Redox oscillation impact on natural and engineered biogeochemical systems

L. CHARLET[1,2].

[1]ISTerre, University of Grenoble, B. P. 53, 38041 Grenoble, France.
[2]Institut Universitaire de France, Paris, France

Many systems fluctuate from oxic to anoxic conditions, in an oscillatory way. Systems becoming seasonally anoxic include irrigated, phreatic- or engineered-flooded soils, seasonally stratified lakes, urban waste sewage pipe and floodplain, macrophyte water treatment plant, and engineered low activity nuclear waste disposal. Conversely, lake "sediments", swamp and peat-bog become oxic "soils" upon urbanization, desertification or agriculture expansion, while anoxic sedimentary formation and aquifers turn oxic upon groundwater over-abstraction or fracking fluid intrusion.

Many reactions in these systems do not reach thermodynamic equilibrium and physical/chemical diffusion, electron transfer kinetics, and solid (e.g. carbonate, sulphide, metallic) phase nucleation control, together with microorganisms, the transitory states of these system. To conduct field work and experimental, analytical or spectroscopic investigation on these systems is a challenge which will be discussed, together with the "natural attenuation"- or release - of toxic elements (such as As, Hg, Se, U..) [1, 2]. (Bio)chemical models of redox oscillatory systems must include a combination of fast reversible reactions (e.g. aqueous and surface complexation equilibria), surface- or microbially- mediated redox kinetic reactions and slow irreversible adsorption/co-precipitation [3]. They should be included in risk assessment and system management of former military or mine sites, waste storage facilities, "green" waste water treatment, floodplains and urban development [4].

[1] Crancon, et al. (2010) *Sci. Tot. Environ*. 408, 2118-2128 [2] Winkel, et al. (2012) *Environ. Sci. Technol (in press)* [3] Burnol *et al.* (2007) *Geochemical Transactions*, **8**:12. [4] Guedron, et al. (2011) *Water research* 45, 2659-2669.

Hydrogen and methane fluxes from the ultramafic-hosted hydrothermal systems on the Mid-Atlantic Ridge

J. L. CHARLOU[1*], C. KONN[1], J.P. DONVAL[1], V. GUYADER[1], F. PEREZ[2], C. MUGLER[2], P. JEAN-BAPTISTE[2], E. FOURRE[2]

[1]Ifremer, Centre deBrest, Département Géosciences Marines, Plouzané, France (*correspondence: charlou@ifremer)
[2]IPSL/LSCE-CEA-Saclay, Gif-sur-Yvette, France (philippe.jean-baptiste@cea.fr)

Mantle-seawater exchanges contribute significantly to the hydrothermal fluxes at slow-spreading ridges. The emplacement of serpentinized mantle at all ultramafic-hosted hydrothermal systems discovered along the slow-spreading Mid-Atlantic Ridge (MAR) where tectonic extension dominates over magmatic construction is a common feature leading to the production of hydrogen and hydrocarbons. To understand the processes controlling the gas generation in ultramafic-hosted active fields, field data including the chemical composition of plumes and fluids are necessary to constraint experimental studies and modeling. The chemical composition of fluids from ultramafic-hosted hydrothermal fields (Rainbow, 36°14'N, Lost City, 30°N, Logatchev I and II, 14°45'N; Ashadze I and II, 12°58'N), all located along the MAR [1] is compared here. Like basalt-hosted fluids, the ultramafic-hosted fluids are controlled by phase-separation. But everywhere H_2 content is extraordinarily enriched in low or high chlorinity phases, demonstrating that the serpentinization process is mainly responsible for hydrogen production. As a consequence of the high reducing power of these systems, isotopic measurements of light hydrocarbons (C_1 to C_4) show that abiogenic hydrocarbons are generated by catalytic Fischer-Tropsch type reaction, considering their isotopic pattern, which is opposite to that for thermogenically-produced hydrocarbons. From plume and fluid data, H_2 and CH_4 fluxes may be calculated. For example, the total hydrogen discharge Φ_{H2} is found to be between 2.5 to 7.5 millions standard cubic meters per year for the Rainbow single site. Based on Rainbow $H_2/^3He$ and ^3He/heat ratios, the global H_2 and CH_4 fluxes for slow-spreading ridges are estimated to be 89 x 10^9 and 8 x 10^9 mol/year, respectively.

[1] Charlou et al. (2010) *AGU Monograph Series* **188**, 265-296.