

DFT calculations and molecular dynamics simulations of the nucleation of hydroxyapatite at a collagen molecule

NORA H. DE LEEUW^{1,2}

¹Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

²Institute of Orthopaedics and Musculoskeletal Science, University College London, Brockley Hill, Stanmore, Middlesex HA7 4LP, UK

Mammalian bone and tooth enamel are biomineralised organic-inorganic composites, comprising the collagen I protein and carbonated hydroxyapatite (HA). Owing to its importance in the natural bone tissue, hydroxyapatite is also used as a synthetic biomaterial, e.g. in hydroxyapatite/glass and hydroxyapatite/polymer composites, and insight at the molecular level into the processes occurring at the interface between hydroxyapatite and bio-molecules is important to gain understanding of the nucleation and growth of the composite material, as well as its interaction with proteins and other soft tissue components.

We first present the results of DFT calculations of the interaction of the HA (0001) and (01 $\bar{1}$ 0) surfaces with four short collagen peptides with distinct functional groups: hydrophobic, uncharged and charged polar side groups. Proton transfer commonly occurs from the peptides to the reactive (01 $\bar{1}$ 0) surface, which adsorbs the peptides more strongly and usually in their anionic form, whereas the more stable (0001) surface adsorbs the peptides mainly as neutral zwitterions or in their cationic form.

We next employed classical Molecular Dynamics simulations to investigate the interaction of one of the peptides HYP-PRO-GLY with the same surfaces in an aqueous environment, where the water was shown to affect both the configuration/location and the strength of adsorption of the peptide at the surfaces. The preference for adsorption at the (01 $\bar{1}$ 0) surface, as determined by the calculations, agrees with experiment and the morphology of the biomineralised HA crystal.

Finally, we have investigated the nucleation of HA at a collagen template, by immersing a complete triple-helical collagen molecule in a stoichiometric solution of Ca, PO₄ and OH ions, where we have observed the formation of calcium phosphate clusters at the collagen template.

Preliminary results are also presented on a new protocol developed for the simulation of a 3-dimensional collagen matrix, which is required for the modelling of the complete HA/collagen composite material.

Linking periodic mineralogical transformations to changes in aqueous lead and arsenic concentrations: Implications for long-term stabilization

J.L. DELEMOS^{1*}, J.E. VIDUMSKY², J. SUN³,
B.C. BOSTICK⁴, W.D. BRADY⁵, G.O. CADWALADER¹
AND M.F. DEFLAUN⁶

¹Geosyntec Consultants, Acton, MA 01720, USA
(*correspondence: jdelemos@geosyntec.com)

²DuPont Corporate Remediation Group, Wilmington, DE 19805, USA (john.e.vidumsky@usa.dupont.com)

³Dartmouth College Earth Sciences, Hanover, NH 03755 USA (Jing.Sun@Dartmouth.edu)

⁴Lamont-Doherty Earth Observatory, Columbia University (bostick@ldeo.columbia.edu)

⁵Geosyntec Consultants, Baton Rouge, Louisiana 70808, USA (WBrady@geosyntec.com)

⁶Geosyntec Consultants, Princeton, NJ 08648, USA (MDeFlaun@Geosyntec.com)

At a former phosphate fertilizer manufacturing facility, arsenic and lead concentrations are elevated in soils (54, 200 and 136, 000 mg/kg) and associated groundwater (> 800 and 100 μ g/L). In this study, solid phase transformations will be linked to transient changes in aqueous contaminant concentrations. Monitoring wells were sampled quarterly for three years to evaluate aqueous geochemistry and soil mineralogy was characterized using sequential extractions and x-ray adsorption spectroscopy. These data reveal that aqueous concentrations of lead, arsenic, iron and sulfate fluctuate sinusoidally in response to seasonal and tidal changes in water table elevation. Changes in pH and Eh indicate that these concentrations are responding to redox transitions. Mineralogical data indicates that iron-sulfides oxidize during the spring and reform during periods of sustained reduction. To study potential remedial strategies, mineralogy and aqueous geochemistry were monitored in microcosm studies amended with variable concentrations of Fe (II) and organic matter. These studies mimic episodic saturation of soils and demonstrate that remedial amendments influence mineralogy and contaminant flux to groundwater. Water table modulations effect the long term stabilization achieved by these amendments, suggesting that system hydrology will be the controlling variable in the success of remedy implementation.