Cl-RSA and the characterization of subsurface systems

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The new Cl-RSA technique (Chlorine Residual Salt Analysis) provides an additional tool for the investigation of formation waters. The characteristics of formation waters (major and trace elements concentrations, isotopic compositions) are commonly used in sedimentary basins, oilfields, reservoirs and aquifers studies. For example, fluid flow barriers within aquifers and/or hydrocarbon columns can be suspected if 87Sr/86Sr or salinity depth profiles show discontinuities (Smalley et al., 1995; Mearns and McBride, 1999; Walgenwitz et al., 2001). Additionally, in oilfield studies, the oil saturation of the reservoir porosity is assessed using resistivity data which themselves depend on the salinity. Although of great potential, the study of formation waters is limited due to limited sampling techniques. The conventional wireline fluid sampling techniques such as MDT (Modular Dynamic Tester) or RFT (Repeat Formation Tester) give access to aquifer waters (if present in the basin). However, this sampling is necessarily restricted in space (to the aquifer) and the few scarce data need to be up-scaled to the whole basin or field. Other standard techniques require the extraction of formation waters from cores. Although providing a better scale resolution compared to wireline techniques, their use is limited to fresh or "preserved cores".

Several studies show the existence of fine-scale heterogeneities in the compositions of formation waters (Smalley et al., 1995; Coleman et al., 1998; Ziegler et al., 2001). The Cl-RSA technique has been developed on the model of the widespread Sr-RSA technique, in order to answer this need for a fine-scale investigation of formation waters. It can be performed on dried cores (e.g. archive cores) and allows a study at a cm-scale resolution. Residual salts, precipitated from pore waters, are recovered by an optimised crush-leach method with ultrapure water. Unlike strontium, chloride, the major anion in these waters, is not involved in diagenetic reactions. However, chlorine

contents and stable chlorine isotopic compositions (delta37Cl) of formation waters may vary in response to water-rock interactions, transport processes (such as ultrafiltration, diffusion, adsorption, ion exchange, osmosis, etc...) and mixing (Coleman et al. 1993; Eggenkamp et al., 1997; Loomis et al., 1997; Eggenkamp, 1998). Chlorine contents and isotopic compositions can thus be used to trace the origin of the waters and model the hydrodynamic history of the system.

Firstly, the validity of the Cl-RSA technique was tested on sandstones and shale samples from the North Sea and the Lower Congo Basin in West Africa. It was then applied to intra-reservoir shale samples from several wells of the West African oilfield. These samples come from thin shale layers inserted in reservoir formations from turbiditic units. They are all located in the hydrocarbon column of these oil reservoirs. The Cl-RSA delta37Cl values vary from -1.93 to +2.30 per mil (+/- 0.05, relative to SMOC). The chemical and isotopic compositions (major, minor and trace elements; delta18O, deltaD, 87Sr/86Sr, delta37Cl) of waters from the aquifer layers that underline the hydrocarbon columns within some of these turbiditic units, were also characterized. The salinity of the aquifer waters increases with depth: 50 to 237 g/L. Their delta37Cl values range from -1.09 to +0.01 per mil. Several processes such as dissolution of evaporites, ion filtration by semi-permeable membranes and mixings with meteoric water from recharge areas and with waters associated to hydrocarbons, can produce changes in the salinity. When considered with Cl/Br, delta37Cl of formation waters (aquifer waters and pore waters from hydrocarbons columns) help trace the origin of the salinity and discriminate the processes involved.

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