

EXPERIMENTAL INSIGHTS INTO THE ORIGIN OF DEFECT-STRUCTURED HIBONITES FOUND IN METEORITES.

J. Han^{1,2}, L. P. Keller², and L. R. Danielson³, ¹Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, USA (jangmi.han@nasa.gov), ²ARES, Code XI3, NASA/JSC, Houston, TX 77058, USA, ³Jacobs JETS, NASA/JSC, Houston, TX 77058, USA.

Introduction: Hibonite ($\text{CaAl}_{12}\text{O}_{19}$) is a primary, highly refractory phase occurring in many Ca-Al-rich inclusions (CAIs) [1]. Previous microstructural studies of hibonite in CAIs and their Wark-Lovering (WL) rims showed the presence of numerous stacking defects in hibonites [2-6]. These defects are interpreted as the modification of the stacking sequences of spinel and Ca-containing blocks within the ideal hexagonal hibonite structure due to the presence of wider spinel blocks [3], as shown by experimental studies of reaction-sintered compounds in the CaO- Al_2O_3 system [7]. We performed a series of experiments in the CaO- Al_2O_3 -MgO system in order to provide additional insights into the formation processes and conditions of defect-structured hibonites found in meteorites.

Methods: Two experiments were prepared by reacting pure alumina crucibles with (1) 2CaO- Al_2O_3 eutectic melt and (2) 2CaO- Al_2O_3 eutectic melt with 5 wt% MgO in a high-temperature box furnace at 1,530°C for 4 hours, followed by air quenching [8]. A new experiment (3) was conducted using the same components, but was held at 1,530°C for ~5 days before quenching. The run products were cut, mounted in epoxy, and polished for detailed petrologic and mineralogical descriptions using a JEOL 7600F SEM. We extracted TEM sections from hibonite in the run product using a FEI Quanta 3D field emission gun SEM/FIB. The sections were then examined for micro-to-nanometer scale structural and chemical characterization by a JEOL 2500SE field-emission scanning TEM equipped with a Thermo-Noran thin window EDX spectrometer.

Results: Experiment (3) produced a reaction zone similar to, but generally thicker than, that observed in the earlier experiments (1) and (2) [8]. Adjacent to the alumina is a thick hibonite layer (20-60 μm thick), followed by a grossite layer (10-40 μm thick), and finally a zone of krotite and quench melt. While in experiment (2) metastable Al-rich spinels with ~10-25 mol% excess Al_2O_3 occur with hibonite and at the hibonite-alumina and hibonite-grossite interfaces, no spinel intergrown with hibonite or in contact with the alumina is observed in experiment (3). Instead, abundant euhedral stoichiometric MgAl_2O_4 spinel crystals occur only as inclusions in grossite in experiment (3). The FIB section 3-1 contains compact intergrowths of randomly-oriented hibonite laths. Despite the longer heating duration in experiment (3) than in experiment (2), hibonite in both experiments showed similar features: i) streaking along the *c* axis in electron diffraction patterns, ii) the presence of abundant stacking faults parallel to the *c* axis, and iii) random variations in spacing of the lattice fringes along the *c* axis. Quantitative EDX analyses reveal that hibonite is nearly $\text{CaAl}_{12}\text{O}_{19}$ with MgO ≤ 0.2 wt%, but defect-rich areas in hibonite are enriched in MgO relative to defect-free, ordered areas in hibonite.

Discussion: Our preliminary experiments in the CaO- Al_2O_3 -MgO system produced hibonites that contain stacking defects and correlated compositional variations, similar to those observed in meteoritic hibonites [2-6]. These observations support the previous interpretations that the presence of stacking defects in meteoritic hibonites is the result of accommodation of wider spinel blocks into the hexagonal hibonite structure [3,7]. In contrast to Mg-free hibonites in experiment (1), Mg-bearing hibonites in both experiments (2) and (3) contain a much higher density of stacking defects. These observations indicate that the introduction of Mg stabilizes the formation of wider spinel blocks in hibonite due to the substitution of Mg with Al on two tetrahedral sites in the spinel blocks [9]. However, no discernible structural difference in hibonite between experiments (2) and (3) is observed, and a heating on the order of days appears insufficient to cause significant structural changes in hibonite. In addition, the difference in the heating duration between experiments (2) and (3) yielded an important difference in the occurrence and composition of spinel. The abundant $\text{Al}_{8/3}\text{O}_4$ - MgAl_2O_4 spinel solid solutions observed in experiment (2) formed metastably owing to high temperature and short reaction time of the experiment. The paucity of these conditions in the early solar nebula likely explains why aluminous spinel is extremely rare in CAIs [e.g.,10].

Conclusions: The observed structural and compositional similarities between synthetic and meteoritic hibonites suggest that defect-structured hibonites can also represent the products of crystallization from a high-temperature aluminous melt as an alternative mechanism to disequilibrium condensation favored by [3,11]. A FIB/TEM study of isotopically characterized CM hibonites [5,11] is underway.

Acknowledgements: This research was supported by NASA grant 14-EW14_2-0122 to LPK.

References: [1] MacPherson G. J. 2014. *Treatise on Geochemistry II* vol.1 pp.139-179. [2] Keller L. P. 1991. *AGU* 72:141. [3] Han J. et al. 2015. *MAPS* 50:2121-2136. [4] Han J. et al. 2015. *MAPS* 50:A153. [5] Kööp L. et al. 2016. Abstract #2005. 47th LPSC. [6] Needham et al. 2016. *GCA*, in press. [7] Schmid H. and De Jonghe L. C. 1983. *Philos. Mag. A* 48:287-297. [8] Han J. et al. 2016. Abstract #2848. 47th LPSC. [9] Doyle P. M. et al. 2014. *AM* 99:1369-1382. [10] Simon S. B. et al. 1994. *GCA* 58:1937-1949. [11] Liu et al. 2012. *EPSL* 327-328:75-83.