Biogeochemical processes in a clay formation *in situ* experiment

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An *in situ* diffusive test in the Opalinus Clay formation was carried out in a packed-off borehole in which traced artificial porewater was circulated for a period of five years. The original focus was to obtain reliable data on the pH/pCO_2 conditions of the porewater by diffusive equilibration between the artificial and *in situ* porewater. Because of observed microbially induced redox reactions, the objective was extended to understanding the biogeochemical processes occurring in the borehole and to investigate their impact on pH/pCO_2..

The observed decrease of conservative tracers e.g. ^2H and Br- could be explained by diffusion into the clay. Diffusive equilibration between the borehole water and the formation occurred within approximately two years. Microbially-induced redox reactions in the borehole, including primarily sulphate reduction considerably altered the composition and pH/pCO_2 of the water. Thus, pH was lower and pCO_2 was higher than indicated by complementary laboratory investigations performed under abiotic conditions.

Obviously, the chemical and isotopic composition of the pore water in the borehole was affected by the complex interplay of diffusion, carbon degradation rates, mineral equilibria and weathering rates (e.g. Fe carbonates), iron sulphide precipitation rates, and exchange reactions with the clay. The ^{13}C signals measured for different carbon species showed significant variations. The main cations, such as Na, Ca and Mg remained remarkably constant during the experiment, thus indicating the strong buffering of the formation via cation and proton exchange, as well as by carbonate dissolution/precipitation reactions.

Atomistic origins of mineral-water interfacial phenomena and their relation to surface complexation models

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An integrated approach has been applied to investigate the aqueous electrolyte interface with isostructural rutile (α-TiO_2) and cassiterite (α-SnO_2). Macroscopic pH titrations of surface charge and ion sorption, and electrophoretic mobility studies of oxide powder suspensions have been extended from room temperature to 250°C. Synchrotron X-ray probes of immersed single crystal surfaces have revealed at sub-Å resolution the extent of surface relaxation and the distribution of interfacial water and ions. Static and dynamic *ab initio* and classical molecular simulations have been linked with these observations to provide a detailed understanding of the average interfacial structure and dynamics.

The (110) face of both phases is the most stable and best developed, but the smaller lattice spacing and higher polarizability of Ti(IV) in rutile result in significant differences in the interfacial structure and dynamics. Protonation of surface oxygens is clearly related to the nature of bonds with substrate metal atoms, but is also strongly influenced by strong hydrogen bonds among surface species and between them and next-layer water molecules, and both are influenced by surface lattice spacing. All ions studied on these surfaces exhibit inner sphere sorption at several sites whose relative abundances change with pH and temperature and are largely dictated by sorbed ion radius and charge, and surface structure. The assignment of inner sphere ions to 'Stern planes' and bond valence models of surface protonation are consistent with the atomic-scale interfacial properties, but the concept of the interfacial solvent as a dielectric continuum appears to have no molecular basis.