# Effective mixing and reaction front kinetics in porous media

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The effective reaction kinetics of chemical species transported in solution in the subsurface depends on the probability of reactants to mix. While chemical reactions ultimately occur by diffusive mixing at the molecular scale, the effective reaction kinetics can be greatly enhanced by the shear and stretching action of the flow field, which increases the surface available for diffusive mass transfer [1]. Understanding and quantifying the effect the flow field heterogeneity on the upscaled mixing and reaction rates is thus a key issue for the prediction reactive transport in the subsurface.

We use pore scale Smooth Particle Hydrodymanic (SPH) simulations to investigate effective mixing and reaction kinetics for reaction fronts where an initially resident reactant is displaced by an incoming reactant. The reaction kinetics is found to be faster than that of homogeneous diffusion-reaction fronts, for which the mass of product grows like the square root of time. At early time, the effective reaction rate is controlled by the formation of fingers of incoming reactant, which invade the porous media, rapidly increasing the reaction front area. At late time, the reaction kinetics is governed by the longitudinal dispersive growth of the mixing area and by the spatial distribution of concentration gradients in the mixing zone, which characterize a persistent state of incomplete mixing [2.3]. We discuss the effect of changing the relative contribution of advective and diffusive motions (quantified by the Peclet number) on the temporal evolution of effective mixing and reaction rates.
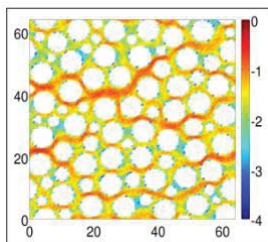


Pore scale flow field
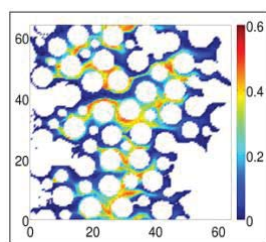
Distribution of product concentration within the reaction front

[1] Dentz M., T. Le Borgne, A. Englert, B. Bijeljic (2011) Review Article J. of Cont. Hydrol., **120-121**, 1–17
[2] Le Borgne T., Dentz M., Davy P., Bolster D., de Dreuzy, J. R. and Bour O. (2011) Phys. Rev. E, **84**, 1
[3] de Anna, P., T. Le Borgne, M. Dentz, D. Bolster and P. Davy (2011) J. of Chem. Phys., **135**, 174104

# Contrasting Biogeochemical Cycling of Iron and Aluminium along the GEOTRACES West Atlantic section

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The thus far longest (13,000 km) complete deep ocean section of iron (Fe), aluminium (Al) and a suite of other trace elements and isotopes was realized in 2010-2011 in the West Atlantic Ocean. The more than 1200 data values reveal the major sources and processes controling Fe and Al in the oceans. Overall Fe is decoupled from Al except in the uppermost surface layer of dust input. Overall the Al shows an amazing inverse relationship with Si.

The background concentrations of Fe are quite uniform around 0.5 nM but there are several major enhancements. In the 10-30 ºN region the uppermost samples (10m depth) have maximum concentrations of Fe exceeding 2nM and Al exceeding 40 nM, respectively, due to partial dissolution of dust supply from the Sahara. This extra Fe supports $N_2$ fixation by diazotrophs in the Sargasso Sea, that upon sinking of plankton debris and mineralization causes a high anomaly of the nitrate/phosphate ratio in the 200-800m depth zone. The Amazon River plume provides a signal of high Fe and Mn but Al is not enhanced. Underlying the equator the strong oxygen minimum zone contains higher Fe concentrations, that by upward mixing may well be the major source of Fe to surface waters supporting plankton growth. The Confluence zone (~30 ºS) of the Brazil and Malvinas Current is a well known region of high biological productivity and chlorophyll biomass. We now find this is supported by very high dissolved Fe from below at ~3 nM or more, the supply of which may also be due to influence of the Rio de la Plata or submarine groundwater discharge. The North Atlantic Deep Water shows a very strong correlation of Al and silicate (Si) in the subArctic Gyre, yet going southwards the NADW content of Al decreases and of Si increases and far south no relationship exists anymore. This is consistent with ocean simulation modeling of steady remineralization of Si versus continuous loss of Al due to adsorptive scavenging. An enhanced Fe pool at 2000-3000m depth below and south of the equator (4ºN - 15ºS) is consistent with hydrothermal input, confirmed by higher Mn but no extra Al.