

Cleaner water, more oil and taking out the garbage

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The electronic age has been driven by developments in technology. The same instruments that have built the foundation for nano-technology have also launched a revolution in science, because for the first time in human development, we can see at the fundamental chemical level. We can see atoms and how they are arranged in a solid, and we can identify molecules and watch them react. This has enormous potential for gaining insight into why things happen and how. We can observe nature at a whole new level, learn its secrets and use our new knowledge to find solutions to society's challenges. Some examples from work in our NanoGeoScience research group include ensuring cleaner water, storing waste more safely, discovering the mysteries of biomineralisation, getting more oil from reservoirs and immobilising CO₂ in rock form, where it will be stable for geologic time.

With ultra-high resolution techniques, we can see changes that with our traditional, macroscopic methods would be visible only after many years. New developments in atomic force microscopy allow us to probe a surface with a chemically functionalised tip and make maps of hydrophobic areas that are only 10's of nanometers in diameter. Maps of elasticity reveal clay laths that are one or two unit cells thick. Surface analysis with X-ray photoelectron spectroscopy and X-ray reflectivity shows how hydrocarbons and water compete for position in the ordered layers that form at the termination of the bulk mineral structure. X-ray micro-tomography shows how pores fill with fluid and how solids dissolve.

From molecular level observations of the solid-fluid interface, combined with macroscopic data about the structure and composition of solids and fluids, we can define the mechanisms by which reactions take place. Over the past century, geochemists have built a thermodynamic database to describe natural systems. However, nature's complexity makes predictions difficult. Kinetics is often blamed for lack of equilibrium. Clearly, one part of this century's geochemical challenge is to build a kinetic database. The other part is to reveal what goes on at the solid-fluid interface, to define the parameters that control geochemical processes. Adsorbed species and layers of precipitates that are only one or a few unit cells thick have been invisible until now, but their relationship with the fluid in contact, defines the equilibrium relationships, not the bulk material beneath them.

Can carbonate coatings inhibit *in situ* mineral carbonation?

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In situ carbonation of basalts has been suggested as a potential CO₂ sequestration method due to their porous and permeable properties and high reactivity [1]. Acid CO₂-saturated waters in contact with basaltic glass will lead to rapid dissolution of basalt and release of divalent cations, (Ca²⁺, Mg²⁺, Fe²⁺) that can react to form stable carbonates like calcite, magnesite and siderite. Clays and zeolites are also likely to form due to basaltic-CO₂ rich water interaction. To assess the degree to which these phases may clog pores and/or influence the reactivity of the basalt due to formation of surface coatings, a series of coupled dissolution-precipitation experiments on basaltic glass were performed in mixed-flow and batch reactors. The experiments were performed at far-from-equilibrium conditions with respect to basaltic glass but at supersaturated conditions with respect to calcite by adding bicarbonate-bearing solutions to the reactors. Calcium was supplied by either 1) release from dissolving basaltic glass or 2) addition of CaCl₂ to the reactive solution. Experiments, where the Ca²⁺ was sourced from dissolving basaltic glass, did not generate calcite in sufficient amounts to influence basaltic glass dissolution rates. In the case where a CaCl₂ solution was added to the reactive solutions, visible amounts of calcite precipitated, but this did not influence measurably basaltic glass dissolution rates after 64 days of experiment. Previous work by Hodson [2] indicates that porous discontinuous coatings do not inhibit the dissolution of the primary mineral. These results indicate that small quantities of precipitated carbonates do not slow the release of divalent metal cations from basaltic glass, suggesting the viability of *in situ* carbonation of basalts.

[1] Oelkers *et al.* (2008) *Elements* 4, 333-337. [2] Hodson (2003) *GCA* 67, 3355-3363.