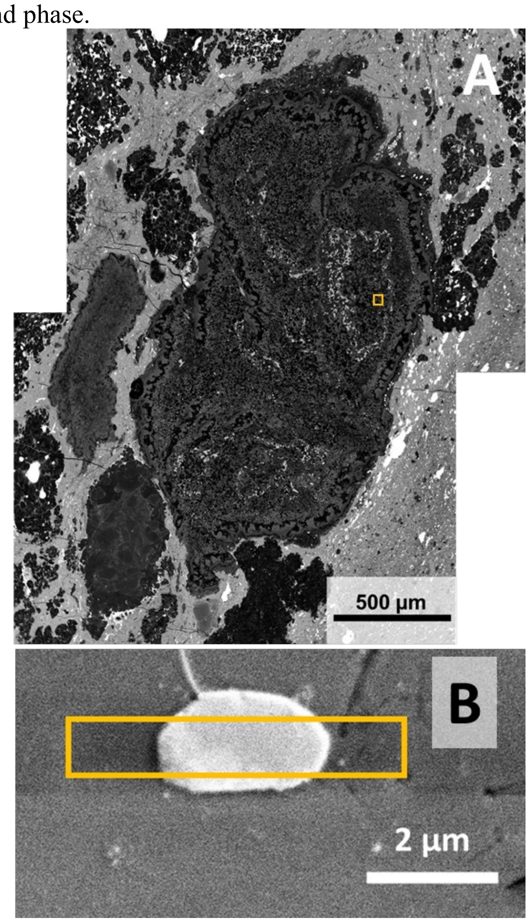
A TRANSMISSION ELECTRON MICROSCOPY STUDY OF A REFRACTORY METAL GRAIN FROM A CALCIUM-ALUMINUM-RICH INCLUSION IN THE LEOVILLE CV3 CHONDRITE. T. Ramprasad[1], L. B. Seifert[2], P.Mane[3,4] and T. J. Zega[1,2] [1]Dept. of Material Science and Engineering, University of Arizona, Tucson, AZ 86719, USA. [2]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 86721, USA. [3]Lunar and Planetary Institute (USRA) Houston, TX 77058, USA. [4]NASA Johnson Space Center, Houston, TX 77058, USA (tarunika@lpl.arizona.edu)

Introduction: Calcium-aluminum-rich inclusions (CAIs) are an important component of chondritic meteorites. They can contain materials that are thermodynamically predicted and isotopically age dated to be among the first-formed solids in our solar system [1-5]. Observed in some CAIs are micron to sub-micron sized inclusions rich in Fe, Ni, and high-Z elements such as Pt, Os, Ir and W, in the form of refractory metal nuggets (RMNs), fremdlinges, and 'nugget like objects' (NLOs) [1,6]. Refractory siderophile elements such as Os, Ir and Ru are thermodynamically predicted to condense at temperatures well in excess of the major CAI phases such as melilite, perovskite, spinel and hibonite [2,7-9]. These refractory metal inclusions in CAIs can therefore serve as probes into the thermodynamic landscape of the early solar protoplanetary disk. Here we report on a refractory grain identified in a CAI of the Leoville CV3 chondrite. This work is part of an ongoing effort to gain insight into the thermochemistry of the early solar system through systematic analyses of the structure and chemistry of various components in CAIs [10-13].

Sample and Analytical Techniques: A fluffy type A CAI (Fig. 1A) was identified in a section of the Leoville, CV3 chondrite (Center for Meteorite Studies, Arizona State University collection, #821_C_3) using a JOEL-JXA 8530F electron microprobe at Arizona State University. Backscattered electron (BSE) imaging and energy-dispersive X-ray spectroscopy (EDS) were used to identify refractory metal grains in the CAI using 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.

We selected one of the larger (micron-sized) refractory metal grains, designated as 'Spud' (Fig. 1B) for further analysis. 'Spud' was extracted and thinned to electron transparency (<100 nm) using the FIB-SEM located in KMICF, following methods described by [14-15]. The FIB section was analyzed using a 200 keV Hitachi HF5000 scanning transmission electron microscope (S/TEM) located at KMICF. The HF5000 is equipped with cold-field emission gun, 3rd-order spherical aberration corrector for STEM imaging, and an Oxford Instruments X-Max N 100 TLE energy-dispersive spectroscopy (EDS) system with dual 100 mm^2 windowless silicon-drift detectors (Ω = 2.0 sr). Selected-area electron-diffraction (SAED) patterns were acquired to aid in determination of crystallinity and phase.



Results: The mineralogy, texture, and morphology of the CAI are consistent with that of a fluffy type A (FTA) CAI [16]. BSE imaging at high magnifications revealed grains with high contrast, indicative of compositions rich in elements of higher atomic number relative to surrounding material. These high-Z grains have sizes that range from ~250 nm to 4 µm. EDS analyses confirm that the bright grains are metal-rich inclusions. A minor fraction of the grains are composed of only Fe and Ni, but the majority (~60%) of the identified inclusions also contained various refractory siderophiles including Os, Ru, Zr, Ir and Mo. EDS analysis on the FIB-SEM of Spud shows that it contains Fe, Ni, Mo and Ru.

High-angle annular dark-field (HAAFD) imaging and EDS mapping in the TEM (Fig. 2) show that Spud occurs in melilite ($Ca_{1.9}Al_{1.99}Si_{1.06}O_7$). Spud contains a subhedral to anhedral morphology and is compositionally heterogenous (polyphasic, Fig. 2). Local spatial correlation occurs among Fe, Ni, and Pt, and also among Os, Ru, and Mo. SAED patterns show that the Fe-Ni-Pt, Fe-Os-Mo-Ru and Fe-Pt regions are crystalline.

Discussion: CAIs can contain various types of inclusions rich in Fe, Ni and refractory siderophiles such as Os, Ru, W and Pt [1]. RMNs are micron-sized, single-phase alloy grains and can contain Os, Ir, Ru and Rh [1,7,17]. NLOs are also micron-sized inclusions, but contain two phases, a refractory metal, and an oxide [6]. Fremdlinge are the largest of such inclusions (tens of microns in size) and are complex aggregates of Fe-Ni alloy, silicates, oxides, and sulfides [1,17]. While the size of Spud matches previous descriptions of RMNs and NLOs, Spud is neither a single-phase alloy like RMNs, nor does it contain one metal phase and one oxide like NLOs. Spud does not match the above described categories of refractory metal inclusions.

The presence of refractory siderophiles such as Mo, Os, Ru, and Pt suggests a high-temperature origin. Thermodynamic modelling by [7] indicates condensation temperatures of 1917 K, 1693 K, 1613 K and 1415 K for Os, Mo, Ru and Pt respectively. These models also show that following the initial condensation of a refractory metal, alloying of solutes such as Fe, Ni and W, occurs in levels proportional to their partial pressures in the surrounding gas. Such alloying occurs at temperatures above the condensation temperatures of common CAI phases such as melilite (1529 K), perovskite (1441 K), spinel (197 K) and forsterite (1354 K) [2]. The polyphasic nature of Spud could be the result of such high-temperature alloying, possibly shortly after the condensation of Mo and Ru at 1693 K and 1613 K respectively. That Spud occurs as an inclusion is consistent with it having formed prior to and at temperature above that of its host melilite in this FTA CAI, which is qualitatively consistent with such prior thermodynamic modeling. Further, the polyphasic nature of Spud is similar to refractory grains from a FTA CAI in the Northwest Africa (NWA) 8323, CV3 chondrite [11-13]. These data suggest that such refractory metal grains could have been widespread in the inner and early solar protoplanetary disk and represent some of the earliest formed solids to have condensed.

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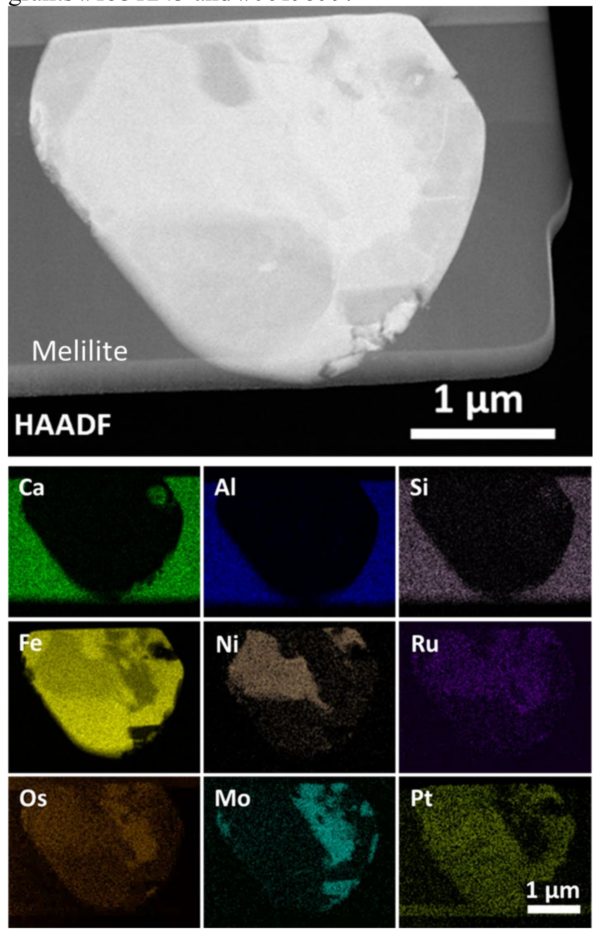

Fig 2. STEM data on ‘Spud’. HAADF Image (Top) False-color EDS Maps (Bottom)

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