

## **Modification of hydroxyapatite surface during the reaction of dissolution at various temperatures**

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Hydroxyapatite (HAP) is considered to be a stable mineral under surface Earth conditions and adopted as a proxy for paleo-environmental reconstructions. The solubility of this mineral, virtually the amount of a solid that can dissolve into a unit volume of solution is very low, with apparent pKs values ranging between 58 and 62. However apatite minerals are also assumed to be the major source of inorganic phosphorous in nature controlling the productivity of many ecosystems. Thus, a clearer description of the solubility properties for HAP can be gained by understanding the basic principals governing the solid-solution equilibrium. In this study, the reaction of HAP dissolution in pure water was investigated at 25, 50 and 70° C using batch reactors and the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy to analyze the evolution of the expose surface.

We found a constant non stoichiometric release of calcium and total phosphorus in all experiments while a different behavior of the dissolved species as a function of temperature. At 25°C, calcium and total phosphorous concentrations rapidly increase in the first stage reaching steady state after 7 days of reaction. At 50° and 70°C both calcium and total phosphorous rapidly increases reaching a maximum values decreasing then to reach steady state after 13 days of interaction.

Comparing the spectra of the pristine HAP surface to that after 7 days of reaction, we observed the presence of new peaks corresponding to the vibrations of the  $\text{HPO}_4^{2-}$  species attributed to the possible presence of calcium hydrogen phosphate ( $\text{CaHPO}_4$ ) formed on the surface. We propose that kinetics of the new layer formation is responsible for low values of the the apparent solubility of hydroxyapatite.