

Electron paramagnetic resonance spectroscopic study of carbonate-bearing fluorapatite: New defect centers and constraints on the incorporation of carbonate ions in apatites

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ABSTRACT

X-band electron paramagnetic resonance (EPR) spectra of gamma-irradiated crystals of carbonate-bearing fluorapatite from the Levant mine, Cornwall, England, revealed the presence of two previously characterized centers (i.e., an O⁻ defect and an O-□_F defect, where □_F represents a vacancy at the F site), a CO₂ radical, and a new oxygen-associated hole-like center in the anion column. The O-□_F center in carbonate-bearing fluorapatite is stable at room temperature, whereas in carbonate-free fluorapatite the stability of this radical is shifted to lower temperatures (<225 K). The CO₂ radical herewith first reported in carbonate-bearing fluorapatite is characterized by an axial symmetry at room temperature but a weakly orthorhombic symmetry at 77 K, similar to its counterpart in carbonate-bearing hydroxylapatite. This CO₂ radical most likely formed from Type A carbonate ions by the loss of an O atom and trapping of an electron during gamma irradiation. The single-crystal EPR spectra of the new hole-like center are characterized by the absence of any hyperfine interactions and a strongly orthorhombic symmetry. The spin Hamiltonian parameters of this new center suggest a structural model involving the trapping of a hole by a substitutional oxygen ion sandwiched between two fluorine ion vacancies in the anion column and strongly disturbed by vacancies at the neighboring Ca2 and O3 sites, suggesting a complex substitution of the type: □_FO²⁻□_F + □_{Ca2} + CO₃²⁻ → F⁻F⁻ + Ca²⁺ + PO₄³⁻.

Keywords: EPR spectroscopy, fluorapatite, CO₂ radical, new O⁻ center, carbonate ions