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**ABSOLUTE DATING of OIL GENERATION and EXPULSION:
The LAST CHALLENGE in GEOCHRONOLOGY?**

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The absolute chronology of terrestrial and extra-terrestrial rocks and fluids has been developed from the first isotope analyses of radiogenic and radioactive elements about half a century ago. Although it is possible now to estimate the ages or the residence times of any kind of rocks, water and gas compound, it is still impossible to date with confidence the different critical ages of a petroleum system, except the age of the rocks sedimentations (source rocks, reservoirs, caprocks, ...). Several attempts have been developed recently, with mitigated success (radiogenic noble gas isotopes, osmium isotopes, lead isotopes). We present here a synthetic view of the most recent examples of attempts for dating oil and gas expulsion out of the source rocks using both noble gas isotopes and the system Uranium/Thorium/Lead.

The noble gas isotopes

Some noble gas isotopes are called radiogenic, as they are the products of the decay of natural radioactive isotopes. The two main ones are ^4He (coming mainly from the radioactive decays of ^{235}U , ^{238}U and ^{232}Th) and ^{40}Ar (product of disintegration of the radioactive ^{40}K). For a given amount of parent isotope (radioactive one), the amount of daughter element (radiogenic one) is a direct function of the elapsed time of isolation of the considered fluid, here an hydrocarbons phase. Even if it could be seen that there is a rough correlation between the concentrations of radiogenic noble gas isotopes and the age of functioning of a petroleum system, no quantitative model could be designed out of the concentrations and isotope data, as noble gas compounds are extremely mobile (mainly helium), and that the problem of the closure of the system is paramount. It seems that the hydrocarbon phase is never completely acting as a closed system in relation with noble gas compounds, a partial leakage of these compounds being associated with an external input of deeper sources. The net result is that no absolute datation may be obtained so far with this methodology. However, relative chronology between different hydrocarbon accumulations of the same basin could be obtained.

The Uranium/Thorium/Lead system

The pioneer work of Dreyfus et al. (2005) has shown that the lead isotopic signature of oil could be analyzed with ICP-MS, and gave important results in terms of mantle contribution in petroleum systems. We decided to apply this new analytical methodology to a tentative dating of oil expulsion with the U/Th/Pb geochronometric system. The advantage of these elements is their relative inertia in terms of migration, mainly when compared to noble gases. It was possible to discover that the parent/daughter ratios (i.e. $^{238}\text{U}/^{206}\text{Pb}$, $^{235}\text{U}/^{207}\text{Pb}$ and $^{232}\text{Th}/^{208}\text{Pb}$) are generally much higher in the kerogen than in the associated oils, where the concentrations of uranium and thorium are very low. This implies that the dating of the age of expulsion

cannot be obtained with the usual isochron method, as the generated oil will remain with the same lead isotopic ratios than at the expulsion time, as the parent concentrations (U and Th) are close to zero. The age of expulsion is obtained through the measurement of the lead isotopic ratios in oils and in the associated kerogen, and with the parent/daughter ratios measured in the kerogen (Figure 1).

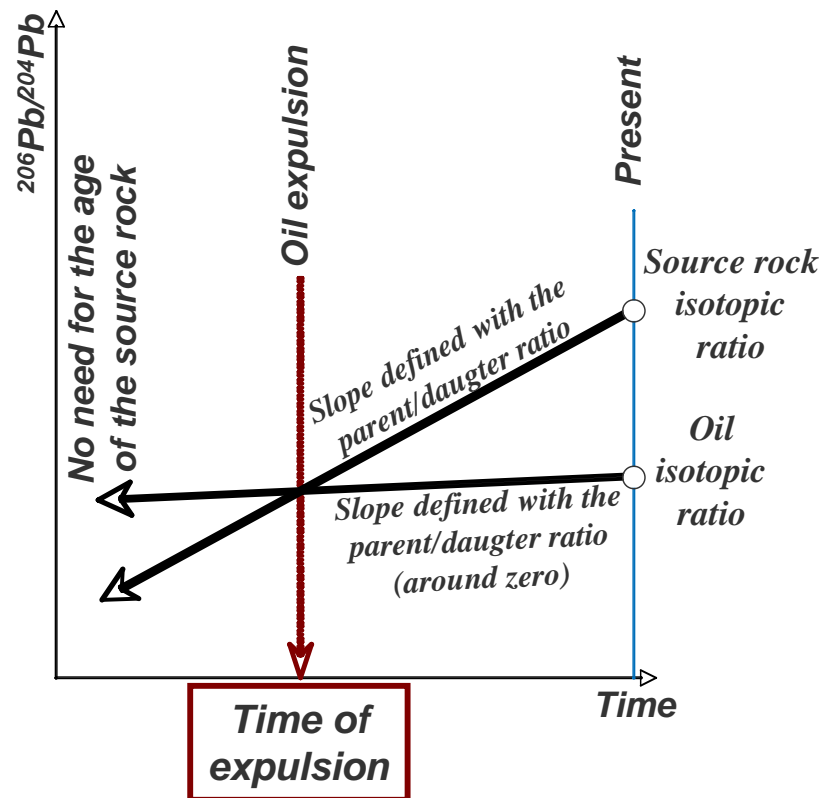


Figure 1: principle of the U/Th/Pb dating of oil expulsion, with the example of the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio.

The preliminary results obtained from different basins (Reconcavo, Brazil, Berkine, Algeria and Alberta, Canada) are presented, and indicate that the age of expulsion can be obtained when the source rocks have been sedimented in a marine environment. When silico-clastic sediments are present in the source rocks, it appears that the calculated ages give incorrect values.

Conclusion

The absolute dating of oil expulsion is still a challenge for geochemistry. Some new methodologies give promising results (U/Th/Pb, Re/Os not discussed in this work). However, it is possible to obtain reasonable ages for some petroleum systems, whereas other ones are still difficult to characterize due to the complexity of the chemical interactions between rocks, water and organic matter affecting the radiogenic isotopes, always in ultra-trace concentrations in the oils.