

## **Atomic-scale structure and non-stoichiometry of meteoritic hibonite: A transmission electron microscope study**

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### **ABSTRACT**

Hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ) is a common refractory mineral in Ca-Al-rich inclusions (CAIs) in primitive meteorites. Transmission electron microscope (TEM) studies have identified enigmatic planar defects in different occurrences of hibonite in the Allende meteorite that give rise to strong streaking along  $c^*$  in electron diffraction patterns. Atomic resolution high-angle annular dark-field (HAADF) imaging and energy-dispersive X-ray (EDX) analyses were used to determine the nature and origin of these planar features. HAADF images of hibonite grains reveal lamellar intergrowths of common 1.6 nm spacing, and less commonly 2.0 and 2.5 nm spacings, interspersed in stoichiometric hibonite showing 1.1 nm (002) spacing. Stoichiometric hibonite consists of alternating Ca-containing (“R”) and spinel-structured (“S”) blocks stacked in a sequence RS. In contrast, the 1.6 nm layers result from a doubled S block such that the stacking sequence is RSS, while in the widest defect observed, the stacking sequence is RSSSS. These intergrowths are epitaxial and have coherent, low-strain boundaries with the host hibonite

Meteoritic hibonite shows common Ti and Mg substitution for Al in its structure. Atomic-resolution EDX maps of hibonite grains in the Allende CAI confirm the preferred site occupancy of Mg on tetragonal M3 sites in S blocks and of Ti on trigonal bipyramidal M2 and octahedral M4 sites in R blocks. Mg is highly concentrated, but Ti is absent in the planar defects where wider S blocks show Al-rich compositions compared to stoichiometric  $\text{MgAl}_2\text{O}_4$  spinel. Therefore, Mg likely played the major role in the formation and metastability of planar defects in hibonite. Electron energy loss spectroscopy data from the Ti  $L_{2,3}$  edge show the presence of mixed Ti oxidation states with ~15–20% of Ti as  $\text{Ti}^{3+}$  in hibonite, suggesting a direct substitution of  $\text{Ti}^{3+} \leftrightarrow \text{Al}^{3+}$  in hibonite. The remaining ~80–85% of Ti is present as  $\text{Ti}^{4+}$  and corresponding EDX analyses are consistent with the well-known coupled substitution  $2\text{Al}^{3+} \leftrightarrow \text{Ti}^{4+} + \text{Mg}^{2+}$  being the major mechanism for Ti and Mg substitution in hibonite.

The formation of planar defects in hibonite occurred during high-temperature nebular condensation or melting/crystallization processes. The occurrence of non-stoichiometric hibonite in the Allende CAI deviates from the mineral formation sequence predicted from equilibrium condensation models. Overall, our atomic resolution TEM observations signify non-equilibrium, kinetic-controlled crystal growth during the high-temperature formation of refractory solids in the early solar nebula.

**Keywords:** Hibonite, spinel, calcium-aluminum-rich inclusions, planar defect, transmission electron microscopy; Origins of our Solar System and Its Organic Compounds