

Substitution of Ti³⁺ and Ti⁴⁺ in hibonite (CaAl₁₂O₁₉)

PATRICIA M. DOYLE^{1,2,†}, PAUL F. SCHOFIELD^{2,*}, ANDREW J. BERRY^{1,2,‡}, ANDREW M. WALKER^{3,§} AND KEVIN S. KNIGHT^{4,2}

¹Department of Earth Science and Engineering, Imperial College London, South Kensington SW7 2AZ, U.K.

²Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

³School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol BS8 1RJ, U.K.

⁴ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, U.K.

ABSTRACT

The structures of eight synthetic samples of hibonite, with variable Ti oxidation state and Ti concentration (2.4–15.9 wt% TiO₂) that span the range reported for natural hibonite found in meteorites, were determined by Rietveld refinements of neutron powder diffraction data. Ti³⁺ was found to exclusively occupy the octahedral face-sharing M4 site irrespective of the presence or absence of Ti⁴⁺. Ti⁴⁺ partitions between the trigonal bipyramidal M2 site and the M4 site. The ratio (Ti⁴⁺ on M2):(Ti⁴⁺ on M4) appears to be constant for all the samples, with an average of 0.18(2) irrespective of the concentrations of Ti³⁺ and Ti⁴⁺. These substitutional sites were shown to be the most stable configurations for Ti in hibonite from calculations using density functional theory, although the predicted preference of Ti⁴⁺ for M4 over M2 is not as strong as is observed. This is attributed to the different Ti contents of the experimental and calculated structures and suggests that the Ti site occupancies might change between these concentrations. Furthermore, it is shown that Ti has a preference to occupy neighboring M4 sites such that Ti-Ti interactions occur with stabilization energies of 83 kJ/mol for Ti³⁺-Ti³⁺ and at least 15 kJ/mol for Ti⁴⁺-Ti⁴⁺. Features in optical spectroscopy and electron spin resonance data from meteoritic and synthetic hibonites that have been used to infer Ti³⁺/Ti⁴⁺ are shown to actually derive from these Ti-Ti interactions. The amount of Ti⁴⁺ in hibonite can be determined from the unit-cell parameters if ΣTi is determined independently. Ti³⁺/Ti⁴⁺ in hibonite may record the oxygen fugacity (f_{O_2}) of the early solar nebula, however, the existence of Ti³⁺-Ti³⁺ and Ti⁴⁺-Ti⁴⁺ interactions and the potential for Ti⁴⁺-Ti³⁺ interactions need to be considered when interpreting spectroscopic data in terms of Ti valence state and f_{O_2} . Hibonite as a single-mineral oxybarometer must be used with caution due to the potential role of crystal chemistry (including Ti-Ti interactions) to stabilize Ti oxidation states independently of f_{O_2} .

Keywords: Hibonite, titanium substitution, site occupancy, CAI, neutron diffraction, density functional theory, oxygen fugacity