

Investigation of coupled flow and geochemical reactions at the pore scale by direct numerical simulation

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Prediction of chemical fate and transport in subsurface environments often relies on reaction rate constants applicable to each grid block of continuum-scale numerical models. Typically, laboratory-determined reaction rates are applicable to a scale smaller than that resolved by the continuum-scale models. Upscaling of these rates to a grid block is possible under certain conditions; otherwise, microscopic and macroscopic scales need be considered simultaneously (e.g. [1], [2]). This is often the case in carbon sequestration or remediation applications where the subsurface geochemical system is driven to far-from-equilibrium conditions in relatively short time scales, which result in short characteristic length scales. In addition, induced geochemical reactions such as mineral precipitation and dissolution can modify the geometry and structure of porous media, which further affects the macroscopic reactions rates.

Direct numerical simulation techniques in which the Navier-Stokes or Stokes equations are solved using conventional methods (e.g. finite volume, differences) allow for incorporation of complex multicomponent reaction networks into pore scale models. We employ pore scale modeling based on direct numerical simulation of flow and multicomponent reactive transport to investigate the two-way coupling between precipitation-dissolution reactions and flow. We focus on calcite dissolution-precipitation as system of environmental relevance. We observe that non-uniformity in the flow field at the pore scale decreases the overall reactivity of the system in equivalent continuum-scale systems. The effect becomes more pronounced as the heterogeneity of the reactive grain packing increases, particularly where the flow slows sufficiently such that the solution approaches equilibrium locally and the average rate becomes transport-limited.

Simulations show that dissolution and precipitation reactions affect the pore space non-uniformly. As a result, a simple porosity-permeability correlation may be insufficient to describe the complexity of the reaction-induced pore space evolution. The relative magnitude of the reaction rate constants affects the evolution of the permeability-porosity relationship. In dissolution simulations, fast reactions result in localized effects and further evolution of permeability is relatively unaffected by subsequent porosity increase. In contrast, slow reactions cause a less localized dissolution, with the result that the permeability increase is consistent with the porosity increment.

[1] Battiato, Tartakovsky (2011), *J. Contam. Hydrol.*, 120-121, 18-26

[2] Wood (2009) *Adv. Water Resour.*, 32, 723-736.

Comparison of three organic geochemical proxies for sea-surface temperatures in a four year sediment trap record

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The most well-established organic-geochemical SST proxy index $U^{K'_{37}}$ based on haptophyte produced long-chain ketones (alkenones) has been shown to yield robust estimates of annual mean SSTs but may be more problematic in high productivity eastern boundary upwelling areas. In the last decade, two types of new organic geochemical SST proxies, i.e., the TEX_{86} index based on archaeal glycerol dialcyl glycerol tetraether (GDGTs) and two indices based on long-chain diols derived from diatoms (DCI) and eustigmatophytes (LDI) have been proposed. Those proxies have been suggested to be applicable in settings where the alkenones are less reliable or absent. On the other hand, each of the new indices has its own caveats. These include, but are not limited to: 1) the fact that GDGT producing archaea thrive throughout the water column and perhaps also in the sediment; 2) limited understanding of the physiological role of the respective lipids in their precursor organisms; 3) incomplete understanding of the export mechanisms responsible for the transport of lipids from the depth of production to the sediments; 4) concerns regarding differential degradation of individual lipids.

Here we address several of these questions using sediment trap samples collected at 1-2 week intervals between June 2003 and March 2007. The trap was moored off Cape Blanc in an area strongly influenced by seasonal coastal upwelling. We measured $U^{K'_{37}}$, TEX_{86} , and the diol indices as well as concentrations and fluxes of the respective lipids. The results are compared with total, carbonate, opal and organic matter fluxes as well as diatom abundances. For all indices, we observe pronounced seasonal cycles, while flux-weighted averages agree well with values measured in underlying surface sediments. Reconstructed SSTs based on $U^{K'_{37}}$ and TEX_{86} correspond generally well with satellite measured SSTs but reveal that $U^{K'_{37}}$ is more uncertain during periods of highest productivity. The DCI shows a well pronounced but reverse relationship with SST than originally proposed. Fluxes of all lipids are closely tied to total fluxes, implying that ballasting is an important mechanism. Delays between observed and reconstructed SST maxima are within the expected range for alkenones and larger but similar for GDGTs and diols, implying that these lipids are predominantly exported as diatom-rich aggregates known to sink at lower velocities than carbonate containing aggregates. We find no evidence for substantial sub-surface export of GDGTs.