

Chlorine isotope fractionation during aqueous fluid transport

M. Coleman
H. Eggenkamp
J. Loomis
J. Rosenbaum

A. Pouya

Postgraduate Research Institute For Sedimentology, The
University of Reading, Reading RG6 6AB UK

G.3S, École Polytechnique, 91128 Palaiseau Cedex, France

Some water co-produced with oil has chemical and isotopic compositions resulting from its migration from mudrocks. In some fields chemical compositions of produced waters may change systematically with time after a well comes on stream and as the water-cut (proportion of water in the total produced fluid) increases. In Forties field (Central North Sea) the variation resulted from an increased proportion of aquifer mixed with oil zone water (Thurlow and Coleman, 1997). As oil is produced from the reservoir, reduction of pressure, localised to the zone around the perforations at the well bottom, draws up a cone of aquifer water and increases water-cut as it mixes with oil-zone water. In Forties oil-zone water is only 40% of the salinity of the aquifer. We developed a method for separating trace water from oil phase which has no visible co-produced water. It is oil-zone water and, in many fields, its composition is noticeably different from aquifer composition (Thurlow and Coleman, 1997). Here we explore the reasons why many oil-zone waters are characterised by unusual, extremely-fractionated chlorine isotope values.

Chlorine stable isotope geochemistry. Chlorine and bromine are relatively un-reactive at the temperatures expected in most sedimentary environments. Thus, they are considered as conservative tracers of solute movement and mixing processes. Cl is measured relative to ocean chloride, which shows no variation within analytical error (approx 0.05‰ 1 σ). Chlorine isotope compositions were measured using standard techniques: precipitation as AgCl, conversion to CH₃Cl, and stable isotope ratio mass spectrometry (Eggenkamp, 1994). Unlike other light stable isotopic elements, chlorine shows relatively little natural variation. Evaporites of all ages show the same limited range of values ($\delta^{37}\text{Cl}$, approx. 0 \pm 0.5‰), so marine Cl has not varied during the Phanerozoic.

Measurement of Cl isotope compositions of oilfield samples showed that many have extremely fractionated values very different from seawater.

Stable isotope compositions, with chemical data, confirm the complexities of spatial variation of composition of oil field brines. In Forties sampling from an in-fill well in the crest of the field confirmed that the range of compositions resulted from mixtures of two end-members, aquifer and oil-zone waters (confirmed by the $\delta^{37}\text{Cl}$ and Cl^{-1} relationship, $r^2 = 0.96$: oil-zone water $\text{Cl} \approx 24,000$ ppm, $\delta^{37}\text{Cl} = -5.3\%$, Fig. 1). Similarly, the most dilute brine in Oseberg field (19,000 ppm Cl) has $\delta^{37}\text{Cl} = -5.0\%$. We have now combined extraction of trace water with Cl isotope analysis of samples from another field. Thereby we have shown that another oil-zone dilute brine, in a complex mixture, has the most negative $\delta^{37}\text{Cl}$ (Rosenbaum and Coleman, 1998). Therefore, oil-zone waters are often dilute brines with extremely negative Cl isotope compositions. However, since all these waters are mixtures, it is not possible to determine whether the true end-member composition is actually more dilute or even more negative in $\delta^{37}\text{Cl}$ than the measured values. The key question is whether these compositions are the results of *in situ* processes or whether the waters are transported from elsewhere.

Origins of isotopically fractionated brines. If the oils had been emplaced in reservoirs with pore-fluids which were either non-saline or were dilute brines, these would have formed both the original oil-zone and aquifer. However, the extreme fractionation precludes this type of fluid from being the oil-zone waters observed today, since no other sub-surface brines have similar isotopic compositions. Subsequent dissolution of salt deposits elsewhere in the basin and movement of brines could have established the current, saline aquifer compositions and established a concentration contrast with the original oil zone waters. This could have provided the opportunity for diffusive mixing. However, there are three arguments against this. (a) If diffusion is allowed to continue, the isotopic and compositional differences diminish: it is improbable that the timing is just right to allow observable large effects in all cases. (b)

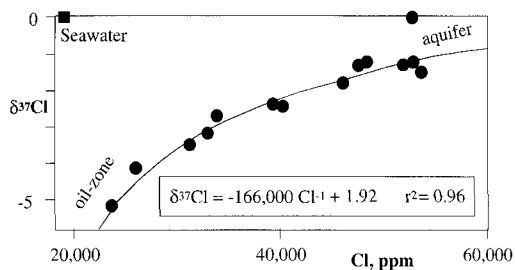


FIG. 1. Binary mixture of two brines, Forties field produced waters.

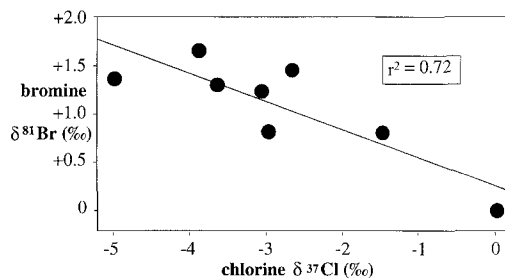


FIG. 2. Anticorrelation of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ for Oseberg field waters.

Laboratory experiments give quantitative isotopic diffusion effects for Cl and Br, in both cases the lighter isotope diffuses faster to give negative δ values and a distinctive relationship with Cl concentration (Eggenkamp and Coleman, 1997a). Dilute samples show negative isotope values, as expected. However, in Forties field, the only oilfield example with good vertical sampling coverage, neither chemical nor hydrogen and oxygen isotope compositions conform to a diffusive mixing law, despite a gradient of chemical compositions in the oil-zone. (c) Most persuasively, the first Br isotope compositions measured on oil-field samples deny diffusion: samples from Oseberg show anticorrelation of Cl and Br isotope compositions (Eggenkamp and Coleman, 1997b; Fig. 2). Since an *in situ* process was not responsible, isotopically fractionated water must have originated outside the reservoir. The most likely origin for this water is the oil source-rock because clearly it has a permeable connection to the reservoir. Despite conventional understanding of the migration process, which considers only oil phase transport, source-rocks in all the cases considered are mudrocks, an environment in which isotopic fractionation processes might occur.

Processes which might fractionate Cl isotopes. Our laboratory experiments have characterised some of the processes which might cause chlorine isotopic fractionation. Diffusion could occur in any permeable pore-space with a concentration gradient. In a sedimentary basin, however, mud-rocks, because of their fine grain size and high clay mineral content, have a large area of chemically active surfaces and are subjected to compaction which might expell porefluids. The experiments, at a preliminary stage, already indicate that relevant isotopically fractionat-

ing processes may occur. We performed an holistic simulation of clay compaction and expulsion of pore-water using kaolinite and NaCl brine mixture, subjected to increasing pressure from 1 MPa to 50 MPa. The initial fluid, produced at relatively low pressure, showed increase in Cl concentration and an increase of $\delta^{37}\text{Cl}$ of 0.05‰. Successive samples at higher pressures showed a trend of decreasing Cl concentration to below the original value and decrease of $\delta^{37}\text{Cl}$ to a final value 0.2‰ less than the starting value. Our preliminary experiments with anion exchange resin (Loomis *et al.*, 1998) produced relatively large isotopic fractionation. The first Cl eluted from a column was fractionated by +4.7‰. Although not yet confirmed, the resin must retain isotopically light Cl. If clays in mudrocks behave similarly this isotopically light Cl would be available for expulsion from the sediment. For all these processes it is important to note that it may be difficult to relate them to the complexity of a real mudrock system: e.g. multi-stage chromatographic processes which could enhance effects or a scale of system in which the bulk product would show only small effects.

Conclusions. There are a number of processes which could produce $\delta^{37}\text{Cl}$ values observed in brines in oil reservoir oil-zones. Although the details of the processes are not completely clear it is probable that migration, or associated transport processes, carry aqueous fluids from mudrocks to the reservoir. The key finding is that a really conservative element, chlorine, shows very distinctive isotopic fractionation as a result of transport processes. Most probably, other less easily noticed effects have occurred. Particularly, hydrogen and oxygen isotopes and Cl/Br ratios, normally considered to be conservative, may be very much changed from the original source values.