# FIRST RESULTS OF A PHYSICOCHEMICAL SURVEY OF CV3 CALCIUM-ALUMINUM-RICH INCLUSIONS: THE REFRACTORY TRACE ELEMENTS Sr, Y, Zr, Nb, Ba, Hf, Ta.

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**Introduction:** Ca, Al-rich inclusions (CAIs) offer glimpses into the earliest chemical and physical processes during solar system formation. We have begun a study of the trace element distribution(s) within CV3 CAIs and their constituent minerals to help constrain the chemical environment(s) of their formation and evolution. We have physically, mineralogically, and chemically characterized 20 individual CAIs in thick sections of 3 different CV3 chondrites using 3D tomography, qualitative x-ray mapping, quantitative electron microprobe and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) techniques. The combination of these techniques on individual CAIs will expand our knowledge of the physical and chemical formation conditions of these enigmatic objects.

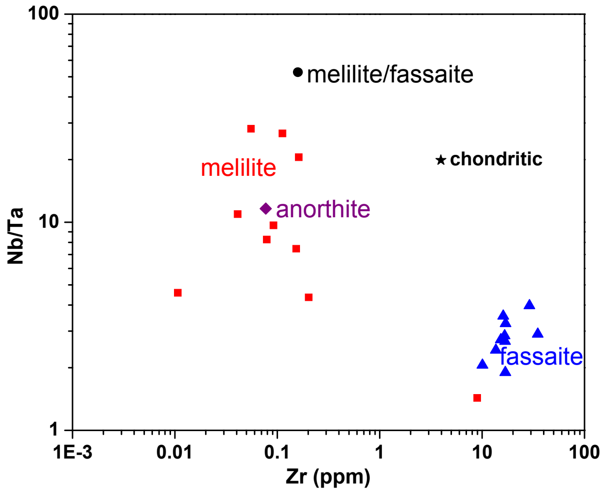
For our initial report, we will focus on the content(s) of the refractory trace elements Sr, Y, Zr, Nb, Ba, Hf, and Ta. Previous investigations of suites of these elements in bulk Allende refractory inclusions have shown that while there seems to be little Zr/Hf variation from the currently accepted chondritic value of ~35 [1], there exist considerable Nb/Ta variations [2,3] within the same samples. As a whole, this variation is consistent with condensation within in a small temperature range, because Nb oxides are predicted to condense at temperatures very similar (14-40 ºC) to Tb oxides [3,4]: [2] suggested that the effect can be explained by efficient condensation of Ta atoms from a gas leaving it enriched in Nb atoms. Here, we investigate the distribution(s) of Zr/Hf and Nb/Ta ratios and their relationships with other refractory trace elements within our suite of 20 CAIs and among the minerals contained in them.

**Methods:** We identified inclusions contained in 6 ~1-2 cm$^3$ slabs of the Allende (CV3, oxidized subgroup AMNH 4948), Axtell (CV3, oxidized, AMNH 4873), and Leoville (CV3, reduced, AMNH 4337) carbonaceous chondrites by x-ray microtomography (e.g. [5,6]) at the GEOCARS beamline of the Advanced Photon Source (APS) at Argonne National Laboratory in Chicago, Illinois. After identification of promising inclusion-rich areas for study, thick sections (200 µm - 5 mm) were cut and surfaces were mapped [e.g. 7] using the AMNH electron microprobe at 15 kV and 20-30 nA beam current for positive identification of candidate CAIs. Table 1 shows a list of meteorites and tentative identification of CAI types within our study. To determine the mineralogy of individual CAI components, we performed quantitative electron microprobe analysis on the 8 major and minor elements Na, Mg, Al, Si, Ca, Ti, Cr, and Fe. Finally, we used the LA-ICPMS technique of [8] to quantify 44 trace elements within CAIs and regions dominated by a single mineral phase in them, subject to constraints of CAI sizes and petrological characteristics.

Table 1. Samples included in this study.

| Sample | # CAIs | Type(s) |
|---|---|---|
| Allende-AC1 (see [4]) | 1 | Large (9 mm) Type B1 |
| Allende-tp2-ps1 | 8 | fine and coarse grained |
| Axtell-1-A | 5 | related(?) fine grained |
| Leoville-CAI2-B | 1 | Large (5 mm) Type B1 |
| Leoville-tp1-psA | 4 | fine and coarse grained |
| Leoville –CAI1A-F1 | 1 | Fluffy Type A |

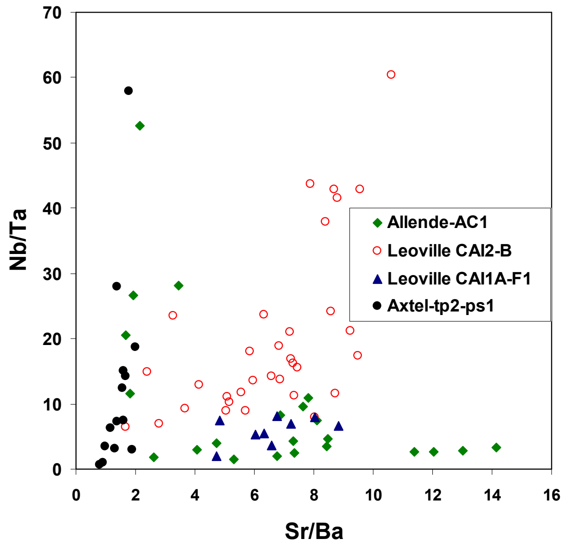
Figure 1: Nb/Ta and Zr content of minerals within the Type B1 Allende CAI (Allende-AC1).



We used the quantitative analysis capabilities of the AMNH microprobe for independent Ca quantification since our LA-ICPMS technique relies on internal standardization with Ca. As with many techniques, in LA-ICPMS there is a trade-off between spatial resolution and limit of detection, so we compromised on a spot size of 80 µm, which corresponds to an ablation depth of ~50µm. Although this spot diameter necessarily means that we have some analysis overlap of mineral species, the combination of tomographic imaging and LA-ICPMS has a distinct advantage: we can clarify questions regarding the homogeneity of our ablation locations by consulting the tomography images. Additionally, we plan follow-up work on the AMNH FE-SEM for further characterization of our samples. The combination of these techniques is a step forward for the analytical analysis of CAIs.

**Results:** We compare our results to the respective chondritic Nb/Ta and Zr/Hf values of 19.9 and 34.3 obtained by [1] and other trace element values to CI1 given by [9]. Mean Nb/Ta ratios of our 114 LA-ICPMS analyses of CAIs are slightly sub-chondritic at 16.1 with a standard deviation nearly as large. Zr/Hf ratios of the same suite yield a somewhat super-chondritic value of 45.3. After removal of outliers, generally resulting from Hf concentrations near our limit of detections, we again obtain a slightly super-chondritic value of 39. Mean Zr/Y values of our analyses are chondritic at 2.0, but Average Sr/Ba in our samples is 5.0, higher than a chondritic value of ~3 likely due to the greater volatility of Ba.

Figure 2: Evidence for volatility-based fractionation of Nb and Ta in CAIs.



Of the 20 individual CAIs we have investigated, only one, AC1 (see table and [4] for description), a Type B1 CAI in Allende, was large enough for the unambiguous analysis of individual mineral phases. In Fig. 1 we show Nb/Ta and Zr content of primary minerals within this CAI. Phases labeled in Fig. 1 also contained an amount of fine-grained (1-10 µm) spinel, which was peppered throughout the sample. Major element analysis of these spinels did not show significant variations of composition with location within the sample and we assume that our results do not reflect variations in the included spinels, but rather their host phases. The Hf content of AC1 was unfortunately often below the limits of detection of our measurements, but the 9 (of 22) spots analyzed yielded a mean super-chondritic Zr/Hf of 45.3. Zr content of the Ti-rich (4-7% $TiO_2$) fassaites is predictability higher than that found in the melilites or the single anorthite measurement, reflecting the similar geochemistry of Ti and Zr. When considered as a whole, Nb/Ta ratios of our analyzed spots in this single CAI range from 1 to nearly 60. When isolated by mineral type (Fig. 1) we find that melilites have generally higher Nb/Ta, while the fassaite seems the carrier of a low Nb/Ta fraction. The spot labeled as melilite/fassaite was an analysis of a mixed phase and is likely ~70% melilite and ~30% fassaite (along with their requisite complimentary spinels). It has been suggested that bulk sub-chondritic Nb/Ta values reflected in CV3 chondrites is due to one or more of their refractory phases [1,3] and our analyses suggest that fassaite is a candidate.

In Fig. 2, we show evidence for volatility controlled fractionation of Nb/Ta, as suggested by [2]. Sr/Ba, a feasible indicator for nebular temperatures, correlates well with Nb/Ta in individual samples and the Axtell sample which contains a likely physically and chemically related CAI assemblage.

**Conclusions:** Although our suite of elements analyzed by LA-ICPMS includes 44 moderately volatile to refractory lithophile elements, we focus here on a suite of refractory elements: in the future we hope to relate the extensive information known about the refractory elements to expand our knowledge of the more cosmochemically volatile elements.

Our measurements demonstrate that the presence of CAIs can influence the resulting Nb/Ta ratios in carbonaceous chondrites, and mineralogical control of the variation of these ratios is likely. Fassaite may be a carrier of low Nb/Ta containing material. The Nb/Ta ratio of early-condensing materials was influenced by both the oxidation state of condensing materials and their volatility.

**References:** : [1] Münker et al. (2003) *Science, 301*, 84-87. [2] Jochum et al. (1991) *Meteoritics, 26*, 352-353. [3] Kornacki and Fegley (1986) *Earth Planet Sci. Lett., 79*, 217-234. [4] Lodders (2003) *APJ, 591*, 1220-1247. [5] Murray et al. (2003) *LPS XXXIV*, Abstract #1999. [6] Ebel et al. (2004) *Meteor. Planet. Sci., 32*, A33. [7] Friedrich et al. (2005) this volume. [8] Jochum et al. (in press) In: *High Resolution ICPMS*, C. B. Douthitt, ed. [9] Anders and Grevesse (1989) *GCA, 53*, 197-214. This work was supported by NASA grant NAG5-12855 (DSE), and by an AMNH Kalbfleisch Post Doctoral Research Fellowship (JMF).