

Chlorine Residual Salts Analysis: a New Geochemical Tool to Characterize Oil Reservoirs.

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Introduction

When hydrocarbons enter and fill a reservoir, aquifer waters are forced down to low levels and their chemical and isotopic compositions are modified. Oil or gas saturates the rock porosity and traps irreducible waters, which become disconnected from the underlying aquifer. As chemical or isotopic exchange is no longer possible between irreducible waters and the "living" aquifer, the composition of irreducible waters is fossilized. Because of this process and the long time required to fill reservoirs with hydrocarbons, the top to bottom variation of irreducible waters compositions provides a mean to reconstruct the evolution of oil field water through time. The SrRSA method commonly used to visualize the oil fields compartmentalization is based on the analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of residual salts precipitated from those irreducible waters as the core dries out (Smalley et al., 1995; Mearns & McBride, 1999). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of residual salts have been shown to be directly representative of the irreducible waters. The Cl-RSA technique (Chlorine Residual Salts Analysis) has been revealed to provide high-resolution salinity profiles (Walgenwitz et al., 2001). This study investigates the use of the stable isotope composition of chlorine. Unlike strontium, chloride is the major anion in reservoir formation waters. Since it is not involved in diagenetic reactions, its concentrations and $\delta^{37}\text{Cl}$ profiles can trace potential mixings between formation waters and/or physical processes occurring during transport in the sedimentary basin (Coleman, 1993; Eggenkamp et al., 1997).

The Cl-RSA protocol was established and tested on natural sandstones from the North Sea. The $\delta^{37}\text{Cl}$ results are compared to SrRSA determinations performed on the same samples following the same protocol. The technique is then applied to sand and shale samples from several cores drilled in angolan offshore reservoirs and the results compared to present-day aquifers.

Cl-RSA Protocol

Samples are formed of common petrophysical plugs, dry cut to prevent salt leaching. After careful crushing, samples are submerged in ultrapure water in order to dissolve the chloride-bearing salts. The solution is stirred and the mixture is then centrifuged and filtered. To recover all of residual salts, a second lixiviation of the solid residue is performed. The sample grain size, sample/water ratio, timings etc were optimized for quantitative recovery of the residual salts and to ensure reliable isotopic determinations (Sr or Cl).

The steps involved in the chlorine isotopic analysis of the chloride in solution are the following: Cl^- are quantitatively precipitated as AgCl which is then converted into CH_3Cl by reaction with ICH_3 . CH_3Cl is then purified from the excess ICH_3 by a double separation method using gas chromatography (Hoering et al., 1961; Taylor et al., 1969; Kauffman et al., 1984; Eggenkamp, 1994).

The isotopic composition of chlorine is measured by dual inlet Isotope Ratio Mass Spectrometry on the pure CH_3Cl gas. The masses of interest are 52 and 50 and correspond to $\text{CH}_3^{37}\text{Cl}^+$ and $\text{CH}_3^{35}\text{Cl}^+$ respectively. The laboratory standard representative of the SMOC is the seawater "Atlantique 2" from the North Atlantic Ocean. The mean reproducibility of duplicate $\delta^{37}\text{Cl}$ analysis on chloride solutions is ± 0.05 ‰. The chloride concentration in solution is measured by HPLC

with an accuracy of 5 %. The quantity of chlorine converted to CH_3Cl is measured using a calibrated pressure gauge thus allowing the determination of a conversion yield ($106 \% \pm 6 \%$).

Tests of Total Extraction and Homogeneity

The Cl-RSA technique has been tested on plugs taken from a well from the North Sea Central Graben, at depth of 5275 to 5375 m TVDSS. The reservoir is formed of arenites from the Fulmar formation, Callovo-Oxfordian in age, and contains gas condensate hydrocarbons under HP-HT conditions. The production area is limited to the west by a NW-SE sealed fault (Hinton et al., 1998).

The efficiency of the residual salt recovery was verified by performing three successive lixiviations on seven samples. The first lixiviation led a mean recovery of $72 \pm 9 \text{ wt } \%$ of the total chloride. The second and third lixiviations gave $22 \pm 7 \%$ and $6 \pm 3 \%$ respectively.

Figure 1 shows that the $\delta^{37}\text{Cl}$ value of the two first lixiviations is representative of the total dissolved residual salts $\delta^{37}\text{Cl}$ (taking into account the third lixiviation). Further applications of this technique (e.g. the Angolan offshore site) will thus involve only two lixiviations.

The homogeneity of the core sample in $\delta^{37}\text{Cl}$ value was tested by leaching (once) different pieces of plug from the seven North Sea samples (randomly taken from the sample or taken from the centre). This also enables an assessment of any possible pollution of the core by drilling muds (more likely to contaminate the rim of the plug than the core). The $\delta^{37}\text{Cl}$ values of different pieces or centres are in perfect agreement and well within the error bars of the analytical technique ($\pm 0.05\%$). In conclusion, every piece of cylinder taken is representative of the total sample.

The mean $\delta^{37}\text{Cl}$ values of the seven samples (leachings 1 + 2) range from -0.80% to -0.50% with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.711715 to 0.713157 (± 0.000020). The $\delta^{37}\text{Cl}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ depth profiles are compared on Fig.2. Both isotopic ratios increase with depth and their direction and amplitude of variation are generally comparable except for the last sample. A physical process such as ion filtration, which is not traced by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, may affect the chlorine isotopic composition of this sample.

The concordance between $\delta^{37}\text{Cl}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ variations is good evidence that the chlorine isotopic composition determined on a residual salt is representative of that of the original irreducible water.

Cl-RSA Technique Applied to the Angolan Offshore Shales and Sands

The second part of our study is another application of the Cl-RSA technique described above. Differently from the first case study, formed of deeply buried HP-HT reservoirs, the second application has been performed on shallow, unconsolidated oil-bearing reservoirs, offshore Angola. The reservoirs are formed of turbiditic sandstones of Miocene age (middle to lower Miocene) alternating with the thick shale intervals. The oil source rock is of upper Cretaceous age.

The comprehensive set of samples concerned by our study comprises aquifer waters (sampled by the MDT method), shales and unconsolidated sands taken from several wells. Some samples representative of the Aptian salt in the lower Congo Basin were also made available from cores cut in a well from the South Gabon. The drilling muds (oil-based) used during the drilling operations were also sampled and characterized.

As shown on Fig. 3a, the salinity of the Miocene aquifers increases with burial depth "Z" following an exponential law: $\text{Sal} = \exp(Z+A)/B$. The salinity values determined in the intercalated shales from the RSA technique (Walgenwitz et al, 2001), roughly match the MDT data and also increase with depth.

As illustrated in Fig. 3b, the $\delta^{37}\text{Cl}$ of the aquifers (well 1 and 2), agree with the $\delta^{37}\text{Cl}$ measured on some adjacent shale-RS. Two sand-RS were characterized and their $\delta^{37}\text{Cl}$ values correspond to the nearest shale-RS. This demonstrates that residual salts are representative of the formation waters.

$\delta^{37}\text{Cl}$ values of aquifer samples range from -1.09 ‰ to -0.20 ‰ (a value at +0.01 ‰ measured on a water sample from an aquifer very close to an evaporitic dome and "contaminated" by halite dissolution, has shown by the bromine geochemistry, has been excluded from the data set). Above about 2200 m TVDSS, an increase of the $\delta^{37}\text{Cl}$ with depth is observed. Below this depth, the $\delta^{37}\text{Cl}$ globally decreases from -0.20 ‰ to -0.49 ‰ (Fig. 3b).

The $\delta^{37}\text{Cl}$ values measured on residual salts from shales range from -1.11 ‰ to +2.30 ‰. However, all data except two (+0.59 ‰ and +2.30 ‰ situated at 2352 and 2315 meters respectively) fall within a restricted zone ranging from -1.11 ‰ and -0.13 ‰ (Fig. 3b). Inside shale layers, the measured $\delta^{37}\text{Cl}$ shows variation. In the deepest layers, the $\delta^{37}\text{Cl}$ values range from that of the underlying aquifer to systematically higher (up to more than a 2‰ jump). The formation waters from the uppermost shale layer give the lowest $\delta^{37}\text{Cl}$ values. These heterogeneous isotopic data fossilized within each shale layer may reflect the occurrence of ion filtration.

Conclusion

The $\delta^{37}\text{Cl}$ variations, observed on samples from Angola, range between -1.11 ‰ and +2.30 ‰. This 3.4 ‰ variation is generally attributed to transport processes like ion filtration, diffusion, advection, mixings etc. In this study, the variations observed inside a shale layer and from one layer to another separated by characterized barriers are partly explained by ion filtration process. Lithologic barriers act as semi-permeable membrane (Hanshaw & Coplen, 1973) and fluids left behind the membrane are enriched in chlorine and depleted in the heavy isotope. Global variations observed on the all area could also include diffusion/mixings processes.

The Cl-RSA technique allows high-resolution salinity and $\delta^{37}\text{Cl}$ profiles in shales (and sands) to be performed the irreducible waters trapped in the hydrocarbon columns. The results could be used (with well pressure measurements and $^{87}\text{Sr}/^{86}\text{Sr}$ profiles) to accurately detect fluids flow barriers in some area where water sampling is difficult or not possible with the conventional wireline sampling techniques. Chemical and isotopic variations of these oilfield waters are the result of a complex history during which, ion filtration, diffusion/mixings occur during burial, reservoir filling and later evolution in the sedimentary basin.

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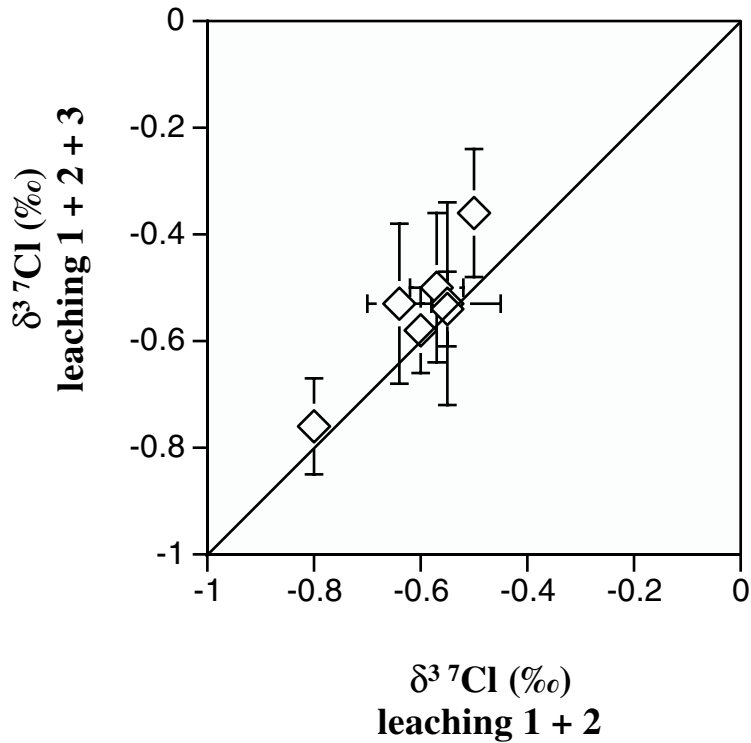


Fig. 1: Comparison of $\delta^{37}\text{Cl}$ (‰/SMOC) calculated by mass balance from leachings 1, 2 and 3 versus the $\delta^{37}\text{Cl}$ calculated from leachings 1 and 2 (for the seven North Sea sandstones). Two lixiviations are thus sufficient to determine the $\delta^{37}\text{Cl}$ value of irreducible waters.

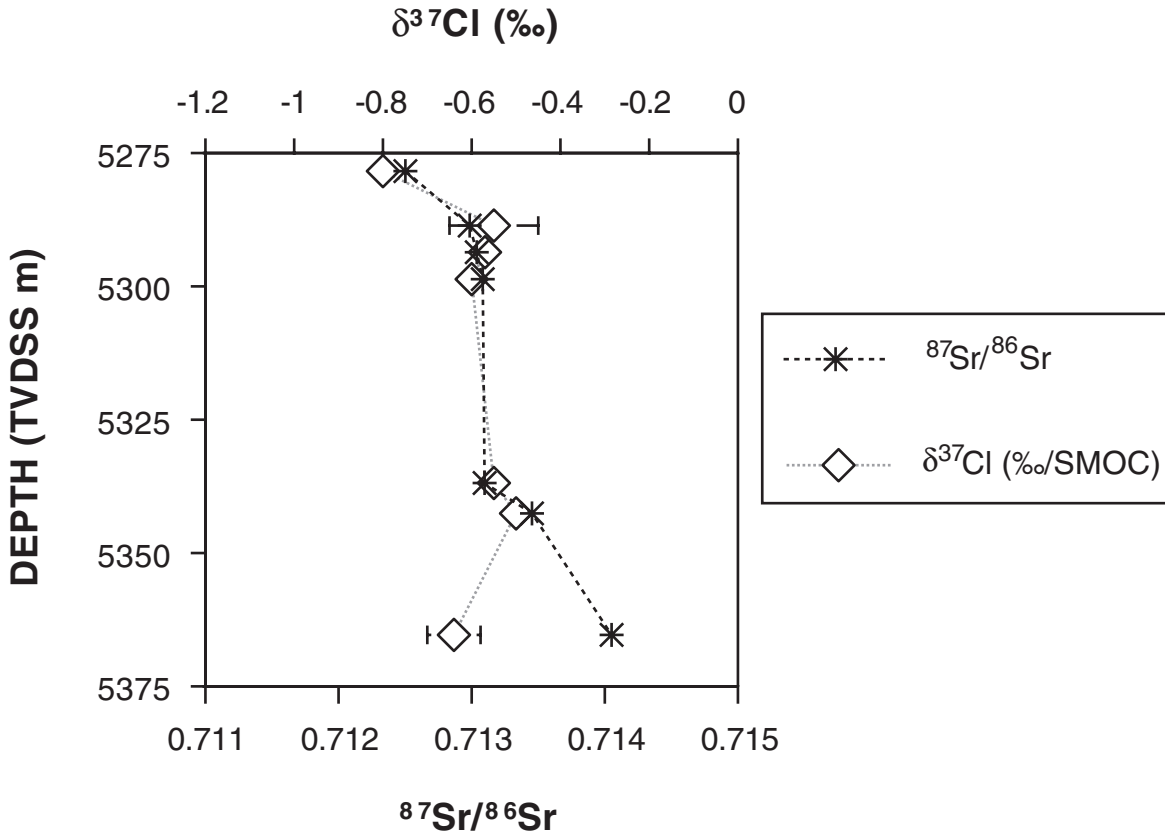


Fig. 2: $\delta^{37}\text{Cl}$ (‰/ SMOC) and $^{87}\text{Sr}/^{86}\text{Sr}$ variations with depth (TVDSS: True Vertical Depth under Sea Surface).

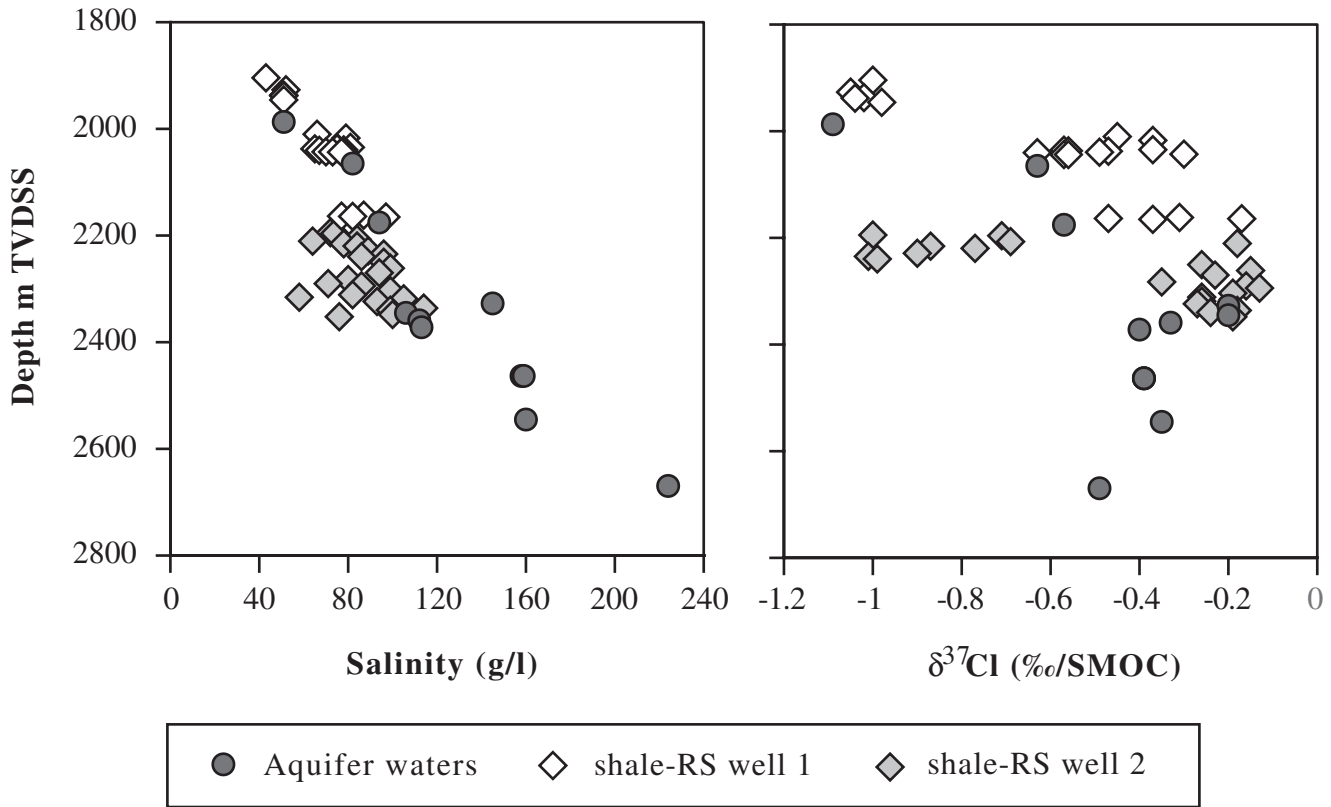


Fig. 3: a) Salinity (g/l) and b) $\delta^{37}\text{Cl}$ (‰/SMOC) variations with depth (m TVDSS: True Vertical Depth under Sea Surface) for aquifer and shale residual salt samples from Angola.