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Synthesis and NMR characterization (^{1}H and ^{31}P MAS) of the fluorine-free hydroxylapatite–britholite-(Y) series

JULIETTE IMBACH,[1] FABRICE BRUNET,[2,*] THIBAULT CHARPENTIER,[1] AND JOSEPH VIRLET[1]

[1]Service de Chimie Moléculaire, CEA Saclay, F-91191 Gif sur Yvette, France
[2]Laboratoire de Géologie, UMR 8538 CNRS, Ecole normale supérieure, 24 rue Lhomond, F-75005 Paris, France

ABSTRACT

Apatites in a fluorine-free chemical system have been synthesized hydrothermally at 650 °C and 1.5 kbar along the hydroxylapatite–britholite-(Y) join [i.e., $Ca_{10}(PO_4)_6(OH)_2$ – $Ca_4Y_6(SiO_4)_6(OH)_2$ join], from oxide mixtures at nominal Si-contents of 0, 0.5, 1, 2, 3, 4, 5.5, and 6 pfu. The hexagonal apatite unit-cell volume decreases by 1.5% from the phosphate to the silicate end-member. A single ^{31}P MAS NMR resonance is recognized at 2.8 ppm in hydroxylapatite. An additional broad line centered around 1.5 ppm is present for Y-rich compositions. Although the ^{31}P MAS NMR spectra could not be fully assigned, the 2.8 ppm resonance that persists even in Si-rich compositions must include the contribution of P atoms involved in P-O-Y bonds. ^{1}H NMR spectroscopy shows that the H content decreases by around 50% from the phosphate to the silicate end-member although all the compounds were synthesized hydrothermally at 650 °C. In addition to the expected $YSiCa_{-1}P_{-1}$ substitution, a second substitution vector, $Y\square Ca_{-1}H_{-1}$, is inferred. It is proposed that the resulting proton vacancies influence neighbor H atoms to give rise to a ^{1}H line at 4.9 ppm. Beside the 4.9 ppm resonance, four other resonances at 0.2, 1.2, 1.5, and 2.0 ppm, are encountered along the series. In the apatite columns, OH groups are bonded to three cations from the Ca2 site and form $(Ca2)_3OH$ groups. In the proposed assignment model, the 0.2 ppm line, the only resonance present in the hydroxylapatite spectrum, is readily attributed to protons from $(Ca)_3OH$ groups. The 1.2 and 1.5 ppm resonances are assigned to $(Ca_2Y)OH$ groups whereas the 2.0 ppm line represents the contribution of protons from both $(CaY_2)OH$ and $(Y)_3OH$ groups.