Diamondoids and Compound Specific Isotope Analyses Applied to Age, Source, Thermal Evolution, Oil Cracking, Oil Mixing and Petroleum System Assessment

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In the last five years, the application of high resolution geochemistry new technologies has caused major impacts on exploration strategy along Brazil and other South American petroliferous basins. Prolific petroleum systems have proved to contain multiple source rock systems which contributed to mixed petroleum accumulations. The investigation of petroleum Systems in Brazilian and others South American sedimentary basins using high resolution geochemical technologies (HRGTs) that include diamondoid analysis for oil cracking and oil mixing, age-related biomarkers and compound specific isotope analysis of biomarkers (CSIA-B) and Diamondoid (CSIA-D) help to promote the idea of deep drilling for light oil and gas exploration in areas never imagined before.

Using diamondoid and CSIA-D is probably the only available technologies to established oil to gas cracking and to correlate the cracked portion of the oil with specific source rock. In these methods diamondoids and isotope of diamondoids are measured in established end-members. The comparison and correlation of the end-members with cracked and mixed oil types revealed, in some Brazilian and others South American basins the occurrence of multiple petroleum systems showing contribution of black oil from shallow sources and highly cracked oils from very deep sources. Such data have open new frontiers of exploration in areas considered to be mature petroleum provinces.

The Use of Bitumens as a Valuable Tool for the Timing of Charge in Basin Modelling

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The Upper Jurassic (Fulmar and equivalent) sandstones are major oil and gas condensate reservoirs in the North Sea, although many of the reservoirs also contain small, but still significant amounts of bitumens. These bitumens have been described as pyrobitumens previously generated by the cracking of an earlier oil charge to generate gas condensate and bitumen, although analytical data from the bitumen that support this formation mechanism have not been published. However, the analysis of the bitumens is very difficult using conventional petroleum geochemical techniques, due to the lack of free hydrocarbons. This problem can be overcome by using hydropyrolysis(hypy)to release bound biomarkers. Using both drill cuttings and core fragments, bitumen-stained samples were successively extracted using n-heptane, toluene and DCM/methanol and the resultant asphaltenes subjected to hypy analysis. Indeed, the bound hydrocarbons releaed via hypy from the bituments have the same maturities as mid-mature oils found in many of the North Sea reservoirs. Thus, a formation mechanism is described in which the bitumens formed as result of an early oil charge that was subsequently degraded during the period of uplift and erosion that generates the base Cretaceous unconformity. This is significantly earlier than predicted by conventional basin modelling, and can only be modelled using the PresRo® kinetic model. Thermal cracking of oils was prohibited by the high fluid pressures that developed during the Plio-Pleistocene subsidence.

Catalytic Gas in Marine Shales

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ABSTRACT

Marine shales are considered passive containers in the decomposition of oil to gas because they show no catalytic activity whatsoever under ordinary laboratory conditions. We report here robust catalytic activity under anoxic conditions where rates of gas generation are accelerated by factors reaching over one million. Activity vanishes irreversibly with even brief exposures to oxygen, which may explain why this remarkable rock property has so successfully eluded detection until now. Measured activity is natural activity carried from the subsurface rather than artificial activity created under analytical conditions. This is consistent with the observation that all activity can be extinguished with oxygen prior to analysis and with the fact that the reactions also proceeds in pure helium under mild laboratory conditions (~ 200oC) without the addition of hydrogen. Activity is independent of rock maturity and geologic age, but increases sharply in rocks deposited in outer-neritic environments under anoxic conditions, conditions that favor the accumulation of transition metals. The catalytic nature of the reaction and its sensitivity to oxygen-poisoning implicates transition metals and our experiments with pure nickel support this possibility. Measured rock activities in the Mississippian Barnett Shale (Fort Worth Basin, Texis, USA) correlate with a regional trend of oil to dry gas from Montague County to Johnson County. That organic rich shales like the Barnett (Mississippian, Texas) and the Monterey (Miocene, California) generate catalytic gas under realistic conditions would suggest that they would similarly generate catalytic gas in the subsurface. The similarity between catalytic gas and produced gas in molecular composition and the association of high-activity shales with dry gas and low-activity shales with wet gas/oil would indicate that they do.

Geochemistry of Wet Sour Gas in the Upper Jurassic Arab-C, Supergiant Shaybah Field, Saudi Arabia

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A geochemical study on the new Arab-C (Upper Jurassic) wet gas discovery in the supergiant Shaybah Field (Rub' Al Khali) was undertaken to explore its origin and for comparison with production from the Lower Cretaceous Shu'aiba reservoir and to Upper Jurassic (Arab-D and Hadriya) oils from Ghawar and the nearby Ramlah Fields. In addition, the relationship between this accumulation and the associated oil residue in the same reservoir has also been investigated.

The Arab-C gas/condensate (1.33% Rc) was found to be chemically and isotopically different from those in the overlying Shu'aiba reservoir (0.82–0.91% Rc) and the stratigraphically-deeper Hadriya reservoir at Ramlah (0.74% Rc), suggesting different origins. A late mature Hanifa carbonate (Upper Jurassic) source is most likely for the Arab-C accumulation,

although a Qusaiba contribution (Silurian) from the western depocenter cannot be entirely excluded. A less calcareous/more arenaceous source is suggested for the Shu'aiba hydrocarbons, which could be either Upper Jurassic or Lower Cretaceous in age.
The Arab-C accumulation may represent a mixture of two hydrocarbon charges. A late charge of more mature wet gas has apparently displaced a paleo-oil column represented currently by liquid residue (1.18% Rc) recovered from core. Alteration processes have affected reservoirs differently. Evaporative fractionation seems to have occurred in the Shu'aiba reservoir, whereas thermochemical sulfate reduction has affected the Arab-C hydrocarbon composition, leading to high H2S content, 13C enrichment and erroneous heptane and isoheptane values. This has been facilitated by high reservoir temperature (130ºC) and a thick anhydrite seal.

Compositional Modeling of Oil to Gas Cracking - Compositional Modeling of Asphaltene and Resin Thermal Degradation

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How deep can we drill before we hit the oil floor? What is the thermal deadline of crude oil under various geological conditions? These are great challenges for exploration geologists and basin modelers. Accurate assessment of oil thermal stability is essential for evaluating the economics of deep petroleum reserves and accumulation. A significant amount of effort has been put into addressing this problem and considerable progress has been made; however, uncertainties in the kinetic parameters related to degradation are still large. Fundamental details of the reaction networks, uniqueness of the kinetic parameters, and the relative importance of specific reaction mechanisms remain as critical unsolved issues. This paper describes a multi-component kinetics model for a specific oil sample from Thailand where the reaction network, reactant coefficients, and activation energies have been determined and calibrated based not only on cracking of the whole oil, but also on sub-fractions of the oil. Details of the thermal cracking of the asphaltene and the resin fractions isolated from the oil will also be discussed.

Advanced interpretations of stable isotopic composition of gases in working petroleum systems

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In petroleum exploration it is critical to determine the source and maturity of any found gas. Several interpretation diagrams have been proposed to infer gas precursors and the degree of their thermal conversion, but most diagrams are qualitative. Chung et al. (1988) proposed that kinetic isotope effects during kerogen thermal cracking should theoretically produce a straight-line relation between the carbon isotopic compositions of thermogenic gases (methane through butane) on a natural gas plot. However, many gases found in oil and gas field deviate from the theoretical straight line. These deviations are interpreted as additions of primary or secondary microbial methane, mixtures of gases of different maturities, or mixtures of gases sourced from several different source rocks. For example, addition of primary microbial gas to thermogenic gas causes a “pull-down” in the carbon isotope values of methane. Using field calibrations, we developed a nomogram to quantitatively estimate thermal stress of a gas. This is a very powerful tool to help us recognize that free and dissolved gases in petroleum accumulations are mixtures representing a range of maturities and origins which may provide a basis for reconstruction of petroleum filling history. Mixing of oil-associated gas with cracked oil gas or lignin-derived gas produces a cross-cutting line on the nomogram. In this paper we compare data from various petroleum systems to show how gas data, when systematically studied, can be used to provide valuable insights into the origin and thermal history of methane through pentanes gases in petroleum fluids.