

Dissolution of biogenic silica in the sediments of the Scheldt continuum

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The riverine fluxes of N and P have been significantly increased by human activities, while the anthropogenic input of Si to the Scheldt estuary is considered to be negligible. This excess delivery of N and P compared to Si has affected the phytoplankton speciation and succession in the Belgian coastal zone. The regeneration and retention of Si in the estuary, and particularly in the sedimentary column, is still poorly known. During the year of 2004, surface sediments and cores were collected along the Scheldt continuum. Dissolution kinetics of biogenic silica (BSi) was carried out in batch reactors for several months on sediments from different locations and depths, and the effect of salinity on the dissolution rate was investigated. Preliminary results show that the salinity effect is stronger for low salinity values, but becomes negligible for higher values. Our results also exhibit high BSi dissolution rates in the second centimetre of the sediments cores, with lower values in the first centimetre but also at depth. These results are coherent with the BSi profiles, as well as the microscopic observations of the sediments that showed a higher abundance of biogenic opal debris in the second centimetre with respect to the first centimetre. A model taking into account a two-phase dissolution was used to fit the experimental data, the two phases considered corresponding to biogenic and lithogenic silica, respectively. Overall, the dissolution rates are low and the amorphous silica saturation concentration is never reached, suggesting that the recycling of the biogenic material in the sedimentary column is very low. Part of the opal reaching the sediments probably dissolves at the surface, while the rest is rapidly incorporated within the sedimentary column where dissolution continues along with other diagenetic reactions.

Controlling and predicting subsurface calcium carbonate precipitation for capture of inorganic contaminants

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In situ manipulation of biogeochemical conditions to induce the formation of mineral phases is one approach for immobilizing metal contaminants in subsurface environments. Examples include U and Tc bioreduction, engineered precipitation of U phosphate minerals, and microbially facilitated coprecipitation of ⁹⁰Sr in calcite. Strategies for controlling the formation and distribution of precipitated minerals usually require introduction of soluble chemical amendments to the subsurface. The challenges involve not only controlling the distribution of amendments and resulting reactions, but also predicting how permeability and flowpaths evolve as solid phases are deposited (including biomass). The changing flowpaths and geochemical environment will impact the propagation of solid phases and contaminant mobility. Computational models that can account for the scale-dependent coupling between physical, chemical and biological processes over a range of spatial and temporal scales are not well developed.

Experiments in 2- and 3-dimensional packed-sand media have been conducted where calcium carbonate precipitation and co-precipitation of Sr²⁺ is induced by one of two mechanisms. The first is by propagating calcium carbonate precipitates within the fluid-fluid mixing zone between two solutions that flow in parallel. The second approach involves *in situ* generation of carbonate, in the presence of dissolved calcium, by enzyme catalysed hydrolysis of urea. This is an analog for a natural biological process. In both cases, within the reaction zone, a wide range of saturation indices and ion ratios can be established at the pore scale depending on the relative rates of solute transport, mixing, and precipitation. Multiple precipitation modes (e.g., homogeneous and heterogeneous nucleation and growth), different carbonate phases, and varying morphologies can occur in close proximity. The thermodynamic, kinetic and physical control of precipitate deposition influences Sr partitioning in the porous media, as well as permeability and flow paths in the porous media.

We have simulated solute mixing and flow modifications at the pore scale using the Smoothed Particle Hydrodynamics (SPH) method. Continuum-scale simulations of the experimental results were also conducted using grid-based methods. A goal is to use SPH simulations as the basis for parameterization of macroscopic finite-element multi-component reactive transport models, correlating results from the two model scales with our experimental results.