Spectroscopic investigations of the adsorption of As onto bovine bone

WENDY J. HARRISON[1], RICHARD F. WENDLANDT,[1] JOHN M. CHARNOCK[2] AND C.M.B. HENDERSON[3]

[1]Dept. of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA (wharriso@mines.edu; rwendlan@mines.edu)
[2]Daresbury Laboratory, Daresbury, Cheshire, WA4 4AD, UK (j.m.charnock@dl.ac.uk)
[3]SEAES, Manchester University, Manchester M13 9PL, UK (c.m.b.henderson@dl.ac.uk)

Batch adsorption experiments of As^{3+} and As^{5+} onto raw bovine bone, collagen-extracted bone, collagen, fired bone (600°C), and synthetic apatite show strong selectivity for arsenic in the sequence collagen > raw bone > extracted bone > fired bone > synthetic apatite (Wendlandt et al., 2002). In this investigation, XANES, EXAFS, and IR techniques were applied to characterize As surface interactions, the kinetics of As^{5+} and As^{3+} uptake, and the rate of oxidation of As^{3+}.

Fired bone and synthetic apatite appear to reach surface site saturation at around 200 ppm As. Arsenate is co-ordinated by 4 oxygens with As-O bond lengths of 1.69A and As^{3+} is co-ordinated by 3 oxygens, with As-O bond lengths of 1.77A. No outer sphere interactions were observed. Arsenate was adsorbed more rapidly than As^{3+} onto extracted bone. Adsorbed As^{3+} oxidized to As^{5+} in times >36hrs and <72hrs on all solids and collagen. Oxidation is probably surface-catalyzed because post-experiment solutions and separated solids retain As^{3+}. Collagen binds both As^{3+} and As^{5+} with preferential binding of As^{5+}. Remnant collagen in extracted bone causes enhanced adsorption by this solid.

Photo-oxidation of As^{3+}, adsorbed onto fired bone during short duration experiments (4 hrs), is induced in the EXAFS beam during analysis times of a few hours. Susceptibility to photo-oxidation is reduced in experiments lasting more than 4 hrs, suggesting that the nature of the As^{3+}-surface interaction has changed. We propose that collagen may stabilize As^{3+} on the bone surface because photo-oxidation of As^{3+} adsorbed onto extracted bone or collagen was not seen. Limited photo-reduction was also observed.

Exceptional adsorption characteristics of bone materials are attributed to the combined effects of collagen binding with arsenic adsorption by the hydroxyapatite. Continued investigation of such materials for remediation of elevated arsenic concentrations in drinking water is warrented.

Reference

Wendlandt A.E. et al., (2002). Geol. Soc. America Ann. Mtg, Abstracts with Program, 34 (6).

Comparison of mineral, biological and precipitated carbonate apatites

J.C. ELLIOTT, R.M. WILSON AND S.E.P. DOWKER

Dental Biophysics, Institute of Dentistry, Queen Mary, University of London, E1 4NS, UK (j.c.elliott@qmul.ac.uk, r.m.wilson@qmul.ac.uk, s.e.p.dowker@qmul.ac.uk)

It seems to be generally agreed that CO_3^{2-} ions in mineral, biological and precipitated carbonate apatites replace PO_4^{3-} ions in the crystal lattice with sometimes a small fraction replacing OH^- ions. Several workers have also proposed that CO_3^{2-} ions can occupy surface, or other poorly defined locations, particularly in the biological apatites that have submicron crystal dimensions. Details of the way in which CO_3^{2-} ions substitute for PO_4^{3-} ions do not seem to be settled. For example, recent Rietveld structure refinements of precipitated apatites have reached different conclusions (Wilson *et al*., 2004), namely that the CO_3^{2-} ion is parallel or vertical to the basal plane, or occupies the "sloping face" of the vacated PO_4^{3-} ion site. Infrared spectroscopy of the CO_3 bands suggests that the environment of the CO_3^{2-} ion is rather variable (Elliott, 2002). For example, the bands in biological and precipitated apatites are distinctly different from those usually seen in minerals: it is not clear if this represents a substantial or trivial difference in the structure. Even within groups of precipitated and some mineral apatites, CO_3^{2-} absorption bands are rather variable. The origin of this variability is not known with certainty. The experimental evidence for the various proposed locations of the CO_3^{2-} ion will be reviewed and inconsistencies and what seem genuine differences will be highlighted. This research was supported by the Medical Research Council (G9824467) and currently by St Bartholomew's and the Royal London Charitable Foundation (RAB03/PJ/18).

References

Wilson R.M., Elliott J.C., Dowker S.E.P. and Smith R.I., (2004), *Biomaterials* **25**, 2205-2213.

Elliott J.C., (2002), Reviews in Mineralogy and Geochemistry **48**, 427-453.