Thermal decomposition of brushite, CaHPO₄·2H₂O to monetite CaHPO₄ and the formation of an amorphous phase

ANJA DOSEN* AND ROSSMAN F. GIESE

Department of Geology, University at Buffalo, 411 Cooke Hall, Buffalo, New York 14260-3050, U.S.A.

ABSTRACT

Brushite, CaHPO₄·2H₂O, is a layered structure in which the layers are held together by water molecules via hydrogen bonds. Brushite loses its water molecules in two steps when heated, to form monetite CaHPO₄. The loss of water results in the formation of an amorphous phase along with monetite. We investigated the dehydration process primarily by means of X-ray diffraction, and quantified the amount of monetite and the amorphous phase as a function of heating rate and temperature via Rietveld refinements. Water loss was recorded by thermogravimetric analysis and the nature of the products was investigated by Fourier transform infrared spectroscopy. Recrystallization, water loss, and the formation of the amorphous phase depend on the heating rate and/or time of exposure at temperature. The conversion temperature is about 220 °C, although brushite can convert to monetite at lower temperatures during prolonged exposure to heat. More amorphous phase forms during slower dehydration at slower heating rates. The amorphous phase forms due to non-linear dehydration of brushite. The amorphous phase is hydrated and can be regarded as a highly disordered monetite with some free water trapped in the structure.

Keywords: Brushite (DCPD), Monetite (DCPA), thermal analysis, amorphous calcium phosphate (ACP), XRD, TGA

INTRODUCTION

In nature, brushite, CaHPO₄·2H₂O (dicalcium phosphate dihydrate, DCPD), forms in guano deposits in caves where it is associated with other phosphate minerals, along with quartz, gypsum, calcite, and other minerals (Dumitras et al. 2004). Brushite can be found in phosphorite deposits and is a by-product formed during the removal of phosphorus from wastewater (Valsamis-Jones 2001). Brushite is also a biologically relevant mineral (Mathew and Takagi 2001) and can form in renal stones (Guan et al. 2008). Along with hydroxyapatite, brushite is used as calcium phosphate cement and as a bone substitute material (Bohner and Gbureck 2008). Heating of brushite is required for the creation of luminescent materials (Berend and Hegedus 1975). Brushite is also used as a component of fertilizers, as a food additive, and as a component of toothpaste (Sainz-Diaz et al. 2004).

When heated, brushite loses structural water in two steps to form anhydrous monetite (dicalcium phosphate anhydrous DCPA), CaHPO₄. These two dehydration steps are complete between 200 and 220 °C, depending on the heating rate. A third dehydration step is the loss of the remaining proton attached to a phosphate group of monetite to form γ-Ca₃P₂O₇ (~350 °C). Heating to higher temperatures produces β-Ca₃P₂O₇ at 700 °C and finally at 1200 °C α-Ca₃P₂O₇ (Schofield et al. 2004). Berend and Hegedus (1975) reported the formation of several amorphous calcium phosphate (ACP) phases during dehydration of brushite to form monetite. They reported that brushite forms “XRD weak, partially amorphous monetite,” which dehydrates upon further heating into amorphous pyrophosphate and finally into γ-Ca₃P₂O₇. Additionally, they found two amorphous phases (Ca₃PO₄·0.75H₂O and Ca₃PO₄·H₂O) that form during the transformation of brushite to monetite. Berend and Hegedus (1975) recorded the diffraction data on film using a Guinier camera, and their report did not specify how the authors determined the presence and compositions of amorphous phases or the method of quantifying the amorphous phases present.

We are investigating the formation of an amorphous phase and monetite during the dehydration of brushite primarily by means of X-ray diffraction (XRD) correlated with the loss of water recorded by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The main goal of our research is to quantify the amount of an amorphous phase that forms during transformation of brushite to monetite during heating, and to attempt to describe the processes that drive its formation.

CRYSTAL STRUCTURE

Brushite (Fig. 1) crystallizes in the monoclinic crystal system with space group Ia, and unit-cell parameters a = 5.812, b = 15.180, c = 6.239 Å, and β = 116.42° (Mathew and Takagi 2001). The brushite structure was first determined and refined to a moderate accuracy by Beevers (1958) using single-crystal X-ray diffraction data. Further investigation by Curry and Jones (1971) showed the positions of hydrogen atoms. Schofield et al. (2004) determined the unit cell and atomic parameters under a range of temperatures during the dehydration of brushite.

Brushite has a layer structure and the layers are comprised of corrugated sheets of CaO₆ polyhedra and PO₄ tetrahedra. Six oxygen atoms from CaO₆ polyhedra are bound to phosphate groups and the remaining two belong to water molecules (Schofield et