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A Correlative Electron Microscopy Study of a Ru-rich Metal Grain from a Calcium-aluminum-rich Inclusion

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Calcium-aluminum-rich inclusions (CAIs) are sub-mm to cm-sized objects composed of highly refractory Ca- and Al-rich mineral phases, hosted in chondritic meteorites [1]. The component minerals of CAIs were thermodynamically predicted to be condense at high temperatures in the cooling solar nebula [2-3]. Isotopic analyses place the age of these objects at 4.567 Ga, making them the first formed solids in our solar system [4-5]. The chemical compositions and crystal structures of the Ca- and Al-rich minerals serve as imprints of the thermochemical environments in which they formed. Therefore, detailed microstructural analyses of CAIs can provide insight into the processes that prevailed in the early solar system.

CAIs can contain metal inclusions rich in Fe, Ni, and refractory siderophile elements Pt, Os, Ir and W [1]. Such inclusions are classified into three types: refractory metal nuggets (RMNs), nugget-like objects (NLOs) and fremdlinge [1,6]. Some of these refractory siderophile elements are thermodynamically predicted to condense at temperatures higher than those of common CAI mineral phases such as hibonite melilite, perovskite and spinel [2, 7-9]. Metal inclusions in CAIs can therefore serve as probes into some of the highest temperature processes in the early solar system. Here we report the coordinated analysis of one such metal inclusion.

A CAI (Fig. 1) was identified in a thin section of the Leoville CV3 chondrite (Center for Meteorite Studies, Arizona State University collection, #821_C_3) using a JEOL-JXA 8530F electron microprobe at Arizona State University. Backscatter-electron imaging (BSE) and energy-dispersive spectroscopy (EDS) were used to identify a metal grain rich in Pt-group elements with a Thermo Fisher (formerly FEI) Helios NanoLab 660 G^3 focused-ion-beam scanning-electron microscope (FIB-SEM) located at the Kuiper Materials Imaging and Characterization Facility (KMICF) at the Lunar and Planetary Laboratory, University of Arizona. The FIB is equipped with an EDAX EDS system. One metal inclusion, designated as 'Mirum', was selected for further analysis in the transmission electron microscope (TEM) and extracted and thinned to electron transparency following previously described methods [10], using the FIB-SEM at KMICF. The section was analysed using the 200 keV spherical-aberration corrected Hitachi HF5000 scanning transmission electron microscope (S/TEM) located in the KMICF. The HF5000 is equipped with twin Oxford Instruments (X-max) EDS detectors, providing a 2.0 sr solid angle for X-ray collection. Selected-area electron diffraction (SAED) was used for determination of crystallinity and phase identification.

The mineralogy and textures show that the identified CAI (Fig. 1) is a fluffy type A (FTA) CAI. Mirum is composed of two adjoining irregularly shaped grains measuring 1.14 μm × 0.3 μm and 0.45 μm × 0.38 μm. EDS analysis on the FIB-SEM, showed that both grains contain Fe and Ni and are rich in Ru.

The metal inclusion was extracted along the longest dimension to determine its chemical composition and crystal structure in the TEM, to understand its high-temperature origin.

STEM high-angle annular dark-field (HAADF) and bright-field (BF) imaging, and EDS mapping of the FIB section show that the metal inclusion initially observed on the surface in the FIB-SEM is shallow at depth (≤ 1 μm). However, the STEM images also reveal an adjoining metal-rich grain and three additional buried grains (Fig. 2). All metal-rich grains in this FIB section are included in 'Mirum'. The metal-rich grains contain subhedral and anhedral morphologies. STEM imaging shows that the metal-rich grains are surrounded by multiple Ca-Al silicate grains (Fig. 2). SAED patterns acquired from the Ca-Al silicates index to melilite and each have different orientations. EDS mapping reveals spatial correlations among Fe, Ni, Pt, Os and Ru (Fig. 2). EDS mapping also reveals that Mirum contains local enrichments in Ni and Ru. SAED patterns acquired from various regions in Mirum show that the inclusion is crystalline. While we were unable to match the SAED patterns to specific phases in line with the compositions, they index to the face-centered cubic structure of Pt.

RMNs are described as sub-micron- to micron-sized inclusions composed of single-phase alloys [1, 11-12]. Some RMNs contain cores enriched in Os, Ir, Ru and Rh, and boundaries enriched in Pt [12], while others are composed of metallic cores surrounded by Ni-rich and Ni-poor Fe sulfides [7]. NLOs are also micron-sized inclusions and are composed of a refractory metal (alloy) and an oxide [6]. Fremdlinge are tens of microns in size, and are complex aggregates of Fe-Ni alloy, silicates, oxides, and Fe sulfides [1, 12]. In comparison, our observations show that although the size of 'Mirum' is similar to previous descriptions of RMNs and NLOs [1, 6], the local enrichments in Ni and Ru, as well as the lack of oxide observed in Mirum deviates from prior descriptions of RMNs and NLOs respectively. Thermodynamic modelling by [7] indicates that Os, Ru and Pt condense at 1917 K, 1613 K, and 1415 K respectively. Their calculations also suggest that once a refractory metal condenses, it is thermodynamically favorable for the metal to incorporate other solutes, e.g., W, Fe and Ni, in levels proportional to their partial pressures in the solar nebula gas. Such alloying occurs at temperatures above those at which the host melilite (1529 K, [2]) is predicted to condense. We hypothesize that Mirum formed via condensation of the refractory siderophiles (Ru, Os and Pt) followed by alloying to incorporate Fe and Ni. Mirum and other such refractory-siderophile-rich grains represent some of the earliest formed solids in our solar system [13].

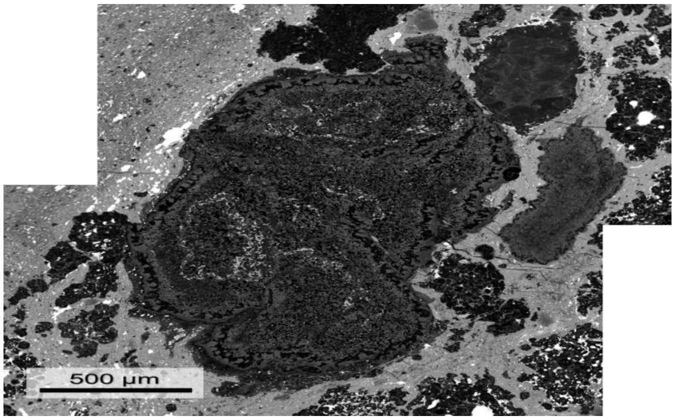

Figure 1. BSE image of the fluffy type A CAI from Leoville.

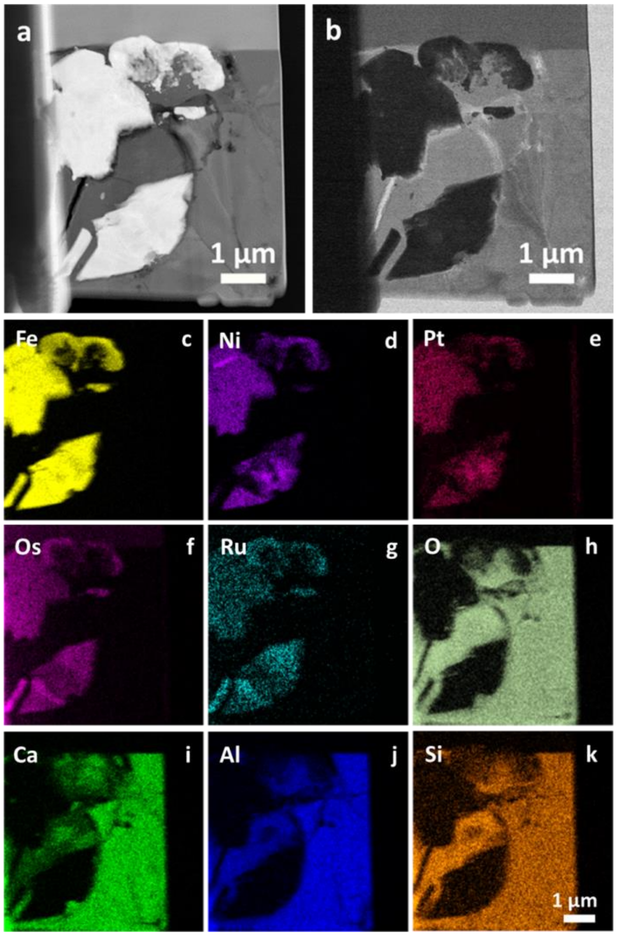

Figure 2. STEM data for 'Mirum'. (a) HAADF image. (b) BF image. (c) to (k) False-color EDS maps.

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