NANOSTRUCTURAL ANALYSIS OF SEVERAL PEROVSKITE GRAINS FROM AN ALLENDE CAI: EVIDENCE FOR EQUILIBRIUM OR NON-EQUILIBRIUM CONDENSATION? T. J. Zega[1,2], V. Manga[2], K. Domanik[1], K. Muralidiharan[2]. [1]Lunar and Planetary Laboratory, [2]Dept. of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA. (tzega@lpl.arizona.edu).

Introduction: With radiometric age dates that exceed those of all other solar materials, calcium- and aluminum-rich inclusions (CAIs) are the oldest solids to have formed in the solar system [e.g., 1]. CAIs are cm-sized objects, composed of mineral phases formed at very high temperatures and which are predicted by thermodynamic models to be among the first solids to have condensed within a cooling gas of solar composition [e.g., 2]. Their analysis can provide a glimpse into some of the earliest chemical and physical processes to have transpired during solar-system formation.

The generic CAI, as described by [3] contains several different oxide and silicate phases. Perovskite, nominally $CaTiO_3$, is the major Ti-bearing phase in fluffy type-A CAIs and is predicted to host rare-earth elements and (minor) lithophile elements [4]. Micron-sized grains of perovskite occur both in the Wark-Lovering rims that surround many of them and within the melilite interior. Here we report on the structure of several perovskite grains in a fluffy type-A CAI from the Allende CV3 chondrite. This work is part of a long-term effort to examine microstructures and crystal chemistry of CAIs at length scales ranging from the micron level down to the atomic, and to use such information to gain insights into their origins.

Samples and Analytical Methods: A petrographic thin section of the Allende CV3 chondrite (TS25, U. Chicago) was examined using an FEI Helios focused-ion-beam scanning electron microscope (FIB-SEM), equipped with an EDAX energy-dispersive spectrometer (EDS), located at the Lunar and Planetary Laboratory, University of Arizona. We acquired backscattered electron images (BSE) and EDS spectrum images of a local part of the melilite inclusion. Selected perovskite grains were extracted using the FEI easylift micromanipulator on the Helios and thinned to electron transparency using previously described methods [5]. All samples were ion polished down to 5 keV to remove the amorphous damage layer created by higher-voltage milling. The FIB cross sections were analyzed using the newly developed 200 keV Hitachi HF5000 transmission electron microscope (TEM) located at Hitachi High Technologies (Mito, Japan). The HF5000 is equipped with a cold-field-emission gun, an aberration-corrector for scanning TEM (STEM) imaging, and a large solid angle Si-drift Oxford EDS system. It is capable of rapid (minutes) X-ray mapping of entire FIB sections and atomic-resolution imaging (80 pm).

To complement our experimental work, density-functional theory (DFT) calculations in conjunction with thermodynamic modeling of phase stability are currently underway. The goal of these calculations is to investigate the condensation and phase transformation temperatures pertaining to solid solutions relevant to this work, namely perovskite and spinel. Further, the role of the well known displacive phase transformations that occur in the perovskite phase and their effects on the phase stability of the solid solution is also being investigated.

Results: BSE imaging revealed a localized region within the inclusion hosting abundant perovskite grains (Fig. 1a).

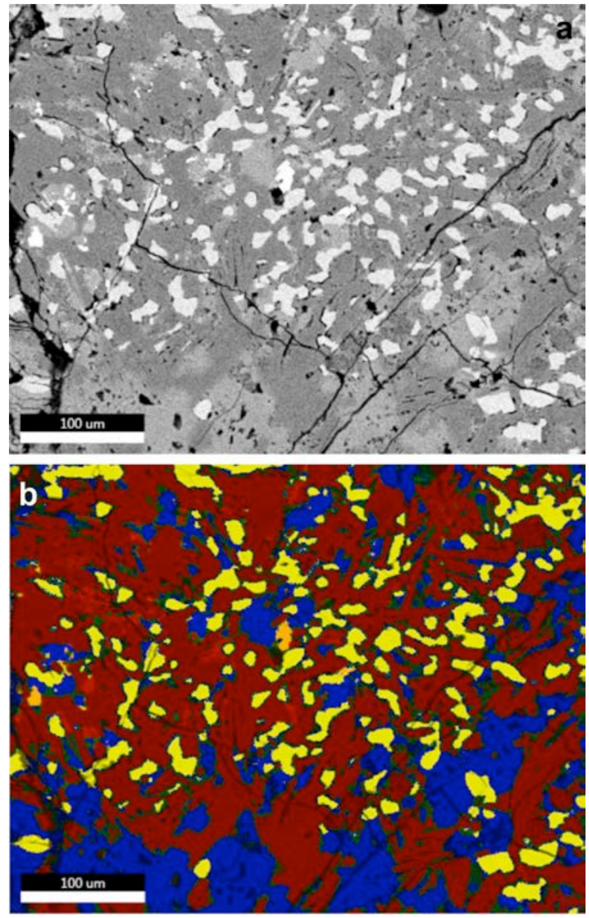

Fig. 1. SEM data on a region of a fluffy type-A CAI from the Allende CV3 chondrite. **(a)** BSE image. High-contrast grains are perovskite. **(b)** EDS false-color spectrum image (yellow = perovskite, red = hibonite, blue = melilite).

The grains are tens of μm in size and contain subhedral morphologies. EDS spectrum imaging reveals that the perovskite is surrounded by abundant hibonite and melilite grains similar to and larger in size than the perovskite (Fig. 1b). Four perovskite grains were chosen for more detailed investigation using TEM. C straps were deposited along lines transecting the perovskite grains and their interfaces with the surrounding material.

Bright-field TEM imaging reveals that the FIB sections of the perovskite and surrounding material have varied microstructural complexity. All are polyphasic with grains that range in size from nm to several μm (e.g., Fig. 2). Perovskite from two of the FIB sections contains inclusions that EDS spectrum imaging reveals are spinel. The inclusion from section 'D' exhibits a lathic morphology, measures approximately 100 × 150 nm in size, and occurs adjacent to a Ca-Mg-Al-silicate. The inclusion from section 'C' is significantly larger, measuring approximately 300 × 400 nm in size.

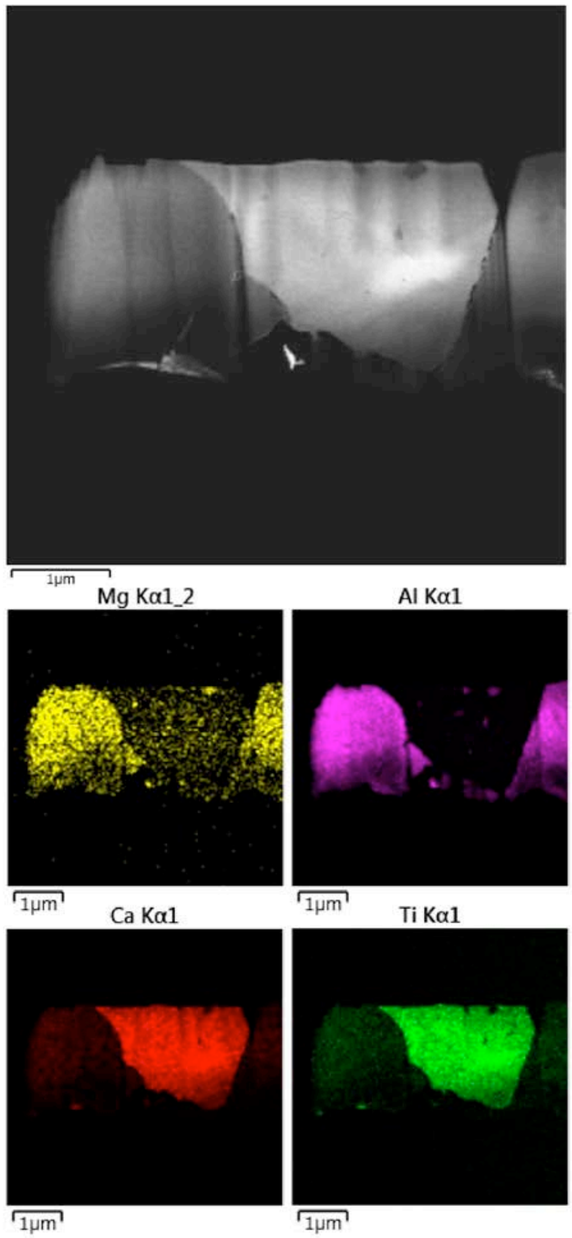

Fig. 2. TEM data on a FIB section of a perovskite grain from a fluffy type-A CAI in the Allende CV3 chondrite. **(top)** High-angle annular-dark-field image. **(bottom)** EDS false-color spectrum images. Spinel inclusions within the perovskite are resolved by EDS (cf., Mg and Al maps).

High-resolution imaging and selected area electron diffraction shows that it is twinned along the [111] direction. EDS spectrum imaging reveals that V is segregated to atomic columns located in a single atomic plane at the twin boundary.

Discussion: [6] described fluffy type-A CAIs in the Allende CV3 chondrite and inferred that they are aggregates of material that condensed in the early solar nebula. The TEM data that we present here shows no signs of secondary alteration that would otherwise argue against condensation. However, the microstructural relationship observed here suggests that spinel condensed first and was later enveloped by condensing perovskite.

Equilibrium thermodynamic calculations predict that both perovskite and spinel will condense from a gas of solar composition. Perovskite is predicted to condense at 1593K and at 1441K, whereas spinel is predicted to condense at 1397K [4]. The high-temperature phase of perovskite is cubic, whereas the lower temperature phase is orthorhombic [7]. The microstructure we observe here is inconsistent with these predictions, raising the question of whether equilibrium condensation occurred for this particular CAI.

We hypothesize that the solid solution of spinel (with dissolved V) exhibits a higher condensation temperature than the solid solution of perovskite. Based on the hypothesis, one can assume that the spinel condensed first as a single crystal at a relatively higher condensation temperature than the perovskite. As temperature of the local system dropped to the condensation temperature of perovskite, the high-temperature cubic form condensed around the spinel. As temperature continued to decrease, the perovskite underwent a displacive phase transition from the cubic to orthorhombic form. This phase transition imparted shear stress to the spinel crystal, and it became twinned in response to the applied stress. Further, we hypothesize that the V, which was originally homogeneously distributed in the spinel, segregated at the induced twin, driven by an energetically favorable diffusion, forming a plane of atomic columns parallel to the [111] direction. Preliminary DFT studies seem to suggest that the presence of solute elements (e.g. V) shift the relative stability of the different solid phases as well as the equilibrium condensation temperatures, in line with the above hypothesis.

Continued examination of perovskite grains should reveal whether the microstructure we observe here is isolated to this inclusion or is common among other fluffy type-A CAIs in CV3 chondrites. Complete DFT studies and thermodynamic modeling will provide full quantitative treatment of the condensation temperature and phase stabilities of these solid solutions.

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Acknowledgements: We thank Drs. Hiromi Inada and Keitaro Watanabe at Hitachi High Technologies (Mito, Japan) for their assistance with the HF5000 TEM. Research supported by NASA grant NNX15AJ22G (TJZ).