FACHSTELLE SEKUNDÄR ROHSTOFFE

UNIVERSITÄT BERN

MSc	Simon Durni
Supervisor	PD Dr. Urs Mäder
	Dr. Urs Eggenberger
Projectpartner	RMS Foundation, 2544 Bettlach

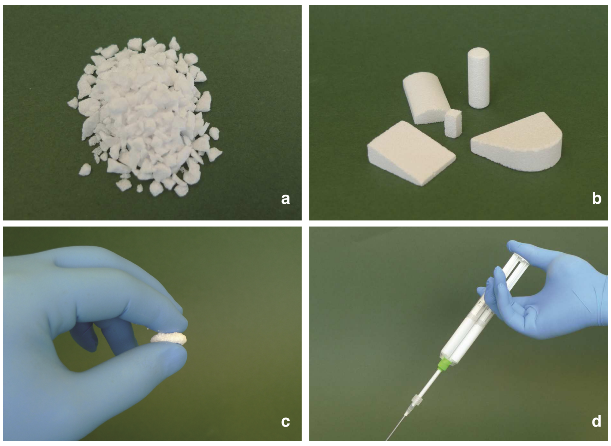
Solubility and Characterization of Monocalcium and Dicalcium Phosphates in the Context of Cementitious Biomaterials

Monocalcium phosphate monohydrate (MCPM) is a highly acidic and soluble synthetic mineral used in calcium phosphate bone cements. Its stability in aqueous solutions is limited to pH regions below 2. In a pH range of ~2-5, the dicalcium phosphates (DCP) brushite and monetite are the stable phases and limit calcium and phosphate concentrations in a solution.

The current study tried to deduce solubility products (K_{sp}) from dissolution and reequilibration experiments of MCPM powders immersed in water. MCPM dissolves and DCPs precipitate. With a higher MCPM/liquid ratio, more DCPs precipitate, the pH is lowered and ionic concentrations increase. The major goal was to approach the invariant singular point between MCPM and a DCP. With K_{sp} of DCPs from the literature, the program PHREEQC can model and deduce the K_{sp} value of MCPM. Since the ionic strength of a solution becomes higher with decreasing pH, the study also focused on the applicability of activity coefficient models on dilute and more concentrated solutions.

The experiments were done by characterizing three commercial MCPM powders and studying their behavior in degassed Milli-Q water with increasing MCPM/liquid ratio. Compositions of solutions equilibrated with a calcium phosphate were analyzed with ion chromatography. X-ray powder diffraction described the mineralogy of precipitates.

Results showed that the K_{sp} literature values of brushite and monetite had to be reconsidered and were adjusted to fit experimental observations. Brushite was the preferable precipitate at pH values above 2.8. Monetite was the main phase in more acidic solutions. Towards lower pH and higher ionic strengths, the transition from a metastable brushite to a stable monetite equilibrium occurred more rapidly. A singular point could not even be reached at a pH of 1.75 at which MCPM still dissolves. The comparison of theoretical models with experimental data revealed that the Truesdell and Jones activity coefficient model and the geochemical parameters implemented in PHREEQC can only predict the behavior of MCPM and DCPs in solutions with ionic strengths up to 700 mmol/kg of water and pH values down to 2.1. The model deviates from experimental results in more acidic solutions. Therefore, further studies need to be done to determine the parameters responsible for the observed deviations.



The four most common CaP bone graft substitutes
a) Granular bone void fillers
b) Solid pre-forms like blocks, wedges or cylinders
c) Putties or non-hardening pastes
d) Hardening cements

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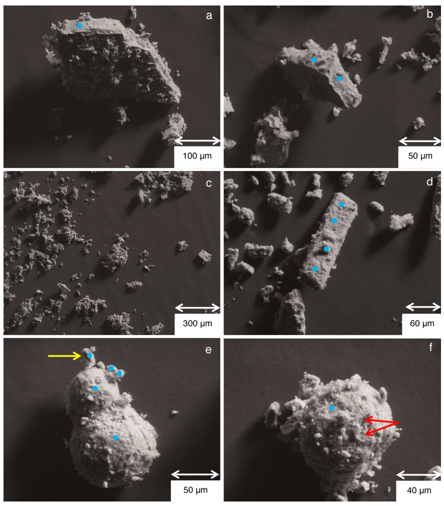

SE images of the three starting powders showing variations in crystal and aggregate shapes. Blue points mark EDX spot analyses. a-c) Powder 882 shows larger tabular and idiomorphic crystals with smaller crystals nucleating and growing on the planar surfaces. Small crystals aggregate to dendritic tangles. d) Larger grains of powder 11095 are rod-shaped. e-f) Grains in powder C51-81 generally show spherical shapes, although the yellow arrow marks a hypidiomorphic crystal growing on top of the sphere. Red arrows mark radiating tabular crystals on the surface of the MCPM spherule.

Institut für Geologie
Fachstelle Sekundärrohstoffe
Baltzerstrasse 1+3
CH-3012 Bern

Tel. +41 031 631 87 98
rohstoff@geo.unibe.ch
www.rohstoff.unibe.ch