## A study on the effect of pore geometry on mineral changes

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Injection of seawater in 130°C offshore chalk oil fields will induce chemical alterations as the seawater is not in equilibrium with the formation. This has been confirmed by core experiments. Furthermore, the core experiments reveal that the chemical alteration induces enhanced compaction and enhanced oil production. Many conceptual models have been suggested for this phenomenon, but quantitative geochemical simulations on the pore scale is missing. We investigate the spatial distribution of the chemical alterations induced by seawater and MgCl<sub>2</sub> flooding at 130°C; the net chemical change in the pore space is compared with the net chemical change observed in the core experiments.

A full geochemical solver integrated with a lattice Boltzmann (LB) model is used to model the pore scale reactive flow. The LB model solves the fluid flow and the advection-diffusion of the chemical species, while the geochemical model gives the interaction between the aqua chemical species and the pore mineral-surfaces. The geochemical solver has been compared successfully with PHREEQC and effluent from core experiments. A simulation on a carbonate sample is shown in Fig.1.



**Figure 1:** 0.219M MgCl<sub>2</sub> is flooded from the left at 130°C, the pore space is initial in equilibrium with distilled water. After 2 pore volumes of flooding magnesite is precipitated non-uniformly in the pore space (blue (opaque) to red (solid) colours). Only calcite is present initially.

## Key impact of soil (Fe/organic C) ratio on REE shallow groundwater patterns

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A number of studies have been carried out over the last two decades on the chemistry of rare earth elements (REE) in stream waters and groundwaters. They occur usually as simple REE (III) species, with the exception of Ce. Indeed, among the REE, Ce is the only element that can be oxidized to the (+IV) state, modifying its behaviour. REE are potentially used as tracers of rock/water interaction processes, groundwater flow and mixing, soil genesis, and notably, as proxies for evaluating paleoceanographic and paleoclimatic change by using Ce anomaly development.

Previous investigations of the REE geochemistry in groundwaters of the Kervidy/Coët-Dan catchment (Brittany, France) showed a systematic, topography related variation of REE signatures, notably a large negative Ce anomaly in the upper part which decreases from top to bottom of the transect. These studies also showed that REE are carried by organic colloids in these waters. A recent study showed that the strong spatial variation of negative Ce anomaly would be due to the input into the aquifer of REE-rich, Ce anomaly-free, organic colloids located in the uppermost, organic-rich soil horizons. Consequently, one major question arises: why organic colloids show a large negative Ce anomaly at the top and Ce anomaly-free at the bottom?

In this context, soil/water interactions performed through soil column experiments, were carried out with several soil samples recovered from top to bottom of two toposequences to understand the origin of the variability of REE patterns in the Kervidy/Coët-Dan catchment. The major carriers phases of the REE pools were determined. Moreover, batch experiments were carried out to investigate the role of organic molecules in the development of Ce anomaly in solution.

The results showed: (i) a strong Ce sequestration in oxidized phases such as secondary minerals formed at the frond of altered shale, (ii) a close relationship between soil Fe/Organic C ratio and Ce anomaly in soil solution. Moreover, this study showed (iii) the strong influence of organic molecules in the lack of Ce anomaly in waters by Fe oxyhydroxide dissolution. Furthermore, the REE signature in the Kervidy/Coët-Dan groundwaters appears to be provided in major part by the upper horizon of soil.

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