Real-time *in situ* volatile characterization and methane carbon stable isotopic composition in the deep sea

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To better understand the nature of geochemical and microbial interactions in the subsurface biosphere, advances in both *in situ* molecular biology and geochemical measurements are needed. To examine these linkages in deep sea ecosystems, we have developed and deployed two *in situ* instruments, a mass spectrometer and a methane stable carbon isotope ($\delta^{13}C$) analyzer. We present real time concentration data for H_2 (20 – 120 μM), CH_4 (300 – 1300 μM) and CO_2 (5.9 – 7.6 mM) collected at sites along the Juan de Fuca Ridge hydrothermal vent system using the *in situ* mass spectrometer operating at a depth of over 2200m. With the ability to collect continuous spectra, we were able to detect areas of diffuse hydrothermal flow in which active H_2 and/or CH_4 oxidation was occurring, setting the stage for future studies focusing on specific metabolisms involving these gases. Second, we have also deployed an *in situ* methane $\delta^{13}C$ analyzer, designed to detect low concentrations of methane (nM), and measure $\delta^{13}C$ of CH_4. A recent deployment at a ~960m deep cold seep in Monterey Bay, CA, in which fluids were directly sampled from the seep orifice yielded both methane concentrations and carbon isotope ratios in real time. Coupled with microbiological data, this approach allows for better constraint of fluxes as well as microbial oxidation of CH_4 occurring at fine scales within sediments. This integrative –and *in situ*-approach will be fundamental to furthering our understanding of the deep subsurface biosphere.

Reactive transport modeling of Cr^{VI} treatment by a PRB in Thun (Switzerland)

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In Thun, Switzerland, a PRB (permeable reactive barrier) for Cr^{VI} reduction by iron shavings was installed in 2008. The barrier design was the same as used in Willisau, Switzerland, reported previously [1]. Both PRBs are composed of a double array of vertical piles containing iron shavings and gravel.

Column experiments performed with variably reactive iron shavings were used to calibrate the geochemical reactive transport model and reaction network of Mayer *et al.* [2], using the modeling software Crunchflow [3]. The aquifer in Thun is almost saturated with dissolved oxygen and the groundwater flow velocities are ca. 10 m/d. Under these conditions, the iron shavings showed a very strong decrease in their reactivity during the first month of operation. These observations could be modelled by adding kinetic Cr^{VI} and $O_{2(aq)}$ reduction by $Fe^{2+}_{(aq)}$. To our knowledge this is the first time that a model for the Cr^{VI} reduction by a PRB in a completely oxidized aquifer has been developed. The calibrated model was used to simulate the hydrodynamics and hydrogeochemistry within the double pile-array of the barrier in 2D. The modeled $Fe^{2+}_{(aq)}$ distribution within the PRB after 20 days of operation is illustrated in fig. 1.

The modeling work clearly points out that the limiting factors in the performance of the PRB are the groundwater velocity, the aquifer dispersivity and the $O_{2(aq)}$ concentration and other competing redox reactions ?
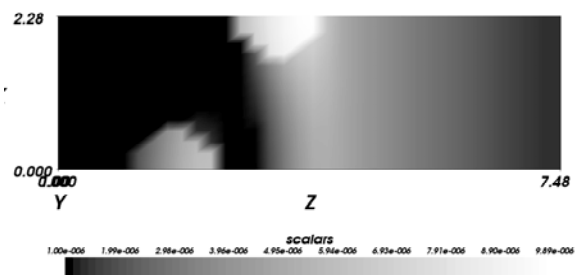

Figure 1: Spatial $Fe^{2+}_{(aq)}$ concentrations [mol/l] after 20 days of PRB operation (horizontal section through PRB).

[1] Flury *et al.* (2008) *Applied Geochemistry* 10.1016/ j.apgeochem.2008.12.020 [2] Mayer *et al.* (2001) *Water Resources Research* **38,** 3091-3103. [3] Steefel (2008) *http://www.csteefel.com.* User's manual 1-90.