# Natural organobromine in terrestrial and marine environments

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In natural systems, bromine (Br) is generally believed to exist in the form of inorganic bromide. The perception of bromide as unreactive in soils justifies its frequent use as a hydrological tracer. Similarly, the oceanographic classification of Br as a conservative element in the water column has persisted for decades. We have recently shown that stable organobromine of natural origin is ubiquitous in terrestrial [1] and marine [2] environments. Using a novel quantitative technique based on XRF and X-ray absorption spectroscopy, we quantified organobromine concentrations in estuarine and marine sediments. Organobromine occurs in correlation with organic carbon and varies with sediment depth (Fig. 1) due to biogeochemical cycling of Br.
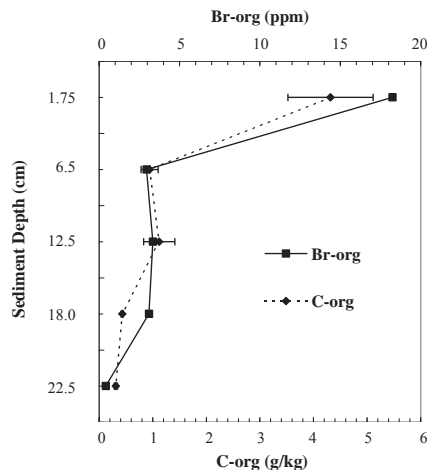


**Figure 1:** Organobromine and organic carbon concentrations with depth in estuarine sediments from Cape Cod, MA, USA.

X-ray spectromicroscopic images of sediment sections reveal a heterogeneous Br distribution, with associations between organobromine and metals such as iron and calcium. Organobromine also appears in particulate material from sediment traps deployed in the water column, suggesting that some fraction of sedimentary organobromine originates in overlying waters.

In the terrestrial environment, the Br in plant litter, organic-rich surface soils, and isolated humic substances is exclusively bonded to carbon. Terrestrial organobromine production is linked with plant litter decay and may be catalyzed by haloperoxidase-like enzymes in the soil environment.

These findings overturn the paradigmatic classification of Br as unreactive in the environment, shedding light on a biogeochemical cycle that may ultimately contribute to our understanding of the environmental fate of anthropogenic organobromine pollutants.

[1] Leri & Myneni (2012) *Geochim. Cosmochim. Ac.* **77**, 1-10.
[2] Leri *et al.* (2010) *Global Biogeochem. Cycles* **24**, GB4017.

# Redox and Ca/Mg/Fe ratios in clay formations

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Redox control and Ca/Fe/Mg ratios remain among sensitive factors to improve modelling of porewaters chemistry in geological clay barriers. The existing models consider pure phases at equilibrium with porewater [1, 2], however accurate observations show more complexe mineralogy. In that way two marine clay formations (Callovian-Oxfordian (COx) clay at Bure, France and Opalinus (OPA) clay at Mont Terri and Benken, Switzerland) were investigated to describe diagenetic minerals, the processes involved in their deposition and the effects of these processes on redox conditions and phase stabilities.

**Mineralogical constraints in COx clay [3] and OPA clay**
Diagenetic sequence defined in the three clay formations consists of: 1) dominant micritic calcite with minor dolomite, and pyrite resulting from bacterial reduction of dissolved marine sulphate; calcite and dolomite are characterized at this stage of low Fe/(Fe+Mg) ratios (<0.4);
2) calcite, Fe-rich dolomite/ankerite, siderite ($Ca_{0.1-0.3}$ $Fe_{0.5-0.7}$ $Mg_{0.2-0.4}$ $CO_3$) and glauconite. Calcite and siderite have Fe/(Fe+Mg) ratios higher than 0.5-0.6 in the both clay formations. At contrary Fe-rich dolomite shows heterogenous Fe/(Fe+Mg) ratios depending of the clay formation: ~ 0.1 in COx clay, ~ 0.35 in OPA Clay of Mont Terri and up to 0.7-0.8 in OPA clay of Benken;
3) galena, sphalerite, celestite, calcite veinlets.

**Redox control**
Redox is controlled by pyrite in the models [1, 2, 4]. When Sphalerite and galena are taking account in the COx porewater model, the three sulfides are not at equilibrium with porewater. Further investigations on the distribution of sphalerite and galena in the clay formation are needed to affine the chemical system (introduction of Zn and Pb or not) to control the redox.

**Ca/Fe/Mg ratios in porewaters**
The cation exchanger of clay rocks reflects the relative amounts of exchanged cations in porewater through exchange equilibrium reactions [3]. Porewater is also at equilibrium with some diagenetic minerals. In Pearson [1] (OPA Clay model) and Gaucher [2] (COx Clay model), porewaters are likely at equilibrium with calcite (for Ca), dolomite (for Mg), siderite (for Fe) and celestite (for Sr). The large chemical variations of carbonates and their distribution (present at the scale of the formation or only at some levels) must be taken account to improve the models. Further work is to precise the carbonate compositions at equilibrium with present-day porewaters, specifically of dolomite in COx, ankerite and siderite in OPA, and to calculate the solubility constants of the carbonate solid solutions for Ca/Mg/Fe ratio control. The Fe control by siderite in the COx model will be discussed, siderite being present at a level of the COx Clay.

[1] Pearson (2011) *Applied Geochemistry* **Volume26**, 990-1008,
[2] Gaucher (2009) *GCA* **Volume73**, 6470-6487,
[3] Lerouge (2011) *GCA* **Volume75**, 2633-2663,