

Geological and Geochemical Controls on Crude Oil Acidity

Dou, Lirong¹, Maowen Li², Dingsheng Cheng³, Dujie Hou⁴, Sneha Achal², Xiandeng Ye⁵ (1) China National Oil and Gas Development Corporation, No.6-1, Fucheng Beidajie, Xicheng District, Beijing, China (2) Geological Survey of Canada, Calgary, AB (3) PetroChina Research Institute of Petroleum Exploration & Development, Beijing, China (4) China University of Geosciences, Beijing, China (5) China National Oil and Gas Development Corporation, No.6-1, Fucheng Beidajie, Xicheng District, Beijing, China

Analyses of various fractions isolated from 82 crude oils from Africa, Asia and North America demonstrate that the carboxylic acid fraction is responsible for the acidity in these oils. Fatty acids are important components in oils with relatively low thermal maturity, but naphthenic acids account for most of the carboxylic acid fractions in all oils. While crude oils with high total acid numbers (TAN = 0.5-5 mgKOH/g) are not limited to heavy oils (<20oAPI), crude oils with extremely high TAN values (>5 mgKOH/g) are often heavily biodegraded. Although biodegradation appears to be the main geochemical process that produces high concentrations of carboxylic acids in crude oils, the increase in the TAN values with increasing biodegradation, as measured from their hydrocarbon compositions, is clearly influenced by the depositional environment of the concerned petroleum systems. Thus, for crude oils at any given biodegradation ranking, their TAN values tend to increase from marine to inland lacustrine oils. Both the sulfur contents and TAN values of the oils increase in the initial stages of oil biodegradation. However, the fact that oils with the highest TAN values are those with the lowest sulfur contents in our sample set suggests that sulfur-containing compounds contribute little to the crude oil acidity. A number of non-biodegraded oils also show relatively high acidities, indicating that factors other than biodegradation, possibly related to the later addition of fresh oils to earlier biodegraded oil reservoirs can control oil acidity in vertically stacked oil reservoirs.

Intra-Delta Versus Sub-Delta Sourcing of Petroleum – a Global Review

Samuel, O. J.¹, G.D. Abbott¹, C. Cornford² (1) University of Newcastle upon Tyne, Newcastle upon Tyne, United Kingdom (2) Integrated Geochemical Interpretation Ltd (IGI), Bideford, United Kingdom

Deltas have seen active petroleum exploration in the last three decades, but whether 'deltaic oils' are sourced within (intra-delta) or from below the delta (sub-delta) remains unclear. For sub-delta sourcing, the role of the delta is primarily one of burial and maturation of a pre-existing source rock. As a group, deltaic oils are characterised by being sourced from a kerogen mix comprising terrigenous plants of the hinterland and delta top, and marine phytoplankton whose bioproductivity may be enhanced by fluvial nutrients. Nearly all the Petroleum Systems identified in Tertiary deltas (e.g. Beaufort-Mackenzie, Niger, Assam, and Mahakam,) have been designated 'hypothetical' with respect to oil-source correlations.

We have harvested the literature for high resolution geochemical analyses, databasing analyses from 229 oils reservoirised within Tertiary deltas worldwide. Molecular and isotopic data suggest intra-delta and sub-delta sourcing operates within most deltas. The sub-delta groups show molecular affinity with marine organofacies (e.g. %C₂₇ and occurrence of C₃₀ Steranes) and higher maturity (C₂₉ Sterane_{20S/S+R}). The intra-delta oils have waxier n-alkane distributions, terrigenous biomarkers and lower expulsion maturities.

Our evidence fits a model where the intra-delta source rocks are either coals, or large volumes of lean shales either containing a mix of land plant and aquatic kerogens, while the sub-delta source rocks tend to be thinner discrete units, rich in TOC and contain marine kerogen. Where sub-delta oils migrate into deltaic reservoirs, molecules may be picked up by leaching (migrational contamination). These conclusions from published data will be augmented by new analyses in the coming months.

Isotopic Fractionation Effect of Primary Migration in Simulation Experiment of Selected Terrestrial Source Rocks

Geng, Ansong¹, Yuhong Liao² (1) Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China (2) Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

Previous studies showed that there are fractionation effects in generation and expulsion of terrestrial kerogen on both chemical compositions and isotopic compositions. This research simulates the primary migration of hydrocarbons by adding deuterated n-C₁₅ into source rocks. The $\delta^{13}\text{C}$ values of both deuterated n-C₁₅ and individual n-alkanes generated were analyzed, the results suggested that there exist strong isotopic fractionation effects (about 3 ‰ less than 10cm distance) in primary migration of vitrinite-rich coal, but there is no obvious isotopic fractionation (≤ 0.3 ‰) in primary migration of fusinite-rich brown coal and mudstone.

Combined together with the previous published experimental results of Liao (2004) from the same simulation experimental system, conclusion is that the maturation of organic matter, secondary crack of hydrocarbons and the adsorption-desorption process of hydrocarbons have influence on the fractionation effect on isotopic compositions in generation and primary migration of hydrocarbons. All of these factors make the n-alkanes retained in residual organic matter richer in ¹³C. Because vitrinite-rich coals have larger internal surface and high adsorptive capacity, the adsorption-desorption process is more complicated and the diffusion of hydrocarbons in kerogen matrix is more difficult, and thus the isotopic fractionation effect is aggravated in vitrinite-rich coals. This isotopic fractionation effects should be considered in oil-source correlation if vitrinite-rich coal is potential source rock.

Diagenesis and Reservoir Quality Evaluation Using Combined Petrographic, Isotopic and Geochemical Records

Zwingmann, Horst¹, Reinhard Gaupp² (1) CSIRO Petroleum, Perth, Australia (2) Friedrich-Schiller-University, 07749 Jena, Germany

Isotopic and geochemical studies are important tools in petroleum exploration. Diagenesis is integrated into larger multi-disciplinary studies to address complex issues such as reservoir management in high cost and risk environments to

evaluate economic success. Isotopic dating and geochemical tracing are effective tools to constrain timing and location of migration pathways of hydrocarbons into reservoirs. Time represents a master value in determining whether hydrocarbons will inhibit further diagenetic reactions, which can significantly effect reservoir quality by increased or diminished porosity preservation. Isotopic age and geochemical tracing data provide implications about the origin of hydrocarbons, fluid flow and mass transfer.

Results of combined K-Ar, Ar-Ar, Rb-Sr, rare earth element and stable isotope data from studies in Europe (NW Germany) and Australia (Copper Eromanga basin) will be presented to demonstrate applications of these tools for reservoir estimation and management. Both areas contain reservoirs with a range of specific high temperature diagenetic illites that significantly reduce reservoir characteristics. These areas allow investigation of illitization processes and thermal histories of deeply buried tight gas sandstone reservoirs. Illite is a major clay mineral component in these sandstone and is responsible for their low permeability. It displays a wide range of morphologies, modes of occurrence and origins, which can be dated and traced by geochemical tools.

Source Rock Studies of the Pedirka Basin, Australia

Middleton, Mike F.¹, Charles E. Barker², John Heugh³ (1) Murdoch University, N/A, Australia (2) U.S. Geological Survey, Denver, CO (3) Central Petroleum, N/A,

The Pedirka Basin is an under-explored Permian-aged basin, located in central Australia. After deposition of the Permian succession, the basin was covered by a thickness of between one to two kilometers of Mesozoic sediments of the Eromanga Basin. During its burial history, the basin has undergone several periods of relatively intense tectonic deformation along specific structural trends. Petroleum is known to occur in the basin from shows, and subsequent analyses, in many of the 14 exploration wells drilled in the basin from 1965 to 1990. The source-rock analysis of 24 samples obtained from exploration wells are consistent with a previous source-rock maceral study, and support the strong possibility of a good liquid hydrocarbon generative potential. This study shows the HI-OI and S1+S2 plots of the data are supportive of a higher than normal (for central Australia) type I kerogen content in the basin's Permian and Triassic source rocks.

Vitrinite reflectance data for the basin indicates that the deepest drilled sediments to date have a maturity in the middle of the Oil Window (0.85-0.90% maximum vitrinite reflectance). Burial history modeling of potential new well locations support maturity levels in this order. Calculations of possible volumes of hydrocarbons that could be generated indicate that volumes of the order of 10^8 m³ (c. 600 MMbbls) of oil equivalent could potentially be generated in the deepest trough of the basin, which is the Madigan Trough. It is concluded that a good petroleum discovery potential remains within the deeper parts of the basin.

Identification and Characterization of Oil Types in the San Joaquin Basin, California

Lillis, Paul G.¹, Leslie B. Magoon², Kenneth E. Peters² (1) U.S. Geological Survey, Denver, CO (2) U.S. Geological Survey, Menlo Park, CA

Analyses of 120 oil samples were used to characterize and map the distribution of oil types in the San Joaquin Basin, California. Geochemical parameters most useful for oil-oil correlation are stable carbon isotope ratios and biomarker ratios that include pristane, phytane, steranes, and terpanes. A subset of 82 oils not significantly affected by biodegradation or severe thermal maturity was selected for chemometric analysis, including hierarchical cluster analysis and principal component analysis. The results show that there are at least four oil types, which are designated as MM, ET, EK, and CM, after the most likely source rocks — the middle and upper Miocene part of the Monterey Formation, the upper Eocene Tumey Formation, the middle Eocene part of the Kreyenhagen Formation, and the Upper Cretaceous to Paleocene Moreno Formation, respectively. Different MM oil subtypes may originate from various members of the Monterey Formation and lower Miocene part of the Temblor Formation. Some of the MM oils reflect the increased contribution of terrigenous organic matter to the marine basin near the Miocene paleoshoreline.

Maps showing the distribution of oil types provide the basis for petroleum system maps that incorporate the geologic framework, source rock distribution and burial history, and migration pathways. These petroleum system maps are used for U.S. Geological Survey resource assessments of the San Joaquin Basin.

Brine and Hydrocarbon Evolution in a Salt Diapir-Oil Field Environment, Southeast Mexico

Levresse, Gilles¹, Julian Bourdet², Jordi Tritlla³, Jacques Pironon², Alex Carrillo-Chavez³, Jaime Patiño⁴, Miguel Varela⁴, Lourdes Clara⁴ (1) Centro de Geociencias, UNAM Campus Juriquilla, Queretaro, Mexico (2) CREGU - UMR G2R, Vandoeuvre-lès-Nancy, France (3) Geociencias-UNAM, Mexico, Queretaro, Mexico (4) Pemex Exploracion y Produccion, Villahermosa, Tabasco, Mexico

The Campeche Bay Cretaceous oil fields consist of dolomitized carbonates with superimposed impact breccias and an ejecta seal on top, thought to be formed after the Chicxulub impact. The structure of this area is principally driven by tectonics and salt diapirism during Miocene. Both oil fields are anticline structures. Chuc and Cantarell oil fields are crosscut by salt diapirs, which act as fluid flow barriers. Fractures are cemented by dolomite and late calcite and host most of the fluid inclusions studied. These are classified as two-phase brine-bearing (LAQ-V), two-phase oil-bearing (LHC-V); and poly-phase (LAQ-LHC-V-S = celestine, anhydrite) fluid inclusions. The petroleum inclusions contain around 30 mole% of methane and 1 mole% of CO₂ and belong to the "black oil" family. The majority of aqueous inclusions are methane-depleted and show no evidence of hypersaline brines. Gas/liquid ratios on fluid inclusions, ranging from 3 to 11%, were determined by confocal scanning laser microscopy at a given temperature. Microthermometric data show two maximum Th distribution around 50-60°C to 115°C for hydrocarbon inclusions and around 100°C-140°C for aqueous inclusions. These facts suggest that the end of the dolomitization process was closely related with the beginning of the main accumulation of oil in the reservoir, displacing the aqueous fluids and precluding the precipitation of carbonates. As

we found no clear evidences of hypersaline fluids related with diapirism, the oil charge would probably occurred before the salt tectonics took place.

P-T Conditions during Methanogenesis and Oil Filling in Mesozoic Dolostones from the Saramako Oil Field, Southeast Mexico

Tritlla, Jordi¹, Gilles Levesse², Jacques Pironon³, Alex Carrillo-Chavez¹, Eduardo Gonzalez Partida¹, S. Teinturier³, Hugo Martinez Kemp⁴, Fernando Gonzalez⁴, Miguel Varela⁴, Lourdes Clara⁴ (1) Geociencias-UNAM, Mexico, Queretaro, Mexico (2) Centro de Geociencias, UNAM Campus Juriquilla, Queretaro, Mexico (3) CNRS - UMR G2R, Vandoeuvre-lès-Nancy, France (4) Pemex Exploracion y Produccion, Villahermosa, Tabasco, Mexico

The Saramako oil field is located onshore the Mexican Gulf, in the Reforma-Comalcalco area, SE Mexican Basin (Mexico). The Tithonian and middle Cretaceous carbonates present a comparable evolution, with two events of pervasive dolomitization and a late calcite event. Dolomite carbon and oxygen isotopic compositions suggest that dolomitization occurred in a burial environment with a low water to rock ratio. Three fluid inclusion types have been found: (1) two-phase brine-bearing (LAQ-V) fluid inclusions; (2) two-phase oil-bearing (LHC-V) fluid inclusions; and (3) poly-phase (LAQ-LHC-V-S1-3= celestine, anhydrite, OM) fluid inclusions. The oil composition spans from black to light oil. Homogenization temperatures for type 2 (LHC-V) and 1 (LAQ-V) inclusions range from 5°C to 165°C and from 56°C to 82°C in the Tithonian reservoirs, and from 32°C to 155°C and from 80°C to 169°C in the middle Cretaceous reservoirs. Calculated salinity for aqueous fluids associated with oil inclusions in Tithonian and middle Cretaceous dolostones range from 5.5 to 7.5 moles of NaCl/kg H₂O and from 0.33 to 2.4 moles of NaCl/kg H₂O respectively. The CH₄ contents in type 1 (LAQ-V) fluid inclusions is similar for Tithonian and middle Cretaceous reservoirs, and varies from 0.009 to 0.242 moles of CH₄ /kg H₂O. Both reservoirs reveal the same filling history. A first, high pressure CH₄-rich brine pulse (ca. 1200 bars) precedes a hydraulic breccia event subsequently followed by a first hydrocarbon pulse (ca 500 bars). The last fluid P-T conditions calculated (ca. 300 bars; ca. 130°C) are thought to represent the main filling episode in the hydrocarbon reservoir history.

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

Scotchman, Iain C.¹, Will Meredith², Colin E. Snape², Andrew D. Carr³ (1) Statoil (UK) Ltd, London, United Kingdom (2) University of Nottingham, Nottingham, United Kingdom (3) Advanced Geochemical Systems Ltd, Leics, United Kingdom

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 hydrolysis(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 released via hypy from the bitumens 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.