

Atomic-scale characterization of the oxidation state of Ti in meteoritic hibonite: Implications for early solar system thermodynamics

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ABSTRACT

Calcium-aluminum-rich inclusions (CAIs) in chondritic meteorites are composed of refractory minerals thought to be the first solids to have formed in the solar nebula. Among them, hibonite, nominally $\text{CaAl}_{12}\text{O}_{19}$, holds particular interest because it can incorporate significant amounts of Ti into its crystal structure in both Ti^{3+} and Ti^{4+} oxidation states. The relative amounts of these cations that are incorporated reflect the redox conditions under which the grain formed or last equilibrated and their measurement can provide insight into the thermodynamic landscape of the early solar nebula. Here we develop a new method for the quantification of Ti oxidation states using electron energy-loss spectroscopy (EELS) in an aberration-corrected scanning transmission electron microscope (STEM) to apply it to hibonite.

Using a series of Ti-bearing oxides, we find that the onset intensity of the Ti $L_{2,3}$ edge decreases with increasing Ti-oxidation state, which is corroborated by simulated Ti-oxide spectra using first-principles density-functional theory. We test the relationship on a set of synthetic hibonite grains with known $\text{Ti}^{4+}/\Sigma\text{Ti}$ values and apply the developed method on a hibonite grain from a compact type A inclusion in the Northwest Africa (NWA) 5028 CR2 carbonaceous chondrite. The STEM-EELS data show that the chondritic hibonite grain is zoned with a $\text{Ti}^{4+}/\Sigma\text{Ti}$ ratio ranging from 0.78 ± 0.04 to 0.93 ± 0.04 over a scale of 100 nm between the core and edge of the grain, respectively. The Ti substitution sites are characterized by experimental and calculated high-angle annular-dark-field (HAADF) images and atomic-level EEL spectrum imaging. Simulated HAADF images reveal that Ti is distributed between the M2 and M4 sites while Mg sits on the M3 site. Quantitative energy-dispersive X-ray spectroscopy shows that this grain is also zoned in Al and Ti. The Mg distribution is not well correlated with that of Ti and $\text{Ti}^{4+}/\Sigma\text{Ti}$ at the nanoscale.

The spatial decoupling of the element composition and Ti-oxidation states suggests a multistage evolution for this hibonite grain. We hypothesize that Ti and Mg were incorporated into the structure during condensation at high temperature through multiple reactions. Transient heating, presumably in the solar nebula, adds complexity to the crystal chemistry and potentially redistributed Ti and Mg. Concurrently, the formation of oxygen vacancies as a result of a reducing gas, led to the reduction of Ti^{4+} to Ti^{3+} . The multiple defect reactions occurring in this single hibonite crystal preclude a simple relationship between the $\text{Ti}^{4+}/\Sigma\text{Ti}$ and the f_{O_2} of formation. However, moving forward, these measurements are fundamental inputs for modeling of the thermodynamic conditions under which hibonite formed in the early solar nebula.

Keywords: Hibonite, Ti oxidation state, STEM-EELS, chondrites, CAIs, thermodynamics, early solar system, atomic scale, DFT calculations