

**HIBONITE AND ITS ASSOCIATED ULTRAREFRACTORY PHASES FROM THE PARIS CM CHONDRITE.** J. Han<sup>1,2,3</sup> and L. P. Keller<sup>2</sup>, <sup>1</sup>Lunar and Planetary Institute, USRA, 3600 Bay Area Boulevard, Houston, TX 77058, USA (han@lpi.usra.edu), <sup>2</sup>ARES, Code XI3, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA, <sup>3</sup>Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204, USA.

**Introduction:** A comprehensive mineralogical and oxygen isotopic study of ultrarefractory (UR) Ca-Al-rich inclusions (CAIs) in carbonaceous chondrites was reported in [1]. The mineralogy of these CAIs is dominated by Zr-, Sc-, Ti-, and/or Y-rich oxides and silicates, and often contain refractory metal nuggets (RMNs). These CAIs occur as isolated inclusions or constituents inside CAIs and chondrules. UR CAIs likely formed by various high-temperature processes, such as condensation, melting, evaporation, and aggregation in a <sup>16</sup>O-rich gaseous reservoir [1].

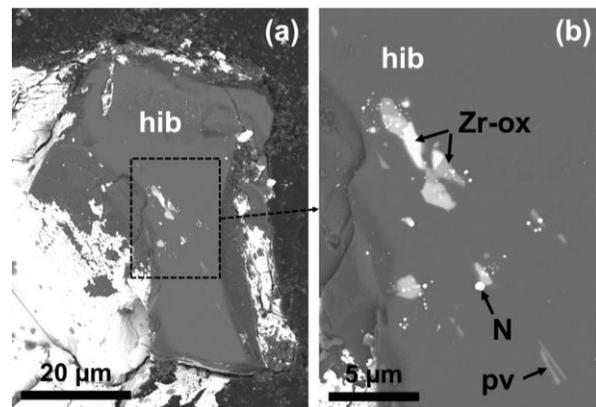
As part of our microstructural analyses of hibonite samples from CM chondrites, we studied a hibonite crystal from the Paris CM chondrite that includes an assemblage of Zr-bearing perovskite, Zr-rich oxide, and RMNs [2]. Here, we report the preliminary TEM studies of hibonite and its inclusions of UR oxides and RMNs. Our goals were to determine the microstructure, chemistry, and crystallography of these UR phases and provide constraints on their formation conditions in the solar nebula.

**Methods:** Following the isotopic studies of the Paris hibonite samples by [3], the mount was re-polished and we conducted petrological and mineralogical characterization of the hibonite samples using JEOL 7600F SEM and JEOL JXA-8530F electron microprobe. Two FIB sections from one hibonite crystal Pmt1-15 were prepared using a FEI Quanta 3D field emission gun SEM/FIB. The sections were examined using a JEOL 2500SE field emission scanning TEM equipped with a Thermo-Noran thin window EDX spectrometer.

**Results and Discussion:** Pmt1-15 is a fragment of a single hibonite crystal with inclusions of Zr-bearing perovskite and RMNs (**Fig. 1**). The different BSE contrast suggests the presence of other Zr-rich oxide phase attached to the perovskite. Clusters of sub-micrometer, rounded RMNs are concentrated near or within these assemblages. Some perovskite crystals are elongated parallel to the elongation direction of the host hibonite. Although no spinel is observed from this study, Pmt1-15 was originally classified as SHIB by [3].

Electron microprobe data show that Pmt1-15 contains 0.58-0.84 wt% TiO<sub>2</sub> and 1.2-1.8 wt% MgO. However, these ranges represent the lowest end reported from SHIBs, but show greater overlap with those measured from PLACs [4-7]. The <sup>26</sup>Mg\* excess of this

hibonite is marginally resolved, with  $\Delta^{26}\text{Mg}^* = 0.31 (\pm 0.37) \text{‰}$  and  $(^{26}\text{Al}/^{27}\text{Al})_0 = 1.54 (\pm 1.84) \times 10^{-5}$ . It is isotopically light, with  $\delta^{25}\text{Mg} = -2.55 (\pm 0.15) \text{‰}$  [3]. While PLACs lack resolvable excesses of radiogenic <sup>26</sup>Mg\*, SHIBs show a spread in <sup>26</sup>Mg\* excesses and <sup>26</sup>Al/<sup>27</sup>Al ratios [3-7]. These chemical and isotopic characteristics suggest that Pmt1-15 may be a PLAC that likely formed by condensation [3-7].



**Figure 1.** BSE images of a hibonite crystal Pmt1-15 from Paris (CM). The white material in (a) is the gold coating residue. Abbreviations: hib = hibonite; pv = perovskite, Zr-ox = Zr-rich oxide, N = RMNs.

Our TEM observations show that the hibonite crystal Pmt1-15 is essentially free of defects and displays a uniform 2.2 nm (001) spacing in lattice fringe images, consistent with well-ordered, stoichiometric hibonite crystal.

Zr-bearing perovskite in Pmt1-15 shows two different occurrences. First, perovskite nanoparticles (<300 nm in size) occur along hibonite grain boundaries (**Fig. 2a**). Some nanoparticles are elongated normal to the *c*\* axis of hibonite and have a crystallographic orientation relationship with hibonite, such that  $[100]_{\text{hibonite}}/[100]_{\text{perovskite}}$  and  $(001)_{\text{hibonite}}/(011)_{\text{perovskite}}$ . However, other perovskite grains elongated along the *c*\* axis of hibonite are not in a crystallographic continuity with hibonite. Second, elongated perovskite laths (up to ~500 nm in width) occur within hibonite crystals and along hibonite grain boundaries (**Fig. 2b**). They are typically elongated normal to the *c*\* axis of hibonite and have a crystallographic orientation relationship with hibonite, such that  $[100]_{\text{hibonite}}/[100]_{\text{perovskite}}$  and

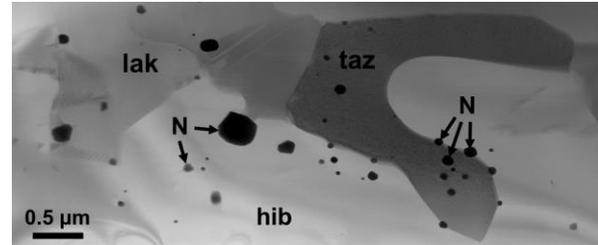
$(001)_{\text{hibonite}}// (011)_{\text{perovskite}}$  (Fig. 2c). We infer that these perovskite grains nucleated and epitaxially grew simultaneously with hibonite. A similar crystallographic orientation relationship between hibonite and perovskite was observed in the Allende FUN CAI SHAL [8], where numerous Zr- and Y-bearing perovskite platelets were observed as epitaxial intergrowths within hibonite. These observations signify the importance of a strong kinetic control on the UR solid formation in high-temperature environments of the early solar nebula.

In addition to perovskite, an assemblage of lakargiite  $\text{Ca}(\text{ZrTi})\text{O}_3$  and tazheranite  $(\text{ZrTiCaYSc})\text{O}_{2-x}$  was also observed in hibonite (Fig. 3). Both grains are highly irregularly-shaped. Lakargiite is twinned and shows strong pseudo-cubic [010] reflections that originate by a mirror operation across (121) in the [101] direction [9], similar to the common twinning operation in perovskite that cools from high temperatures through the cubic-orthorhombic phase transition [10].

Numerous RMNs (up to 400 nm in size) occur as isolated metal alloys in hibonite, lakargiite, and tazheranite (Fig. 3). They are compositionally homogenous and contain 72-80 wt% Os, 8-11 wt% W, 8-15 wt% Ir, 2-4 wt% Mo, and  $\leq 0.4$  wt% Fe. These compositions are very Os-rich, compared to RMNs reported previously from CAIs in carbonaceous chondrites that contain  $< 55$  wt% Os [11]. Because Os condenses at higher temperatures than any other refractory siderophile elements, except for Re [12], the RMNs in Pmt1-15 represent the highest temperature ( $> 1600$  K at  $10^{-4}$  bar) component that served as the nucleation sites for the other UR phases.

**Conclusions:** Our preliminary TEM observations reveal that the hibonite crystal Pmt1-15 contains the UR mineral assemblages of Zr-bearing perovskite,

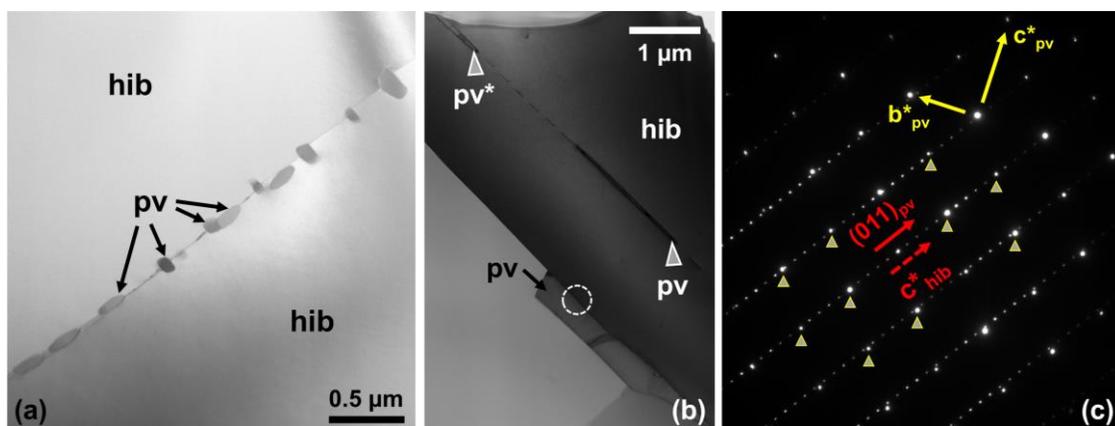
lakargiite, tazheranite, and Os-Ir-W-Mo alloy. We conclude that this hibonite sample represent the highest temperature component that formed in the early solar nebula, where kinetic effects, as well as thermodynamic stabilities, were important.



**Figure 3.** BF-STEM image of lakargiite and tazheranite as highly irregularly-shaped grains enclosed in hibonite. Numerous RMNs are observed, as black grains in this image. Abbreviations: hib = hibonite; lak = lakargiite; taz = tazheranite; N = RMNs.

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**References:** [1] Krot A. N. et al. (2019) *Geochemistry* 79, 125519. [2] Han J. et al. (2017) *MetSoc*, abstract #6380. [3] Liu M.-C. et al. (2012) *EPSL* 327-328, 75-83. [4] Ireland T. R. (1988) *GCA* 52, 2827-2839. [5] Ireland T. R. (1990) *GCA* 54, 3219-3237. [6] Kööp L. et al. (2016) *GCA* 184, 151-172. [7] Kööp L. et al. (2016) *GCA* 189, 70-95. [8] Keller L. P. et al. (2012) *MetSoc*, abstract #5313. [9] Galuskin E. V. et al. (2008) *Am Min* 93, 1903-1910. [10] Keller L. P. and Buseck P. R. (1994) *Am Min* 79, 73-79. [11] Schwander D. et al. (2015) *GCA* 168, 70-87. [12] Berg T. et al. (2009) *Astro J* 702, L172-L176.



**Figure 2.** (a, b) BF-STEM images of two occurrences of perovskite in Pmt1-15. (c) Diffraction patterns obtained from the circled area in (b), indexing as  $[100]_{\text{hibonite}}//[100]_{\text{perovskite}}$  and  $(001)_{\text{hibonite}}/(011)_{\text{perovskite}}$ . Abbreviations: hib = hibonite; pv = perovskite.