INVESTIGATIONS INTO THE FORMATION MECHANISMS OF CM HIBONITES AT THE MICRO- TO NANOSCALE USING THE SEM AND TEM L. Kööp[1,2,4], A. M. Davis[1,2,3,4], S. S. Rout[2,4], K. L. Villalon[1,2,4], and P. R. Heck[1,2,4], [1]Department of the Geophysical Sciences, [2]Chicago Center for Cosmochemistry, [3]Enrico Fermi Institute, University of Chicago, Chicago, IL, [4]Robert A. Pritzker Center for Meteoritics and Polar Studies, Field Museum of Natural History, Chicago, IL (E-mail: koeoep@uchicago.edu)

Introduction: Hibonite (Hib)-rich CAIs from CM chondrites such as PLACs (platy hibonite crystals), SHIBs (spinel-hibonite inclusions), and fractionated Hib-rich objects show a remarkable variety of isotopic properties [1,2], indicating that they record snapshots of the isotopic homogenization of the early solar nebula. For example, PLACs and related Hib-rich CAIs are ^{26}Al-depleted and show a large range of nucleosynthetic anomalies (>100‰) [1,2]. In contrast, SHIBs and highly fractionated Hib-rich CM CAIs show a range of inferred ^{26}Al/^{27}Al ratios (0–supracanonical), with smaller nucleosynthetic anomalies than in PLACs [1,2,3].

Contrary to many other types of CAIs, there is a fairly good relationship between the isotopic character and petrologic features of Hib-rich CAIs [e.g., 1]. For example, (1) PLACs rarely contain spinel (Sp) and (2) the MgO and TiO_2 abundances are more restricted and on average lower in PLACs than in SHIB Hibs. While these petrological differences are likely indicative of different formation conditions, the formation processes of Hib-rich CAIs have remained controversial. In particular, both melt [4] and direct condensation [5] origins have been considered for PLACs. The nature of their formation mechanism(s) is an important consideration for the interpretation of isotopic data, as it could help distinguish between mass-dependent and nucleosynthetic variations (e.g., for O isotopes [6]).

Taking advantage of an isotopically well-characterized set of Hib-rich CM CAIs [e.g., 3,6–8], we have started to investigate the structure and chemistry of these CAIs on a finer scale. Our goal is to evaluate if distinct petrologic differences exist that might help to identify the formation mechanism(s) of these CAIs. Here, we present initial results for a PLAC and a SHIB.

Samples and methods: CAI 2-7-1 is a PLAC and appears as a single crystal of Hib in the polished section (Fig. 1a). It was chosen for this study because of its margin, which consists of Sp and perovskite (Pv; Fig. 1a). FeO-rich silicate material is present along one edge of the CAI (likely matrix or an altered rim; Fig. 1a). This CAI has no resolvable radiogenic ^{26}Mg excess, and no resolvable anomalies in Ti or Ca isotopes [7,8].

CAI 1-9-5 (Fig. 1b) is a SHIB with a Δ^{17}O value of ~–23‰, with no significant displacement from the CCAM line [6]. It was chosen for this study because it contains multiple refractory metal nuggets (RMNs; compositions were presented in [9]).

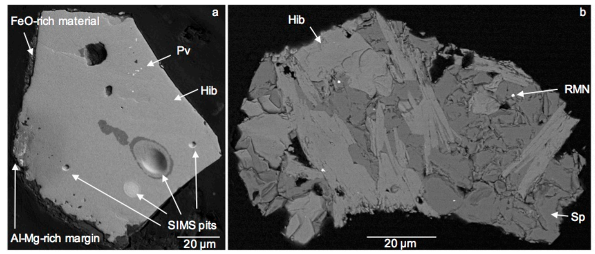

Figure 1. BSE images of PLAC 2-7-1 (a) and SHIB 1-9-5 (b).

Both CAIs were separated from the Murchison meteorite (2-7-1 from ME 2644, 1-9-5 from ME 2752, both from the Field Museum collection) by freeze-thaw disaggregation and density separation. ME 2752 was also treated with HF-HCl. The CAIs were mounted in epoxy and polished. The scanning electron microscopy (SEM) and focused ion beam (FIB) work presented here was performed with a JEOL JSM-5800LV SEM and a Tescan LYRA3 FIB-SEM at the University of Chicago, the latter is equipped with Oxford Nordlys-Max^2 electron backscatter diffraction (EBSD) and Oxford XMax energy-dispersive x-ray spectroscopy (EDS) detectors. In addition to EBSD, which was performed at a 70° sample tilt angle, the system allows transmission Kikuchi diffraction (TKD), which was performed at a 20° tilt.

Electron transparent lamellae were extracted from both samples by FIB lift-out. For 2-7-1, a protective layer of Pt was deposited prior to lift-out, and the lamella was attached to a copper grid using Pt. The lamella extracted from 1-9-5 was attached to a copper grid using C to avoid Pt contamination of the RMNs. Both lamellae were thinned to electron transparency using a 30 keV Ga^+ beam and final polishing was done with a 2 keV Ga^+ beam. The lamella of 1-9-5 was imaged with a 300 kV FEI Tecnai F30 G2 transmission electron microscope (TEM) at the University of Chicago.

Results and discussion: *2-7-1:* Figure 2a shows that the margin of 2-7-1 consists of Sp (confirmed by EBSD on polished mount and by TKD on the extracted lamella), which is pervaded by interwoven bands of submicron-sized Pv (confirmed by TKD on the extracted lamella). An EBSD map obtained on the polished mount shows the same orientation for Sp in this region. The boundary between Hib and the Sp is irregular (Fig. 2a) and the lamella reveals that the depth of the Sp-Pv assemblage is shallow (<1 µm; Fig. 2b). Below the assemblage is more Hib, followed by FeO-rich silicate material that is similar to the material that is exposed at a different location in the polished mount (Fig. 1a). The silicate extends into the CAI, possibly along a grain boundary or cleavage plane.

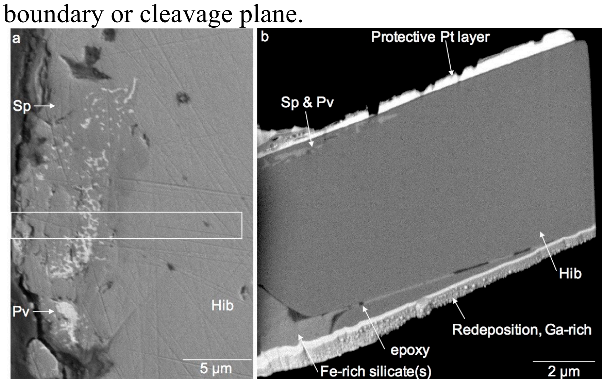

Figure 2. BSE images of the Sp- and Pv-bearing margin of PLAC 2-7-1 (a) and the lamella lifted out of 2-7-1 (b). The white box in (a) indicates the area that the lamella was lifted out from. The lamella is tilted relative to the post of the grid due to a problem with the gas injection system.

The Sp-Pv assemblage at the margin of this PLAC is of interest because it could be a result of high-temperature gas-solid reactions between Hib and the cooling solar nebula gas. Condensing Mg may have reacted with Hib to form Sp (taking up Al), while Pv formed to accommodate the other abundant cations not taken up by spinel, i.e., Ca and Ti. The interwoven texture of Pv and Sp may support such a scenario. A reaction between Hib and the gas was also favored by [10] for the origin of Sp-Hib-bearing CAIs from a CO chondrite, but Pv grains in these CAIs are usually larger and not part of a pervasive network as observed here. If 2-7-1 is a condensate, the lack of resolvable anomalies in Ca and Ti in this ^{26}Al-depleted CAI may indicate that isotopic anomalies were efficiently homogenized in the gas phase before condensates formed.

1-9-5: The lamella lifted out of SHIB 1-9-5 contains multiple Hib and Sp crystals as well as one RMN enclosed within a single Sp crystal (Fig. 3a). Sp crystals are anhedral, with rounded Sp-Sp boundaries. Bright-field TEM images of the Hib grains in 1-9-5 commonly show straight lines parallel to the elongation direction of the crystals (Fig. 3b), which could be the result of lattice stacking faults as observed by [10]. The diameter of the RMN is ~300 nm (Fig. 3c), but it was larger before final thinning of the lamella. EDS analyses of this RMN (in wt%: Mo 20, Ru 18, Os 17, Ir 14, Pt 12, Fe 8, Rh 4, W 3, Re 3, Ni 1) are within the typical range of RMNs in SHIBs [9]. TKD shows that the studied RMN has a hexagonal structure (Space Group P6_3/mmc). The RMN does not appear uniform in bright-field (Fig. 3c); instead, it shows small dark areas towards the edge of the RMN. At this point, it is not clear whether this is a preparation artifact or a result of chemical heterogeneity within the RMN.

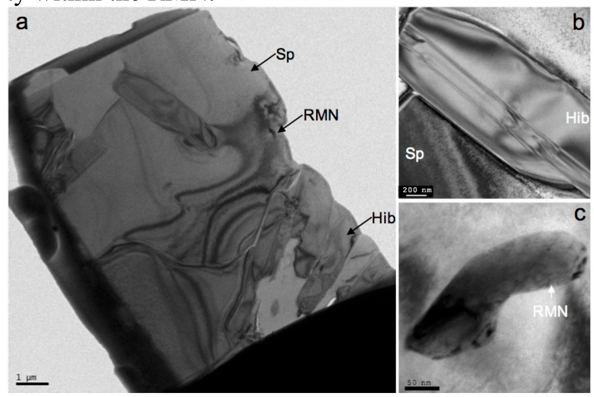

Figure 3. TEM bright-field images of the lamella from SHIB 1-9-5. a) Overview. b) Magnification of a hibonite grain. c) The RMN, set within a Sp grain.

Conclusion and outlook: The relationship between Hib, Sp and Pv in PLAC 2-7-1 may be indicative of a gas-solid reaction between Hib and the cooling solar nebula gas. Further TEM work is planned to look for traces of melilite, which is expected to occur before Sp during equilibrium condensation and could be present on the TEM scale as observed for CO CAIs by [10].

A condensation origin of 2-7-1 could support a scenario in which condensate CAIs are isotopically homogenized due to efficient mixing in the gas phase. However, additional work is needed, for example, to evaluate whether condensation features are absent in isotopically anomalous PLACs.

The hexagonal structure inferred from TKD for the RMN in SHIB 1-9-5 is in agreement with the structure of RMNs inferred by TEM [11]. This suggests that TKD is a useful tool for microstructural investigations of RMNs. We plan to apply TKD to other RMNs, especially from mass-fractionated Hibs, which have refractory compositions but are devoid of Mo and W [9].

We further plan to extend the study of the lamella lifted out of SHIB 1-9-5. The presence of RMNs in this CAI may indicate that it formed by melting [9], making it suitable for comparing and contrasting it to possible gas-solid condensate Hibs.

References: [1] Ireland T. (1990) *GCA, 54*, 3219-3237. [2] Liu M.-C. et al. (2009) *GCA, 73*, 5051–5079. [3] Kööp L. et al. (2015) *LPI Contrib. 1832,* #2750. [4] Ireland T. et al. (1988) *GCA, 52*, 2841-2854. [5] Hinton et al. (1987) *ApJ, 312*, 420–428. [6] Kööp L. et al. (2014) *LPI Contrib., 1777,* #2508. [7] Kööp L. et al. (2014) *LPI Contrib., 1800,* #5384. [8] Kööp L. et al. (2015) *LPI Contrib., 1856,* #5225. [9] Schwander D. et al. (2015) *GCA, 168*, 70–87. [10] Han J. et al. (2015) *MAPS, 50*, 2121–2136. [11] Harries D. et al. (2012) *MAPS, 47,* 2148–2159.