

## **Residual Oil Analysis Reveals Complex Filling History of Multi-Reservoir Fields in the Southwestern Cooper Basin, South Australia**

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We have analysed a suite of produced and residual oils from stacked Cambrian, Carboniferous, Permian and Jurassic reservoirs in eight fields along the southwestern flank of the Cooper Basin. Here hydrocarbons expelled from Permian coal measures in adjacent troughs can migrate up section past the erosional edge of the Triassic seal and into Jurassic and Cretaceous non-marine sandstones of the overlying Eromanga Basin. In addition, several fields appear to have received charges from marine Cambrian source beds in the underlying Warburton Basin. Residual oils were recovered sequentially from the intact pore system of sandstone core plugs by high-pressure solvent flow-through extraction (SFTE). This analytical approach is based on the 'first in, last out principle' which assumes that the last oil to enter the reservoir (free oil) is the first to be extracted, whereas the initial charge (adsorbed oil) is recovered last. Molecular distributions of saturated and aromatic hydrocarbons in the residual oil fractions (n = 2-4) recovered from each core plug were compared with those of DST oils from the host and adjacent reservoirs. Differences in maturity (0.6-1.1% equivalent vitrinite reflectance) and source affinity (30-100% Permian) help constrain the charge histories of the fields in question. The same oscillating balance between Jurassic and Permian charge previously reported for Cretaceous reservoirs along the Murteree Ridge, 50-75 km to the southeast of the study area, is evident in Jurassic reservoirs of the Muteroo, Spencer and Taloola fields.

## **Formation of CO<sub>2</sub> in Sedimentary Basins and Assessment of CO<sub>2</sub> Risk in Gas Prospects**

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The unexpected occurrence of CO<sub>2</sub> in gas reservoirs is a major risk in exploration for natural gas, particularly in SE Asia. We developed a computer code in which we calculate the CO<sub>2</sub> risk using mineral equilibria from the hydrothermal literature that control the partial pressure of CO<sub>2</sub> in fluids. We expand this concept to sedimentary basins in general for predicting CO<sub>2</sub>. Our model infers that CO<sub>2</sub> is mostly released by the decomposition of disseminated carbonates from deeply buried clastic sediments at temperatures > 300°C. The CO<sub>2</sub> migrates with other fluids to shallower depths and can be sequestered through reversible reactions with silicates which buffer the CO<sub>2</sub> content of the fluid phases. These buffers usually restrict the CO<sub>2</sub> content of a gas phase to between 3 and 15 mole percent. However, the CO<sub>2</sub> content of a gas phase can rise above 70 mole percent if the CO<sub>2</sub> buffer capacity of a rock-water system is exceeded. We developed a new modeling capability that calculates the CO<sub>2</sub> partial pressures based on known mineral equilibria with generic assumptions on the carbonate content of various types of sediments. This code has been integrated as a module into the Cornell/GBRN BASIN VIEW computer code so that CO<sub>2</sub> risk assessment can be performed using industry-standard basin modeling. The new code computes a risk factor that ranks the relative risk of encountering high concentrations of CO<sub>2</sub> at a particular location in a basin. Examples of model results with case histories from SE Asia will be discussed.

## **Elemental Fingerprinting of Brazilian Petroleum: A Linkage to Gondwana ?**

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Trace elements, such as V and Ni, are commonly used in reservoir geochemistry for source identification. The availability of new and powerful analytical techniques, like ICPMS with its different instrumentation (quadrupole, high resolution, time-of-flight) and hyphenated techniques (GC, HPLC) opened a new perspective for elemental characterization of crude oils, allowing their direct analysis at the ultra trace level. In parallel, systematic studies on elemental distributions in crude oil fractions showed that most elements concentrate up to ten times in the heaviest ones, asphaltenes and resins, without altering the elemental compositions when compared to the corresponding crude oil. The inorganic petroleum geochemistry of Brazilian basins was investigated based on these results. Up to 50 petroleum samples from sedimentary basins of the Brazilian Atlantic passive margins and of Venezuela, Peru, Ecuador, Mexico, Iran, Yemen, Niger and Angola were analyzed by ICP-MS and ICP-OES. In order to have elemental distributions representative of the oil phase, the emulsified water was separated before fractionation of the sample; asphaltenes were separated by precipitation in heptane. Alkaline, alkaline earth and Fe-Sr-Ba were mostly concentrated in emulsified water. Trace and ultra-trace elements of the transition series were determined in the oil and its heavy fractions. In general trends, V was related to biodegradation, Ni, Co, Mo and Ga were associated to maturation processes and Zn-Cu-Pb-U-Th, to hydrothermal activity. Similar chondrite normalized elemental patterns were observed in crude oil and asphaltenes of samples from Rio Grande do Norte/Ceará and Niger, and from Rio de Janeiro (Campos) and Angola, respectively, suggesting a common origin of these oils from Gondwana basins.

## **Geochemistry of Western Australian Crude Oils: Use of Carbon Isotope Models to Delineate Active Petroleum Systems**

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Bulk carbon isotopic compositions of crude oils and their sub-fractions (saturate, aromatic and polar fractions) have long been used in conjunction with conventional biomarker data as an interpretive tool in the oil industry. Many geochemical models however, tend to be developed using data from specific regions such as the Gulf of Mexico or North Sea. Australian basins however, can boast a number of unusual factors that are difficult to compare with the more explored northern hemisphere basins, such as the relatively low TOC contents and high terrigenous affinity of many known source rocks. As a consequence, some of the better known interpretative tools often cannot be applied effectively to Australian oil accumulations. For example, whilst Jurassic marine sediments remain the most widely attributed source rocks on the North West Shelf, numerous source horizons ranging from Permian to Cretaceous age, and containing varying degrees of terrigenous influence, are also known to contribute to commercial oil accumulations. This influence is generally more clearly reflected in the carbon isotopic compositions of respective sediments and crude oils.

Over the years, a large amount of carbon isotope data has been collected from most basins within Australia. Here we present data and interpretive models for a number of Western Australian basins to highlight the combined use of biomarker and bulk carbon isotope analyses to, for example, delineate marine and terrestrial influenced source horizons. Thus models may be successfully applied, in a regional context, to distinguish for example, active petroleum systems in Western Australia.

### **Divergent Fluid Regimes and the Formation of Hydrothermal Dolomite: Examples from Devonian Reservoirs in the Western Canada Sedimentary Basin**

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Hydrothermal dolomites and apparently allied processes, such as effluent leaching and hot silicification have been described from numerous Devonian carbonate reservoirs in Alberta and British Columbia. Its presence has been used as an indicator of the interaction of high-temperature hydrothermal fluids with host carbonates due to tectonic influences in the Western Canada Sedimentary Basin (WCSB). The timing of the fluid flow events that precipitated these dolomites and the chemistry of these fluids has been the basis of many arguments. The Wabamun Group of WCSB is no stranger to dolomitization. In southern and southeastern Alberta the Wabamun carbonates are almost exclusively dolostone. To the north and west in Alberta and into British Columbia, quite the opposite is true, with less than an estimated 0.5% of the total Wabamun Group represented by dolostone. One would suspect that the agents and fluid-flow regimes responsible for these different occurrences would be substantively different. Basin-wide, ongoing Wabamun study, suggest that this discrimination may be possible but is commonly obscured by "significant" recrystallization. Dolomitization by very saline brines occurred under a broad continuum of temperature regimes (as determined by fluid inclusion and stable isotope studies), that were prevalent during shallow to intermediate burial. Superhot (165oC or greater) conditions apparently prevailed in the northwest (e.g. Monias), indications of scalding temperatures (85-125 oC) are common over much of the Peace River Arch area (e.g. Tangent, Eaglesham, Gold Creek, Pine Creek), whereas hot temperatures (60-90oC) predominate in pools surrounding the Wild River Basin (e.g. Medicine Lodge, Berland River). Lukewarm temperatures (30-50oC) are observed for the Crossfield trend.

### **Geochemical Processes Responsible for the Sour Gas Accumulation in the Bohai Bay Basin: A Case Study from the Northern Jinxian Sag**

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Sour gases from the northern Jinxian Sag of Bohai Bay Basin (China) are highly unusual as they contain up to 92% hydrogen sulfide and are associated with extremely sulfur rich oil. Because the current temperatures of most sour gas reservoirs in this area are below 100°C, many researchers believe that these gases were originated from bacterial sulfate reduction of mildly biodegraded S-rich oil at a location outside the current reservoirs. However, it is uncertain how the transport of hydrogen sulfide from the reaction site to the current reservoir could change the hydrogen sulfide concentration of a gas from <3% to 92%, whether this compositional fractionation has had any impact on their sulfur isotope values, and where the unaccountable methane could have gone. An alternative source could be the thermochemical sulfate reduction occurring in deeper parts of the Eocene reservoirs. This manuscript contributes to this fascinating debate on the prevailing geochemical processes by reviewing on the reservoir temperature distribution, regional geothermal history, and available molecular and isotopic data of various reservoir fluids and sulfur species.

### **An Investigation of Petroleum Systems of the Permian Basin, U.S.A**

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The Permian Basin, located in western Texas and southeastern New Mexico, USA, is one of the most prolific petroleum provinces in North America, having produced 35 billion barrels of oil, 91 trillion cubic feet of gas and 5.5 billion barrels of natural gas liquids through 1990. Hydrocarbons are produced from reservoirs of Cambrian through Cretaceous age, although most production is from Paleozoic reservoirs. Potential source rocks for Permian Basin oils include the Ordovician Simpson Group, Silurian Fusselman Formation, Devonian Woodford Shale, Mississippian Barnett Shale, a source of Wolfcampian (Permian) age, two facies of the Permian Bone Spring Formation, two facies of Guadalupian (Permian) age, and a Pennsylvanian (?) source. Despite the prolific hydrocarbon production, little published information is available regarding petroleum systems of the Permian Basin. In this study, geochemical data from approximately 400 oils, including biomarker parameters, sulfur content, and saturate and aromatic carbon isotope ratios, were used to differentiate oil types as a first step in defining Permian Basin petroleum systems. Hierarchical cluster analysis and principle components

analysis were used to differentiate oil families utilizing the detailed geochemical analyses, and revealed the complexity of Permian Basin petroleum systems. Mixing of oil types is widespread and biodegradation has occurred in some reservoirs. The recent exploration focus on unconventional shale gas resources in the Permian Basin highlights the need for understanding details of the petroleum systems.

### **New Insights into Source and Maturity of Sedimentary Organic Matter from the Vulcan Sub-Basin (Timor Sea) Using Stable Isotope Ratios of Individual Hydrocarbons**

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Recent work demonstrates the use of delta values of sedimentary hydrocarbons (n-alkanes, pristane and phytane) to evaluate the maturity of marine source-rocks from the Perth Basin (Western Australia). Distinct deltaD signatures were observed for immature source-rocks (%Ro = 0.53) where pristane (Pr) and phytane (Ph) were significantly depleted in deuterium (D) relative to the n-alkanes. With increasing maturity (up to %Ro = 1.13) the difference between the deltaD values of n-alkanes and isoprenoids reduces as Pr and Ph become progressively enriched in D. The enrichment of D in isoprenoids was attributed to isotopic exchange associated with thermal maturation.

This work has been extended further to a series of highly-matured sediments (%Ro = 0.6–1.6) from the Vulcan Sub-basin (Timor Sea), where the deltaD values of n-alkanes and isoprenoids show similar trends to those observed in the Perth Basin and indicate that D-enrichment in isoprenoids continues at much higher maturities. Further work is being carried out on additional sediment extracts from the Vulcan Sub-basin, to enable a detailed comparison of the isotopic profiles. Crude oils from this region have also been studied to evaluate their source and thermal maturity, adding new ideas on exploration plays and enhancing previous studies at this locality based on molecular and carbon isotopic analysis. In addition, these new isotopic results may be used in conjunction with molecular parameters to provide insights into migration pathways.

### **Isotopically Light Methane Expelled from Thermogenic Mature Coal! What Is Going on?**

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Gas composition and isotope values of gas liberated from coals on the Norwegian Continental Shelf (NOCS) by simple crushing have been analyzed and compared to those from fluid inclusion gases. The fluid inclusions were extracted from sandstones in contact with the coals. The coal gas was found to be isotopically similar to that liberated from inclusions. The methane is very light with d13C values in the range of -58 to -72‰ and isotopically very different from most of the gas discovered on the NOCS in which methane values generally fall in the range of -42 to -45‰. Most of the coal samples have a vitrinite reflectivity of 0.8 to 1% Ro. The inclusion samples contain dominantly methane (70 to 90%) while the coal gas is much wetter. The study shows that the examined coals have expelled biogenic gas: 1) over a temperature window where quartz overgrowth formation takes place (80-120degC), 2) in sufficient amounts to become trapped in inclusions and 3) over a sufficient time interval to become trapped. This suggests that volumes of biogenic produced methane have been expelled from the investigated coals at a surprisingly high temperature (depth of burial ~4000m) and that this light methane besides being trapped in inclusions also can migrate – potentially into commercial traps and mix with thermogenic high maturity gas – which is isotopically heavy and thereby skew the overall gas isotope values towards lighter values (values in the -45 to -55‰ range). No isotope fractionation during expulsion is observed.