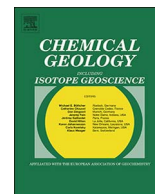




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Mineralogical transformation during hydroxyapatite dissolution in simple aqueous solutions

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ABSTRACT

Hydroxyapatite (HAP) is considered to be a stable mineral under surface Earth conditions and adopted as a proxy for paleo-environmental reconstructions and in choice of remediation strategies. A clear description of the solubility properties for HAP is fundamental and can be gained by understanding the basic principals governing the solid-solution interface.

In this study we investigated the early stage of HAP dissolution at 25°, 50° and 70 °C using solubility and ATR-FTIR spectroscopy measurements. We found a non-stoichiometric release of calcium and total phosphorus in solution in the experimental close to neutral pH conditions. The ATR-FTIR measurements revealed the presence of new peaks corresponding to the vibrations of HPO_4^{2-} group. Comparing HAP spectra of the pristine surface to those obtained after 7 days of hydration we propose the presence of monetite (CaHPO_4). This rapidly formed new phase would affect the observed low solubility of HAP and its presence could validate the use of this mineral in paleo-environmental reconstructions and ecological remediation strategies.

1. Introduction

Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is considered one of the less soluble calcium phosphate minerals found in nature (Filippelli, 2002; Adcock et al., 2013). Detailed knowledge of the mechanism controlling the stability of this mineral is fundamental in predicting phosphorus release and ecosystem regulation (Bengtsson et al., 2009) as well as in remediation strategies for polluted wastewaters (Valsami-Jones et al., 1998; Harouiya et al., 2007; Nzihou and Sharrock, 2010; Zhu et al., 2016). Besides the low solubility and enhanced radiation tolerance resulting from the structural flexibility (Jolley and Smith, 2016), hydroxyapatite is also a potential matrix for radioactive ion removal (Nishiyama et al., 2016) and for nuclear-waste storage under geological depository (Oelkers and Montel, 2008).

A number of studies focused on hydroxyapatite (HAP) solubility proposing controversial interpretations on the dissolution mechanisms (Kaufman and Kleinberg, 1979; Dorozhkin, 1997; Fulmer et al., 2002; Chairat et al., 2007a; Harouiya et al., 2007). Because of its low solubility, the dissolution kinetics of hydroxyapatite may be controlled by reactions occurring at the mineral surface (Berner, 1981) requiring the identification of active sites at the surface (Christoffersen et al., 1999). Several authors suggested that, during HAP dissolution, a proportion of

released ions could be 'readsorbed' to the mineral surface forming Ca-phosphate coatings (Mafe et al., 1992; Thomann et al., 1993; Bertazzo and Bertran, 2006; Bertran et al., 2006). The formation of coatings was also considered to be responsible for the difference in solubility between hydroxyapatite and fluoroapatite (Gray et al., 1962; Rootare et al., 1962; La Mer, 1962; Neuman and Bareham, 1975; Kaufman and Kleinberg, 1979; Larsen and Jensen, 1989; Bertazzo et al., 2010; Chairat et al., 2007b). In this work, we investigated the earlier stage of the hydroxyapatite dissolution: the evolution in solution composition was analyzed and the surface modifications were investigated by ATR-FTIR spectroscopy (Attenuated Total Reflectance Fourier Transform Infrared). To avoid the heterogeneity of the natural hydroxyapatites, we chose Prayon TCP308, a synthetic phosphate made industrially by a reproducible proprietary method which only contains calcium, phosphate and hydroxide ions.

2. Experimental methods

2.1. Solid preparation and characterization

As above mentioned, synthetic hydroxyapatite TCP308 (Prayon, Belgium), not thermally treated, was used in this study. The initial solid

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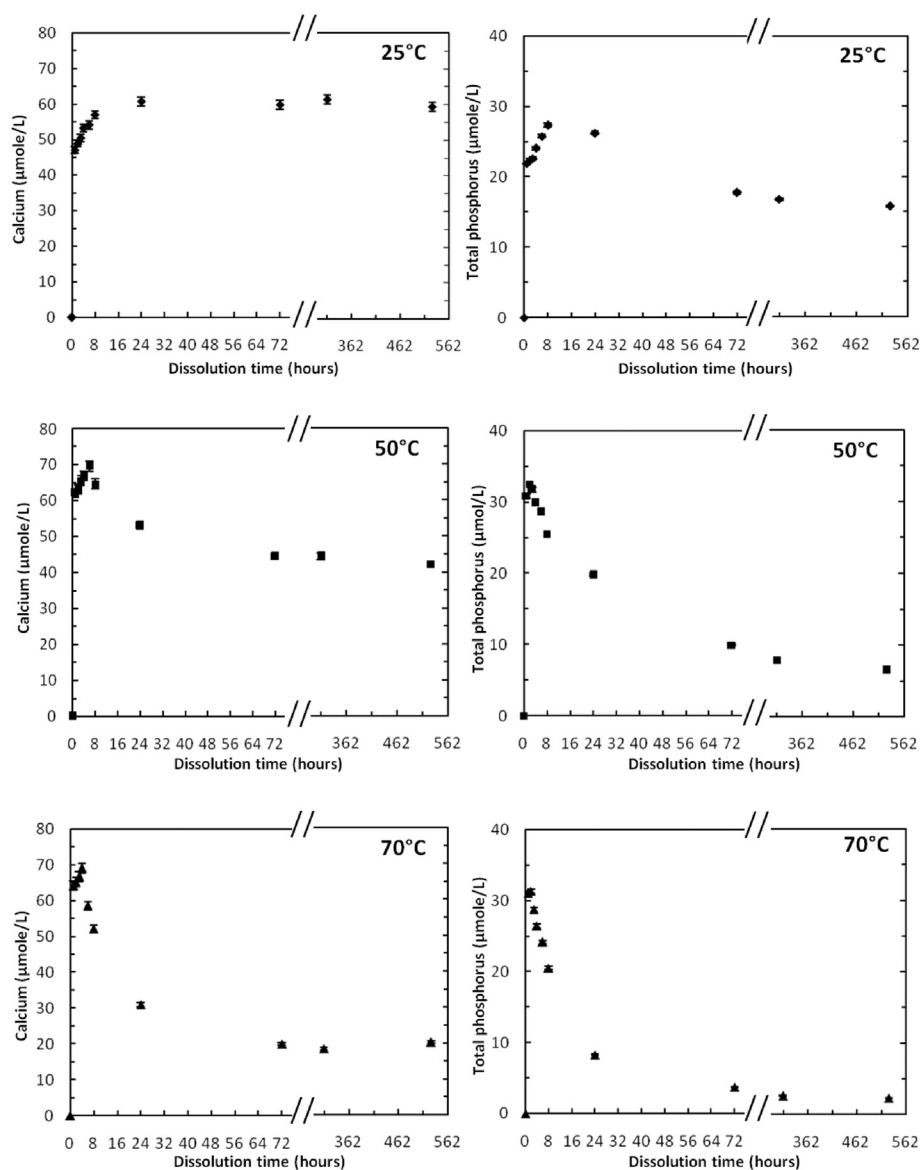


Fig. 1. Evolution of calcium and total phosphorus vs time at different temperature.

was analyzed by powder X-ray diffraction (XRD) with a Bruker D2 X'PertPRO diffractometer using Cu K α radiation (40 kV and 40 mA). The crystallographic identification of TCP308 was accomplished by comparing the experimental XRD pattern to card#9001233 of hydroxyapatite standard (Crystallography Open Database, COD). In our starting material we found in the typical 2θ regions only the characteristic peaks at 21–29°, 32–34°, 39–41°, 46–54° corresponding to hydroxyapatite phase (space group P6₃/m).

The grain morphology observed by scanning electron microscopy (SEM, Zeiss Supra 55VP) revealed the presence of well-formed euhedral grains with an average size between 200 and 800 nm. The specific surface area, determined by BET method (Micrometrics Gemini Vacprep 061) was 7 m²g⁻¹.

2.2. ATR-FTIR spectroscopy

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were obtained on a Nicolet Impact 410 FTIR. Spectra were recorded with a horizontal ATR accessory and a diamond crystal as the reflection element. All absorption spectra were obtained at 8 cm⁻¹ resolution covering the 4000–500 cm⁻¹ range and then subtracting a blank scan obtained without samples. OMNIC 8.1 (Thermo Fisher

Scientific Inc.) software analytical procedures were used to convert the spectra from ATR to transmittance and to perform additional analysis such as peak resolution. In order to identify calcium phosphate species present on the ATR-FTIR spectra, several species were considered: Ca (H₂PO₄)₂·H₂O bis (dihydrogenphosphate) monohydrate or MCPM monocalciumphosphate monohydrate (Sánchez-Enríquez and Reyes-Gasga, 2013); CaHPO₄ calcium hydrogenphosphate, or monetite (Petrov et al., 1967; Tortet et al., 1997; Hsu et al., 1998; Xu et al., 1999; Zavgorodniy et al., 2012); CaHPO₄·2H₂O, calcium hydrogenphosphate dihydrate, or brushite (Petrov et al., 1967); Ca₈(HPO₄)(PO₄)₅·5H₂O or octacalcium phosphate, OCP (LeGeros, 1985; Drouet, 2013); Ca_xH_y(PO₄)_z·nH₂O, $n = 3–4.5$, or amorphous calcium phosphate (ACP) (Gadaleta et al., 1996; Sinyaev et al., 2001); Ca_{10-x}(HPO₄)_y(PO₄)_{6-y} calcium deficient hydroxyapatite, or HA(HAP) (Domashevskaya et al., 2014).

2.3. Dissolution experiments and solution analysis

Dissolution experiments were carried out introducing 1 g of solid and 25 ml of deionized water into 50 ml polypropylene flasks. The flasks were agitated with a Memmert shaking water bath at the constant speed of 240 rpm for a time range between 1 h and 22 days at a

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