

COMPLEX INTERGROWTHS OF NON-STOICHIOMETRIC DEFECT-STRUCTURED HIBONITE AND Al-RICH SPINEL IN AN ALLENDE Ca-Al-RICH INCLUSION.

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Introduction: Hibonite is a primary ultra-refractory mineral occurring in many Ca-Al-rich inclusions (CAIs) [1] and is predicted to condense as the second major phase from a cooling gas of solar composition [2]. Our previous microstructural studies of hibonite in carbonaceous chondrites revealed its unique microstructures consisting of numerous defects that contain Mg-enriched, wider spinel blocks in stoichiometric hibonite [e.g., 3-5]. [6,7] demonstrated experimentally that defect-structured hibonites can grow easily in the presence of minor Mg and are kinetically more stable than equilibrium assemblages predicted by thermodynamic calculations [2]. However, a thermodynamic vs. structural stability of defect-structured hibonite relative to other early-condensed Al-rich phases such as corundum, grossite, and spinel remains poorly constrained. Here, we present the results of atomic resolution TEM imaging of hibonite in a compact Type A CAI in the Allende CV3 chondrite in order to better understand the crystal structure and chemistry of defect-structured hibonite and its associated Al-rich phases, especially non-stoichiometric, Al-rich spinel, in the context of the formation of first refractory solids in the early solar nebula.

Sample & Methods: In the Allende CAI, elongated hibonite crystals up to ~60 μm long are intergrown with spinel and minor perovskite as inclusions in a ground mass of coarse-grained melilite. The hibonite crystals show oscillatory zoning, readily shown by SEM BSE imaging and EDS mapping, with MgO and TiO₂ contents up to 3.2 wt% and 7.2 wt%, respectively. We prepared a FIB section from hibonite using a FEI Quanta 3D SEM/FIB at NASA JSC. The section was analyzed using a JEOL 2500SE scanning TEM at NASA JSC and a JEOL JEM-ARM300F Grand ARM TEM at JEOL.

Results & Discussion: Based on our initial analyses using the 2500SE STEM, the FIB section consists of two hibonite subgrains surrounded by spinel and melilite. The first hibonite crystal contains an Al-rich spinel inclusion (160 nm long and 20 nm wide), which shares the crystallographic orientation relationship with the host hibonite such that $[110]_{\text{hib}}//[011]_{\text{sp}}$ and $(001)_{\text{hib}}//(111)_{\text{sp}}$. The hibonite crystal is nearly defect-free, but the spinel inclusion is associated with a few defects along the (001) plane of the host hibonite that are extended up to ~1.5 μm from its top and bottom tips. In contrast, the second hibonite crystal contains a higher number of defects that show a range of (001) spacings. Most defects are developed across the entire crystal, but a few are terminated within the crystal.

Atomic resolution high angle annular dark-field images provide direct information about the spatial distribution of heavy atoms in hibonite, which allows us to determine the structure and chemistry of layers having a range of (001) spacings in comparison with stoichiometric hibonite and spinel. In the first hibonite crystal dominated by 1.1 nm wide (001) layers, the spinel inclusion is decorated by a single layer of 1.6 nm (001) spacing along its top, as well as stepwise layers of 2.0 nm (001) spacing extended from its bottom end. In the second hibonite crystal, isolated layers of 1.6 nm and rarely 2.5 nm (001) spacings are randomly intergrown within the prominent hibonite layers of 1.1 nm (001) spacing. The 1.6 nm wide (001) layers are commonly observed in hibonite from many CAIs [e.g., 3-5], but wider layers of 2.0 nm and 2.5 nm (001) spacings appear extremely rare.

Stoichiometric hibonite contains five Al sites (three octahedral M1, M4, and M5 sites, a trigonal bipyramidal M2 site, and a tetragonal M3 site) that are distributed within basic Ca-containing and spinel blocks [8]. The common 1.6 nm wide (001) layers are interpreted as forming wider spinel blocks in non-stoichiometric, Mg-enriched hibonite that contain twice as many M1 and M3 sites and 50% more M5 sites compared to stoichiometric hibonite having 1.1 nm (001) spacing [5,9]. The 2.0 nm and 2.5 nm wide (001) layers lack Ca-containing blocks and are therefore interpreted as distinct lamellae of Al-rich spinel up to 6 unit cells that formed contemporaneously and are intergrown with hibonite.

The defect-structured hibonite and Al-rich spinel intergrowths observed in this study imply that both of these phases were kinetically stable at high-temperatures, which conflicts with thermodynamic calculations showing essentially no stability of Al-rich spinel even in dust-enriched systems [10]. The metastability of such non-stoichiometric assemblages in which kinetics were important may have suppressed grossite and krotite formation, but enhanced the abundance of spinel in CAIs.

References: [1] MacPherson G. J. (2014) *Treatise on Geochemistry II* vol.1 pp.139-179. [2] Yoneda S. & Grossman L. (1995) *GCA* 59:3413-3444. [3] Han J. et al. (2015) *MAPS* 50:2121-2136. [4] Han J. et al. (2017) 80th MetSoc, abstract #6380. [5] Keller L. P. et al. (2018) 49th LPSC, abstract #2392. [6] Han J. et al. (2016) 79th MetSoc, abstract #6534 [7] Han J. et al. (2017) 48th LPSC, abstract #2895. [8] Nagashima M. et al. (2010) *Mineral Mag* 74:871-885. [9] Schmid H. & De Jonghe L. C. (1983) *Philos Mag A* 48:287-297. [10] Ebel D. S. et al. 77th MetSoc, abstract #5268.