MICROSTRUCTURAL ANALYSIS OF A REFRACTORY-SIDEROPHILE GRAIN, FOUND IN A CALCIUM-ALUMINUM-RICH INCLUSION.

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Introduction: Calcium-aluminum-rich inclusions (CAIs) are mm- to cm-sized objects composed of Ca- and Al-rich minerals [1]. CAIs were isotopically age dated to be the earliest formed solids in the protoplanetary disk and thermodynamically predicted to condense at high temperatures [2-5]. The structures and chemical compositions of CAIs and their various components can provide insight into the earliest processes in our solar system.

CAIs can contain grains rich in Fe and Ni, and some with refractory siderophile elements such as Os, Re, Pt, Ir, Mo and W [1]. These grains can range in size from sub-micron to a few microns in diameter. Early work on these refractory metal nuggets (RMNs) suggested that they were single-phase alloys, rich in Os, Ir, Ru and Pt [6,7]. Isotopic measurements on one-such object from the Allende meteorite suggests that it formed in the solar nebula [8]. Refractory metals are predicted to condense at high temperatures [3, 9-10].

RMNs can serve as thermal probes of the solar nebula. However, given their small size, nanoscale analysis is required to better understand the structures and chemistries of these objects, as well their relationship to the host CAI. This work is part of an ongoing effort to understand the composition and structures of CAIs and what they can tell us about the earliest processes in our solar system.

Sample and Analytical Techniques: A fluffy type-A (FTA) CAI ('Cloud', Fig. 1A) was identified in a thin section of the Northwest Africa (NWA) 8323, CV3 chondrite (Center for Meteorite Studies, Arizona State University collection, #1895_1_2) using a Cameca SX-100 electron microprobe (EMP), 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. Grains rich in transition and rare-earth metals were identified using WDS.

We selected a refractory metal grain ('Bright1') to determine its structure and chemistry. Bright1 was cross sectioned, extracted, and thinned to electron transparency (<100 nm) using previously described methods [11] with a Thermo Fisher (formerly FEI) Helios NanoLab 660 G^3 focused-ion-beam scanning-electron microscope (FIB-SEM) located at LPL. The FIB section was analyzed using a 200 keV spherical-aberration-corrected Hitachi HF5000 scanning transmission electron microscope (S/TEM) located at LPL. The HF5000 is equipped with an Oxford Instruments X-Max N 100 TLE EDS system with dual 100 mm^2 windowless silicon-drift detectors ($\Omega = 2.0$ sr). Selected-area electron-diffraction (SAED) patterns were acquired for determination of crystallinity and phase.

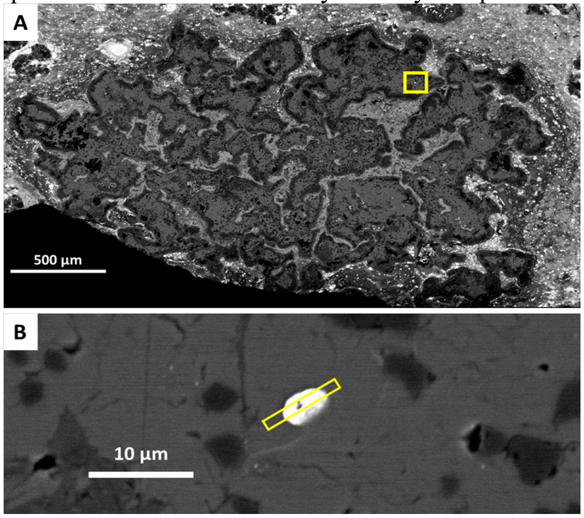

Fig 1. (A) BSE image of FTA 'Cloud' and surrounding matrix. The yellow box indicates the region in which Bright1 occurs. (B) BSE image of a local part of Cloud containing Bright1. The yellow rectangle indicates the FIB transect.

Results: The mineralogy (80 to 85 vol% melilite, 15 to 20 vol% spinel, and 1 to 2 vol% perovskite) and the nodular morphology of 'Cloud' are consistent with previous descriptions of fluffy type-A (FTA) CAIs [12]. Bright1 occurs within the melilite interior. WDS analysis of Bright1 shows that it contains Fe, Ni, Pt, Os, Ir, Ru and Rh.

High-angle annular dark-field (HAADF) imaging and EDS mapping in the TEM show that Bright1 is compositionally heterogeneous (Fig. 2). Spatial correlations occur among Fe, Ni and Pt, and also among Ir, Os, Ru and Rh. Si, Mg and O correlate locally and SAED analysis of the region indicates that the mineral is forsterite. SAED patterns acquired from the Fe-Ni-Pt metallic regions show rings, indicative of polycrystalline material and index to a Fe-Ni-Pt alloy. Thus, the TEM data indicate that Bright1 contains a mixture of metal alloys, oxides, and a silicate.

Discussion: FTA CAIs are believed to be direct condensates from the solar nebula, as characterized by their irregular shapes and increase of Al/Mg in melilite from core to rim [13]. Many FTAs also show evidence for secondary alteration in the form of minerals such as nepheline, grossular and sodalite [13]. Neither Na- nor Cl-rich minerals occur in the FTA Cloud, indicating that it is unaltered.

CAIs can contain inclusions rich in high-Z elements [1]. For example, refractory metal nuggets (RMNs) were reported by [1,6-7] as sub-micron to micron-sized objects composed of single-phase alloys. Some grains consist of cores enriched in Os, Ir, Ru and Rh, and boundaries enriched in Pt [7], whereas others contain metallic cores surrounded by sulfides [14]. RMNs rich in Os, Ru and Mo also occur within presolar graphites in the form of single-phase hexagonal crystals [15]. In comparison, fremdlinge are characterized as complex aggregates with irregular morphologies, often with cores composed of Fe-Ni alloys and Fe sulfides, surrounded by silicates, phosphates, sulfides and oxides [7, 16-18]. They are large objects, typically tens of microns in size and have only been reported within CAIs in oxidized CV3 chondrites [1].

The composition and morphology of Bright1 does not precisely match previous descriptions of fremdlinge or RMNs, but its characteristics are more similar to the latter than the former. Compared to fremdlinge [7, 16-18], Bright1 is smaller and does not contain secondary phases or a fluffy aggregate morphology. Compared to RMNs, Bright1 is a polyphasic metal and itself contains a silicate inclusion, which is contrary to previous descriptions of single-alloy RMNs.

The presence of refractory siderophiles Os, Ir, Ru, and Pt points towards a high-temperature origin. Early thermodynamic equilibrium calculations by [14] indicates condensation temperatures of 1917K, 1639K, 1613K, 1415K, and 1346K for Os, Ir , Ru, Pt, and Rh respectively. These calculations also suggest that once a solid grain of a refractory metal is formed, there is thermodynamic favorability for it to incorporate other metals solutes in proportion to their partial pressures in the nebular vapor. The alloys that result do so at temperatures mostly above that at which melilite condenses (1529K, e.g., 2) and so form before their host silicate. Exactly how Bright1 and other RMNs become incorporated within melilite is therefore perplexing. If condensation was occurring according to equilibrium, Bright 1 may have served as a seed nucleus for condensation of its host melilite. In such a scenario, the polyphasic nature of Bright1 with intermixed O-rich and purely metallic regions suggests that oxidation of the grain occurred locally prior to the condensation of melilite. Additional work on this and other refractory metal-bearing grains will help test these hypotheses.

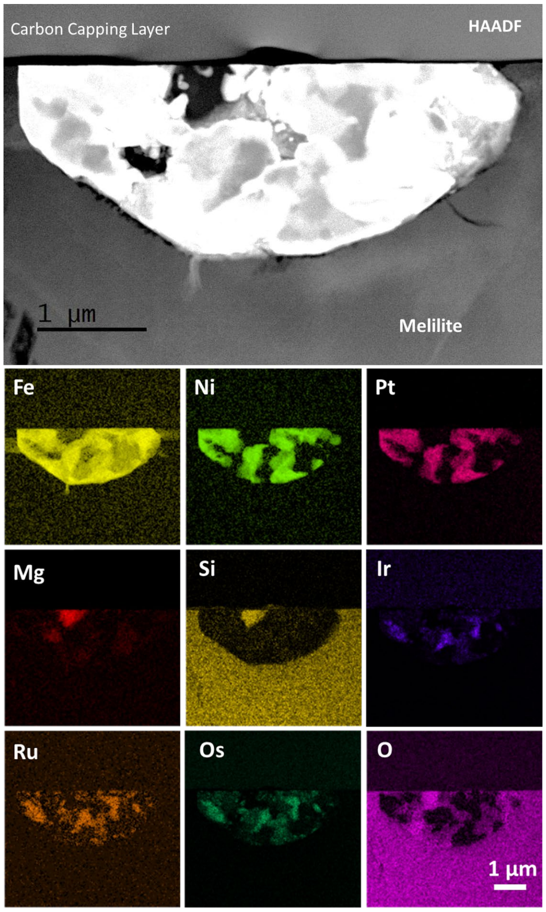

Fig 2. TEM data on Bright1. HAADF image (top); False-color EDS maps (bottom).

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