Analytical electron microscopy of inorganic-organic interfaces

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We present an overview of the application of analytical electron microscopy to the study of the interfacial interaction between organic materials and inorganic mineral phases. Two overall themes are considered: biomineralisation and bio-mediated demineralisation involving studies of the structure of the iron storage protein ferritin [1] and an investigation of biotite mineral weathering by mycorrhizal fungi [2].

The current generation of (scanning) transmission electron microscopes (S/TEMs) can readily provide atomic scale resolution to study the projected structure of crystalline mineral surfaces potentially in contact with an organic phase. In addition to this structural information, it is important to be able to extract analytical chemical information on the distribution of elements and their bonding at such interfaces using energy dispersive X-ray (EDX) and electron energy loss spectrometries (EELS). This is most easily achieved by forming a small probe and employing STEM spectral imaging techniques; in addition energy filtered TEM (EFTEM) is also a possible method of analysis. Finally, a key aspect is electron fluence during both imaging and, more importantly, fine probe analysis as it is crucial that the mineral structure (and ideally also the organic material) remains unaltered/ immobilised during investigation. We demonstrate the need for preliminary studies of the electron beam induced changes as a function of both overall electron fluence and also fluence rate [3]. Furthermore we highlight the potential of smart acquisition STEM for low dose analysis [4].

With correct instrumental methodologies in place, sample preparation is an overiding issue. We will discuss different approaches to the production of interfacial cross-sections ranging from microtomy through to the use of focused ion beams for site specific S/TEM sample preparation.

[1] Pan *et al*. (2009) *J. Struct. Biology* doi: 10.1016/j/ jsb.2008. 12.001. [2] Bonneville *et al*. (2009) *Geology*, (accepted). [3] Eddisford *et al*. (2008) *J. Phys. Conf. Ser*. **126**, 012008. [4] Sader *et al*. (2008) *EMC2008* **1**, 425-426.

Cycling of Fe by siderophilic cyanobacteria: Implications for an early biosphere

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Prior to 2.4 Ga, terrestrial oceans were likely significantly enriched in soluble Fe (Rouxel, Bekker & Edwards 2005), a condition that is not conducive to the growth of most contemporary fresh water and marine cyanobacteria (CB). That is why siderophilic CB (SCB) (Brown *et al.* 2007) which inhabit iron-depositing hot springs (Pierson and Parenteau, 2000) may constitute the most appropriate natural model to shed light on possible mechanisms of the adaptation of ancient CB to high [Fe^{2+}]. Besides, the study of the interaction of SCB with igneous rocks may help us to understand the mechanisms of SCB adaptation to low concentrations of dissolved Fe.

SEM and TEM techniques, combined with EDS analysis of the cells of SCB grown in DH medium supplemented with 0.6 mM $FeCl_3 \cdot 6H_2O$, revealed Fe-rich extracellular coatings most consistent with ferrihydrite. In addition, accicular Fe-oxides have lattice spacings and external morphologies consistent with goethite. This study also revealed, for the first time, the generation of intracellular Fe-rich phases with quasi-circular shapes ranging from ~40 to 200 nm in diameter. P, Fe, and O are the major constituent elements of those phases with minor amounts of Al and Ca.

SEM-EDX studies of the interaction of SCB with Fe-rich minerals and rocks revealed, for the first time, their ability to leach ilmenite, olivine, FeS, ZnS and ferrosilicates. We found, in parallel, that the SCB studied can secrete organic acids such as 2KGA and malate which possess chelating properties. As result, Fe release from dunite incereased by a factor of X50.

We hypothesize that the ability of SCB to mineralize Fe within their cytoplasms could be a protective mechanism to survive oxidative stress induced by high [Fe^{2+}] in the Precambrian ocean. The ability to leach Fe-rich minerals could have supported the proliferation of SCB on land with low levels of [Fe^{2+}]. Both processes could have created the presumptive biosignatures of ancient CB.