Behaviour of rare earth and trace elements during fluid venting at cold seeps

D. Birot[1], G. Bayon[1], L. Ruffine[1], J.-C. Caprais[2], C. Bollinger[3,4], E. Ponzevera[1], E. Rongemaille[1] and M. Voisset[1]

[1]Département Géosciences Marines, IFREMER, Plouzané, France
[2]Département Etudes des Ecosystèmes Profonds, IFREMER, Plouzané, France
[3]Université Européenne de Bretagne, 35000 Rennes, France
[4]Université de Brest, IUEM, CNRS UMR6538, 29280 Plouzané, France

Venting of methane-rich fluids is a widespread phenomenon at ocean margins. Seafloor expressions of focused fluid venting on continental margins are commonly referred to as cold seeps, which include a large range of geological structures such as pockmarks, mud volcanoes, gas chimneys, and brine pools. Because methane, as a greenhouse gas, plays a key role in the Earth's climate, there have been significant efforts to quantify methane fluxes at continental margins, and assess their relevance to the global carbon budget. In marked contrast, however, very little is known about trace element biogeochemistry at cold seeps, and the impact of fluid seepage on ocean chemistry.

Here, we report dissolved and total dissolvable (TD) rare earth and other trace element concentrations, Nd isotopic compositions, and data for well-established tracers of fluid seepage (TDFe, TDMn) for seawater samples collected in the water column above deep-sea fluid-escape structures from the Niger Delta (Gulf of Guinea, West African margin). These results indicate that fluid seepage in this area acts as a source of dissolved REE to bottom waters. Our data suggest however that the net input of dissolved REE from sediment to the ocean is quantitatively buffered through iron and manganese-oxide scavenging at vent sites. The importance of fluid seepage at continental margins on the global marine REE and trace element cycles will be discussed.

Reactivity of clay minerals towards technetium immobilization

Michael E. Bishop and Hailiang Dong*

Department of Geology, Miami University, Oxford, OH 45056, USA (*correspondence: dongh@muohio.edu)

^{99}Technetium (^{99}Tc) is a fission product of uranium-235 and plutonium-239 which poses high environmental hazard due to its long half-life ($t_{1/2} = 2.13 \times 10^5$ y), abundance in nuclear wastes, and environmental mobility under oxidizing conditions. Tc (VII) valence state is stable in oxic environments and exists as the pertechnetate anion [Tc $(VII)O_4^-$] and is highly soluble. However, under anoxic conditions, Tc (VII) can be biologically and chemically reduced to insoluble Tc (IV).

In this study we evaluated the reactivity of clay minerals toward technetium immobilization utilizing a range of clay minerals including montmorillonite, iron-rich smectite (nontronite), rectorite (50:50 illite/smectite), mixed layered I-S (70:30), and illite, chlorite (ripidolite), and palygorskite. Many of these clay minerals are present at DOE technetium-contaminated sites. The clay minerals were characterized to determine mineralogy, and total iron and Fe (II) contents. Fe-Oxides were removed prior to utilization using a modified dithionite-citrate-bicarbonat (DCB) method. Fe (III) contents in the oxide-removed clay minerals ranged from 0.5 wt% to 19.7 wt%. Structural Fe (III) in the clay minerals was first bioreduced to Fe (II), and biogenic Fe (II) was then used to reduce Tc (VII). In a typical bioreduction experiment, lactate was used as electron donor, and anthraquinone-2, 6-disulfate as electron shuttle in select tubes in bicarbonate buffer (pH-7) with *Shewanella Putrifaciens* CN32 cells. The largest iron reduction occurred in chlorite (~43%). In the smectite to illite (S:I) series, nontronite-Fe (III) was reduced the most (~31 wt%) followed by mixed-layer illite/smectite, with illite being the least bioreducible. Structural Fe (III) in playgoskite was only slightly bioreducible (~4%). Fe (II) in the bioreduced clay minerals was used to reduce Tc (VII) to Tc (IV) in PIPES (pH 7) buffer. In the S:I series, the smectite end member was most effective in reducing Tc (VII) and the illite member the least effective, parallel to the extent and rate of Fe (III) bioreduction of these minerals. Despite a large amount of Fe (III) bioreduction in chlorite, most bioreduced Fe (II) was not available for Tc (VII) reduction. The amount of biogenic Fe (II) in playgoskite was available for Tc (VII) reduction, but with a very low rate. For all the clay minerals, the ratio of oxidized Fe (II) to reduced Tc (VII) was 3, as expected based on the stoichiometric reaction between Fe (II) and Tc (VII). These kinetic results are important for our understanding of how various clay minerals may be used to immobilize heavy metal Tc at DOE sites.