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Time-resolved in situ studies of apatite formation in aqueous solutions

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Abstract

Formation of hydroxylapatite through the precipitation and evolution of calcium phosphate precursor phases under varying conditions of temperature (25–90 °C), pH (6.5–9.0), and calcium to phosphorus ratio (1.0, 1.33, 1.5, and 1.67) comparable to those found in many sediments and soils were studied. The products of low-temperature precipitation were analyzed by ex situ X-ray diffraction and SEM, as well as time-resolved in situ synchrotron X-ray diffraction. Rietveld refinement was used for quantitative evaluation of relative abundances during phase evolution. The results of ex situ investigations conducted at ambient temperature and near-neutral pH indicate formation of amorphous calcium phosphate, which over the course of experiments transforms to brushite and ultimately hydroxylapatite. The results of in situ X-ray diffraction experiments suggest a more complex pathway of phase development under the same conditions. Some of the initially formed amorphous calcium phosphate and/or crystalline brushite transformed to octacalcium phosphate. In the later stage of the reactions, octacalcium phosphate transforms quite rapidly to hydroxylapatite. This is accompanied or followed by the transformation of the remaining brushite to monetite. Hydroxylapatite and monetite coexist in the sample throughout the remainder of the experiments. In contrast to the near-neutral pH experiments, the results from ex situ and in situ diffraction investigations performed at higher pH yield similar results. The precipitate formed in the initial stages in both types of experiments was identified as amorphous calcium phosphate, which over the course of the reaction quite rapidly transformed to hydroxylapatite without any apparent intermediate phases. This is the first application of time-resolved in situ synchrotron X-ray diffraction to precipitation reactions in the $Ca(OH)_2$-H_3PO_4-H_2O system. The results indicate that precursors are likely to occur during the natural or induced (e.g., with application of Ca+PO_4 amendments) formation of hydroxylapatite in many sedimentary environments.

Keywords: Calcium phosphates, precursor phases, hydroxylapatite, time-resolved in situ X-ray diffraction, synchrotron