Hydrogen generation at clay minerals of sandstone cements

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Hydrogen availability is crucial for the activity of anaerobic chemolithoautotrophes. These microbes are able to tolerate extreme environmental conditions, prevailing in e.g. hydrothermal vent systems, deep aquifers, underground mines and mine residues. If microbial or hydrothermal H_2 supply is lacking, mineral - water reactions could sustain anaerobic chemolithoautotrophic metabolism. In sandstones, iron rich clay minerals of the cements are suspected to be the most reactive minerals in respect to H_2 formation, since water reduction is commonly related to oxidation of mineral bound ferrous iron.

Methods

Rock samples from the Westfal C sandstone formation (2,800 m depth) were analyzed for their cement minerals using XRD and sequential extractions. Milled rock samples and iron rich chlorite samples were reacted in headspace vials with a pH=3.5 buffer solution for 30 days. The headspaces were analyzed for H_2 by gas chromatography. Non-sterile and sterile test systems were used. Additional tests with Westfal C sandstone rock samples and ground water were preformed at 90 bar and 40°C in a high pressure reactor (CO_2/Ar gas phase) for 5 months. The gas phase was sampled regularly for GC analysis of H_2.

Results

In all test systems, hydrogen generation was observed at levels of 100 to 500 nmol H_2 / g $_{\text{sample}}$. Test systems unfavourable for autochthonous microbial activity (sterile mineral tests, low pressure rock sample tests) contained higher H_2 concentrations then test systems that favour autochthonuos autotrophic metabolism (non-sterile mineral tests, high pressure rock sample tests). In addition, H_2 levels declined with time, indicating microbial H_2 consumption during the tests by autochthonous autotrophes. The figure shows H_2 concentrations over time in sterile and non-sterile Fe-chlorite - water interaction tests. Dissolved hydrogen concentrations in the test systems (10-60 µmol / L) clearly exceeded literature reported environmental H_2 levels of e.g. sulphate reducing or methanogenic aquifers and of basaltic ground waters. Generated H_2 concentrations are comparable to calculated H_2 fluid concentrations of midocean ridge basalt.

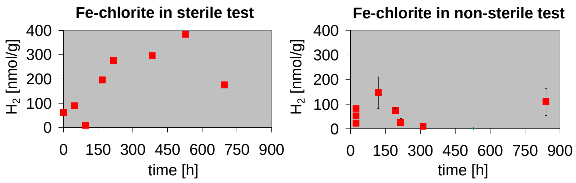

Figure 1: H_2 generation from Fe-chlorite - water interaction

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Geochemistry of barium in sediments of the western Black Sea

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During two cruises with RV POSEIDON and RV METEOR to the western Black Sea (west of Crimean Peninsula) in 2004 and 2007, respectively, sediment cores were taken along a transect from 500 to 1700 m water depth. Pore water and solid phase investigations aimed at unraveling the geochemical behaviour of barium in this anoxic water column and sedimentary environment. In particular, our study focussed on the following questions: (1) In which way does the anoxic water column of the Black Sea control the flux of particulate barium phases to the seafloor?, (2) Does barite form in the anoxic water column and - if so - is the amount of barite reaching the sediment surface dependent on water depth as reported for oxic marine depositional environments?, (3) Can barium/barite be used as a sedimentary tracer of past productivity in the Black Sea?, (4) How is barium redistributed post-depositionally at the sulfate/methane transition (SMT) which is typically located around 2 m sediment depth?, (5) Can we use diagenetic barite to trace the downward migration of the SMT which occurred in the Black Sea deposits since the transition from the last glacial freshwater lake situation to the Holocene anoxic marine period? Understanding the geochemistry of barium in sediments underlying anoxic water bodies – like is the case in the Black Sea – will significantly contribute to improving interpretations of fossil sedimentary records laid down under oxygen-depleted water column conditions, like below or within oxygen minimum zones or during Cretaceous Oceanic Anoxic Events.