Stable chlorine isotopes as tracers of solute transport in a clay-rock formation (Paris Basin, France)

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The Callovo-Oxfordian (C-O) clay-rock formation in the eastern Paris basin (France) was selected for extensive study to assess its potential interest for siting a radioactive waste disposal facility. The C-O is a very low permeability homogeneous marine clay-rock sequence over- and underlain by two low permeability limestones.

The aim of this study is to evaluate the solute transport history in this unit using chlorine stable isotopes. Our samples covered the whole clay formation (130m in thickness) from 342m to 472m in depth as well as the bordering limestones.

Chlorine has two stable isotopes ^{37}Cl and ^{35}Cl and is a conservative tracer in this context. In a sedimentary context, differences in their transport characteristics lead to chlorine isotope fractionation during mixing, diffusion and ultrafiltration processes.

Pore water chlorine was extracted by leaching and was converted into chloromethane for mass spectrometry analysis.

Pore water Cl concentrations are low and constant throughout the C-O, between 300 and 500 mg/l, but greater in border limestone pore waters (up to 2700 mg/l). C-O δ^{37}Cl ranges from -0.34‰ to +0.65‰/SMOC. Three parts in the C-O formation can be identified. The center shows very homogeneous δ^{37}Cl (+0.22±0.2‰) whereas the bottom and the top δ^{37}Cl are more negative (0 down to -0.35‰). The higher δ^{37}Cl (+0.6‰) are found at the center/bottom and center/top limits. There is no evident isotopic link between the C-O and bordering limestones.

The δ^{37}Cl variability shows that the concentration and δ^{37}Cl of primary pore water (probably ocean water) have changed due to transport processes after the sediment deposit. The low pore water chlorine concentration, very different from marine concentration, and the δ^{37}Cl indicate a complex diagenetic history for the C-O. Since data cannot be explained by simple diffusion or ordinary mixing processes, several processes undoubtedly occurred to lower chlorine concentration and to fractionate chlorine isotopes, ultrafiltration probably playing a role for the latter. It is difficult to identify these processes but they have probably to do with the progressive effacing of the diagenetic effects on concentration and isotope composition.

Aromatic hydrothermal petroleum from a mercury deposit (Idrija, Slovenia)

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High concentrations of polycyclic aromatic hydrocarbons (PAHs) are found in fossil and active hydrothermal systems, often associated with mercury mineralization. An ongoing petroleum-geochemical study of the fossil hydrothermal vents (~150°C) in the Middle Triassic Idrija mercury deposit investigates the formation and alteration of the Hg-associated petroleum.

Rock Eval parameters and $R_0 = 1.3$ to 2.0% place barren and Hg-mineralized host rocks in the mature to postmature region. The isotopic compositions of the kerogens ($\delta^{13}C_{KER} =$ –29.0 to –23.1‰, $\delta^{15}N_{KER} =$ –1.2 to +4.6‰) indicate a mixed marine-continental organic source. In all samples the bitumens are enriched in ^{13}C (up to 3‰) relative to the associated kerogens, pointing to allochthony of the hydrothermal petroleum. In the mineralized samples the higher TOC and bitumen contents, anomalously low T_{max} values, and higher δ^{13}C values of bitumens and kerogens suggest a substantial contribution of less mature migrated/reworked (^{13}C-enriched) hydrothermal petroleum. The GCs of saturated HCs have a unimodal distribution of *n*-alkanes in the range *n*-C_{12} to *n*-C_{30}, and variable amounts of pristane (Pr) and phytane (Ph). The samples from profiles across the mineralization show variations of the molecular maturity parameters (Pr/Ph, Pr/*n*-C_{17}, Ph/*n*-C_{18}), and low to complete lack of hopanes and steranes content. This indicates an enhanced thermal alteration of the HCs along the mineralizing fluid pathways. In mineralized samples the $C_{<17}$ *n*-alkanes are isotopically lighter (up to 3‰) compared to the higher C-number homologues, probably representing later petroleum pulses. The aromatic HCs in mineralized samples are characterized by low unresolved humps and high concentrations of PAHs (fluorene, phenanthrene, fluoranthene, pyrene, triphenylene, chrysene, benzofluoranthene, coronene), aromatic sulfur compounds (dibenzothiophene, benzonaphtothiophene), and their alkylated homologues. The presence of reduced and oxidized compounds (dihydrophenanthrene and benzenedicarboxylic acid) point to hydrogen and oxygen exchange between organic matter and water (hydrolytic disproportionation), which is currently being investigated by δD analyses. The observed molecular signatures of the Idrija bitumens indicate that aromatic petroleum formed by medium temperature hydrolytic disproportionation during interaction of the organic matter and the mercuriferous fluids in the subsurface of hydrothermal vents, and later long-term re-equilibration at elevated burial temperature.