

Mechanism of microbial hydroxyapatite manufacture and its application to radionuclide remediation

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Introduction

Hydroxyapatite (HAP) shows potential for the remediation of metal contaminated waters [1, 2]. *Serratia sp.* contains high levels of an atypical phosphatase enzyme located in the bacterial periplasmic space and attached to extracellular polymeric substance; this enzyme cleaves glycerol-2-phosphate, liberating inorganic phosphate and providing the nucleation site for the growth of biological hydroxyapatite (Bio-HAP) crystals [1, 3]. Evidence suggests that the growth of Bio-HAP is controlled within spatial localisation of the biological space on and in close proximity to cells [1, 3]. Crystalline HAP [Ca₁₀(PO₄)₆(OH)₂] is described as ten calcium cations aligned in 2 non equivalent sites denoted as Ca(1) and Ca(2). The Ca(1) site contains four cations each surrounded by nine oxygen atoms, whereas, the Ca(2) site contains six cations each surrounded by 7 oxygen atoms [4].

Experimental

Various techniques (Atomic force microscopy, scanning and transmission electron microscopy, BET surface area, X-ray diffraction) were used to characterise the properties and structure of HAP. To investigate how HAP properties influence metal uptake, portions of biomineral were heated at different temperatures ranging from 200-700 °C before the sorption of key radionuclides (Eu³⁺ as an analogue for trivalent actinides, U⁶⁺, Sr²⁺ and Co²⁺). The amount of absorbed species was determined by inductively coupled plasma mass spectroscopy and synchrotron X-ray absorption spectroscopy (XAS) was used to determine the local environment.

Results and Conclusions

Controlled biomineral growth produces amorphous HAP, with a large surface area and more reactive surface. Untreated HAP viewed under TEM and AFM appeared as chain/needle structures of < 50nm length. As the HAP was heated from 200-700 °C the organics content and HAP surface area decreased and the mineral became more crystalline. Heat treating to 700 °C caused the HAP to anneal and larger spheres >100 nm in length formed. The potential of microbial HAP to remediate radionuclides and the stability of bound metals will be presented.

[1] Handley-Sidhu et al., (2011) *Environ. Sci. Technol.* **45**, 6985-6990. [2] Handley-Sidhu et al., (2011) *Biotechnol. Lett.* **2011**, **33**, 79-87. [3] Thackray et al., (2004) *J. Mater. Sci. Mater. Med.* **15**, 403-406. [4] Terra et al., (2009) *Phys. Chem. Chem. Phys.* **11**, 568-577.

Redox Conditions and Metasomatic Activity beneath the Wesselton kimberlite, South Africa

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The redox state in mantle-derived garnet peridotite can be determined using the ratio of Fe³⁺/ΣFe in garnet, which can be measured using Fe K-edge X-ray Absorption Near Edge Structure (XANES) [1] spectroscopy. This is a synchrotron based method which allows for *in-situ* measurement with high spatial resolution. Redox state is expressed as oxygen fugacity (*f*O₂) and is an important control on carbon speciation in the mantle, particularly defining the boundary between carbonate stability relative to diamond or graphite.

A suite of garnet harzburgite and lherzolite xenoliths from the Wesselton kimberlite pipe, South Africa was analysed using electron probe microanalysis, LA-ICP-MS and Fe K-edge XANES spectroscopy with the aim of investigating the relationship between metasomatic enrichment and changes in redox conditions in the cratonic mantle beneath the Wesselton kimberlite pipes.

The suite shows evidence of multiple metasomatic events, including zonation in some garnet grains in which Ca, Fe and Ti enriched rims have overgrown highly refractory cores. Two distinct garnet REE patterns occur within the suite, 'sinusoidal' patterns typical of harzburgitic garnet in the cores, with 'normal' patterns typical of lherzolithic garnet on the rims. We quantitatively mapped the Fe³⁺ distribution in these grains using XANES and calculated average rim and core *f*O₂ values using the oxybarometer of Gudmundson and Wood [2]. The results indicate Δlog*f*O₂ of -1.37 (relative to FMQ) on the rim and -3.79 in the core at 1060 °C and 50 kbar. These values both fall in the diamond stability field in P-T-*f*O₂ space, however the rim *f*O₂ value is close to carbonate stability. Our results are in broad agreement with those of McCammon *et al.* [3] on similar samples.

We interpret this data in terms of quenching of the xenoliths caused by eruption of the kimberlite, during a strongly oxidising metasomatic event.

[1] Berry *et al.* (2010) *Chem. Geol.* **278**, 31-37.

[2] Gudmundsson and Wood (1995) *Contrib. Mineral. Petrol.* **119**, 56-67.

[3] McCammon *et al.* (2001) *Contrib. Mineral. Petrol.* **141**, 287-296.