

History of Solute Transport in a 400m Mudrock Sequence, Calibrated by Laboratory Chlorine Stable Isotope Diffusion Experiments

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To determine diffusion coefficients, we created a concentration gradient of NaCl in a 40cm length of polyacrylamide gel (about 85% porosity) in a borosilicate glass tube, 16mm internal diameter. Concentrations and temperature were varied in different experiments. After a time calculated to allow formation of a distinctive diffusion profile, the tube was broken and the gel sliced into small lengths which were leached to give their Cl concentrations. The same samples were analysed for $\delta^{37}\text{Cl}$ values. The results gave ideal diffusion profiles and could be modelled perfectly by Fick's Diffusion Law, allowing us to calculate diffusion coefficients (D) for overall Cl concentration and also the ratio of the coefficients for ^{35}Cl and ^{37}Cl . Those experiments with concentrations near to present-day seawater, covering the temperature range 2°C to 80°C, gave D varying from 0.91×10^{-9} to $5.25 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. The ratio of the isotopic diffusion coefficients (D-35/D-37) varied from 1.0014 to 1.0019.

The results were applied to investigate solute transport processes in low-permeability sedimentary rocks: a silty-clay sequence of Vraconian (Cretaceous) age in the Rhone valley, France. The formation studied, "Couche Silteuse de Marcoule" (CSM), is an homogeneous, compacted marine mudrock with very low permeability ($K < 10^{-12} \text{m.s}^{-1}$), bounded at top and bottom by highly permeable marine formations which now carry non-saline water. Cores were taken which covered the whole section, from about 380m to 790m depth. Previous work (Tevissen *et al.*, 1997) had indicated a chloride profile, which was interpreted as the result of a double-sided diffusion profile. However, it was not possible to confirm that the process was diffusive rather than advective, and there were potential problems about the process of sampling porewaters, since two approaches, squeezing and leaching give different results.

Due to its very low permeability, pore-water could not be extracted directly from the CSM. We overcame the sampling problems by determining porosity and total chloride content very precisely on each sample. Helium porosity of dried core samples was measured. Subsequently, Cl concentration and $\delta^{37}\text{Cl}$ determination was made by leaching the rock samples, mixing crushed and ground rock with de-ionised water. Porewater concentration was calculated from the extracted chlo-

ride value by relating it to the porosity of the relevant core sample, assuming only that all the Cl extracted had originated in the porewater. Extracted chloride was converted into chloromethane (Eggenkamp, 1994) for mass spectrometric analysis.

The porewaters are all sodium chloride brines and could have evolved from an original marine composition. Cl concentration shows a peak at about 600m depth while Cl isotope compositions show a wide range of values from a maximum value (approx. +1.7‰) at a depth near to 450m and decreasing systematically both upward and downward (approx. -0.7‰) as shown in Figure 1. The results can be interpreted as a diffusion process by using the measured values for helium permeability of the core samples but calculating Cl permeability by relating D values for Cl to those of He. In addition, it is necessary to assume an initial porewater composition; we assumed sodium chloride brine of present-day marine concentration. However, the data set must be modelled as the results of two processes.

A double-sided diffusion process operated, superimposing the distinctive peaks of concentration and positive chlorine isotope values on a profile of chloride concentration and isotope values, which resulted from burial compaction of a sedimentary sequence. Although there are no detailed profiles porewaters of deeply buried undisturbed sediments, there are other data from laboratory experiments of simulated compaction (Coleman *et al.*, 1998) and analyses of a limited number of deeply buried mudrock cores from oil exploration wells. These results indicate an expectation that the effects of burial compaction might be expected to give more positive chlorine isotope values in shallow sediments and negative ones from deeper samples.

Preliminary overall interpretation of the results suggest that burial compaction produced a chlorine concentration and isotope profile of limited extent in the mudrock sequence. After a period of quiescence, tectonic activity at about 15 Ma allowed the sequence access to surface waters. The permeable beds above and below the CSM had connate marine pore-waters replaced by freshwater which initiated a concentration contrast at its top and bottom and started the double diffusion system.

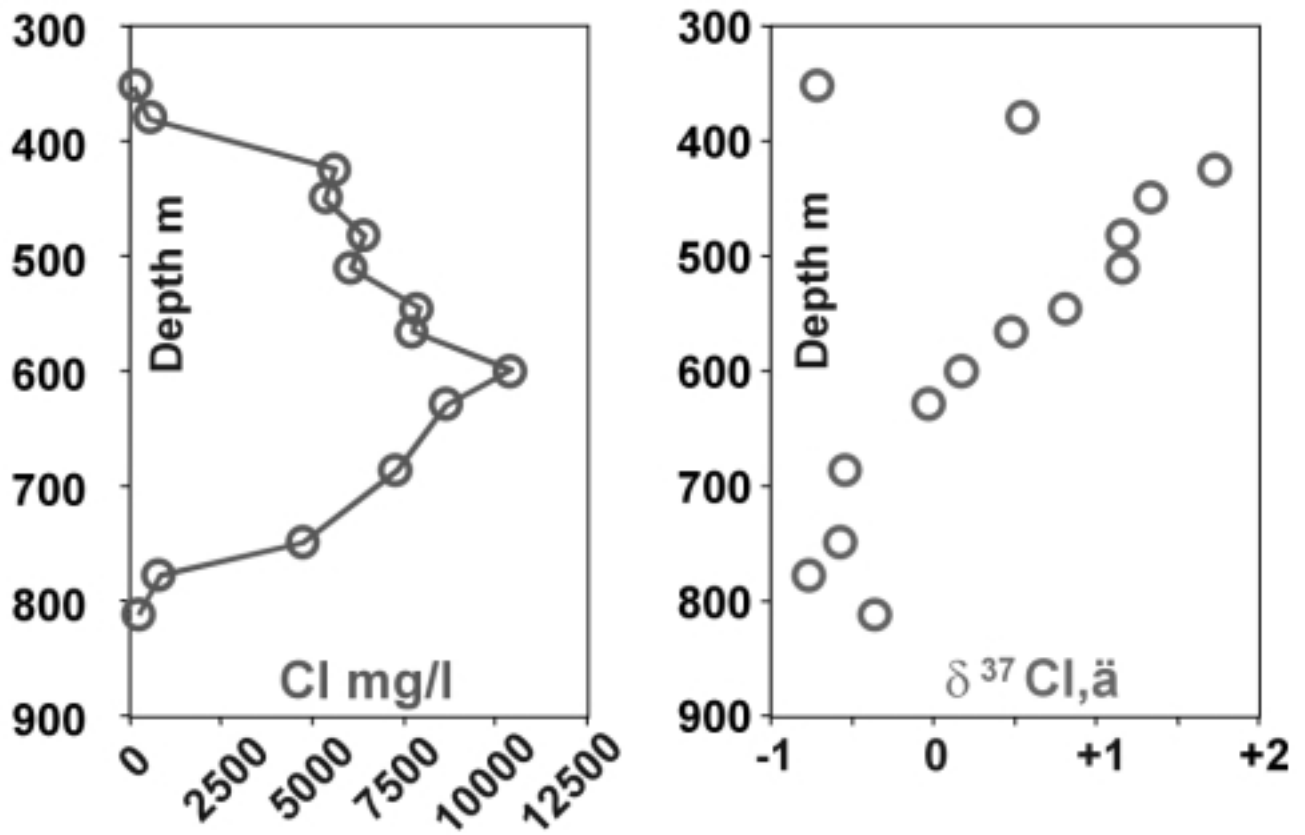


Figure 1: Chloride concentration and Cl stable isotope profiles in CSM samples

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