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Abiotic Hydrocarbon Generation: Do We Need To Consider It in New Oil and Gas Plays?

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Introduction

A long debate, which started in the XIXth century about the mineral or organic origin of oil and gas, was concluded some decades ago with definite proofs of the organic origins of petroleum and associated natural gas. However, the possibility of a purely mineral generation of organic molecules is still vivid in Earth Sciences, as it is the only way to generate life in the universe, and as hydrocarbon plumes have been evidenced in plutonic rocks as well as above hydrothermal sites on mid-oceanic ridges, where the high temperature and the absence of any sediments precludes an organic origin for these compounds. Chemists have been able to artificially generate hydrocarbon normal-alcanes through Sabatier and Fisher-Tropsch reactions for a long time. The remaining question is to know if these processes are important in the mass balance of hydrocarbons on Earth, and what kind of hydrocarbon compounds are preferentially generated by natural processes.

Natural hydrogen gas and associated methane

Natural hydrogen gas seeping out of oceanic hydrothermal sites, ophiolites and some plutonic cratons has been documented in various places of the Earth, associated with high pH (11-12) low Eh (-0.5V) water springs. The origins of this hydrogen gas is interpreted as due to the oxidation of the ferrous iron of the olivine from the peridotites into ferric iron (linked to serpentinization), associated with the reduction of associated water into H_2. A systematic association of this hydrogen with methane and nitrogen in various proportions is present in all these emanations. The easiest way to understand the generation of this methane is through the reduction of surrounding carbon dioxide with H_2 as the reducing agent. The measurement of the carbon stable isotopic ratios of this H_2-associated methane presents extremely heavy $\delta^{13}C$, up to +7 in some cases. An organic origin of this methane carbon is not possible, as any organic source would have much lighter carbon isotopic signature. A correlation may be evidenced for all these seeps between the carbon isotopic ratio of methane and the influence of mantle fluids expressed with the helium isotopic ratio $^3He/^4He$, normalized to the atmospheric ratio Ra=1.4 10^{-6} (Figure 1). The purely crustal value of the helium isotopic ratio R/RA is around 0.02, whereas the upper mantle has values between 5 and 8. The carbon stable isotopic ratio of methane is also positively correlated with the hydrogen isotopic ratio of H_2 (Figure 2), inducing a genetic link between these two compounds. The necessary reducing agent for abiotic methane generation (H_2) is thus mainly related with formations associated with the upper mantle. An isotopic distillation of the carbon of CO_2 could be calculated, inducing a temperature in the range of 300°C. These examples represent a clear evidence of purely abiotic hydrocarbon generation, affecting only methane: no evidence of any C2+ compounds could be detected in these gas seeps.

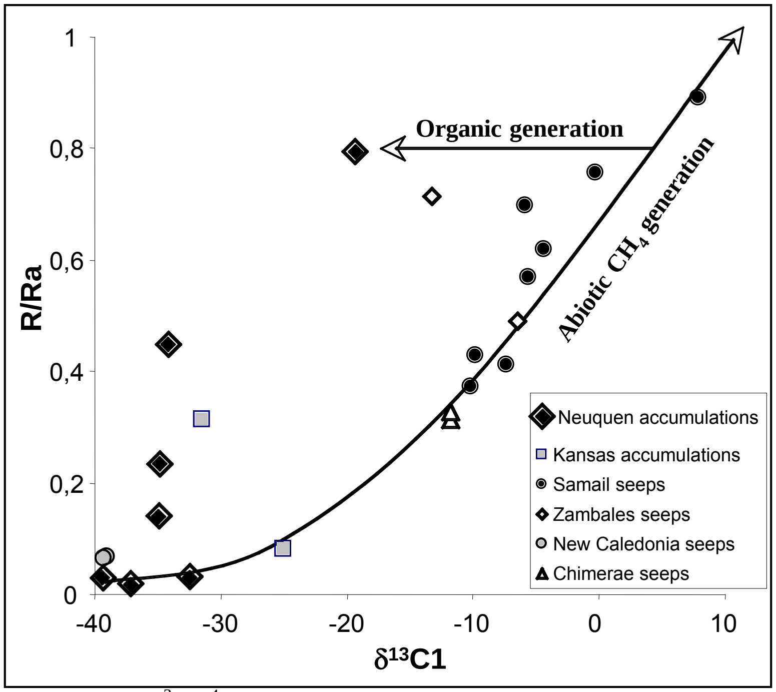

Figure 1: helium isotopic ratios $^3He/^4He$ expressed as R/Ra, Ra being the atmospheric isotope ratio of 1.4 10^{-6}, versus the carbon isotopic ratios of methane $\delta^{13}C$, expressed in per mil versus PDB.

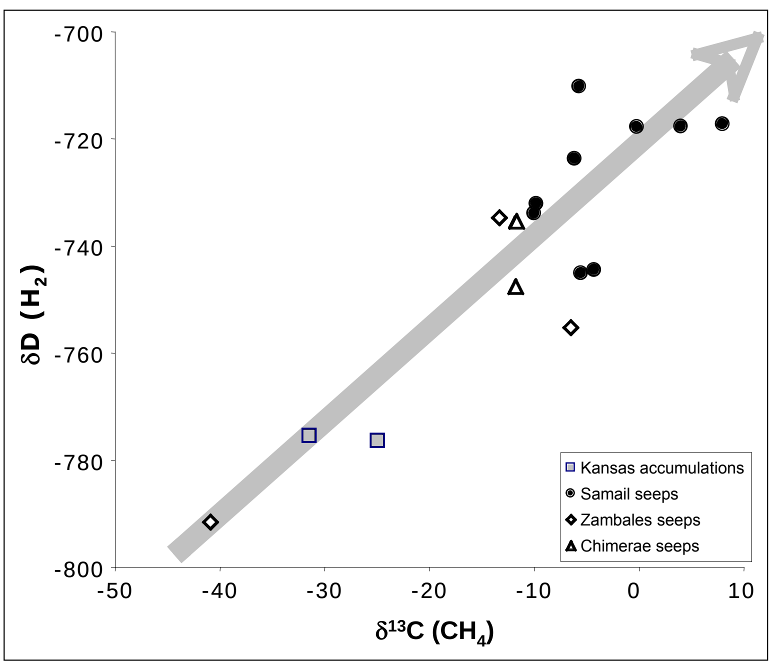

Figure 2: D/H isotopic ratios of H_2 expressed in per mil (δD) versus the SMOW standard, versus the $^{13}C/^{12}C$ isotopic ratios of CH_4, expressed in per mil ($\delta^{13}C$) versus the PDB standard.

Petroleum systems and mantle fluids: the Neuquen case study

The Neuquen Basin is a foreland sedimentary basin, associated with numerous volcanic intrusive and extrusive formations. It has been possible, using both carbon isotopes of hydrocarbon gas compounds and associated noble gases, to characterize the influence of mantle fluids in the petroleum systems. CO_2, which may present concentrations close to 100% in the gas phase, is demonstrated to be mainly of mantle origin. The mantle fluid influence in the basin increases smoothly from the South to the North, with a very large wavelength (500km) not directly correlated with the volcanic intrusions but with a halo of hydrothermal impregnation. Natural lead isotopes in the oil matrix present also a clear mantle contribution, indicating that the mantle fluids invade the sedimentary formations as hydrothermal fluids. The system CO_2/noble gases may be modeled with a simple mixing between a crustal and a mantle end-member respectively. On the opposite, the same mixing model does not fit the chemical and isotopic signatures of the system hydrocarbons/noble gases. The carbon isotopic ratios of methane range from a normal thermogenic signature to heavy $\delta^{13}C$ up to -19, without any possible bacterial alteration of the fluids. Also, these heavier $\delta^{13}C$ methane samples present lighter values of $\delta^{13}C$ for ethane and propane. We interpret these patterns as a mixture between a usual generation of hydrocarbons through the thermal cracking of organic matter, associated with an abiotic generation of light hydrocarbons (mainly methane). On Figure 1, it is possible to see that the Neuquen gas samples show the same trend than the hydrogen seeps, with a positive correlation between the carbon isotopic ratio of methane and the helium isotopic ratio, with heavier methane associated with mantle-contaminated fluids. However, a larger scatter for the Neuquen samples is interpreted as an addition of an organic contribution of hydrocarbons, linked with the commonly studied petroleum systems.

Conclusion

It has been possible to study, without any sedimentary and organic interference, a purely abiotic hydrocarbon generation through natural hydrogen seeps. This abiotic hydrocarbon generation concerns only methane, without any generation of larger compounds. In several petroleum systems affected by mantle hydrothermal fluids (back arc basins, deep offshore), the contribution of an abiotic methane generation may be quite significant, changing the amount and the GOR properties of the accumulated fluids.