Hydroxylapatite in few fossil bat-guano deposits from caves in Romania

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Hydroxylapatite, ideally $Ca_5(PO_4)_3(OH)$, is the most important phosphate species occurring in the guano-bearing caves world-wide. The aim of this paper is to document the physical properties, the infrared behavior and the crystallographic parameters of hydroxylapatite from fossil bat guano deposits in twelve caves from Romania. In all cases, the initial deposits, of both biogenic and authigenic origin, were chemically equilibrated during diagenesis. Individual crystals are tabular, roughly hexagonal, platy on (0001) and usually between 3 and 15 μm across and up to 1 μm thick. The mineral is in all cases Ca-deficient, carbonate- and sulfate-bearing. The Ca-deficiency is proved by a low sum of the six- and nine-fold coordinated cations (lower than 10 *apfu*), which is quite common in the case of the precipitated hydroxylapatite. Less than 3% of the phosphate groups are protonated and less than 5% are replaced by sulfate. The cumulative substitution by other cations in the Ca sites accounts for up to 5% of these (mean 2%). The mineral contains less Ba than Sr, which is quite normal in hydroxylapatite in the fossil bone. Both unit-cell parameters and thermal behavior are characteristic for a hydrous A-type carbonated hydroxylapatite, with molecular water and carbonate substituting for hydroxyl in the structural channels. The multiplicity of the bands in the infrared absorption spectrum ($3\nu_3 + 1\nu_1 + 3\nu_4 + 2\nu_2$) is consistent with a C_6 punctual symmetry of the phosphate anion. CO_3 bands in the infrared absorption spectrum ($\nu_3 \sim 1465$ cm^{-1}, $\nu_3' \sim 1430$ cm^{-1}, $\nu_2 \sim 875$ cm^{-1}) show that hydroxylapatite from all the analyzed caves is carbonate-bearing. The ν_3 antisymmetric stretching of the carbonate group is split in two fundamentals, which is due to the different structural positions occupied by carbonate in the structure. Generally, the obtained unit cell parameters differ from the data reported in literature for the synthetic hydroxylapatite, *a* being greater and *c* smaller than the reported values. Whitlockite, obtained by thermal breakdown at 1000°C, is sulfate-bearing.