Adsorption and segregation at surfaces in minerals and biominerals

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Surfaces and interfaces often determine the growth and behaviour of minerals. Molecules and arrays of molecules at surfaces can control the growth of minerals in the process of biomineralization. Here the differing absorption strengths can stabilise particular surfaces and produce different growth morphologies. Surfaces and internal interfaces (such as grain boundaries) will also affect the distribution of atoms and ions incorporated into minerals. Such species will often segregrate to such interfaces, particularly if the bulk solubility is low. We demonstrate the essential role simulation can play in unravelling the complex mechanisms involved with two examples.

Recent experimental work [1] suggests that the the solubility of argon in minerals like forsterite is much higher than would be expected if it were simply incorporated into the bulk. This also contradicts the frequently made assumption that noble gases are completely insoluble in minerals. We show that the energies of incorporation of noble gases at interfaces are much less than in the bulk mineral, suggesting the importance of grain boundaries in understanding the mineral behaviour.

Aqueous mineral surfaces present a challenge to simulation. It is essential to consider both the mineral surface and the detailed structure of the solvent close to the surface. Previous calculations showed the importance of energies of adsorption in determining whether organic molecules can control the surface structure and morphology of minerals[2]. Such calculations ignored entropy effects. These should be important, since the adsorption of molecules requires the displacement of water, with release of entropy as the water moves from a relatively ordered surface layer to the bulk. We present free energy calculations of adsorption of mono-saccharide molecules and discuss the importance of enthalpy and entropy effects in molecular adsorption and hence control of the growth of surfaces in biominerals such as calcite.

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[2] Freeman, Harding & Duffy (2008) *Langmuir* **24**, 9607.

Redox- and metal-dependent surface modifications of *Shewanella putrefaciens* CN32

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Metals in subsurface environments are challenging to remediate. One approach relies on the activity of dissimilatory metal-reducing bacteria to shift chemical equilibria to favor metal precipitation. During this process, high concentrations of metals develop at the interface between bacteria and the extracellular environment, initiating mineral nucleation at reactive surface sites [1]. In environments where redox conditions can fluctuate, it is expected that the adaptability and metabolic versatility of bacteria will allow them to rapidly modify their surfaces in response to extracellular conditions. It is, therefore, necessary to understand the impacts of oxygen and metals on the biochemistry of the bacterial surface, when assessing the potential for metal immobilization.

The facultative anaerobe *Shewanella putrefaciens* CN32 is a dissimilatory metal-reducing bacterium that was isolated from a terrestrial environment [2]. We have examined how CN32 modifies its membranes in response to oxygen presence, when supplemented with U(VI), V(IV), or Mn(II), with respect to lipid, protein, and lipopolysaccharide (LPS) compositions. We observe that CN32 significantly alters: 1) the degree of saturation and fatty acid chain length of its membrane phospholipids; 2) the fluidity and thermal stability of the membrane, and 3) membrane protein composition in response to oxygen presence. These changes in turn impact the sorption of metals to CN32 envelopes.

Bacterial surfaces are highly dynamic; bacteria respond to their environment by continuously reorganizing and synthesizing membrane components with unique properties. Our research suggests that metal mobility should be assessed in light of the adaptability of the bacterial surface when confronted with inconsistent environmental conditions.

[1] Beveridge (1989) *Annu. Rev. Microbiol.* **43**, 147-171.
[2] Glasauer *et al.* (2002) *Geochim. Cosmochim. Acta* **67**, 1277-1288.