Release of As(III) in groundwater: An energetically driven model tested on Bengal delta sediments

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Decoupling of Iron and Arsenic Release

Recent observations on the incubation of Bengal delta sediments have demonstrated that anaerobic dissimilatory iron reducing bacteria (DIRB) can play a key role in the mobilization of arsenic [1, 2]. Incubation experiments have revealed that arsenic and iron release can be decoupled: arsenic release can appear after Fe(III) reduction, rather than simultaneously. Our batch experiments with synthetic As(V)-doped ferrihydrite (2LFh) and a community of DIRB bacteria (FR) revealed the same decoupling of iron and arsenic release as shown in the figure below [3].

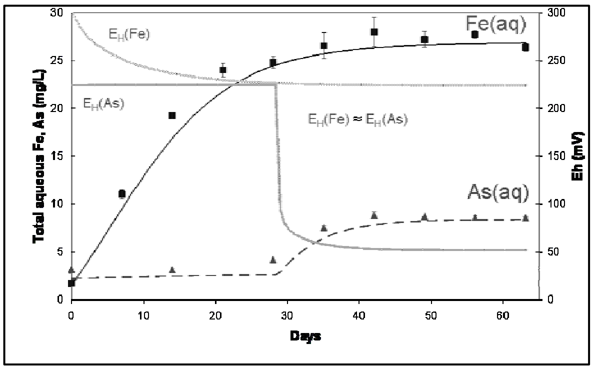

Figure 1: Fe and As release during As(V)-2LFh incubation experiments.

An Energetic Biogeochemical Model

Inorganic reaction processes included in the model are aqueous speciation, surface complexation onto 2LFh and mineral dissolution/precipitation. These reactions are coupled to microbially mediated redox kinetic reactions controlled by the electron donor, i.e acetate and both terminal electron acceptors, i.e Fe(III) and As(V). The same energetic explanation was also successfully applied to the results of Bengal delta sediments incubations [1].

[1] Islam *et al.* (2004) *Nature* **430**, 68-71. [2] Van Geen *et al.* (2004) *GCA* **68**, 3475-3486. [3] Burnol *et al.* (2007) *Geochemical Transactions*, **8**:12.

Carbon and hydrogen isotopic reversals in deep basin gas: Evidence of limits to the stability of hydrocarbons

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Hydrocarbon gases in reservoirs of Silurian and Ordovician age deeper than 3 km in the northern Appalachian basin have carbon isotopic compositions in the sequence: δ^{13}C methane (C_1) > δ^{13}C ethane (C_2) > δ^{13}C propane (C_3) and δ^{13}C butane (C_4). This is reversed from the normally observed sequence of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$ that is predicted by kinetic isotope effects (KIEs) during gas generation and observed in, shallower reservoirs in the basin. The concentration of C_2 and C_3 decreases as the reversal in δ^{13}C increases in deep samples. The hydrogen isotopic composition (δ^2H) of CH_4 observed in other basins increases with depth, but reverses in deep (~4 km) samples so that $\delta^2H\ C_2 < \delta^2H\ C_1$. Trends of $\delta^{13}C_1$ vs $\delta^2H\ C_1$ in gases with normal isotopic sequence show two trends offset by 4 permil that extrapolate to the δ^{13}C and δ^2H of two distinct types of organic matter in source rocks of middle Ordovician age.

A cracking model for gas generated from the two types of organic matter reproduces the range of δ^{13}C observed in gases with the normal isotopic sequence. Combined analysis of the molecular and isotopic compositions of individual gases allows identification of two end-members compositions. One is generated by breakdown of the original source material to gas and oil with normal δ^{13}C, and the second from breakdown of higher hydrocarbons (HHC) in gas accumulations at high temperatures producing the reversed trend. The reversed sequence appears to be produced by Rayleigh-type fractionation with theoretically predicted fractionation factors between $\alpha = 1.022$ (227°C) and $\alpha = 1.015$ (327°C). Decreasing $\delta^2H\ C_1$ in deep samples is consistent with isotopic exchange between CH_4 and H_2O with fractionation factors calculated from exchange experiments ($\alpha = 1.142$, T=250°C). We hypothesize that the reversed trends in δ^{13}C and δ^2H are due to reduction-oxidation (redox) reactions during deep burial in the Appalachian basin with estimated maximum temperatures of 200°C to 300°C. The most reasonable reactions promoting exchange between CH_4 and H_2O are redox reactions between H_2O and residual organic carbon. Simultaneous reversals in δ^{13}C and δ^2H between hydrocarbon gases may be an important signal of limits to stability of hydrocarbon gases and limits to natural gas resource potential in deep basins.