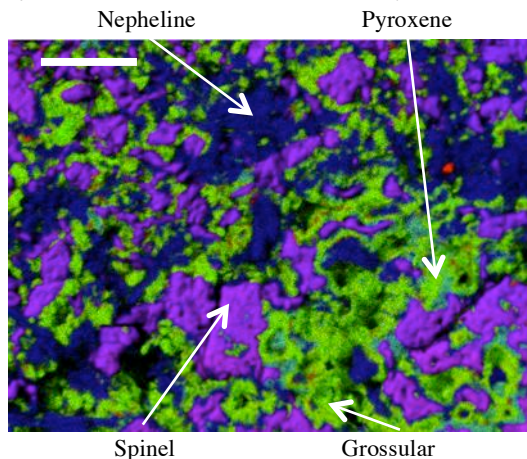


Fig. 2. Typical RGB image (Mg,Ca,Al) of the fine-grained CAIs analyzed in this study. The scale bar is 50 μm .

Powder of each samples were collected on weighing paper before being transferred into triple cleaned Teflon beakers. Great care was brought into collecting only the CAI and any matrix accidentally extracted was removed from the collected fraction using cleaned tweezers. Sample masses ranged from 15 to 760 mg. All samples were then fully digested using optima quality acids with two one-week attacks in HF/HNO₃ 3:1 (+ drops of HClO₄) followed by two one-week attacks in HCl/HNO₃ 2:1 on hot plates at 160°C. The samples were then taken back in concentrated HNO₃ and put back on hot plates for 4 days, before dilution to 3 M HNO₃. All samples were transferred into cleaned centrifuge tubes and centrifuged for 5 min at ~1500 rpm. No residue was visible.

A small aliquot (~1 %) of the solution was sampled for concentration analyses. One fifth of the solution was saved for future work and the remaining 80% was spiked with IRMM-3636 double spike (50.45 % ²³³U and 49.51 % ²³⁶U). To ensure full equilibration of the spike with the sample, the samples were dried completely after spike addition, taken back into concentrated HNO₃ and diluted to 3M HNO₃. No residues were visible after this new digestion step.

Since the total amount of U was low (as low as 0.2 ng of U), the samples were passed through column chemistry only once to minimize blank contributions. Purification was done on U/Teva resin [2, 10] and as follows: (1) sample loading in 3 M HNO₃, (2) matrix elution with 30 ml of 3 M HNO₃, (3) resin conversion to HCl with 5 ml of 10 M HCl, (4) Th elution in 12 ml of 5 M HCl and (5) U elution with 32 ml of 0.05 M HCl. Two geostandards, the two coarse-grained CAIs and a sample of Allende were prepared in the same way to ensure that no systematic biases were introduced by the sample preparation. Results are given in $\delta^{235}\text{U}$ relative to CRM-112a:

$$\delta^{235}\text{U} = \left[\left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right)_{\text{sample}} / \left(\frac{{}^{235}\text{U}}{{}^{238}\text{U}} \right)_{\text{CRM-112a}} - 1 \right] \times 10^3.$$

Quality control: (1) As described in detail in [11] we compared the ²³⁵U/²³⁸U ratios obtained from the raw intensities bracketed by standard measurements, with the ²³⁵U/²³⁸U ratios obtained from double-spike data treatment. Since the spike isotopes (²³³U and ²³⁶U) are different from the naturally occurring isotopes (²³⁵U and ²³⁸U), the data reduction using the double spike is sensitive to artifacts affecting any of the four isotopes, while the ratio obtained by standard bracketing is sensitive to fractionation during sample digestion and purification, and artifacts affecting only ²³⁵U and ²³⁸U. Agreement between these two values in a measurement is a strong internal validation of the result. All analyses passed this validation test.

(2) The four samples with the most U (8 to 20 ng) were analyzed twice. Half the sample was analyzed

after one purification step, while the other half was subjected to a second column chemistry before analysis. For all samples, both results are identical within error bars (~0.1 ‰).

(3) As one CAI showed an extremely large anomaly (>50 ‰), we took part of the unspiked aliquot, passed it through column chemistry twice and measured it again using a new cup configuration with ²³⁵U on the SEM and ²³⁸U on a faraday cup. Both measurements were identical within error bars.

(4) For each of the four most U depleted CAIs, we recombined the matrix cuts obtained from chemistry and doped them with a quantity of U standard similar to the amount initially present in the sample (~0.2 ng of U). These “doped” samples were passed through chemistry once before analysis. Three of these tests showed no anomaly, but one presented a large negative $\delta^{235}\text{U}$ (both in bracketing and by double spike). Further tests are being conducted to understand this result.

Results and discussion: The range of $\delta^{235}\text{U}$ observed in meteorites is small (from -0.2 to +1 ‰) [3], with most samples at $\sim +0.4 \pm 0.2\text{‰}$. In contrast, most of the samples we analyzed show variations between -1 to +6 ‰. Though overall, the samples fall on the trend of $\delta^{235}\text{U}$ vs ¹⁴⁴Nd/²³⁸U defined by [4], we observe a greater scatter in the data. In particular, samples with very low Nd/U ratios (~30) show $\delta^{235}\text{U}$ varying by up to 3 ‰. At this Nd/U ratio, if decay of ²⁴⁷Cm was the only process affecting the U isotopic composition, we would expect (based on the initial ²⁴⁷Cm abundance from [4]) all samples to display an anomaly of $\sim +0.6\text{‰}$. The spread in the data even at low Nd/U is thus hard to reconcile with the decay of ²⁴⁷Cm being the only process leading to ²³⁵U enrichment, and it is plausible that both fractionation during condensation and ²⁴⁷Cm-decay were at play in the early SS.

Four of our CAIs have high Nd/U ratios (>400). At such a U depletion level, the measurements are challenging, and we are still in the process of assessing whether all systematic biases are accounted for or not.

References: [1] Stirling, C.H. et al (2007) *EPSL* 264, 208-225. [2] Weyer, S. et al (2008) *GCA*, 72, 345-359. [3] Goldmann, A. et al (2014) *GCA*, 148, 145-158. [4] Brennecka, G.A. et al (2010) *Science*, 327, 449-451. [5] Grossman, L. (1975) *GCA*, 39, 433-454. [6] Mason, B. and Taylor, S.R. (1982) *Smithsonian Contr. Earth Sci.*, #25. [7] Boynton, W.V. (1975) *GCA*, 39, 569-584. [8] Davis, A.M. and Grossman, L. (1979) *GCA*, 43, 1611-1632. [9] Grossman, L. and Ganapathy, R. (1976) *GCA*, 40, 967-977. [10] Telus, M. et al (2012) *GCA* 97, 247-265. [11] Tissot, F.L.H. and Dauphas, N. *Submitted to GCA*.