More oil from Chalk: Studying the holes – and the borders of the holes, the particle interfaces

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Current methods for extracting oil from chalk leave behind as much as 75% of the total oil available. It remains as small droplets in pore spaces or as thin films on particle surfaces. This oil is inaccessible at present, but if it could be extracted, the impact on global resources would be significant. It will take many years before sustainable energy forms become mature enough to eliminate the need for fossil fuels and society will continue to depend on petrochemicals for many decades. Trapped oil has driven 30 years of chalk research and although the properties of chalk and oil are well characterised and relationships between porosity, permeability and oil production are well-defined, the character of the interface between the pore spaces and their boundaries with the solid, i.e., the surfaces of the chalk particles, is not understood. Nanotechnology is revolutionising our understanding of complex systems in many fields. Likewise, it has promising potential for improving oil recovery.

In the NanoGeoScience group, we have applied nano-scale techniques in an interdisciplinary attack on an old problem: how to recover more of the oil. Our aim is to understand the behaviour of the pore/particle interface well enough to develop an environmentally friendly product or process that can modify particle surface behaviour so more oil is released. Nano-scale X-ray tomography, a non-destructive, *in situ* technique, has shown us the pore spaces before and after treatment. Rietveld refinement of X-ray diffraction data has revealed particle size and its change with time. X-ray reflectivity has shown the thickness of a water film on calcite. And a selection of techniques (including atomic force microscopy, X-ray photoelectron spectroscopy, transmission electron microscopy and molecular mass spectroscopies) has revealed ultra-thin layers of organic and inorganic compounds at the interface between the chalk particles and the pore fluids. These results, and their implications for pore fluid behaviour, will be presented and discussed.

Glutamate surface speciation on amorphous titanium dioxide and hydrous ferric oxide

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The attachment of aqueous amino acids to mineral surfaces is of fundamental interest in a variety of natural and artificial processes ranging from biomineralization to the viability of implants of metallic titanium in the human body. Amino acid-mineral surface interactions may also have played a central role in life's origins, either in determining chiral selection of left-handed amino acids in proteins or in facilitating the formation of peptide bonds. However, very little is known about the way amino acids attach to even the simplest mineral surfaces in water.

Hydrous ferric oxide (HFO) and titanium dioxide exhibit similar strong attachment of many adsorbates including biomolecules. Using recent advances in surface complexation modeling [1], we have integrated published adsorption data for glutamate on HFO over a range of pH and surface coverage [2] with a published *in situ* ATR-FTIR study of glutamate speciation on amorphous titanium dioxide [3]. We found that the same three inner-sphere surface species of glutamate inferred for the titanium dioxide can describe adsorption on HFO. The predicted proportions of these vary with pH and the amount of glutamate consistent with trends inferred from the spectroscopic study. For example, glutamate adsorbs on HFO as a deprotonated divalent anion at pH=3 to 5 and 0.2 μmoles.m^{-2} in the form of chelating-monodentate and bidentate-binuclear species attached to the surface through three or four of the carboxylate oxygens, respectively. However, at similar pH values and >2 μmoles.m^{-2}, glutamate adsorbs mainly by chelating to a single surface site by the γ-carboxylate group. In this configuration the α-carboxylate and amine groups might be free to interact above the surface with the free ends of adjacent glutamates, suggesting a possible mechanism for chiral self-organization and peptide bond formation.

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