NATURAL GEOCHEMICAL TRACERS (STABLE ISOTOPES, NOBLE GASES, METAL TRACE ELEMENTS) AS LIMIT CONDITIONS FOR BASIN MODELING: DIRECTIONS OF MIGRATION, LEAKAGE AND RESIDENCE TIMES OF HYDROCARBONS

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The development of more and more sophisticated basin models for oil and gas exploration gives rise to several questionings about the pertinence of the chosen scenario to represent the geological history of a sedimentary basin. Several key processes cannot be quantified directly from the actual knowledge of the fluid properties, and need extra characterizations, which allow to test the favorite model at the light of geological constraints obtained through high-tech innovative geochemical studies. We present several of these news methodologies which may be used in order to assess parameters as the direction of hydrocarbon migration at the basin and at the reservoir scale (Prinzhofer & Pernaton, 1997; Battani et al., 2000), partial leakage of an accumulation, interaction between hydrocarbons and water (water leaching, biodegradation) and residence times of hydrocarbons in a geological structure (Prinzhofer & Battani, 2003). These approaches take into account the carbon stable isotopes of hydrocarbons, the chemical and isotopic composition of associated noble gases (from Helium to Xenon), and the concentrations and isotopic ratios of several trace and ultra-trace metal elements in the oils.

Partial leakage out of a reservoir characterized by the carbon isotopes of hydrocarbons and with noble gas geochemistry

A series of four oil and gas fields A, B, C and D have been analyzed in several gas phases for chemistry, carbon isotopes and noble gas isotopes. Carbon isotopes of C_1-C_4 indicate that fields A and B contain more mature fluids than fields C and D, and that the degree of openness of fields A and B is greater than for fields C and D (as shown by the Gastar diagrams as defined in Prinzhofer et al., 2000). The associated study of fossil noble gases (^{20}Ne, ^{36}Ar, ^{84}Kr and ^{136}Xe), when correlated with the concentrations of radiogenic ^{4}He, confirm a fractionation due to partial leakage (Figure 1). It is possible to calculate from this kind of trend the absolute proportion of hydrocarbons lost out of the structure, as the expected ratios between two fossil noble gases without any leakage should be the ratio of air-equilibrated water. With a decreasing proportion of helium, indicating an increasing importance of partial leakage, all the heavy/light ratios between fossil isotopes increase, indicating this leakage process. The calculation indicates that the proportion of leakage varies from 0 (for field D) to 40% (for field A) of the accumulated fluids.

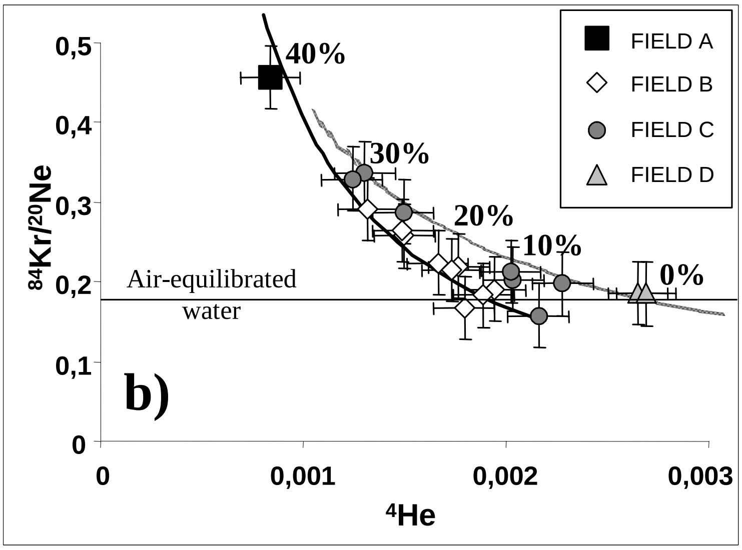

Figure 1: Ratios of the two fossil isotopes ^{84}Kr and ^{20}Ne versus the ^{4}He concentrations, indicative of a partial leakage. The values in per cent represent the proportion of leaked hydrocarbons.

Residence time of hydrocarbons

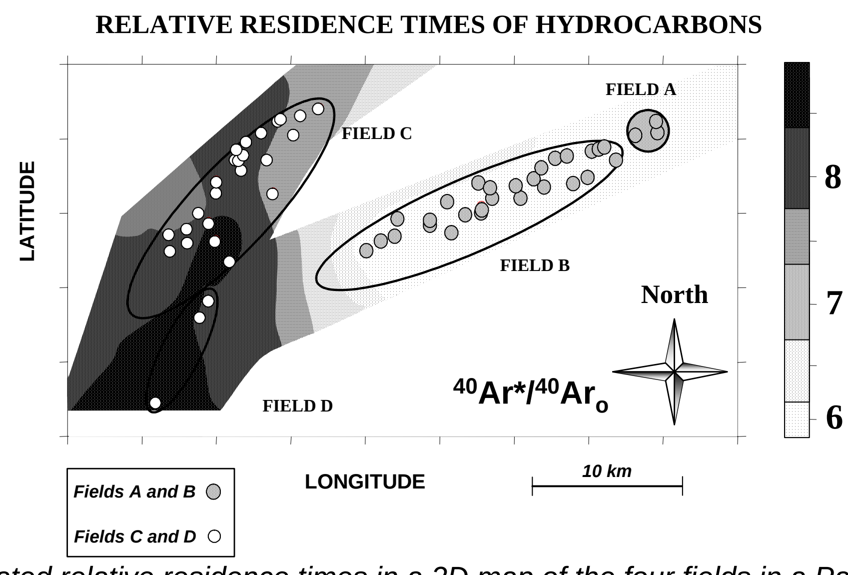

Figure 2: Calculated relative residence times in a 2D map of the four fields in a Paleozoic basin

Looking at the concentrations of radiogenic noble gas isotopes as ^{4}He or $^{40}Ar^{*}$, it is possible to quantify the relative residence time of hydrocarbons in a structure. Figure 2 shows, for the same four fields, the calculated residence times for each collected hydrocarbons. The fluids in the reservoirs A and B have shorter residence time, which is compatible with a higher leakage through the geological history of reservoir filling. A hydrocarbon accumulation sees its chemical composition linked not only to the history of maturity of the source rocks, but also with the "memory" of the reservoir, which may accumulate and keep in its structure all the generated hydrocarbons, or the last pulse generated in the source rocks. The average maturity of the fluids, and its quality in terms of GOR and possible nitrogen amount is directly dependent on this residence time parameter.

Metal trace elements in crude oils, and its implications for oil exploration

Metal trace elements are always present in oils, but only recently measurable, except Nickel and Vanadium, whose concentrations were high enough to be analyzed by usual techniques. ICP-MS high resolution and multi-collection allow to reach sensitivities around several parts per trillion (ppt), associated with selected isotopic ratios (Dreyfus et al., 2005). An intensive research area has been initiated to use these trace elements to characterize the geological history of liquid hydrocarbons, i.e. their source, maturity, alteration and distance of migration. Some ratios as the Mo/Sn ratio seem to correlate with more usual maturity parameters based on organic biomarkers analysis (Figure 3). The analysis of these metals may be performed in oil fractions as asphaltenes (which contain the main part of them) and maltenes. The concentration of Barium in maltenes seems to increase with an increasing amount of biodegradation, giving a new and quantitative tool to characterize the proportion of biodegraded and remaining oil in a reservoir (Figure 4). The concentrations of Barium in the asphaltene, or in the whole oil are not affected by this process.

The last example presented here represents the Lead isotopic ratios of Brazilian oils. The samples contaminated by anthropic activity (tubings, sampling device, etc...) are well identified, and the non-contaminated samples show an isotopic trend corresponding to a mixture between two source rocks (Figure 5).

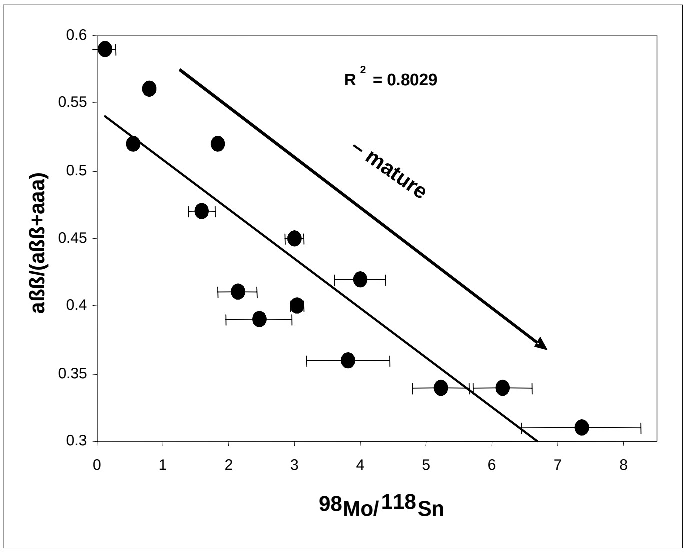

Figure 3: Correlation between an organic maturity index ($\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$) and a trace metal ratio (Mo/Sn).

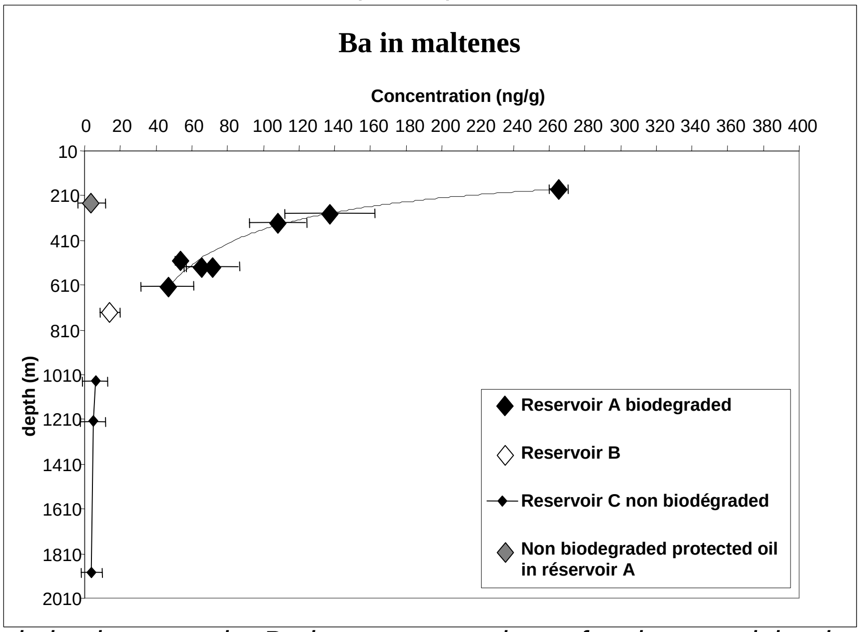

Figure 4: Correlation between the Barium concentrations of maltene and the degree of biodegradation of Brazilian oils.

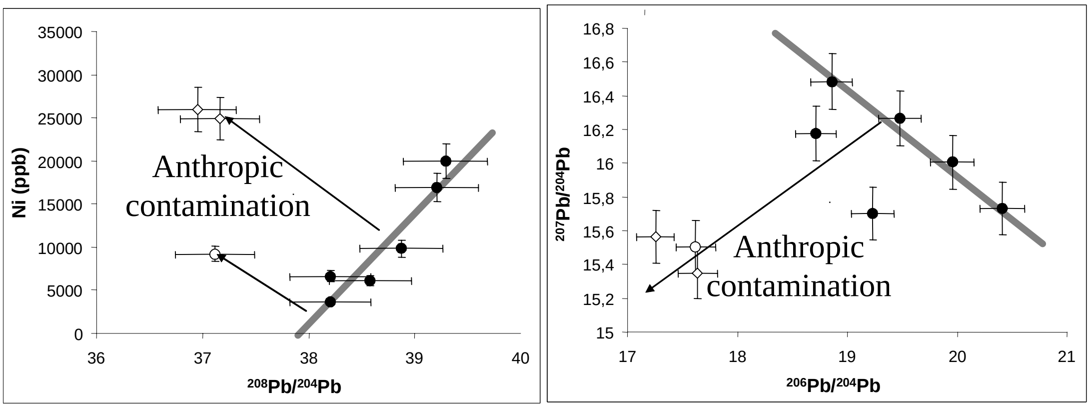

Figure 5: Pb isotopic ratio cross-plotted, or plotted versus the Nickel concentrations of Brazilian oils

Conclusions

The use of different natural tracers allows to better characterize the geological history of a petroleum system. These data represent valuable limit conditions for basin modeling, as they may be used as controls for a given geologic scenario and entrance parameters for a basin modeling. Some are already in a mature use, as stable isotopes of carbon, some begin to be used routinely in different petroleum systems like noble gas isotopes. Others like metal trace elements in oils are under development . Most are very likely promising tools for the future R&D in geochemistry.

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