

REE geochemistry of deep ocean sediments in Brazil Basin

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Geochemical studies are essential for understanding the processes of sedimentation and diagenesis in Brazil Basin in Quaternary. Brazil Basin (South Atlantic) is characterized with low sedimentation rate and the low organic matter concentration in sediments that leads to oxidizing diagenesis. Here we focus on REE geochemistry in the surface and subsurface sediments obtained from 8 sediment cores along 24° W in the Basin from the depths 4500-5800 m. The recovered sediments are represented with red clays, partly reduced hemipelagic clays and carbonate and ethmodiscus oozes.

The sediments at southern stations of the profile are oxidized and reveal the presence of Mn (IV) oxyhydroxide. Shale normalised REE patterns are flat and have positive Ce anomaly. Phosphorus concentrations are low (0.02-0.08%) relative to typical red clays. Sediments of northern part of profile bear evidence of hydrothermal influence: high Fe and Mn concentrations and the characteristic REE pattern. This implies that REE concentrations are increased relative to south station sediments and REE patterns have negligible Ce-anomaly. Phosphorus concentrations are also increased probably due to sorption by hydrothermal Fe-oxyhydroxides. Sources of hydrothermal matter could be volcanic structures at the Basin bottom at 12°W observed during seismic profiling.

Reduced sediments with traces of pyrite were recovered on two stations. They reveal both the absence of Ce-anomaly coupled with Mn-Fe reduction and the anomalous preservation of Ce-enrichment. In first time there were examined REE composition of ethmodiscus oozes of Brazil Basin. The oozes are enriched with manganese that probably controls the positive Ce anomaly.

In this study it has been observed the anomalous Ce enrichment of REE in Brazil Basin sediments relative to World Ocean sediments. Positive Ce anomaly is controlled by scavenging on Fe-Mn-oxyhydroxides. Presence of hydrothermal oxyhydroxides leads to reduction of Ce-anomaly and slight HREE enrichment.

Characterization of sea spray OM from selected algal cultures

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Recent investigations showed that submicron sea spray, generated from biologically productive waters, can be extremely enriched in organic matter [1, 2].

Selected microalgal cultures, namely *Emiliania huxleyi* and *Leptocylindrus danicus*, in the exponential phase of growth, were used to produce sea spray aerosol in bubble-mediated laboratory experiments, with a similar setup as described by Facchini *et al.* [1].

After six hours, seawater were characterized by higher particulate organic carbon (POC) and lower dissolved organic carbon (DOC), as compared to oceanic water samples collected during a cruise in the north-east Atlantic [1]. Aerosol particles generated by bubble bursting show an organic matter (OM) contribution less than 10% of the total submicron sea spray mass, very low compared to the sea spray aerosol generated by the oceanic water samples [1, 2]. Nevertheless, some of the sea spray features described in sea spray aerosol generated by natural waters have been confirmed: submicron sea spray OM resulted mainly water insoluble (WIOC).

¹H NMR analysis highlighted that the WIOC in *E. huxleyi* sea spray consisted of unsaturated lipids, less complex and less oxidized with respect to the oceanic water sea spray [1]. Identical features characterize the spectra of POC extracted from the bubbled water. Aerosol WIOC resulted extremely different from WIOC, and its composition is consistent with a mixture of lipopolysaccharides, proteins and amino acid derivatives (metabolites), which plausibly derived from DOC.

These results confirm that the chemical components of phytoplankton exudates and the biological hydrophobic material (e.g. membrane lipids) forming POC are efficiently transferred to air-sea surface films and into sea spray particles.

[1] Facchini *et al.* (2008) *Geophys. Res. Lett.* **35**, L17814. [2] Keene *et al.* (2007) *J. Geophys. Res.* **112**, D21202.