

Stable isotope (C, O) and monovalent cation fractionation upon synthesis of carbonate-bearing hydroxyl apatite (CHAP) via calcite transformation

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Carbonate-bearing hydroxyl-apatite (CHAP) is of fundamental and applied interest to the (bio)geochemical, paleontological, medical and material science communities, since it forms the basic mineral phase in human and animal teeth and bones. In addition, it is found in non-biogenic phosphate deposits. The stable isotope and foreign element composition of biogenic CHAP is widely used to estimate the formation conditions. This requires careful experimental calibration under well-defined boundary conditions.

Within the DFG project EXCALIBOR, synthesis of carbonate-bearing hydroxyapatite was conducted via the transformation of synthetic calcite powder in aqueous solution as a function of time, pH, and temperature using batch-type experiments. The aqueous solution was analyzed for the carbon isotope composition of dissolved inorganic carbonate (gas irmMS), the oxygen isotope composition of water (LCRDS), and the cationic composition. The solid was characterized by powder X-ray diffraction, micro Raman and FTIR spectroscopy, SEM-EDX, elemental analysis (EA, ICP-OES) and gas irmMS.

Temperature was found to significantly impact the transformation rate of calcite to CHAP. Upon complete transformation, CHAP was found to contain up to 5% dwt carbonate, depending on the solution composition (e.g., pH), both incorporated on the A and B type position of the crystal lattice. The oxygen isotope fractionation between water and CHAP decreased with increasing temperature with a tentative slope shallower than those reported in the literature for apatite, calcite or aragonite. In addition, the presence of dissolved NH_4^+ , K^+ or Na^+ in aqueous solution led to partial incorporation into the CHAP lattice. How these distortions of the crystal lattice may impact stable isotope discrimination is subject of future investigations.