A new approach for deducting *in situ* pH value of hydrothermal fluid in the reaction zone at mid-ocean ridges

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A new approach was developed to predict the pH $_{(P, T)}$ for fluid in subseafloor hydrothermal reaction zones at mid-ocean ridges. This approach involves three steps: (1) obtaining the pH value at the seafloor vent orifice using in situ pH sensor; (2) determining the P-T conditions at the reaction zone from constraints imposed by quartz solubility and phase equilibria in NaCl-H₂O system; and, (3) applying a corresponding theoretical calculation based on the pH value and P-T conditions from step 1 and 2 to estimate $pH_{(P, T)}$ at the depth. Adiabatic cooling is assumed, as is also for conservation of acidity. Thus, using this approach at P-vent (EPR 9°N) indicates a sub-seafloor (reaction zone) pH (P, T) of 6.4, in comparison with a lower value (5.1) that was measured in situ at the seafloor with a YSZ-pH sensor deployed using the submersible Alvin (Fig. 1). The predicted $pH_{(P,T)}$ indicates that the fluid is still relatively acidic compared to the neutrality. pH is a critical parameter, which is needed to constrain a wide range of mass-transfer processes in sub-seafloor reaction zones. Our study shows in situ pH measured at the vent site offers a better opportunity to constrain the deep processes.

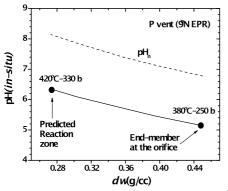


Figure 1: *In situ* pH measured at P vent orifice $(380^{\circ}\text{C}-250 \text{ b})$ in 2008 and the corresponding value predicted for source conditions at higher temperature and pressure $(420^{\circ}\text{C}-330 \text{ b})$. The solid line indicates the pH path in changes of the pH value during fluid ascending to the vent site. For the comparison, pH neutrality is also plotted with dashed line.

Subsurface contaminant transport across physical, chemical and mineralogical heterogeneities

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Subsurface contaminant transport involves the interaction of solutes with geomedia, and is studied either in conventional batch and column tests, or on atomistic so called nano scales. Application to reality is impeded by natural system heterogeneity and micro/macro scaling difficulty. The principal impediment is enhanced reactivity of perturbed samples used and inability to provide the crucial spatial and temporal concentration distributions of contaminants of concern in geomedia, needed for contaminant transport models.

As alternative experimental route, radiotracer diffusion tubes provide the required spatial and temporal concentration. Crucially, it enables exploring reactive transport across heterogeneous matrices. A layered acidic jarosite/alkaline coal fly ash shows the impact of matrix heterogeneity on chemical constituent transport and mobility. Discontinuous chemical gradients between porous media, will significantly affect transport properties by interfacial pore filling precipitates in the reaction zone. Thus radiotracer diffusion tube experiments can provide modellers with reliable boundary conditions needed to incorporate local heterogeneity. The principle of a self-forming layer with lower permeability at the interface between two matrices can be used to design *in situ* reliable and robust engineering sealing for waste disposal sites as well as manipulate subsurface flow.