American Mineralogist, Volume 98, pages 1066–1069, 2013

LETTER

A carbonate-fluoride defect model for carbonate-rich fluorapatite

**HAOHAO YI,[1,*] ETIENNE BALAN,[1] CHRISTEL GERVAIS,[2] LOÏC SEGALEN,[3] FRANCK FAYON,[4]
DAMIEN ROCHE,[3] ALAIN PERSON,[3] GUILLAUME MORIN,[1] MAXIME GUILLAUMET,[1]
MARC BLANCHARD,[1] MICHELE LAZZERI,[1] AND FLORENCE BABONNEAU[2]**

[1]Institut de Minéralogie et Physique des Milieux Condensés (IMPMC), UMR CNRS 7590, UMR IRD 206, UPMC Université Paris 06,
4 place Jussieu, 75252 Paris, cedex 05 France
[2]Laboratoire de Chimie de la Matière Condensée de Paris, UPMC Université Paris 06 and CNRS, Collège de France, 11,
Place Marcelin Berthelot, 75005, Paris, France
[3]UPMC Université Paris 06, UMR 7193 ISTEP, Biominéralisations et Environnements Sédimentaires, 4 place Jussieu,
75252 Paris, cedex 05 France
[4]Conditions Extrêmes et Matériaux: Haute Température et Irradiation (CEMHTI), UPR 3079 CNRS, 1D Avenue de la Recherche Scientifique,
45071 Orléans cedex 2, France

ABSTRACT

We propose a microscopic model of the dominant carbonate for phosphate substitution in fluorapatite. A well-crystallized sedimentary fluorapatite sample containing ~2.3 ± 0.8 wt% of carbonate was investigated using Fourier transform infrared spectroscopy (FTIR) and ^{13}C and ^{19}F magic angle spinning nuclear magnetic resonance (MAS NMR). About 75% of the carbonate groups replace the phosphate group ("B-site"), whereas a lesser contribution from carbonate groups located in the structural channels ("A-site") is observed. Beside the dominant ^{19}F NMR signal of channel ions at ~–102 ppm, an additional signal corresponding to ~8% of fluoride ions is observed at –88 ppm. ^{19}F double quantum-single quantum (DQ-SQ) MAS NMR and ^{13}C{^{19}F} frequency-selective Rotational Echo DOuble Resonance (REDOR) experiments prove that this additional signal corresponds to isolated fluoride ions in the apatite structure, located in close proximity of substituted carbonate groups. Density functional theory (DFT) calculations allow us to propose a composite carbonate-fluoride tetrahedron defect model accounting for these experimental observations. The planar carbonate ion lies in the sloping face of the tetrahedron opposite a fluoride ion occupying the remaining vertex, together replacing the tetrahedral phosphate ion. This "francolite-type" defect leads to a diagnostic narrow IR absorption band at 864 cm^{-1} that could be used as a guide to, e.g., detect the incipient transformation of fossil bone and teeth samples.

Keywords: Apatite, NMR, first-principles calculation, carbonate, FTIR