

Atomistic simulation of the mineral-water interface in contact with charged surfaces

DAVID J. COOKE¹, SEBASTIEN KERISIT^{1,2},
ARNAUD MARMIER¹ AND STEPHEN C. PARKER¹

¹Department of Chemistry, University of Bath, BA2 7AY, UK
(s.c.parker@bath.ac.uk)

²Pacific Northwest National Laboratory, 902 Battelle Blvd,
P.O. box 999, K8-96, Richland, WA 99352, USA.
(sebastien.kerisit@pnl.gov)

We describe recent work using atomistic simulation methods based on the Born model of solids to study the effect of the surface charge on first, the interaction of the solution with a mineral surface and secondly, on the distribution of ions in solution. We have performed a series of molecular dynamics simulations on the (100) surface of goethite, (α -FeOOH), in contact with a 0.9M NaCl solution. The potential models, describing the interatomic interactions for the species in contact with water are shown to be in good accord with both experiment and *ab initio* simulations. We initially considered the stable stoichiometric, charge neutral, surface of goethite, which is terminated by hydroxyl groups. The charged surfaces were then generated by either removing surface protons or hydroxyl groups to make the surface either negatively or positively charged. The molecular dynamics simulations of neutral and charged surfaces were run for over 1 ns, and to ensure that the simulations were converged we considered different starting distributions and different thicknesses of water covering the surface up to a maximum of 20nm.

The results of the simulations show clear layering of water at the mineral surface, in accord with the recent work from both experiment and simulation albeit on different minerals. We also found that unlike classical double layer models, the ion distribution also oscillated away from the surface. However, in keeping with classical double layer models, the ion distribution is controlled by the electrostatic distribution, perhaps suggesting that their failure at high ionic strengths is due to the neglect of electrostatic interactions of the solvent. Finally, varying the surface charge to around $4.5\mu\text{C}\cdot\text{cm}^{-2}$ did not make a highly significant change to the surface properties and behaviour. The effect, which will be discussed further, was largely localised to the near surface region.

Identification of active site and reaction mechanism for epitaxial apatite nucleation at the pseudowollastonite bioceramic-bone interface

NITA SAHAI^{1,2} AND MICHEL ANSEAU³

¹Department of Geology and Geophysics, 1215 West Dayton Street, ²Department of Chemistry, 1101 University Avenue, University of Wisconsin, Madison, WI 53706
(sahai@geology.wisc.edu)

³Department of Organic and Biomedical Chemistry, University of Mons-Hainaut, 24 Avenue du Champ de Mars, 7000 Mons, Belgium (michel.anseau@umh.ac.be)

Ceramics that bond to bone by the formation of an interfacial layer of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) are called bioactive. Using the example of pseudowollastonite (α - CaSiO_3), we present here a model of the properties that make a ceramic bioactive. Hydroxyapatite grows epitaxially on pseudowollastonite surfaces *in vitro* in simulated body fluid, human parotid saliva and cell-culture medium, and *in vivo* when implanted in rat tibias. We have used crystallographic constraints with *ab initio* molecular orbital calculations and a modified Born solvation model to determine the active site and mechanism for nucleating calcium phosphate on psW [1].

We propose that the active site is the planar, cyclic, silicate trimer (Si_3O_9) on the (001) face of psW, where the surface silanols arranged at 60° from each other, provide an epitaxial match to the Ca-O positions on the HAP (001) face. The reaction is modeled stepwise as Ca^{2+} leaching from the psW surface, silicate ring protonation ($\text{Si}_3\text{O}_9\text{H}_3$), inner-sphere sorption of Ca^{2+} at $\text{Si}_3\text{O}_9\text{H}_3$, and HPO_4^{2-} attachment resulting in the calcium phosphate nucleus. The overall reaction is favorable because of a large exothermic contribution from the first step. We propose that the cyclic silicate trimer may be the universal active site on silicate-based bioactive ceramics, and that a critical site-density is required for bioactivity.

Interestingly, some ceramics such as alumina that contain a similar geometry of oxygen atoms arranged in an equilateral triangle are found not to be bioactive. The point of zero charge of alumina is ~ 9 compared to physiological pH = 7.2. We propose, therefore, that in addition to a critical active site-density, the point of zero charge of the bioceramic must be less than physiological pH in order to promote epitaxial, heterogeneous apatite nucleation at its surface.

Reference

[1] Sahai N. and Anseau M. (2005) *Biomaterials*, in review.