Exploring carbonate aquifers and their susceptibility for metal release during CO_2 leakage

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Metal transport resulting from potential CO_2 leakage into freshwater aquifers is a major concern accompanying carbon sequestration operations. Acidity resulting from dissoluton of leaked CO_2 into aquifer waters may result in release of metals from aquifer minerals. Carbonate aquifers have the ability to buffer increased acidity through calcite and dolomite dissolution, and are therefore theoretically “safer” than non-buffering aquifers. However, carbonate minerals are rarely found as pure phases in nature, often containing impurities in the solid phase. These impurities substitute for either calcium or carbonate in the crystal lattice. Buffering of acidity requires dissolution of carbonate minerals, resulting in potential release of trace elements. Whole-rock analysis of natural carbonate rock samples show solid-phase concentrations of Pb and Cr on the order of several ppm, and of Ba, Co, Ni, Rb, Sc and Zn on the order of tens or hundreds of ppm. Prediction of the behavior of these metals through modeling is difficult, as there are several models of co-precipitation and dissolution in solid solutions. Simple stoiciometric dissolution predicts very different release behavior of these metals from calcite dissolution at various CO_2 partial-pressures. For example, at low P_{CO2}, cobalt concentrations in solution are as high as 776 ppb, and decrease with increasing P_{CO2}, whereas barium concentrations in solution increase with increasing P_{CO2}, following a trend similar to that of calcium. In this work, batch dissolution experiments are combined with SEM and electron microprobe analyses, to investigate dissolution rates and equilibrium release of metals from carbonate rocks and to determine their solid-phase source.

Uncovering the key processes involved in manganese biogeochemical cycling in the Ocean

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Mn forms a critical part of many redox enyzmes most notably for photosynthesis, where as part of Photosystem II it converts H_2O to O_2. Many marine organisms also contain Mn superoxide dismutases (SOD), that act as part of the intracellular defences against reactive oxygen species (ROS) and in particular rapidly convert superoxide (O_2^-) into O_2 and H_2O_2. While laboratory studies have shown that the growth of marine phytoplankton is reduced for some species at the low Mn concentrations found in open ocean seawater, currently there is little evidence from fieldwork to suggest Mn limitation occurs, but this possibility remains, particularly for the Southern Ocean.

The supply of Mn to the open ocean is predominantly via the deposition of aeolian dust and subsequent dissolution of Mn(II) from the particles. The released Mn(II) is slowly oxidized (via biota or chemically) to insoluble MnO_2 which precipitates out of the water column. In the sunlit ocean, H_2O_2 can reduce MnO_2 back to Mn(II) completing a redox cycle. New work by a number of groups suggest that transient Mn(III) species, intermediate in the cycling between Mn(II) and MnO_2 may play an important role in both the Mn and Fe biogeochemical cycles in surface waters. In coastal waters Mn(II) can diffuse from reducing sediments with subsequent mixing into the photic zone.

In this presentation we will present data for Mn concentrations, speciation and kinetic reactivity from two research cruises in the Tropical Atlantic (M83-1 and MSM17-04) and from a dust deposition experiment performed in trace metal clean mesocosms in the Mediterranean (DUNE2). We will use our combined dataset to determine the predominant source of Mn to shelf waters in the Mauritanian upwelling region and the adjacent open ocean in the Tropical Atlantic, which are impacted by both Saharan dust and potentially coastal sedimentary sources that are advected offshore by the upwelling waters. Finally we will examine the evidence for Mn(III) in the euphotic zone of the open ocean and the implications this had for Mn biogeochemical cycling in the ocean.