Introduction: Primitive asteroids are remnants of the early solar system, capable of providing insight into the various processes and environments prevalent at their time of formation. Sample-return missions such as Hayabusa2 and OSIRIS-REx (O-Rex) are dedicated to understanding the early solar system by analyzing pristine material recovered from their target asteroids Ryugu and Bennu [1,2]. Detailed understanding of the crystal structures and chemistries of the constituents of the return samples is vital to inferring the conditions prevalent in the early solar system. In order to better analyze and interpret data for samples collected from return missions, it is necessary to study the proxies currently available to us. One such proxy are calcium-aluminum-rich inclusions (CAIs), mm- to cm-sized objects found in primitive chondrites [3] and expected to be found in the samples returned by Hayabusa2 and O-REx.

CAIs are composed of Ca- and Al-rich refractory materials that have been thermodynamically predicted and isotopically dated to be among the first-formed solids in the solar protoplanetary disk [4-7]. The structure and chemistry of these inclusions contain a record of the environments in which they formed and the processes to which they were subsequently exposed. Their analysis can help us better understand and constrain the early stages of solar-system formation.

While the components of CAIs are widely accepted to have initially formed via gas-phase condensation, multiple origins were proposed for the multilayer rims surrounding many of them [8-10]. Additionally, many CAIs are known to have experienced subsequent thermal and aqueous processing, resulting in changes to the morphologies, structures, and compositions of CAIs [11-13]. Here we present data on spinel and perovskite assemblages from the interior and rim of a CAI in the Northwest Africa (NWA) 5028 CR2 chondrite. We identified assemblages of spinel and perovskite in both the interior and rim of TR01 for more detailed studies using transmission electron microscopy (TEM).

Four regions (Fig. 1) were extracted, and thinned to electron transparency (<100nm) using previously described methods [14] with a FEI Helios NanoLab 660 focused-ion-beam (FIB) scanning electron microscope (SEM) located at LPL. The sections from the CAI were analyzed using a 200 keV spherical-aberration-corrected Hitachi HF5000 scanning transmission electron microscope (S/TEM) located at LPL and the Hitachi SU9000 30kV SEM/STEM, formerly located at LPL. The HF5000 and SU9000 are both equipped with Oxford Instruments (X-max) energy dispersive X-ray spectroscopy (EDS) detectors. Selected-area electron-diffraction (SAED) patterns were acquired for determination of crystallinity and phase.

Sample and Analytical Techniques: A compact type-A (CTA) CAI (TR01, Fig. 1) was identified in a thin section of the NWA 5028 (Center for Meteorite Studies, Arizona State University collection #1845-5) using a Cameca SX-100 electron microprobe, located at the Lunar and Planetary Laboratory (LPL), University of Arizona. Wavelength-dispersive spectroscopy (WDS) maps and backscattered electron images (BSE) of the CAI were acquired. We identified assemblages of spinel and perovskite in both the interior and rim of TR01.

Fig 1. BSE image of CTA TR01. Boxes in red indicate regions from which the FIB sections were extracted.

Results: The mineralogy (80 to 85 vol% melilite, 15 to 20 vol% spinel, and 1 to 2 vol% perovskite) and rounded morphology of the inclusion are consistent with previous descriptions of CTA CAIs [15]. Several spinel-perovskite assemblages were chosen to sample the heterogeneity of the CAI.

TEM reveals the detailed microstructure and composition of the CAI phases. FIB section #1 (interior) consists of a spinel grain with a silicate-perovskite inclusion and a perovskite grain. It does not show any signs of alteration [16]. FIB section #2 (rim) consists of three perovskite grains (one with a spinel inclusion and another with a hibonite inclusion) embedded in a large spinel grain, and contains veins and rims around the grains of material with compositions consistent with Fe-rich silicates [16]. The Fe-silicates have needle-like morphologies and occur in crosslinked patterns. FIB section #3 (interior) consists of two spinel grains and a perovskite grain partially surrounded by a
Ca-Al silicate phase with regions rich in Cl, as seen from the high-angle annular-dark-field (HAADF) image and energy-dispersive spectroscopy (EDS) maps (Fig. 2) [17]. FIB section #4 (rim) consists of a perovskite grain between two spinel grains.

**Discussion:** The condensates in CTA CAIs are thought to have experienced some amount of thermal processing. The evidence for such processing includes: their rounded morphology, inward zoning of Åkermanite content, lathic melilite, and symplectite morphology [18]. Except for the rounded morphology of the CAI, TR01 lacks these characteristics, suggesting that the interior of TR01 was not significantly affected by thermal processing. Below we explore signatures of nebular condensation and secondary alteration.

According to equilibrium thermodynamic calculations, perovskite condenses at 1593 K, whereas spinel forms at 1397 K [2]. Therefore, the presence of the perovskite inclusion within the spinel grain in section #1 (interior) is consistent with these predictions. In comparison, the spinel inclusion within the perovskite grain in section #2 (rim) is not consistent with these predictions. The hypotheses for rim formation include condensation [8], melt solidification [9], and evaporative residues [10]. The sequence of minerals seen in the rim is consistent with that listed in [9] as being evidence of melt solidification. Further, recrystallization experiments conducted on CAI melts show that spinel solidifies before perovskite [19]. The microstructure that we observe in section #2 (rim) is consistent with a formation through melt solidification.

NWA 5028 is a CR2 chondrite and it contains evidence of aqueous alteration, in the form of secondary phases such as hydrated minerals in the matrix and CAIs [20,21]. TR01 also shows clear signs of aqueous alteration. The veins in section #2 (rim) are suggestive of fluid flow [22]. Moreover, their morphology and Fe-rich composition are similar to Fe-rich phyllosilicates previously described as products of aqueous alteration [13]. In comparison, section #4 (rim) shows no signs of alteration. Section #3 (interior) contains Cl-rich silicate regions. Chlorine is a highly volatile element and its incorporation into the inclusion is consistent with low-temperature processing, e.g. [23]. Thus, we hypothesize that these Cl-rich regions are remnants of low-temperature iron-alkali-halogen metasomatism such as those described by [13,22]. The data point towards a complex history involving equilibrium condensations and non-uniform secondary processing.

Studies have shown that the spectral properties of Bennu and Ryugu are similar to CM chondrites [24,25]. CM chondrites have experienced alteration and the CAIs found in them contain mineral phases consistent with aqueous processing [3,22]. Therefore it is possible that any CAIs found in samples from Hayabusa2 and O-Rex missions experienced alteration. Consequently, understanding of the evolution of meteoritic samples will aid in the interpretation of asteroid evolutions through the study of samples from Hayabusa2 and O-Rex.

![Fig 2. TEM data on FIB section #3. HAADF image (top); EDS maps (bottom).](image)

**References:**

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