

The OH-stretching region in infrared spectra of the apatite OH-Cl binary system

ROBERT C. TACKER¹, JOHN RAKOVAN^{2,*}, DANIEL HARLOV^{3,4,5,†}, JOHN M. HUGHES⁶, AND SARAH B. CICHY^{3,7,8}

¹North Carolina Museum of Natural Sciences, 11 West Jones Street, Raleigh, North Carolina 27612, U.S.A.

²New Mexico Bureau of Geology and Mineral Resources, Socorro, New Mexico 87801, U.S.A.

³Deutsches GeoForschungsZentrum, Telegrafenberg, Potsdam 14473, Germany

⁴Faculty of Earth Resources, China University of Geosciences, 430074 Wuhan, China

⁵Department of Geology, University of Johannesburg, P.O. Box 524, Auckland Park, 2006, South Africa

⁶Department of Geology, University of Vermont, Burlington, Vermont 05401, U.S.A.

⁷Institute for Geosciences, University of Potsdam, 14476 Potsdam-Golm, Germany

⁸Bundesgesellschaft für Endlagerung mbH (BGE), Department Site Selection, Eschenstrasse 55, 31224 Peine, Germany

ABSTRACT

Polarized Fourier transform infrared (FTIR) microspectroscopy of the OH-stretching region of hydroxylapatite-chlorapatite solid solutions presents novel problems for the assignment of peaks to specific OH-Cl pairs. Crystal structure refinements of Hughes et al. (2016) identified new positions for column anions in synthetic mixed Cl-OH apatites, with three different column anion arrangements depending on composition. These structural refinements, combined with bond-valence calculations, allow for interpretation of the OH-stretching region.

A peak at 3574 cm⁻¹ is identified as that from end-member hydroxylapatite. A second major peak at 3548 cm⁻¹ is only found in mixed chlorapatite-hydroxylapatite solid solutions, as is a third peak at 3592 cm⁻¹. Both represent perturbations of the OH-stretching vibration as compared to hydroxylapatite, to lower and higher frequency, respectively. Both of the new peaks are the result of a Cl_b-OH sequence, with adjacent anions in crystallographically similar positions, both above or both below adjacent mirror planes. One configuration has the hydrogen atom pointed toward the chlorine atom. The second has the hydrogen of the OH group pointed away from the chlorine atom.

Both configurations present novel problems. The shift to lower wavenumber at 3548 cm⁻¹ is characteristic of hydrogen bonding in fluorapatite-hydroxylapatite mixtures, yet the distance between O(H) and Cl_b is too great to allow it. The shift of OH-stretching vibrations to lower wavenumber is produced through changes in polarization of intervening Cl-Ca2' (or Ca2) and Ca2(')-O3 bonds, which are affected by the presence of the large chlorine atom. Lowering the OH-stretching vibration mimics the expected effect of chlorine on a neighboring OH group in the apatite *c*-axis column, though without hydrogen bonding. The shift to higher wavenumbers, i.e., higher frequency at 3592 cm⁻¹, is the opposite of that expected for hydrogen bonding between column anions in the apatite mineral group. It is ascribed to the interaction between an adjacent Cl_b and the oxygen end of an adjacent OH dipole. This pairing places an oxygen and a chlorine atom in close proximity. Possible means of accommodation are discussed.

A ubiquitous peak at 3498 cm⁻¹ represents hydrogen bonding between an OH and the OH_a site, with an interoxygen distance of about 2.9 Å. Published modeling supports the hypothesis that the OH_a site is occupied by an O rather than an OH. However, no clear counterpart to this pairing is observed in crystal structure refinements for specimens lacking OH_a, although the infrared absorbance is present. The existence of oxyapatite is inferred from studies of plasma-sprayed biomaterials, but the crystallographic details of the substitution have remained elusive.

A minor shoulder at 3517 cm⁻¹ does not have a clear counterpart in the structural refinements. Sequences of three columnar anions (e.g., OH-Cl-OH or Cl-OH-OH) can be ruled out, but an unequivocal assignment awaits further research.

Keywords: Apatite, solid solution, FTIR, structure refinements, hydrogen bonding, oxyapatite