

**Ti ISOTOPES: ECHOES OF GRAIN-SCALE HETEROGENEITY IN THE PROTOPLANETARY DISK.**

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**Introduction:** Calcium-aluminum-rich inclusions (CAIs) are the oldest surviving solids to have formed in the Solar System. Their chemical and isotopic compositions provide a record of the conditions present in the protoplanetary disk where they formed and can aid our understanding of how solids formed in the solar nebula, an important step in the eventual process of planet building.

The isotopic compositions of CAIs are primarily controlled by volatility. Evaporation/sublimation are well understood through both theory and experimental work to produce an enrichment in the heavy isotopes of an element, but less is understood about the effects of condensation. Mass-dependent fractionation can potentially provide a record of nebular condensation.

Ti is not likely to experience evaporation due to its refractory nature, making it a useful tool for assessing the effects of condensation. We have undertaken a study of the stable isotope fractionation of Ti isotopes as a tracer of processes that predate the last evaporation events affecting CAIs. We compare the <sup>49</sup>Ti/<sup>47</sup>Ti stable isotope ratio with excess <sup>50</sup>Ti common in CAIs.

We have collected Ti, Mg, Si, and Ca isotope data for a suite of CAIs in order to search for heterogeneity in each of these isotope systems, and for potential correlations among them. We compare our results to expectations for condensation.

**Sample Descriptions:** We measure Ti isotope ratios in a varied group of CAIs including Type A CAIs (EK5-2-1R, KAM L2-B), several Type B1 CAIs (AL4884, 461 “B,” KAM J1, L1, L2-A), a fine-grained inclusion (3B3), and a forsterite-bearing Type B CAI SJ101, and a type B2 (AMNH 4947 Bocce Ball), all from Allende. Additionally, the data set contains a “reworked” Type B CAI (Crucible) from Northwest Africa (NWA 2364), a type B1 CAI from Efremovka (E44), and a type A CAI from Leoville (L144A).

**Analytical Methods:** In-situ analyses were conducted using laser ablation multiple-collector inductively coupled plasma-source mass spectrometry (LA-MC-ICPMS, ThermoFinnegan Neptune™). We used a 193 nm excimer laser to extract Ti from the sample. The laser was operated at a UV fluence of 28 J/cm<sup>2</sup>. Material was ablated at a pulse repetition rate of 3-6 Hz, using a spot sizes ranging from 86-172 μm. Helium (0.29 l/min) carried ablated material from the sample chamber to a mixing chamber where it combines with Ar (0.6 l/min) before being introduced into the ICP torch. The mass resolving power was ~7000 and sam-

ple-standard bracketing was used to correct for instrumental mass bias.

<sup>49</sup>Ti/<sup>47</sup>Ti is essentially free from nuclear anomalies at the 0.1‰ level or greater [1,2]. Comparing our UCLA Glass #5 standard against pure TiO<sub>2</sub> allows us to demonstrate the lack of matrix effects on <sup>49</sup>Ti/<sup>47</sup>Ti within our current analytical precision of ~0.15-0.2‰.

In order to measure <sup>50</sup>Ti/<sup>47</sup>Ti excesses, we peak strip interferences from <sup>50</sup>Cr and <sup>50</sup>V by monitoring <sup>52</sup>Cr and <sup>51</sup>V during each analysis and correct for instrumental fractionation in the usual way (exponential law).

**Condensation Theory:** We consider the isotopic consequences of condensation from a nebular gas in terms of the kinetics of condensation, the degree of undercooling, and potential reservoir effects [3,4].

In addition to the kinetic isotope effects, the model to which we are comparing the data also accounts for reservoir effects, such as those resulting from Rayleigh distillation.

Comparisons of systems with similar volatilities to each other and to the model allows us to assess whether the elements condensed in different reservoirs.

**Data:** δ<sup>49</sup>Ti is reported relative to terrestrial rutile reference material (USNM 83191) and plotted in Figure 1a. The ε<sup>50</sup>Ti data are plotted in Figure 1b. Lines for both ε<sup>50</sup>Ti = 0 and ε<sup>50</sup>Ti = 10 are shown for reference in Figure 1b.

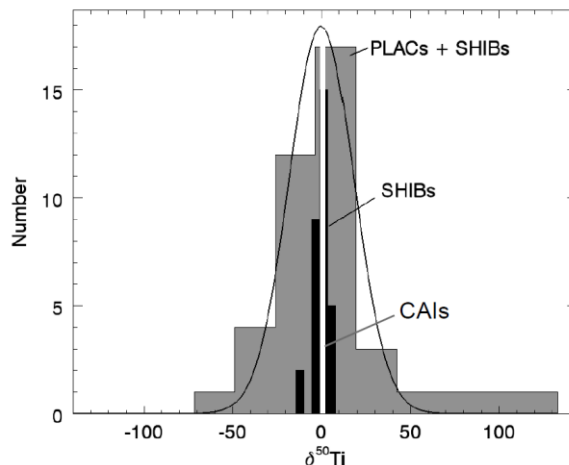
**Discussion:** The data show little variation in δ<sup>49</sup>Ti, with the majority of the analyses having values between ±1 per mil deviation from the terrestrial standard. In the context of our condensation model, there is a general lack of correlation between δ<sup>44</sup>Ca and δ<sup>49</sup>Ti despite their similar volatilities [5]. Thus, the Ca and Ti in CAIs did not necessarily experience the same condensation history and may have been inherited from different reservoirs. This suggests that CAIs are aggregates of pre-existing materials as opposed to being original condensates.

This idea is further perpetuated by the ε<sup>50</sup>Ti data. The majority of the data have values of ~8-10, consistent with averaging. Some CAIs have ε<sup>50</sup>Ti values above or below the typical value, including 461\_13 B, which has a significantly different ε<sup>50</sup>Ti value of ~41. This indicates that there was likely heterogeneity in the disk and in the precursor material from which the CAIs formed. We also observed heterogeneity within CAIs. Notably, the data for L144A show a distinction be-

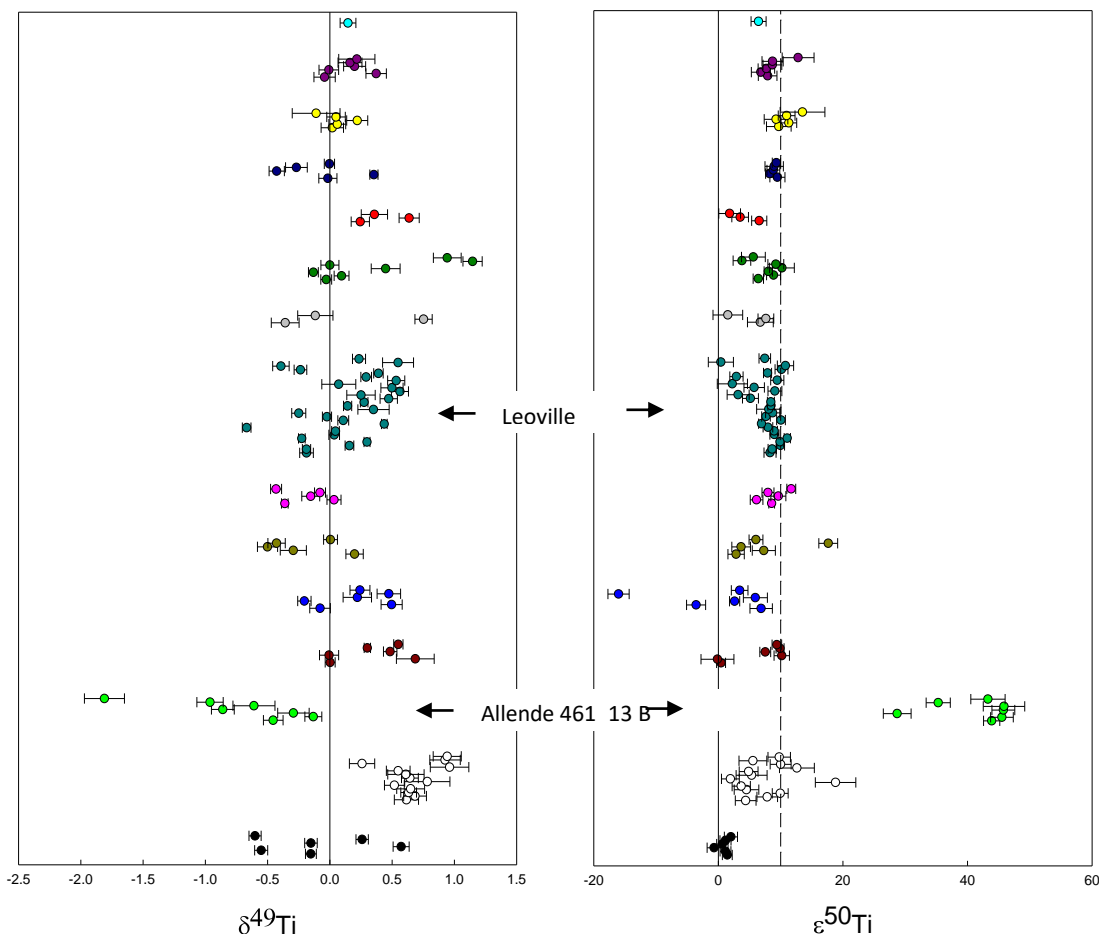
tween the core and mantle of the CAI, with the mantle having a larger excess relative to the central material. These varying compositions within and among CAIs are echoes of even larger heterogeneities in the precursor material that have been dampened due to averaging.

This averaging effect is apparent when comparing CAI and hibonite  $\delta^{50}\text{Ti}$  ( $\epsilon^{50}\text{Ti}/10$ ) data (Figure 2) from Liu (2008) [6]. Although the overall range in  $\delta^{50}\text{Ti}$  is large among hibonites, they define a Gaussian-like distribution with a peak at the typical CAI values of  $\epsilon^{50}\text{Ti} = 10$  ( $\delta^{50}\text{Ti} = 1$ ). This implies that CAIs experience averaging as they are collections of millions of grains that formed in a heterogeneous molecular cloud.

**References:** [1] Zhang J. et al. (2011) JAAS, 26, 2197-2205. [2] Williams, N. H. et al. (2014) LPS XLV, Abstract #21831. [3] Young E. D. and Schauble E. A. (2012) MetSoc, Abstract #5382. [4] Simon J. I. and DePaolo D. J. (2010) EPSL, 289, 457-466. [5] Jordan M. K. et al. (2015) LPS XLVI, Abstract #24722. [6] Liu, M.-C. (2008) PhD thesis, Univ. California, Los Angeles.



**Figure 2.**  $\delta^{50}\text{Ti}$  ( $\epsilon^{50}\text{Ti}/10$ ) data for hibonite grains from Liu (2008). The average CAI value is plotted with a white line at  $\epsilon^{50}\text{Ti} = 10$  ( $\delta^{50}\text{Ti} = 1$ ).



**Figure 1.** (a) LA-MC-ICPMS  $\delta^{49}\text{Ti}$  data for a suite of CAIs from Allende, Efremovka, Leoville, and NWA 2364. (b) LA-MC-ICPMS  $\epsilon^{50}\text{Ti}$  data for the same suite of CAIs.