

Geochemical characterization and origin of high saline pore fluids from the Chapopote asphalt volcano – Southern Gulf of Mexico

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High saline pore fluids in marine deep-sea sediments are well known, especially when evaporites exist in the underlying deep sub-surface. Nevertheless, the classification of brines is matter of debate over and over again. A major question in this context is, if the high content of total dissolved solids is generated by dissolution of evaporites or derived from evaporation residues.

During RV Meteor expedition M67/2 we have taken sediment and pore water samples from an isolated diapiric elevation within the Campeche Knolls area in the southern Gulf of Mexico. At this structure, named Chapopote, asphalt volcanism and hydrocarbon seepage has been documented. Here we present and discuss results from pore water analysis on sediments which have been recovered in the vicinity of the active vent sites. The most conspicuous feature is that interstitial waters from Chapopote knoll exhibit a strong, almost linear increase in salinity (from 37 g l⁻¹ to about 83 g l⁻¹). Modeling of transport and reaction processes give clear evidence that the pore water composition at these sites is controlled by diffusion only. Correspondingly, strong gradients observed for ratios of geochemically almost inert constituents, like Na:Cl, are solely explainable by differences in specific diffusion coefficients. Furthermore, these correlations let assume that the composition of surface pore waters at Chapopote knoll are not significantly influenced by the dissolution of salt minerals. Based on oxygen- and hydrogen-isotope data, which indicate to simple dilution effects, clay mineral dehydration processes seems to be negligible.

In combination with the application of geochemical equilibrium calculation, the similarity of the relative composition of the Chapopote brine to formation waters of Jurassic and Cretaceous age would seem to suggest a local upward percolation of the later. Accordingly, high saline waters at Chapopote would originate from a dilution of a Cretaceous or Jurassic residual brine, which would have to be expected 40-50 m bsf. Based on bromide concentrations its degree of evaporation can be approximated to 25-45 times.

Nature and reactivity of ferrous iron forms through a subsurface redox transition zone probed by contact with the pertechnetate anion

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Aquifer systems can display marked changes in redox properties over relatively short distances as a result of variation in electron donor and oxygen concentrations, microbiologic activity, and sediment texture and mineralogy. Under anoxic conditions, variations in redox potential couple with the biogeochemical speciation of Fe to strongly effect the sorption and transport behavior of certain organic compounds and polyvalent metals and radionuclides. Here we describe results of a laboratory study with subsurface sediments carefully retrieved from an unusual redox transition and fluctuation zone (~18 to 55 m bgs) in an unconfined aquifer at the U.S. DOE Hanford site through which contaminants migrate. The sediments were extracted with weak acid (WA) over time to define acid-soluble Fe(II)_{WA}/Fe(III)_{WA} and co-associated elements (e.g., Si, Al, Mg/Ca, etc). Sediment masses were adjusted to be equal in Fe(II)_{WA}, and kinetic reduction experiments performed in suspension at circumneutral pH with pertechnetate [Tc(VII)O₄⁻(aq)] as a probe reactant. Technetium is a polyvalent radionuclide that is highly sensitive to Fe(II) forms as heterogeneous reductants, and is an important contaminant associated with uranium fission products. Reduction rates normalized to Fe(II)_{WA} varied dramatically between different sediments. The nature of reactive Fe(II) was determined by XRD and SEM/TEM in combination with variable temperature transmission Mossbauer spectroscopy (TMS). Fe(II) smectites and unusual discrete Fe(II) phases were the reductants. The molecular speciation of the Tc(IV) redox product (as determined by EXAFS) was dependent on the reactive Fe(II) form and reduction rate, and varied between Tc(IV)O₂(s) polymers and Tc(IV)-Fe(III) complexes of different type. This speciation, in turn, had a primary influence on the oxidation kinetics of redox product Tc(IV). Microbial characterization of this variable redox zone has been performed and the origin of the various reactive Fe(II) forms will be briefly discussed.