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**APPORT DES MESURES DU ^{37}Cl A LA CARACTERISATION DU
TRANSPORT DE SOLUTES DANS LES FORMATIONS
SEDIMENTAIRES ARGILEUSES**

**CHLORINE STABLE ISOTOPE CHARACTERISATION OF SOLUTE
TRANSPORT IN MUDROCKS**

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ABSTRACT

Chlorine stable isotope analyses were made of pore-waters in a thick silty-clay Cretaceous formation, part of the South-East sedimentary basin, located at the “Gard site” in the Rhone valley. This formation, the “Couche Silteuse de Marcoule” (CSM), is an homogeneous compacted marine mudrock with very low permeability, bounded at top and bottom by highly permeable formations which carry non-saline water. The CSM had been examined by ANDRA for its suitability as a potential host for an underground laboratory for studying the possibility of geological disposal of nuclear wastes.

Due to its very low permeability ($K < 10^{-12}$ m.s⁻¹) pore-water could not be extracted directly from the CSM. Initially, He porosity of the 14 dried core samples was measured. Subsequently, $\delta^{37}\text{Cl}$ determination was made by leaching the rock samples, mixing approximately four times (mass ratio) of crushed and ground rock (grain size $\sim 40\mu\text{m}$) with de-ionised water. Porewater concentration was calculated from the extracted chloride value by relating it to the porosity of the relevant core sample. Extracted chloride was converted into chloromethane (Eggenkamp, 1994) for mass spectrometric analysis.

Cl isotope compositions show a wide range of values from a maximum value ($\sim +1.7\text{‰}$) at a depth near to 450 m and decreasing systematically both upward and downward ($\sim -0.7\text{‰}$).

Isotopic diffusion coefficients for Cl were determined experimentally in the laboratory using polyacrylamide gel (Coleman et al., 1998). On the contrary, convective transport of Cl does not induce any fractionation and thus it is possible to distinguish if a chlorinity gradient corresponds to diffusive or convective processes.

The CSM results imply a diffusive process. These results demonstrate that the variation cannot be the result of advective mixing of more saline and less saline waters. **The $\delta^{37}\text{Cl}$ profile indicates that a diffusive process has occurred in the CSM.** This finding confirms and refines the concepts interpreted from Cl and Br concentration profiles by TEVISSEN *et al.*, (1997), who proposed finite double-sided diffusion as the solute transport process in the CSM.

INTRODUCTION

Natural tracers of solute transport

Natural geochemical tracers can be used to monitor movement of solutes in sediments, but the attempts may be hampered because the tracers may react with the rocks. This is overcome partly by use of isotopic characterisation of solutes or even the water itself. Strontium and other radiogenic isotope ratios have been used (MATRAY *et al.*, 1993) but suffer from the possibility that there may be inputs from detrital or diagenetic minerals. Even identifying the sources of water by use of hydrogen and oxygen stable isotope compositions may be hindered because the process of mineral dissolution or growth of diagenetic minerals can affect these values (ZIEGLER and COLEMAN, *in press*). The use of conservative tracers (unreactive species), especially chloride and bromide and the ratio Cl/Br, overcome problems of loss or addition of the tracer, but even this approach has some problems. For example, a halite source should have a very high Cl/Br ratio which would reflect the source of solutes and the direction of fluid flow: but there can be difficulties because fluid inclusions containing residual evaporitic brine with a much lower Cl/Br can contribute significantly to distort the values measured (FONTES and MATRAY, 1993). Another problem is that within a massive homogeneous sedimentary formation, there may not be significant variation to indicate flow.

Chlorine isotopes

Chlorine stable isotope compositions offer a possible new way to characterise solute transport processes. The element chlorine has only two stable isotopes (^{35}Cl , ^{37}Cl) and $^{35}\text{Cl}/^{37}\text{Cl} \approx 3$. Stable isotope variations generally are very small, so that the actual isotope ratio is not measured, but rather the difference between the ratio of the sample and that of a standard, as this difference can be determined more accurately than the absolute value. This difference is expressed in per mil units (‰) as shown below:

$$\delta^{37}\text{Cl} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} * 1000$$

In this equation R is the ratio, $^{37}\text{Cl}/^{35}\text{Cl}$. Measurements are made using a stable isotope ratio mass-spectrometer, which alternately measures R for an unknown sample and for the standard.

.Seawater chloride is used as standard, since KAUFMANN (1984) and KAUFMANN *et al.* (1984) proved that the chlorine isotopic composition of seawater is constant. They called this standard SMOC (Standard Mean Ocean Chloride). A formal isotopic standard does not exist yet. In all our work, measurements are given as differences from Kimmeridge Bay seawater sampled in the south of England. Comparisons with other seawater samples in our laboratory (including the General Purpose Seawater standard GPS-1 from Ocean Scientific Ltd., Azores deep ocean water and Newfoundland ocean water) showed no measurable variations. The natural range of isotope values of chloride is very small normally and because of its of unreactive nature, it seems that any measurable variation of isotope compositions will have resulted from operation of physico-chemical rather than chemical reaction processes.

PROCESSES OF SOLUTE TRANSPORT

The potentially-important physico-chemical processes are diffusion, shale ultrafiltration, membrane filtration, and ion-exchange. In theory, both diffusion and membrane filtration can cause large fractionation of Cl isotopes (EGGENKAMP 1994; PHILLIPS & BENTLEY 1987). Small fractionations have been observed (~1‰) in natural systems due to diffusion (BEEKMAN *et al.* 1992; EGGENKAMP *et al.* 1994). However, the largest fractionations have been observed in oil-

field brines which showed relatively large, and usually negative Cl isotope variations (COLEMAN 1993; MATRAY *et al.* 1993; EGGENKAMP & COLEMAN 1993; COLEMAN *et al.* 1994; ZIEGLER & COLEMAN 1998). For all these oil-field brines there is no single explanation for the extremely negative values (down to -5‰), however, it has been possible to show that the *range* of compositions resulted from advective mixing of two components.

Theoretical diffusion

Molecular diffusion is the process in which matter is transported from one part of a system to another as a result of arbitrary molecular movements (CRANK 1956). It was first described by Adolf Fick in 1855. This work is now referred to as Fick's First and Second Laws, and was published even before quantitative experimental measurements had been made. According to Fick's First Law the amount of matter moving through a plane perpendicular to the direction of diffusion during an element of time (dm/dt) is proportional to the concentration gradient across the plane and the area of the plane.

$\frac{dm}{dt} = -DA \frac{\partial c}{\partial x}$ D is the diffusion coefficient, A is the area of the plane, c is the concentration and x is the migration distance. The amount of matter moving through the plane per unit of time is the flux (j): $j = \frac{dm}{Adt}$ From which it

follows that: $j = -D \frac{\partial c}{\partial x}$ This is the mathematical formulation of Fick's First Law. The

diffusion coefficient D gives the amount of matter that moves through a unit of area in a unit of time in a unit of concentration gradient. Its dimension is $[\text{length}]^2/[\text{time}]$. It is not possible to measure the value of dm/dt in the above equation directly. This is addressed by Fick's Second Law, which can be derived from the First Law and the Law of conservation of mass. The second law implies that if more matter is supplied than removed the concentration

increases, and vice versa. $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$ This is Fick's second law for linear diffusion. In

this equation x represents the distance to the diffusion plane. Diffusion can be modelled as movement of solute from one **reservoir** to another (or others) from the time when the reservoirs first come into contact with each other. This is shown schematically in Figure 1, where the time when the reservoirs are first in contact is designated as t_0 (Figs. 1a, 1b); The two main types of diffusive process relevant to interpretation of the data discussed in this paper are: - **finite diffusion**, where the concentration is kept constant at the boundary between the two reservoirs and there is a finite diffusion length (Figs. 1c, 1d); and - **infinite diffusion**, where the boundary concentration can vary and there may be an infinite diffusion length, in theory (Figs. 1e, 1f).

For each type it is possible to consider two sub-types:- **single sided**, where there is just one boundary (Figs. 1c, 1e) and- **double-sided**, where there is planar body of finite thickness from which diffusion can occur in two opposite directions, perpendicular to the plane (Figs. 1d, 1f).

Finite diffusion is defined here as diffusion from a reservoir into another reservoir, where the concentration is kept constant at the boundary between the two reservoirs, and within the reservoir into which Cl is diffusing. For example, this may be the case if the lower concentration reservoir is well mixed (advectively), as in diffusion of Cl in the saline pore-fluid of a marine sediment into the non-saline waters of an adjacent sediment as described by EGGENKAMP *et al.* (1994). It is beyond the scope of this paper to treat in detail all the four models shown in Figure 1 and only one-sided finite diffusion (Figs. 1c, 1d) will be described as an example here. It can be solved mathematically by use of the Errorfunction

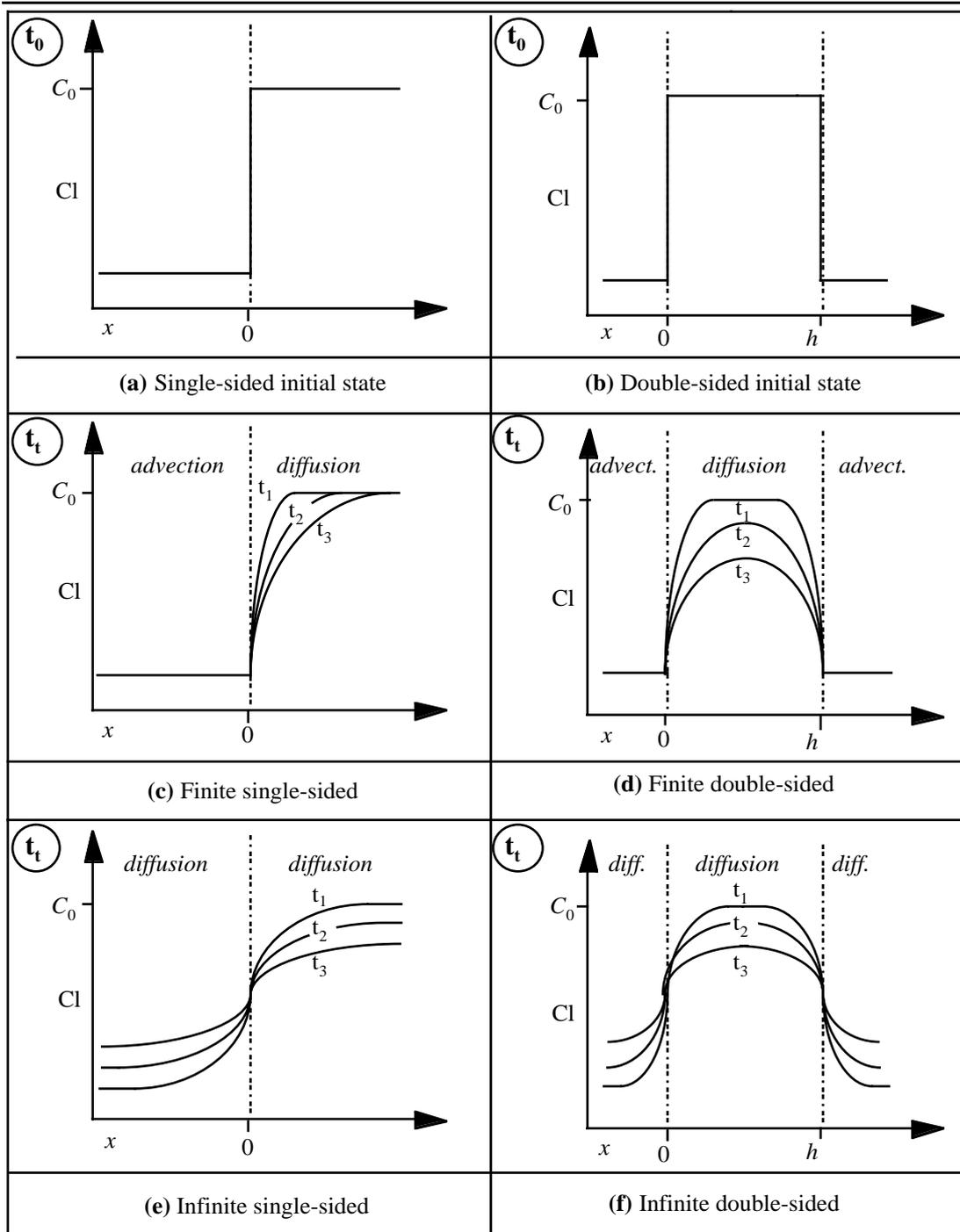


Figure 1. Various diffusion models

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$$C_{t,x} = C_0 \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad (\text{Figs. 1a, 1c})$$

where;

- x is the distance from the diffusion boundary and $x \geq 0$
- t is the time since the start of diffusion
- C_0 is the concentration at t_0 , $x > 0$
- $C_{t,x}$ is the concentration at t , x
- D is the diffusion coefficient

The mathematical descriptions of this and the other diffusion processes are described in detail in textbooks (e.g. JOST, 1957; CRANK, 1956). The key point is that diffusive processes can be modelled as changes in solute concentration as a function of spatial distribution and as a quantitative function of time, provided that the appropriate diffusion coefficient, D , is known. In addition, it might be expected that ^{35}Cl might diffuse more rapidly than ^{37}Cl .

Laboratory diffusion experiments

We have performed a number of experiments to measure isotope fractionation of Cl in a laboratory environment that is comparable to the situation in nature. To that end, we established pure concentration-derived diffusion of a chloride solution, captured in a gel, from which, after a period of diffusion, the Cl or Br isotope composition was determined. The diffusion experiments were similar in some ways to those used to measure diffusion of actinides in clay (SCHREINER *et al.*, 1982), but our approach a polyacrylamide gel (DAVISON *et al.*, 1994, ZHANG & DAVISON, 1995) was used as the porous medium. A borosilicate glass tube (inner diameter 16 mm) was filled with liquid gel. When it had set, usually after two to three hours, more of the same type of gel, but made up in a NaCl or NaBr brine instead of water, was added to the tube (Fig. 2). Diffusion of Cl⁻ or Br⁻ was allowed to proceed for a specific time calculated to allow a clear diffusion profile to be achieved. The tube was held horizontally and after the diffusion allowed to progress. When the experiment had finished, the glass was broken and removed from the gel which was sliced into 1-2 cm slices. The Cl was recovered from the portions of gel by equilibration with distilled de-ionised water (KROM *et al.*, 1994). The Cl concentration of the solutions were determined by colorimetry and converted to the original values in the gel. Cl isotope values were then measured as described in the Sample Treatment section.

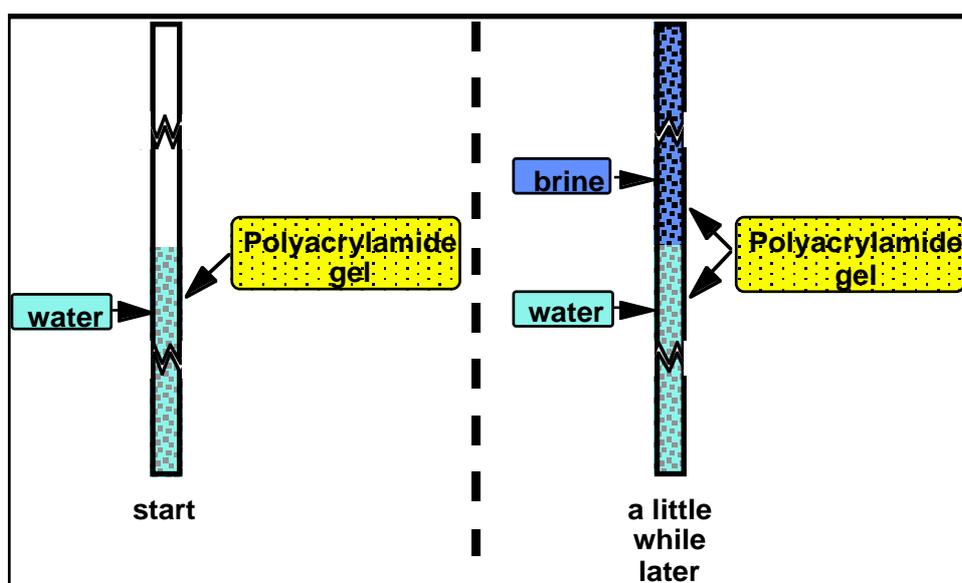


Figure 2. Diagram of laboratory diffusion experiment method

Diffusion experimental results

Very clear diffusion profiles were found. The fractionation can be large (~ 4‰ from a 1:100 ratio in Cl concentration between two end-members); fractionation magnitude depends on the concentration ratio (EGGENKAMP 1994) which controls the extent of diffusion. Therefore, the most negative data appear in the samples with low concentrations, effectively the low concentration end-member (Fig. 3, after EGGENKAMP & COLEMAN 1997). This is a result of the more rapid diffusion of ^{35}Cl , relative to ^{37}Cl , from the higher into the lower concentration environment, which gives the latter a more negative $\delta^{37}\text{Cl}$ value. Figure 3 shows that theory and experiment agree excellently.

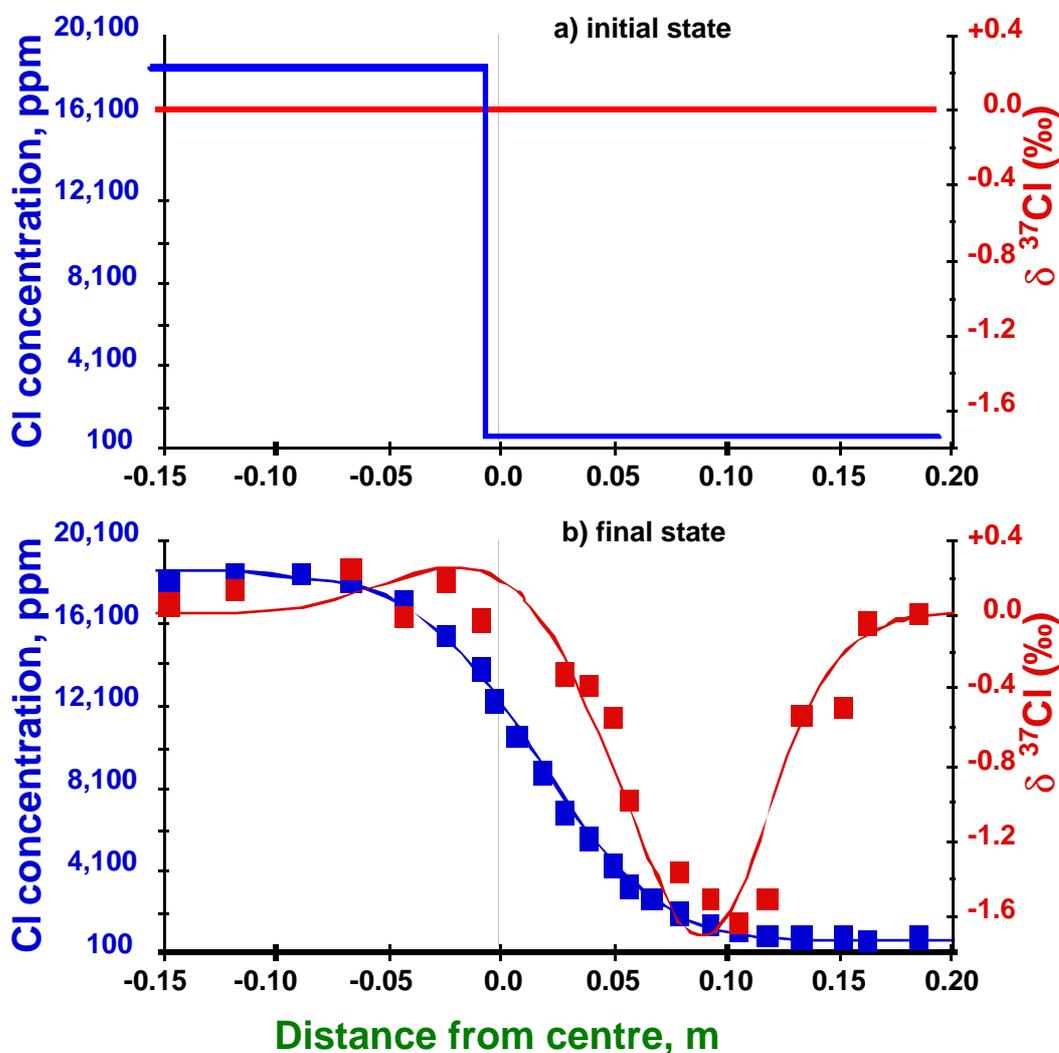


Figure 3. Cl concentration and $\delta^{37}\text{Cl}$ distribution in a diffusion experiment. Blue and red squares indicate the Cl concentration and $\delta^{37}\text{Cl}$ as a function of diffusion distance from the concentration interface. Solid lines are theoretical calculations of the process.

The ratio of the diffusion coefficients of ^{35}Cl and ^{37}Cl , D^{35}/D^{37} , measured under a range of conditions varies only between 1.0014 and 1.0019 while the D value for chloride varies by more than a factor of five for the same experiments.

Advective mixture of two end-members

In the case of advective mixing, samples can only show isotope variations if the end-members have different isotopic compositions. This applies to a series of formation waters from four different areas of the Forties oil-field in the Central North Sea (COLEMAN *et al.*, 1993). Two end-members with Cl concentrations of about 25,000 and 60,000 ppm and $\delta^{37}\text{Cl}$ values of about -5‰ and -1‰, respectively could be recognised. Cl shows a concentration profile with depth (Fig. 4). Plotting the reciprocal concentration (1/Cl) against $\delta^{37}\text{Cl}$ gives a straight line in this case, a binary mixture (Fig. 5).

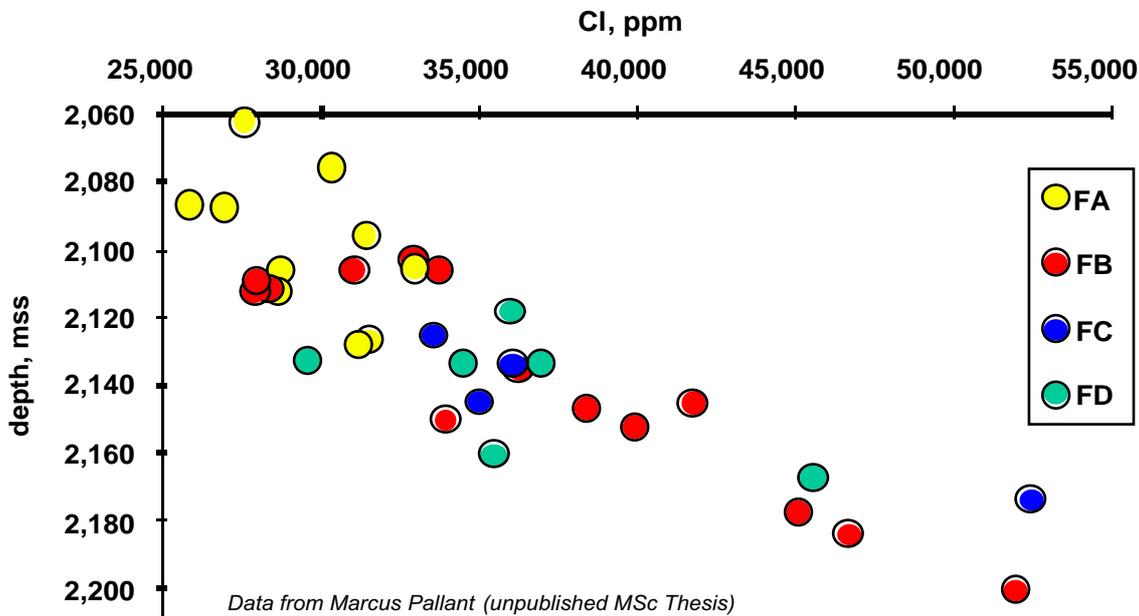


Figure 4. Cl profile with depth in Forties oilfield.

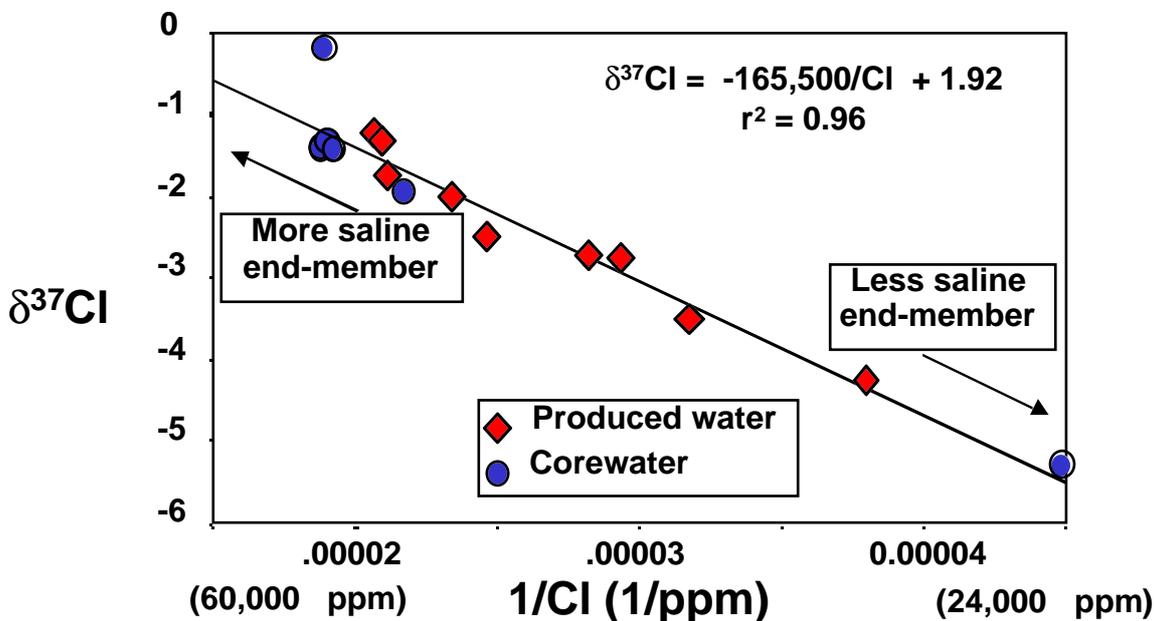


Figure 5. Cl and $\delta^{37}\text{Cl}$ data confirm a mixture of two end-members.

Obviously, if the two end-members have similar $\delta^{37}\text{Cl}$ values, no variations in $\delta^{37}\text{Cl}$ of intermediate samples would be visible. This is shown in the Cl depth profile from the ANDRA Vienne site (Fig. 6a).

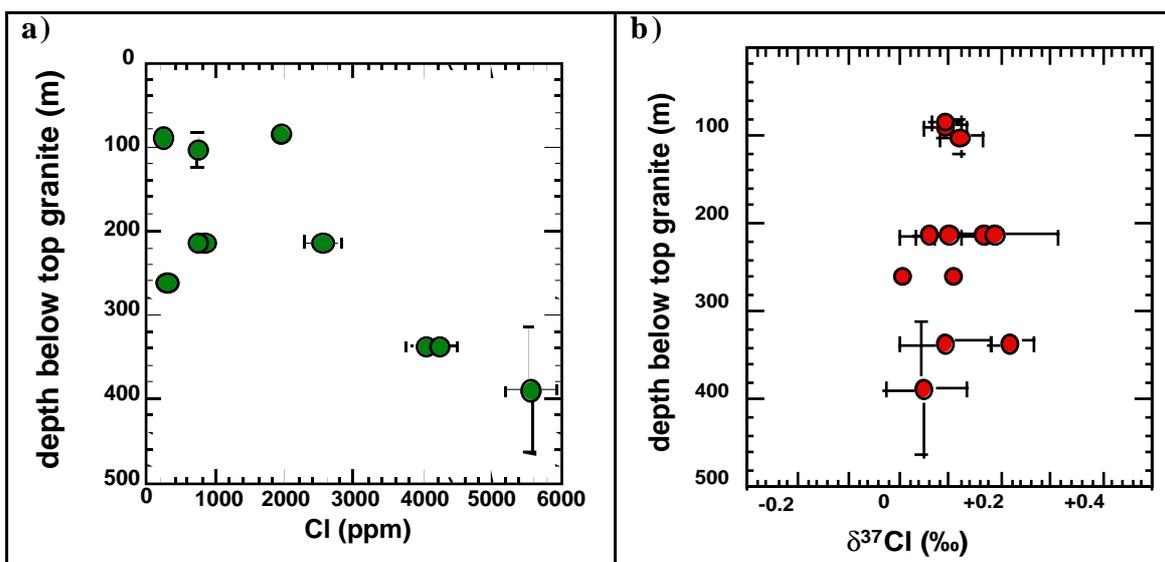


Figure 6. Cl profile at the Vienne site showing no evidence of diffusion and implying an advective mixing process.

Since there is a large concentration profile it is reasonable to ask if diffusion had been operating. However, the limited range of $\delta^{37}\text{Cl}$ (Fig. 6b) and lack of any relationship of either positive or negative values with depth indicates that diffusive mixing did **not** occur here. It seems most probable that there is advective mixing of a more saline brine at depth and fresh water above.

Effects of movement of fluids from mudrocks

Experiments undertaken in collaboration with colleagues at the École Polytechnique subjected slurries of clay minerals and water to successive stages of increased compaction. The fluids which were squeezed from the samples were analysed for Cl concentration and $\delta^{37}\text{Cl}$. A typical result is shown in Figure 7. The initial solution is more concentrated than the original composition and is slightly enriched in ^{37}Cl . This result has implications both for understanding natural systems and the processes of extracting water samples from rock for analysis.

There are a number of factors which might affect chloride concentration. The method of squeezing water from core may release a fluid which is more concentrated than the bulk composition. High pressure squeezing experiments using clay mineral slurries made up in brine expelled initial aqueous solutions more concentrated than the original (COLEMAN et al., 1998). Two possible processes might contribute to this effect, loss of pore fluid while pure water was retained as a bound layer on clay mineral surfaces and ion exclusion. This could explain why the initial concentrations were higher while the later solutions were more dilute since there was proportionately less of the original Cl left in the system. Although, there are systematic changes in $\delta^{37}\text{Cl}$, it is important to note that the effects are small in absolute terms and in comparison to the concentration changes. We have not yet measured a sequence of samples which would form an undisturbed natural analogue of the laboratory experiment, however, we would expect it to show a trend in Cl concentrations but relatively little change in $\delta^{37}\text{Cl}$.

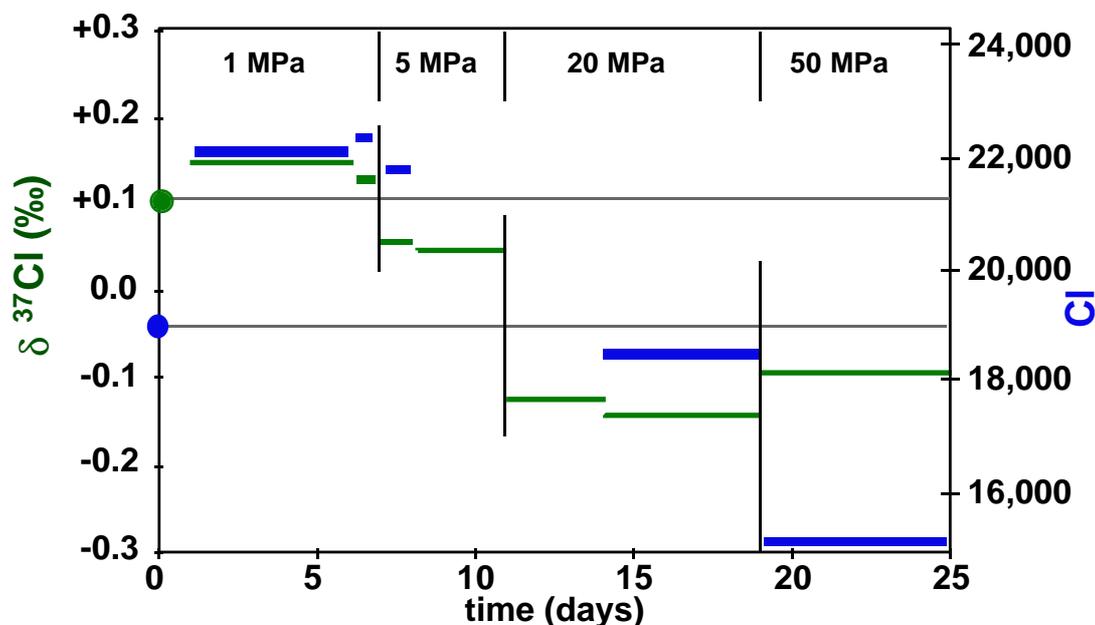


Figure 7. Effects of simulated compaction of a mudrock on Cl concentration and $\delta^{37}\text{Cl}$

SAMPLING AND SAMPLE TREATMENT

A series of cores was chosen from a borehole at the ANDRA Gard site. The location of the sample points is shown in Figure 8. It can be seen that the stratigraphic succession consists of the low permeability Couches Silteuses de Marcoules (CSM) with higher permeability beds above and below. The borehole was chosen as a test of the chlorine isotope approach to characterisation of solute transport because previous work had shown the presence of a chloride concentration profile in the CSM (HARMAND *et al.*, 1997; REEDER *et al.*, 1997a; REEDER *et al.*, 1997b; TEVISSSEN *et al.*, 1997).

Because of the low permeability of the samples and our doubts about the validity of squeezed samples, we used the following procedure for extraction and analysis of chloride concentration and isotopic composition. In this approach we measure porosity very precisely and then leach chloride from the same sample.

Porosity measurement

Core-plugs were cut from the core samples. The volume of each core-plug was measured in two ways: by measuring its dimensions and by the Archimedes method, weighing in air and in water. The samples were then heated in air at 110°C to constant weight. Initial experiments attempted to dry rocks at 60°C, but even after six days full loss of water had not occurred. Even a temperature of 90°C was not effective. The weight of water lost was recorded. Subsequently, the pre volume of the same sample was measured by Helium porosimetry, in which the dried rock sample is placed in chamber of known volume, which is then evacuated. Connection of the sample chamber to another with a known volume of helium at known pressure and temperature and measurement of the new pressure and temperature, gives an accurate measure of pore-volume. Samples were measured in quadruplicate. Our calibration of this method with samples measured by He porosity and by weighed loss of pore water showed that the methods were comparable for samples that had been preserved sufficiently well to avoid loss of water by evaporation. The tests showed that the method was accurate to better than 0.1% and that natural heterogeneity between subsamples was usually greater than this amount.

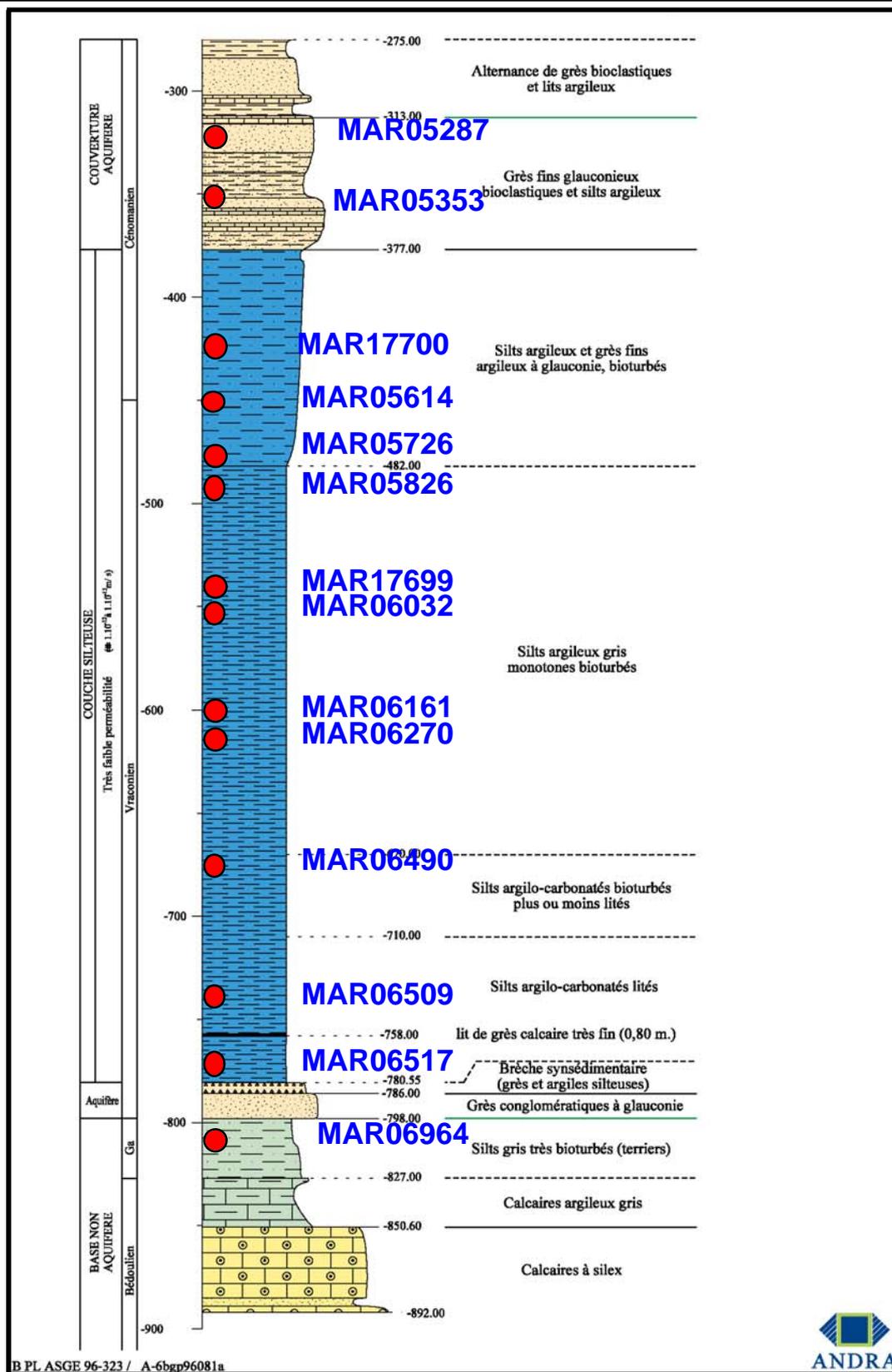


Figure 8. Stratigraphic succession and sampling points in the Gard borehole

Leaching chloride from sediment samples

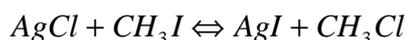
Each rock was mechanically crushed to $\leq 5\text{mm}$ and was then ground in a TEMA mill to $\leq 40\mu\text{m}$. About 25g of ground rock was weighed ($\pm 0.001\text{g}$) and about four times the weight distilled deionised water added by weighing. The rock/water slurry was mixed with a blended for about two minutes and then left to settle for two days. The supernatant solution was decanted and a sub-sample taken for chloride concentration determination.

Chloride concentration measurement

Chloride was separated from other interfering species by ion chromatography on a Dionex AS4A-SC column fitted with a conductivity detector. For Cl^- levels above 10 mg/l the injection volume was adjusted such that the peak area for Cl^- fell within the calibration range. Quantification was by reference to a calibration of external standards taking into account the blank. The results have a relative precision of $\pm 3\%$, or 0.01 mg/l absolute, whichever is the greater. The values were used in recalculating the concentrations for the extracted anions from the sediment samples.

Chlorine stable isotope value measurement

For isotopic analysis, $\delta^{37}\text{Cl}$ was determined by converting chlorine in the samples to chloromethane (CH_3Cl), after which masses 52 and 50 were measured as positive ions in the mass spectrometer. The method uses the reaction of silver chloride, AgCl , with iodomethane, CH_3I (KAUFMANN, 1984; EGGENKAMP, 1994).



CH_3Cl is purified by separating CH_3Cl and CH_3I on a gas chromatograph. The CH_3Cl is trapped in the sample-tube. After all gas has been trapped the sample-tube is taken off the line and the pure CH_3Cl can be analysed on a mass spectrometer. All samples were measured on a VG SIRA 12 triple-collector isotope-ratio mass spectrometer. All samples were measured at least in duplicate. For replicate analyses the precision is usually between 0.05 and 0.1‰. For the rock samples it may be larger, because of the lower Cl concentration, and the potential presence of interfering ions in solution.

SAMPLE RESULTS

Porosity results

Among some of the cores there was considerable variation between different core-plugs. Variations as much a factor of two existed in some cases. Close examination of the samples showed that the lower porosity samples contained a large amount of carbonate cement forming a concretionary zone. For all samples the values used for reconstruction of porewater chloride concentrations were the higher porosity values. In some cases, these results are very different from the average values made previously by mercury porosimetry and density measurements (GROS *et al.*, 1996). The porosity values are shown together with the standard ones in Figure 9.

Chloride concentration results

The new chloride results confirm the existence of a concentration profile as described previously (TEVISSSEN *et al.*, 1997) and are shown in Figure 10. It is interesting to note that there are small, but significant, irregularities in the otherwise smooth trend of values. These

small variations may be related to fine-scale lithostratigraphic heterogeneity. The values range from a maximum of approximately half present seawater chlorinity to very low values.

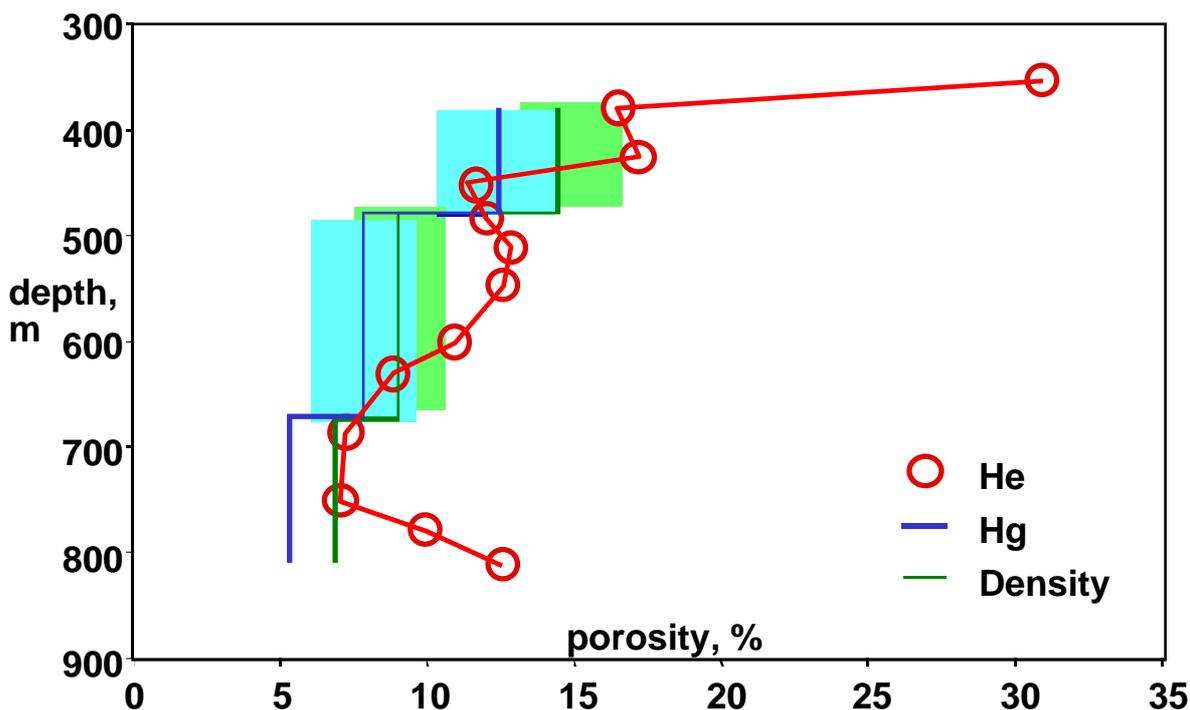


Figure 9. Comparison of porosity measurement results

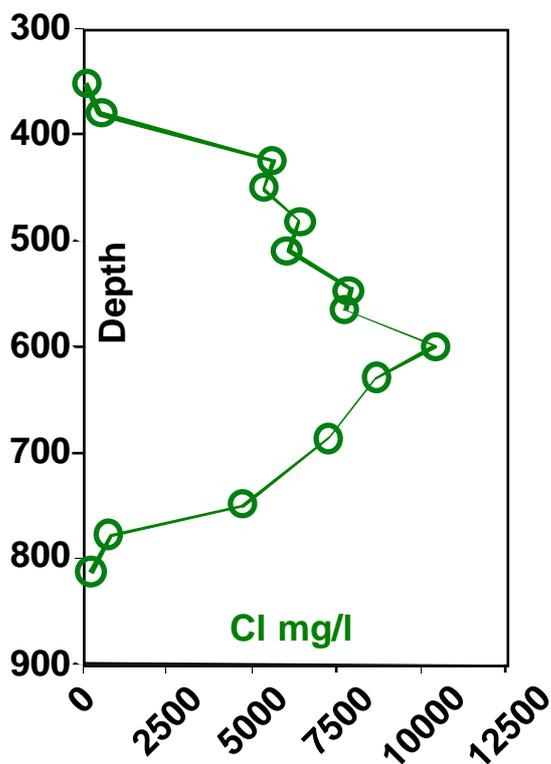


Figure 10. Chloride profile in Gard samples

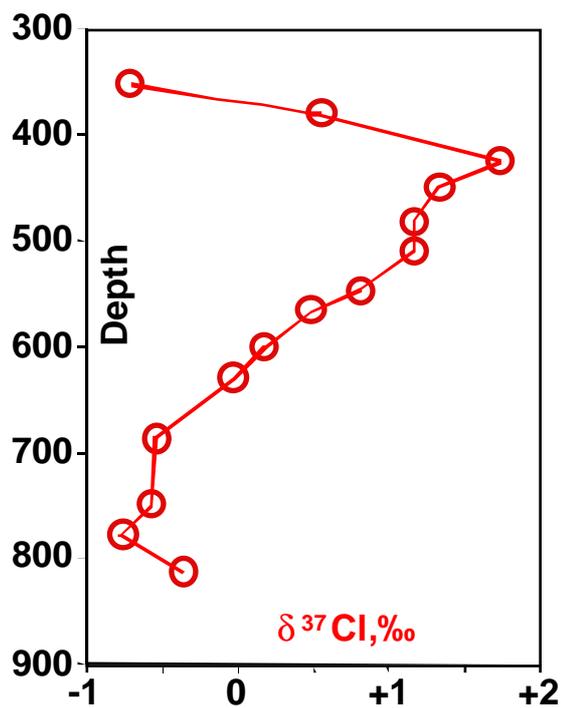


Figure 11. Chlorine isotope profile in Gard samples

Chlorine stable isotope results

The isotope results show an extremely large variation range of values, spanning nearly 3‰. Of particular significance is the fact that there are many positive values which are much higher than the normal range of pore fluid chlorine isotope values. However, it is essential to note that the peak value for isotope composition does not coincide with that for chloride concentration.

INTERPRETATION OF RESULTS

The combination of chloride concentration and chlorine isotope trends suggests that significant transport processes must have operated to modify the porefluids of seawater composition which must have been present in the original marine sediments at deposition. It seems highly unlikely that an advective process might have been responsible for the observed distribution of data, as can be seen in Figure 12, which should be compared with Fig. 5. Because the range of concentrations is so great, it is difficult to see the relationships for the higher concentration points (lower $1/Cl$), so they are re-plotted as $\log(1/Cl)$ to expand that part of the distribution in Figure 13. It is clear that advective mixing did not cause the observed range of values.

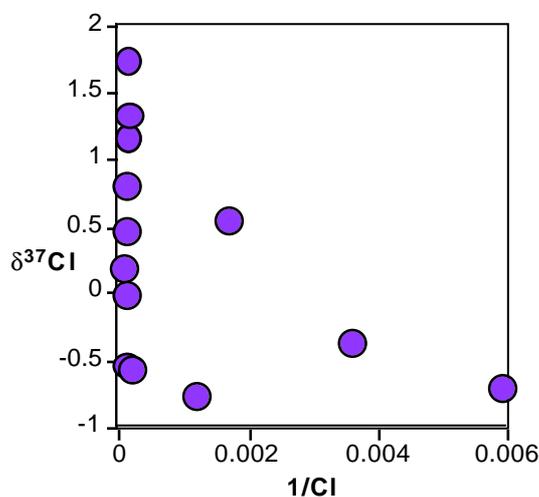


Fig. 12. Plot of $\delta^{37}Cl$ against $1/Cl$

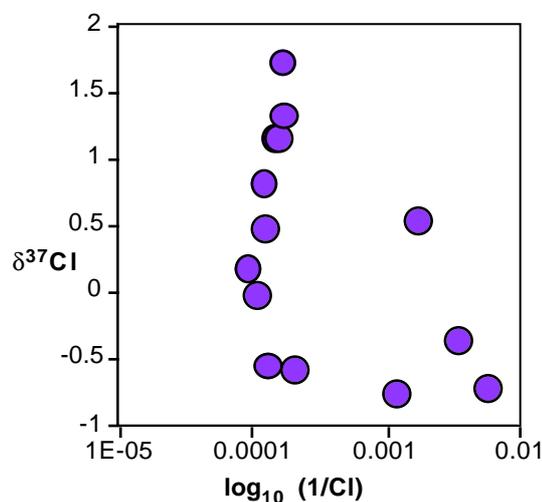


Fig. 13. Plot of $\delta^{37}Cl$ against $\log(1/Cl)$

Because the peak values for concentration and isotope values do not coincide, it is necessary to invoke a more complex model than just simple diffusion. Nevertheless, it seems that diffusive mixing is likely to have been the most significant process that controlled solute transport, since there are no other known processes which might have produced such large isotope variations. In order for this to have operated there must have been an initial profile of chloride produced by another process.

An initial modelling attempt showed that it would be possible to get an approach to the data. The model assumes a double sided diffusion process which started about 15 million years before present with a concentration contrast established at the top and bottom of the CSM, which had stayed fully marine up till then. The results of the model are shown in Fig. 14.

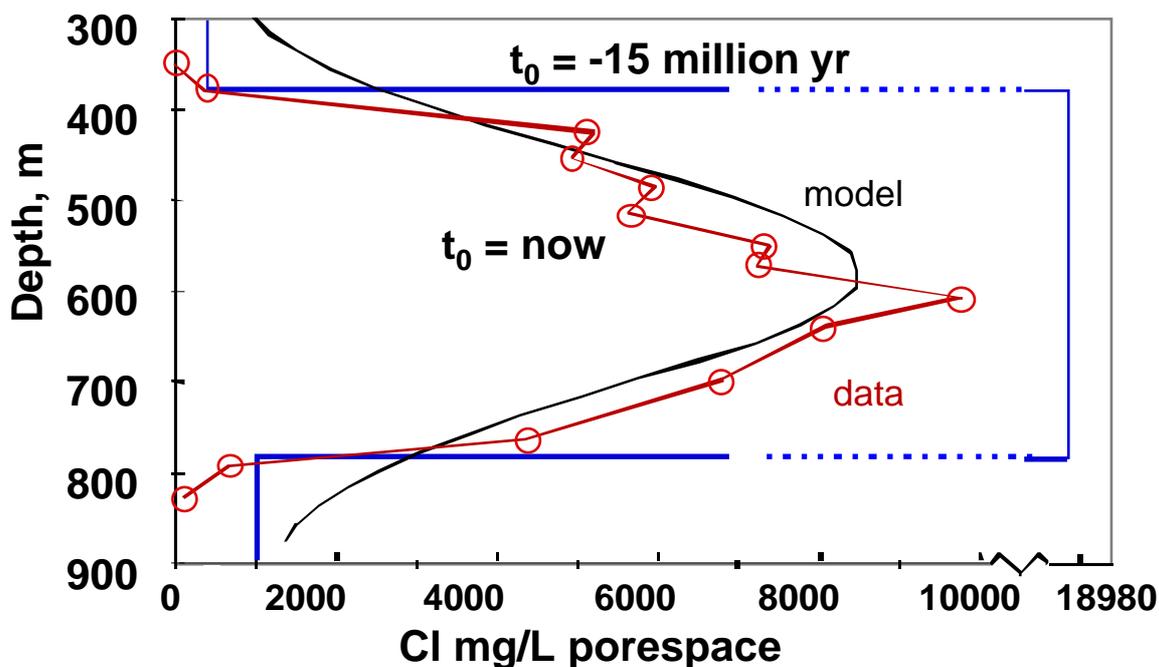


Figure 14. Preliminary model of chloride diffusion in the CSM.

Clearly, this model is not sufficiently good to act as a definitive model of the relevant processes. However, it does show the potential for this approach. It also implies certain predictions, which may have to be modified as the model itself evolves. If the isotope data are honoured then there is the need for an initial chloride profile. As discussed in the section above, *Effects of movement of fluids from mudrocks*, it is likely that the compaction of mudrocks will produce a variation of chloride concentration in the porewaters, but relatively little effect on the isotope compositions. The expected profile of chloride needed to reconcile the model is shown in Figure 15.

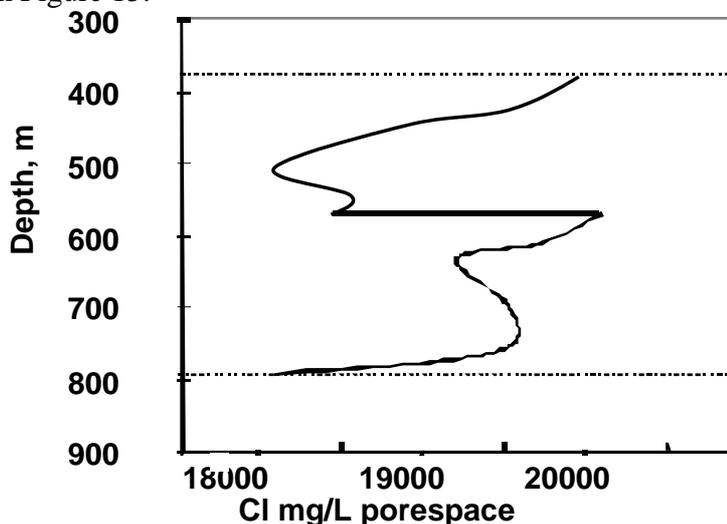


Figure 15. Modelled initial chloride profile in the CSM at the Gard Site

The range of chloride concentrations needed in the initial profile are well within the scope of variation expected from the laboratory simulation of compaction. It seems that there may be some lithostratigraphic control of the detail shown, since the rate of burial and generation of

overpressure would be expected to be a significant effect. However, it must be stressed again that it will be necessary to find an unaltered compacted sequence to test this hypothesis.

The overall model implies a plausible scenario which accords with the known geological history. The sedimentary sequence was compacted which led to minor loss of solutes from the CSM to the more permeable formations above and below. About 15 millions years before present, tectonic activity caused restructuration such that the lateral extensions of the beds examined in the borehole accessed the surface which allowed ingress of fresh water replacing the formerly marine porefluid. This established concentration gradients at the boundaries of the CSM which initiated a diffusive mixing process.

CONCLUSIONS

- The combination of chloride concentration and chlorine isotope values has the power to characterise processes of transport of solutes in porefluids in mudrocks.
- There are distinctive Cl and Cl isotope profiles at Gard Site
- There is no evidence for advective mixing at the Gard Site
- Positive Cl isotope values measured in porefluids imply a diffusive process
- There is the implication that there was an initial Cl concentration profile before the diffusive process started
- The implied initial profile is compatible with the few measurements made so far on laboratory simulation of compaction
- It seems likely that diffusion was the main process operating and confirms earlier hypothesis (Tevissen et al., 1998)

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