INITIAL ANALYSIS OF A REFRACTORY INCLUSION RICH IN $CaAl_2O_4$ FROM NWA 1934: CRACKED EGG.

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Introduction: Calcium monoaluminate, $CaAl_2O_4$, was predicted to exist in refractory inclusions [1,2] but not reported in nature until 2002 [3]. Its extreme rarity is likely due to limited stability fields during condensation in nebular gases [2,3] or crystallization from a liquid [4]. Here we present a preliminary study to characterize the primary petrology and geochemistry of a truly unique calcium monoaluminate-rich CAI, named Cracked Egg, from the CV3 chondrite NWA 1934. Our goals are to constrain the formation of this inclusion and the environment in which it formed.

Analytical Technique: Two thin sections of NWA 1934 containing a 4 mm refractory inclusion were mounted on one inch round slides (Fig. 1). The inclusion's oval shape and visible brittle deformation inspired the name Cracked Egg. Optical microscope and high magnification BSE imaging were performed at the AMNH and Caltech. X-ray mapping (Fig. 2) and quantitative analyses of major

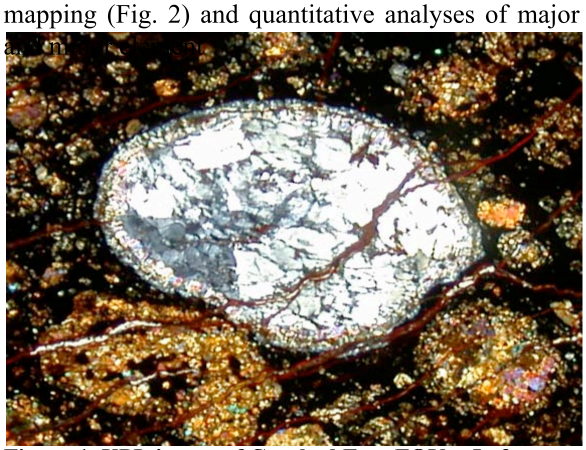

Figure 1. XPL image of Cracked Egg. FOV ~ 5x 3mm.

abundances using natural and synthetic standards were performed on the Cameca SX-100 EMP at the AMNH and JEOL 8200 EMP at Caltech. Raman spectroscopic microanalysis was carried out using a Renishaw M1000 micro-Raman spectrometer system at Caltech. An ~5 mW of 514.5 nm laser illumination (at the sample) focused with a 100x objective lens provided satisfactory spectra. The spot size was about 2 µm. Peak positions were calibrated against a silicon standard. A dual-wedge polarization scrambler was used in the laser beam for all spectra to minimize the effects of polarization. Single-crystal electron backscatter electron diffraction (EBSD) analyses at

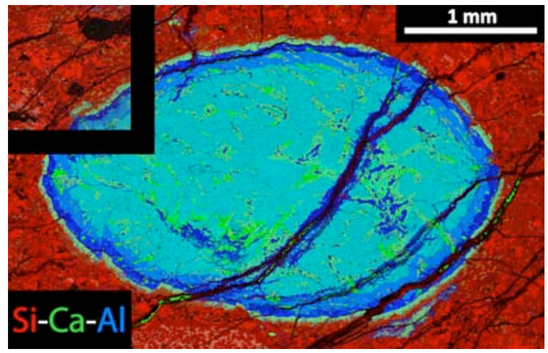

Figure 2. False color X-ray map of Cracked Egg showing relative silicon, calcium, and aluminum concentration in red, green, and blue.

a sub-micrometer scale were preformed using an HKL EBSD system on a ZEISS 1550VP SEM, operated at 20 kV and 6 nA in a focused beam with a 70º tilted stage at Caltech. The EBSD system was calibrated using a single-crystal silicon standard.

Results: Cracked egg is composed primarily of calcium-aluminum oxides and a few silicates, arranged in sub-millimeter-thick concentric ovals, each dominated by a single mineral species. The

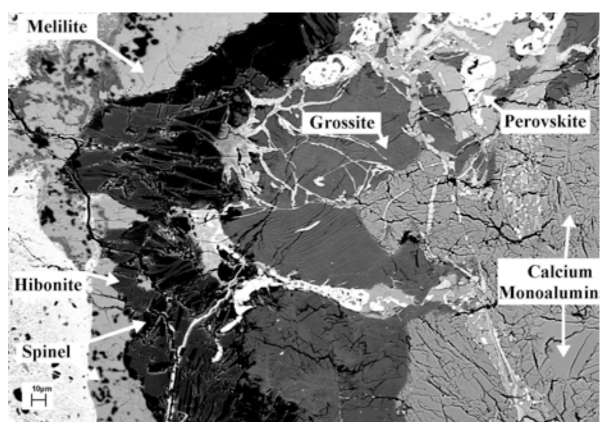

Figure 3. BEI of the rim sequence with 10 µm scale bar.

$CaAl_2O_4$-rich refractory inclusion, Sweeny Smith et al.

outermost ring is composed of aluminous melilite (Ak ~2.8 near the hibonite-spinel layer – 6.6 near the outer edge of the object), which occurs as a granular mass with tiny (<5 μm) euhedral to subhedral spinels (Fig. 3). The next layer inward is anhedral hibonite with spinel. The spinels occur as subhedral 'teeth' pointed outward, towards the edge, and are present throughout the hibonite layer. The third layer inward is composed of grossite, also anhedral. The central portion of the egg is dominated (~ 80 area%) by $CaAl_2O_4$, with smaller anhedral melilite (Ak ~ 0.03), spinel, and perovskite inclusions. Perovskite is also present as anhedral grains cross-cutting the outer layers.

Optical analysis shows that the calcium-monoaluminate is a biaxial crystal with positive 2V ~60 degree and micro-Raman reveals that the $CaAl_2O_4$ crystal has a monoclinic structure. The structure of the calcium monoaluminate was determined by matching the experimental EBSD patterns with structures of synthetic $CaAl_2O_4$. EBSD reveals that the $CaAl_2O_4$ phase is dmitryivanovite (a recently-approved new mineral), a high-pressure polymorph of $CaAl_2O_4$ (a = 7.95, b = 8.62, c =10.25 Å, β = 93.1°, space group P21/c, and Z = 12) [6,7]. Here we present the second natural occurrence of dmitryivanovite.

The cracks from which, in part, Cracked Egg derives its name vary in size and distribution. Tiny submicron- scale cracks riddle the polished surface of the inclusion. Larger, μm-sized cracks are more sparsely distributed and appear most frequently near the boundaries between rim sequences. Several larger 10 to 50 μm cracks filled with hydrated iron oxides originate in the meteorite matrix and pass entirely through the inclusion. Cl-bearing mayenite, $Ca_{12}Al_{14}O_{32}Cl_{l2}$, occurs within the central $CaAl_2O_4$-rich region often associated with perovskite. This is the first natural occurrence of this potentially preterrestrial alteration phase. It was identified by FE-SEM and EMPA. Its EBSD pattern was not observed, indicating it has a poorly defined diffraction structure. Zn-bearing hercynite, also likely a secondary phase, is associated with the mayenite.

Discussion: The Ca-Al oxides comprising the bulk of Cracked Egg progress outwards in rings from a $CaAl_2O_4$-rich center to progressively less calcic more aluminous phases (calcium monoaluminate → grossite → hibonite). All of these species are predicted to occur as condensates from a cooling nebular gas [1,2,3]. However, whereas hibonite and grossite are common in CAIs, calcium monoaluminate is exceedingly rare.

Spinel 'teeth' present in the hibonite rim have an elongate habit, and the fact that they often taper towards the outside of the inclusion may indicate nucleation on the surface of the grossite rim and growth truncated by an overgrowth of hibonite. The melilite rim is the most silica-rich section of Cracked Egg, and may represent a later growth on the surface of an already crystallized inclusion.

The possibility that this inclusion is highly primitive and may represent an original condensate should not be overlooked. The formation of Cracked Egg presumably involved either condensation from nebular gas and/or evaporation, although its size may suggest that it was a liquid droplet. It may be that it was mostly $CaAl_2O_4$ that reacted with nebular gases to produce the observed rings or layers of minerals. It is also possible that Cracked Egg is igneous, or at least the melilite-spinel rim may have been melted (spinels are euhedral to subhedral which may be interpreted as growth from a liquid). If the entire object is igneous, then (1) at what temperature did it melt and (2) what was its cooling rate? Condensation calculations show that the production of Ca, Al-rich melt requires formation within a dust-rich region of the disk [1,2]. Variations in Mg and Si isotopes in other inclusions have been interpreted to suggest that the region in which many inclusions formed was actually dust-poor [8,9]. Thus, Cracked Egg and other $CaAl_2O_4$-bearing inclusions may have formed in slightly different regions or times than $CaAl_2O_4$-poor inclusions.

Dmitryivanovite is the high-pressure form of $CaAl_2O_4$. It is possible that $CaAl_2O_4$ originally formed as the low-pressure polymorph but that a subsequent shock event on the parent body converted it to the high-pressure form (nebular pressures of ~ $< 10^{-3}$ bar would have been far too low for its formation). Numerous cracks cross-cutting the object that continue into the rest of the rock and the generally ellipsoidal shape of the chondrules in thin section are clear evidence that the rock did experience shock post-lithification. Shock features are also endemic in the CH chondrite NWA 470, which is host to the only other known occurrence of dmitryivanovite [3].

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