

Origin and implications of $^{238}\text{U}/^{235}\text{U}$ variations in CAIs

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Calcium-aluminum rich inclusions (CAIs) are submillimeter- to centimeter-sized inclusions that condensed from gas in the hot, inner region of protoplanetary disk and are a major constituent of carbonaceous chondrites. Believed to be the first formed solids in our Solar System, they have been a prime target for absolute Pb-Pb geochronology to establish the age of the Solar System [eg. 1] as well as a time anchor for several relative chronometers. It is now known that CAIs display significant variations in their $^{238}\text{U}/^{235}\text{U}$ ratio [2], a critical parameter in all Pb/Pb age calculations. Whereas this variation was first attributed to the decay of the short-lived radionuclide ^{247}Cm to ^{235}U [2], it is likely at least part of this variation is due to mass dependant fractionation that occurred during the CAI forming process [1]. Therefore, beyond the importance of this ratio for geochronology, understanding the origin of uranium isotopic variations in CAIs may offer insights into CAI forming processes and conditions.

Ten large CAIs have been selected for this study from the pristine carbonaceous chondrite (CV3) NWA 3118 [3], all with sizes large enough for accurate determination of their $^{238}\text{U}/^{235}\text{U}$ ratios. The sample has been cut dry into 3 mm slabs using a diamond wire saw and CAIs selected on the basis of their size have been imaged using a scanning electron microscope. Using the procedure of [1], U is separated from the samples and measured by HR-MC-ICP-MS using a Thermo-Fisher Neptune Plus. To determine the degree of mass-dependent isotope fractionation experienced by individual inclusions, stable Mg and Nd isotope composition are measured for each CAI and compared to the uranium isotopic ratios. Correlations between the Mg, Nd and U isotope ratios will support a model of mass-dependent fraction of U to explain the isotopic variations observed in CAIs from CV chondrites. A lack of correlation will support ^{247}Cm as the primary cause of U isotopic variability. In addition, the CAIs measured for U isotopes will also be dated using the Pb-Pb system based on the Pb step-wise dissolution procedure by [1].

[1] Connelly *et al.*. (2012) *Science* **338**, 651. [2] Brennecka *et al.*. (2010) *Science* **327**, 449. [3] Russel *et al.*. (2005), *MAPS* **40**, A201.

The relationship of goethite surface structure, habit and adsorption capacity

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It is well established that the adsorption capacity of goethite ($\alpha\text{-FeOOH}$) per m^2 increases significantly with decreasing specific surface area (SSA, determined by N_2 -adsorption). For example, the adsorption of chromate increases three-fold as SSA decreases from 94 to 50 $\text{m}^2\cdot\text{g}^{-1}$ [1]. This has led to recent explanations postulating the possible roles of different faces with different surface site densities and affinities [1-3]. The current model assumes that small particles with $\text{SSA} > 80 \text{ m}^2/\text{g}$ are “ideal” prismatic crystals elongated parallel to the **b**-axis (Pnma setting) with {101} and/or {001} forms [4]. It is assumed that the more reactive goethites, which have larger particles and $\text{SSA} < 80 \text{ m}^2/\text{g}$, may have different crystal face distributions to the “ideal” crystals.

We report electron microscopy observations on a suite of synthetic goethites with SSA ranging from 40 to 100 $\text{m}^2\cdot\text{g}^{-1}$. Transmission Electron Microscopy (TEM) confirms that the crystals are well-formed elongate blades: the 40 $\text{m}^2\cdot\text{g}^{-1}$ and the 100 $\text{m}^2\cdot\text{g}^{-1}$ crystals have length modes of about 1 μm and 100 nm, respectively. The 40 $\text{m}^2\cdot\text{g}^{-1}$ sample has single-domain crystals elongated parallel to the **b**-axis as expected. However, the 100 $\text{m}^2\cdot\text{g}^{-1}$ sample contains numerous crystals that have mosaic-domain structure and are instead elongated parallel to the [610] direction. Atomic-Resolution Scanning TEM analysis of the steps on the long edges of two crystals of the 40 $\text{m}^2\cdot\text{g}^{-1}$ sample revealed only 66% terraces parallel to either {001} or {101} forms and 33% parallel to {210}. In contrast, steps on two crystals of the 100 $\text{m}^2\cdot\text{g}^{-1}$ sample with [610] habit were 96% {210}-type and 4% {110}. The change in habit and increase in {210}-type steps in high SSA samples, although surprising, must now be taken into account in assessing the adsorption behavior of goethites.

[1] Villalobos & Pérez-Gallegos (2008) *J. Colloid Interface Sci.* **326**, 307-323. [2] Villalobos *et al.*. (2009) *J. Colloid Interface Sci.* **336**, 412-422. [3] Salazar-Camacho & Villalobos (2010) *Geochim. Cosmochim. Acta* **74**, 2257-2280. [4] Schwertmann (1984) *Thermochim Acta* **78**, 39-46.