

Microbial diagenesis of evaporitic gypsum

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Large amounts of evaporitic gypsum are present in sedimentary basins worldwide. When gypsum comes into contact with hydrocarbon-rich fluids (methane, petroleum) there is a potential for subsurface microbial communities of sulphate reducing bacteria to develop.

We have investigated sulphur-bearing authigenic carbonates from Spain (Lorca basin) and Egypt (Ras Zeit and Gemsa) which are in close stratigraphical relation to Miocene evaporitic gypsum deposits and are a by-product of this microbial activity [1, 2]. We present mineralogical and petrographical evidence for the microbial substitution of gypsum in the form of carbonate pseudomorphoses of gypsum rhombohedra. We developed a new semi-automatic method which allows us to differentiate the isotopic composition of distinct carbonate phases (calcite, dolomite) in sedimentary samples. All carbonates analysed are strongly depleted in ¹³C (-24.5‰ < δ¹³C < -2.8‰) indicating that their carbon source comes from the oxidation of reduced organic compounds.

We are carrying out lipid biomarker analyses to identify potential microbes which are involved in this diagenetic transformation. Preliminary results indicate the presence of archeol and diethers, known to be associated to the oxidation of reduced organic substrates in other diagenetic settings. These results suggest the setting up of a complex subsurface microbiological community whose existence relies on the mineral source of sulphate and organic source of carbon.

This diagenetic process can be of economic importance because the porous carbonates that are produced may form petroleum reservoir rocks [2].

[1] Rouchy *et al.* (1998) *Sediment. Geol.* **121**, 23-55. [2] Aref (1998) *AAPG Bulletin* **82**, 336-352.

Redox activity of humic substances shows a strong dependence on ionic strength

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Humic substances (HS) are redox-active natural polymers present in almost all terrestrial and aquatic environments. They can be reduced chemically or microbially and undergo redox reactions with pollutants or minerals, e.g. Fe(III) (hydr)oxides. However, the influence of geochemical parameters (e.g. ionic strength) on HS redox activity has not been investigated in detail yet.

We therefore tested the redox activity of reduced HS using dissolved and solid Fe(III) compounds as electron acceptors for HS at different concentrations of phosphate buffer and NaCl solutions. We found a strong dependence of HS redox activity on ionic strength with HS being significantly more reactive at higher salt concentrations. Particle size measurements by dynamic light scattering revealed a larger heterogeneity in size distributions at increased salt concentrations including a higher fraction of large HS molecules containing a high inner and/or outer surface-area due to unfolding of molecules during reduction.

From these findings in combination with zeta-potential measurements we hypothesize that the increased redox activity of reduced HS at higher ionic strengths is likely due to changes in the spatial structure of HS. Particles present at high ionic strengths resemble large network-like structures that have a high affinity for Fe(III) ions which can intrude and react with reduced functional groups more easily the higher the ionic strength.

Our results suggest that the redox activity of HS strongly depends on the ionic strength present in a certain environmental system. In particular in low ionic strength systems such as aquifers HS are likely to show a lower redox activity compared to HS in freshwater or in particular in marine systems.