Stable isotope signals of metal contaminants in the environment: The search continues

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The pace of analytical and conceptual progress in the field of metal stable isotope biogeochemistry over the past decade has been breathtaking. The resulting metal stable isotope 'toolbox' is increasingly being used to help determine sources, transport mechanisms and fates of metal contaminants in the environment. Although many metal sources have already been found to have diagnostic stable isotope compositions and the processes leading to those compositions have in some cases been determined, there remains much to explore in terms of yet unrecognized distinctive metal pools and isotope tracer approaches. For example, a growing body of experimental work has demonstrated that metal electroplating partitions isotopically light metal from the plating bath onto the substrate, creating a potentially large pool of isotopically light metal in the environment. To test for this possible isotope signal in industrial materials, we determined the Cr, Zn and Cd stable isotope compositions in acid leachates of an assortment of screws, nuts and bolts from a particular American distributor. In each case, the isotope composition was lighter than the accepted isotope standard for those metals and among the lightest values yet reported for natural materials. Another developing approach for determining sources of aqueous metal contaminants is to consider the isotope composition of each component of a tightly-bound molecule in a multi-tracer framework, for example, to determine the oxygen and Cr isotope compositions of the chromate molecule. The problem in the case of aqueous chromate is that concentrations in all but the most contaminated groundwaters are typically less than 1μM, requiring processing of several liters of water to obtain the ~10 micromoles of chromate required for oxygen isotope analysis by standard TCEA gas mass spectrometry. We are attempting to tackle this problem by developing a negative-ion, thermal ionization mass spectrometry (N-TIMS) method for analysis of nanomolar amounts of purified chromate. Using our 'total evaporation' N-TIMS routine, we are currently able to reproduce the oxygen isotope compositions of our chromate reagents previously measured by TCEA gas mass spectrometry. The next step will be to determine the oxygen and Cr isotope compositions of chromate from natural and contaminated groundwaters.

A modeling study of organic matter remineralization in deeply-buried marine sediments

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In the application of reactive-transport models to the study of biogeochemical processes in marine sediments, it is generally assumed that sediments are isothermal with depth. However this is not the case for deeply-buried sediments (100's of meter sediment depths) in which there is a significant temperature increase (geothermal gradient) with depth. Assuming that the temperature dependence of sediment organic matter (OM) remineralization can be described by the Arrhenius equation, results from nearshore sediments suggest that the activation energy for this process is ~60-130 $\mathrm{kJ\cdot mol^{-1}}$. Based on an increase of ~20-30°C over several hundred meters of sediment, rates of OM remineralization should increase ~10- to ~200-fold with burial. The incorporation of this temperature dependence of reaction rates has not, to my knowledge, been included in reactive-transport models of deeply-buried marine sediments.

I have examined this problem using a coupled, non-linear model that incoporates diffusion, advection, OM remineralization by bacterial sulfate reduction and methanogenesis, and anaerobic oxidation of methane (AOM). Model results show that OM which is highly refractory at seafloor temperatures (~2°C) becomes reactive towards remineralization at depths of several hundred meters due to burial/heating. This results is a deep zone of methanogenesis separated by a relatively large region in which methane diffuses upwards to be oxidized by downwardly diffusing sulfate. The sediment depths at which this AOM occurs are generally <100 m, and sulfate profiles here are highly linear. Furthermore, because of the temperature dependence of OM remineralization, little OM is directly degraded by sulfate reduction during burial. This is in sharp contrast to nearshore marine sediments, where sulfate reduction occurs in the upper several meters of sediment and is more directly coupled to OM remineralization, and further, methanogenesis occurs immediately below the zone of sulfate reduction.

Model results are consistent with field observations in deeply-buried marine sediments, and provide a quantitative framework in which to examine the factors controlling linear pore water sulfate profiles seen in many continental margin sediments. The model also has applications to the study of gas-hydrate containing sediments. All of these considerations will be discussed in this presentation.