Compound-specific transverse dispersion in porous media: Darcy-scale experiments and pore-scale modeling interpretation

M. ROLLE[1]*, D. HOCHSTETLER[2], G. CHIOGNA[1],
P.K. KITANIDIS[2] AND P. GRATHWOHL[1]

[1]Center for Applied Geosciences, University of Tübingen,
72076 Tübingen, Germany
(*correspondence: massimo.rolle@uni-tuebingen.de)
[2]Department of Civil and Environmental Engineering,
Stanford University, CA 94305, Stanford, USA

Multitracer laboratory bench-scale experiments and pore-scale simulations in different homogeneous saturated porous media were performed to (i) gain an improved understanding of the role of basic transport processes (i.e. advection and molecular diffusion) at the sub-continuum scale and their effect on the macroscopic description of transverse mixing in porous media; (ii) quantify the importance of compound-specific properties such as aqueous diffusivities for transport of different solutes.

A non-linear compound-dependent parameterization of transverse hydrodynamic dispersion is required to capture the lateral displacement observed in the experiments over a wide range of seepage velocities (0.1-35 m/day). With pore-scale simulations we can prove the hypothesis that the interplay between advective and diffusive mass transfer results in vertical concentration gradients leading to incomplete mixing in the pore channels. We quantify mixing in the pore channels using the concept of flux-related dilution index and show that different solutes undergoing transport in a flow-through system with a given average velocity can show a different degree of incomplete mixing. We conclude that physical processes at the microscopic level significantly determine the observed macroscopic behavior and, therefore, should be properly reflected in up-scaled parameterizations of transport processes such as local hydrodynamic dispersion coefficients. These findings are relevant also for the interpretation of isotopic signatures in groundwater [1] and for mixing-controlled reactive transport. In the latter case, a correct quantification of transverse mixing is of utmost importance to assess the length of contaminant plumes [2].

[1] Rolle *et al.* (2010) *Environ. Sci. Technol.* **44**, 6167–6173.
[2] Chiogna *et al.* (2011) *Water Resour. Res.* **47**, W02505, doi: 10.1029/2010WR009608.

Boron isotopes as pH proxy: Combination of boron speciation and isotope composition data

C. ROLLION-BARD[1]*, D. BLAMART[2], J. TREBOSC[3],
G. TRICOT[3], A. MUSSI[4] AND J.-P. CUIF[5]

[1]CRPG-CNRS, BP20, 54501, Nancy, France
(*correspondence: rollion@crpg.cnrs-nancy.fr)
[2]LSCE, 91198 Gif-sur-Yvette, France
[3]UCCS, 59652 Villeneuve d'Ascq, France
[4]UMET, Univ. Lille 1, 59655 Villeneuve d'Ascq, France
[5]IDES, Univ. Paris XI, 91405 Orsay, France

Reconstructing past atmospheric CO_2 level and elucidating its link with climate evolution is one of the most fundamental questions in Earth sciences. Boron isotopic composition ($\delta^{11}B$) of marine biocarbonates is considered to be a proxy for ocean pH. This technique has mainly been used in foraminifera and in tropical corals during previous climatic cycles and on longer geological time scales.

Dissolved boron in modern seawater occurs in the form of two species, trigonal boric acid $B(OH)_3$ and tetrahedral borate ion $B(OH)_4^-$, the proportion of which is dependent on pH of the solution. One of the key assumption in the use of $\delta^{11}B$ of carbonates as pH proxy is that only borate ions are incorporated into the carbonate. Here, we investigate the speciation of boron in deep-sea coral microstructures (*Lophelia pertusa* specimen) by using high field magic angle spinning nuclear magnetic resonance (^{11}B MAS NMR) and electron energy-loss spectroscopy (EELS). We observe both boron coordination species, but in different proportions depending on the coral microstructure, i.e. centres of calcification versus fibres. These results suggest that careful sampling is necessary before performing boron isotopic measurements in deep-sea corals. By combining the proportions of $B(OH)_3$ and $B(OH)_4^-$ determined by NMR and our previous ion microprobe boron isotope measurements, we propose a new equation for the relation between seawater pH and boron isotopic composition in deep-sea corals.