

Dynamic subsurface biosphere fuelled by organic matter from the past

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Microbial degradation of organic matter deposited on the seafloor and buried over geological time within marine sediments leads to the onset of a redox zonation. This zonation may strongly shift over geological timescales due to variations of organic matter composition and burial rate. However, such dynamics in subsurface redox zonation is generally not obvious from measured porewater profiles.

Redox zonations may leave characteristic imprints in the geological record and therefore document the diagenetic history of a particular biogeochemical setting. We report the finding of diagenetic barite and dolomite layers that document past positions of the sulphate/methane transition zone (SMTZ) at ODP Site 1229 drilled on the Peruvian continental shelf. The layers co-occur with a focussed enrichment in isotopically light archeol, a lipid biomarker indicative of anaerobic methane oxidation.

Using a time-transient reactive transport model for sulphate and methane allowed to reproduce a SMTZ migrating upward and downward over a depth range of 30 m (below seafloor) over a time period of 100 ka. These variations were caused by variation in the organic matter content, the initial age of organic matter, and burial rate. Organic matter was assumed to decay according the reactive continuum model [1] whereby the different parameters were constrained by bulk TOC and ³⁵S radiotracer rate data.

The diagenetic imprints and modelling results are evidence of a sub-surface redox zonation more dynamic than we would expect from measured porewater profiles. Therefore, the diagenetic record in combination with non-steady state geochemical modelling must be taken into account for an assessment of diffusive fluxes between marine sediments and the water column and their contribution to global biogeochemical cycling.

[1] Boudreau and Ruddick, (1991) *Am. J. Sci.* **291**, 507-538.

Development of methodologies based on Field-Flow Fractionation for the characterization of engineered nanoparticles in complex samples

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Engineered nanoparticles (ENPs) are more and more introduced into consumer products, leading to environmental and health concern. This development has been so rapid that methods to detect, quantify and characterize ENPs in environmental and biological media are still widely lacking. Field Flow Fractionation (FFF) is one of the most promising techniques currently developed for these tasks.

The strategy adopted for the analysis of ENPs in complex matrices depend strongly on the type of the ENPs and the nature of the matrix. Therefore, different methodologies have to be specifically developed for the e.g. analysis of nanoparticles of silver (AgNP) in an environmental matrix and nanoparticles of silica (SiO₂NP) in a biological matrix. These new developments have been performed on reference samples and are presented here.

Standard AgNP (i.e. 15-20 nm NM300 from OECD repository) were spiked to a standard soil (i.e. IME RefeSol from the German Federal Environment Agency) while Standard SiO₂NP (here 40 and 100 nm) were spiked to tomato soup (preparation from JRC in the course of FP7 Nanolyse project). The sample preparation can be done by density separation (AgNP) and by acid digestion (SiO₂NP). Flow-FFF coupled to UV-DAD spectrometry, online static and dynamic light scattering and ICP-MS were used to characterize compositions and properties of nanoparticles as a function of size.

Conventional ICP-MS coupled to FFF seems to be suitable for complex samples containing AgNP, because Ag has a low background in the environment.

These optimized methods helped in the investigation of complex mixtures of ENPs and matrix which finally led to the conclusion that ENPs do not always intensively interact with natural nanoparticles coming from the matrices and can occur as stable single particles in the environment. This results mitigate the current assumption that hetero-aggregation will be the most probable mechanism occurring in the environment. This is important in order to predict the impact of ENPs on the environment and human health.