

Reality or myth: The role of minerals in petroleum generation

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The prevailing hypothesis regarding the role of minerals in petroleum generation is that the source rock mineral matrix is an *inert container* for the kerogen, and that minerals do not significantly influence petroleum generation reactions. This is despite contrary observations including (1) the demonstrated catalytic effect of various minerals in laboratory petroleum generation experiments, resulting in petroleum-like distributions of gases and liquids, (2) the presence of compounds like diasteranes, diamondoids, and benzene and naphthalene isomers in crude oils that form through carbocation reaction mechanisms, and (3) the distribution of light hydrocarbon isomers in crude oil and the composition of gases produced from shales, that indicate mineral-organic reactions are occurring during petroleum generation.

Mineral surface area-total organic carbon relationships suggest there is an intimate association between organic matter and the mineral matrix of source rocks from the time of deposition. Extrapolating that result to petroleum generation, favorable conditions for the interaction of minerals with kerogen during petroleum generation may be established during source rock deposition. The goal of this paper is to evaluate the arguments for and against the role of minerals in petroleum generation, present new data that address the question and discuss the implications of mineral-organic reactions for petroleum generation.

Clay mineral control of organic carbon deposition and preservation in petroleum source rocks

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Previous work has shown a strong positive correlation between mineral surface area and adsorption of organic carbon in modern marine sediments. Our studies of black shales of varying thermal maturity and stages of diagenesis show a strong positive correlation between mineral surface area and total organic carbon in representative black shale deposits. This relation suggests that adsorption of dissolved carbon compounds or other mechanisms of preservation by clay mineral surfaces played a fundamental role in the burial and preservation of organic carbon. Additionally we have focused on the interlayer space of 2:1 smectitic clays. Our results imply that both polar and non-polar organic compounds are capable of gaining entry to the interlayer sites of smectite clay minerals. The MSA-TOC (mineral surface area) association implies organic carbon sequestration in an important class of black shales and petroleum source rocks may be more closely related to patterns of continental weathering and secular clay mineral trends than to the traditional models that consider only ocean water chemistry or marine productivity.

Molecular retention processes in source rocks: Can they explain fractionation during expulsion?

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Multi-component experimental generation patterns often disagree with observed reservoir composition, the latter being much less rich in aromatics and NSO compounds than the generated fluids. Adsorption has frequently been suggested to account for retention in coal, but the concepts brought forward to date are rather unspecific and not quantifiable. Absorption in the kerogen matrix based on polymer solution theory has been suggested for type I and II kerogen. This presentation looks at the interaction of adsorption in nanopores and polymer-solution-type absorption in source rocks and suggests quantifiable processes of fractionation.

Vitrinite is distinctly porous from the nano- to micrometer scale. Basic structural units (BSU) with widths around 1 nm and d002 spacing of 0.34 to 0.38 nm in bituminous coal and anthracite make up nanoporosity. Similarly, organic molecules may replace anorganic cations in inter-layer porosity of clays. If pore diameter approaches the diameter of molecules and the adsorption system is dominated by van der Waals forces, the Dubinin-Radushkevich (D-R) equation can be applied.

We used proprietary software PriMig to validate the processes, which to date reveals the following relationships: In coals, an absorption model based on Polymer Solution theory only, fails to eliminate heavy compounds sufficiently. A model based on D-R theory only leads to rather aromatic oils and condensates. However, a combination of adsorption- and absorption processes explains why coal expels gas, even if its chemical model may suggest generation of large amounts of C₁₅₊ hydrocarbons. Coals with >5% porosity expel gas irrespective of composition of the original chemical generation model. Coals with initial potential around 300 mg/gTOC and with porosity <2% expel high-GOR petroleum fluids. GOR decreases with increasing initial potential.

The results obtained to date are encouraging and point in the right direction. Improved quantitative predictions need better knowledge of multi-component swelling ratios and adsorption, as well as temperature- and maturity-dependence of adsorption and solution systems. The presentation will show the newest available modelling examples of application and validation of the model.

Fluid-rock interactions in petroleum reservoirs: Alkylphenols

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Proxies for monitoring fluid-rock interactions

The interaction of petroleum compounds with mineral surfaces is one of the key mechanisms determining which phase, oil or water, wets mineral surfaces in petroleum reservoirs. Using a number of approaches we describe how polar surfactant molecules (i.e. alkylphenols) behave during crude oil / brine / rock interactions in petroleum reservoirs.

Results and Discussion

A core-flood experiment was designed to monitor the chemical and physical changes during oil migration (Bennett et al., 2004). Wettability alteration shown by Environmental Scanning Electron Microscopy is consistent with changes in C₀-C₃-phenol distributions. In natural systems, alkylphenols display similar behaviour to those described from the core-flood. Molecular modelling experiments (van Duin and Larter, 2001) provide a fundamental explanation of wettability alteration observed during the core-flood. We propose that C₀-C₃-phenol serve as proxies for describing crude oil / brine / rock interactions in petroleum accumulations.

Conclusions

The C₀-C₃-phenols represent an important class of surfactant molecules that can provide information regarding the nature of crude oil / brine / rock environment of petroleum reservoirs.

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Phase relations in the system CHO and the generation of petroleum in hydrocarbon source rocks

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Thermodynamic analysis of metastable equilibrium phase relations among petroleum, CO_{2(g)}, water, and kerogens with various (H/C)s along the U.S. Gulf Coast fluid-pressure (p_f) geotherm indicates that oil generation by melting of immature kerogen in hydrocarbon source rocks occurs at $p_{CO_2(g)} = p_f$ over a narrow interval of $\log f_{H_2(g)}$, which decreases and becomes negligible with increasing depth, temperature, and $\log f_{H_2(g)}$. It follows that the corresponding phase assemblages constitute $f_{H_2(g)}$ buffers in hydrocarbon source rocks. For example, at $\sim 25^\circ < T < 100^\circ \text{C}$, incongruent melting of either a type-I kerogen corresponding to C₁₇₁H₂₈₈O_{9(c)} or a hydrogen-rich type II-kerogen represented by C₂₀₀H₂₆₀O_{10(c)} produces petroleum + water + a kerogen with a lower H/C (C₂₉₂H₂₈₈O_{12(c)}). With increasing temperature from ~ 100 to $\sim 150^\circ \text{C}$ the metastable equilibrium phase assemblage generated by incongruent melting of both C₁₇₁H₂₈₈O_{9(c)} and C₂₀₀H₂₆₀O_{10(c)} generates petroleum + C₂₉₂H₂₈₈O_{12(c)} + CO_{2(g)}. As temperature continues to increase above $\sim 150^\circ \text{C}$, a metastable mature kerogen (C₁₂₈H₆₈O_{7(c)}) is produced by incongruent melting of the C₁₇₁H₂₈₈O_{9(c)}, C₂₀₀H₂₆₀O_{10(c)}, and C₂₉₂H₂₈₈O_{12(c)} kerogens, which results in metastable equilibrium at depth among C₁₂₈H₆₈O_{7(c)}, petroleum, and CO_{2(g)}. With further burial of the source rock at temperatures $> \sim 225^\circ \text{C}$, both C₁₇₁H₂₈₈O_{9(c)} and C₂₀₀H₂₆₀O_{10(c)} melt congruently to produce petroleum + CO_{2(g)}, but C₂₉₂H₂₈₈O_{12(c)} continues to melt incongruently to form petroleum, C₁₂₈H₆₈O_{7(c)}, and CO_{2(g)}. However, in the latter case, the volume of C₁₂₈H₆₈O_{7(c)} produced in the process progressively decreases with increasing temperature as the volume of petroleum generated increases. It can be shown that the distribution of the hydrocarbons in the petroleum produced compares favorably with its natural counterpart. It can also be demonstrated that the volume of crude oil derived from the incongruent melting process can account for all of the oil produced and in proven reserves in the world's oil fields.

The case for catalytic gas

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The currently accepted paradigm for the origin of natural gas may be in trouble. Its central theme is this: hydrocarbons thermally crack to lighter hydrocarbons and ultimately to methane (CH₄) over geologic time and this explains the progressive conversion of oil to gas (C₁ – C₄) and gas to methane with increasing basin temperatures.

It has three serious flaws. First, hydrocarbons are too stable to decompose at the observed temperatures. Second, when oil does thermally crack, it gives a gas unlike natural gas. Finally, ethane and propane are extraordinarily stable and should not crack to methane over geologic time.

The case supporting the alternative hypothesis, that natural gas is formed catalytically by low-valent transition metals (Mango, 1992), is now compelling:

1) Source rocks in their natural state convert oil to gas catalytically.

2) They accelerate cracking rates by factors reaching well over one million.

3) The catalytic gas generated is identical to natural gas.

While the thermal paradigm cannot explain the composition of natural gas (Mango, 2001) and the conversion of wet gas to dry gas without invoking untested hypotheses, catalysis by transition metals can. Source rocks in their natural state generate natural gas catalytically (Mango et al., 1994) and convert wet gas to dry gas under the same conditions (Mango & Hightower, 1997). Thus, the evolution of petroleum (oil to wet gas and wet gas to dry gas) is uniquely replicated in catalytically active source rocks under natural conditions.

Of the two hypotheses competing for paradigm status, the catalytic hypothesis is the more economic; it explains more, needs less in the way of auxiliary help, and has broader experimental support.

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Hydrogen isotopes in organic matter maturation: A synthesis

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The D/H ratio of live biomass correlates well with D/H of ambient water used by organisms for primary production and metabolism of biochemicals. As ocean water and meteoric waters occupy a very wide range of D/H ratios, the D/H ratios of immature sedimentary organic matter (SOM) provide valuable paleoenvironmental and paleoclimatic information, especially on the molecular, compound-specific level. The biogeochemistry and isotopic composition of SOM change, however, during long-term maturation from early diagenesis into metamorphism.

Much has been learned from laboratory experiments and naturally matured samples about isotopic exchange between organic hydrogen and inorganic hydrogen at higher temperatures since Tom Hoering's (1984) pioneering hydrous pyrolysis experiments. On the compound-specific level, significant isotopic exchange of C-bound organic hydrogen with other ambient hydrogen is apparent at higher temperature, but seems to have affected many hydrocarbons only during their chemical genesis from precursor molecules. Some organic hydrogen moieties are prone to continually exchange (e.g., some aromatic hydrogen), whereas others seem to retain their D/H ratios over geologic time (e.g., *n*-alkanes; Sessions et al., 2004).

Published data from field studies document that increasing thermal maturity tends to transfer deuterium from inorganic sources into coal, kerogen, NSO-compounds and hydrocarbons, in qualitative agreement with hydrous pyrolysis results. However, D/H ratios of moderately mature fossil organic matter can still (i) distinguish kerogens from marine and freshwater paleoenvironments, (ii) identify oil families, (iii) correlate petroleum to their source rocks, and (iv) retain sufficient hydrogen isotopic information from the original biomass to assist in paleoenvironmental reconstruction (e.g., Schimmelmann et al., 2004).

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Carbon and hydrogen isotope measurements in abiogenic hydrocarbon synthesis

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Controversy surrounds the issue of possible contributions of abiogenic hydrocarbons to economic hydrocarbon systems, in large part because the characteristics of proposed abiogenic hydrocarbons have not been well defined. In particular, one of the key tools used for differentiating hydrocarbons of diverse origin – stable isotope signatures – are still largely unconstrained for abiogenic end-members. Based on field observations, an abiogenic isotopic signature of carbon isotope depletion in ¹³C and hydrogen isotope enrichment in ²H from methane to ethane has been proposed. This is based on the hypothesis that during polymerization of methane to produce higher hydrocarbons there will be a preferential rate of reaction for the light isotopes resulting in preferential incorporation of ¹²C into the products of the reaction but preferential loss of ¹H. To date however there has been very little laboratory verification of fractionation in abiogenic processes in general, particularly for hydrogen isotope effects.

This presentation describes the analytical developments involved in measuring both carbon and hydrogen isotopes on small sample volumes produced by experimental apparatus used for a variety of processes of abiogenic hydrocarbon synthesis. Synthesis of higher alkanes from methane in a spark discharge apparatus was a key experiment in developing the earliest models of carbon isotopic fractionation during polymerization. In this study we have revisited those experiments to verify the carbon isotope fractionation patterns and to incorporate measurement of hydrogen isotope effects for the first time as well.

Hydrogen and carbon isotope compositions of hydrocarbons in hydrothermal carbon reduction processes

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To understand the reaction pathways and isotopic fractionation for abiotic organic synthesis under hydrothermal conditions, two experiments involving carbon dioxide reduction at 400°C, 500bar were carried out. Formic acid was used as carbon precursor in the first experiment, with magnetite as a catalyst. The second one was conducted by injecting CO₂ and then H₂ into the reaction cell, and magnetite was purified to remove potential organic contaminations prior to the experiment.

CO and hydrocarbons (C₁-C₄) were observed in both experiments. Only when the H₂/CO₂ ratio passed a critical threshold in the second experiment, did the formation of hydrocarbons from CO₂ reduction proceed. More CO and hydrocarbons were produced by adding more H₂. XPS analysis indicates carbon enrichment and hydrocarbon formation on magnetite surfaces following the reactions.

A pattern of carbon isotope depletion between C₁ - C_n has been debated as a potential indicator of abiogenic hydrocarbon synthesis. Recently it has become feasible to measure δ²H isotope signatures as well. This presentation will show some of the first results for δ²H isotope analysis of samples produced during hydrothermal solution experiments. In the first experiment, the hydrocarbon isotopic compositions were clearly impacted by mixing with biogenic hydrocarbons sorbed to the magnetite surface. After removal of this source of contamination in the second experiment, results do not show a pattern of C isotope depletion and H isotope enrichment, but rather a 5‰ enrichment between C₁ (-28.5‰) and higher hydrocarbons (C₂ and C₃) with identical δ¹³C values. Results show a pattern of C isotope enrichment and H isotope depletion between C₁ and higher hydrocarbons in our experiments, suggesting that different abiogenic hydrocarbon formation reactions may well have different isotopic patterns associated with them.

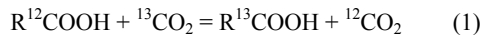
Experimental investigation of organic acid carboxyl carbon exchange with aqueous CO₂

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Previous laboratory experiments have demonstrated rapid exchange of carboxyl carbon in organic acids with aqueous carbonate species during hydrous pyrolysis of petroleum source rocks (Dias 2000). To build on these initial findings, we conducted a series of experiments that constrain the roles of minerals, aqueous and vapor phase reactions, and temperature during carboxyl exchange reactions. Experiments were conducted at 250 to 350°C with and without a vapor phase present. All experiments initially contained 20 to 70 mmolal of C₂-C₅ straight chain organic acids and 100 mmolal H₂ and 99.9 % ¹³C labeled CO₂. No minerals were added to the experiments.

Variations in the isotopic composition of C₂-C₅ organic acids revealed extensive exchange of carboxyl carbon at 250 to 350°C according to the reaction:



The rates of reaction (1) increased with increasing temperature and decreased with increasing organic acid chain length. The rate of carboxyl exchange decreased slightly upon creation of a headspace, a likely result of reduced reaction rates for volatile acids that had partitioned into the vapor phase. Rates of reaction observed during this study were comparable to rates during the mineral-bearing experiments of Dias (2000), suggesting carboxyl exchange via an aqueous reaction that is not mineral catalyzed.

Extensive reduction of aqueous organic acids to their corresponding n-alkanes resulted in the production of ¹³C labeled hydrocarbons during the experiments. Formation of these hydrocarbons demonstrates the availability of aqueous reaction pathways that may allow incorporation of carbonate carbon into petroleum hydrocarbons. Examination of carbon isotopic trends for short-chain n-alkanes, carboxylic acids, and CO₂ associated with petroleum from a variety of environments suggests similar exchange reactions may be occurring in nature. Accordingly, models that describe the isotopic evolution of short-chain hydrocarbons during the thermal maturation of petroleum may need revision to include the effects of carboxyl exchange reactions.

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Effect of aqueous chemistry on the thermal stability of hydrocarbons in petroleum reservoirs

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The thermal stability of hydrocarbons under geologic conditions is of significant interest for petroleum geochemists due to its effect on the gas to oil ratio (GOR) and the maximum depth of oil occurrence within sedimentary basins. While most previous research in this area has focused on the kinetics of organic thermal reactions, the effects of inorganic species contained in formation waters and reservoir minerals are increasingly being recognized as a significant contributor to this process. The oxidation of hydrocarbons via the reduction of sulfate (TSR) is one example of an organic-inorganic reaction that plays a critical role in controlling the thermal stability of hydrocarbons in some reservoirs. Gibbs free energy calculations suggest that these reactions are energetically favorable at typical reservoir temperatures, yet non-catalyzed TSR reactions involving anhydrite have never been simulated in the laboratory at temperatures below 800°C. This suggests that the rate of TSR must be controlled by some unidentified kinetic factors.

We have conducted a series of hydrous pyrolysis laboratory experiments in order to investigate the role of formation water chemistry on the thermal stability of petroleum hydrocarbons. Our results show that the chemical composition of aqueous solutions in contact with hydrocarbons significantly affects the rates and pathways of hydrocarbon cracking and oxidation. More specifically, the ionic strength and major ion concentrations (e.g., SO_4^- , Ca^+ , Mg^{2+} , etc.) can influence the onset temperature of oil cracking to form natural gas, and the amount and composition of gas generated (e.g., CO_2 , H_2S , CH_4 , etc.). The predominant mechanism appears to be the reduction of reactive sulfate ion-pair species coupled with hydrocarbon oxidation.

Oil-anhydrite TSR reactions in the Permian Khuff Fm, Saudi Arabia

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Thermochemical sulfate reduction (TSR) occurs when anhydrite reacts with petroleum resulting in calcite, H_2S and other reduced sulfur compounds. Analysis of data from 10 wells from the sour Permian Khuff Fm from Ghawar and neighboring fields in Saudi Arabia using geochemistry, stable isotopes, fluid inclusions and petrography has confirmed that H_2S is due to TSR. Anhydrite has been replaced by calcite and sulfur. However, of all the various types of anhydrite, only nodules composed of microcrystalline anhydrite have undergone TSR. Replacive calcite is poorly developed in many cases with much anhydrite remaining even in reacted nodules. Some wells have no finely crystalline anhydrite, and thus have no H_2S . Fluid inclusion analysis revealed that: (1) the initial charge was oil, later displaced or diluted by gas, (2) TSR occurred in the presence of oil between 113°C and 135°C. TSR thus occurs at a lower temperature with oil than with dry petroleum gas (Worden et al. 1995). Based on petrography and fluid inclusion analysis, TSR is only at an early stage in Ghawar. This may be due to one of: lower temperatures than in other sour gas provinces, recent cooling, the recent emplacement of less reactive petroleum (i.e. gas) or the isolating effect of TSR calcite that grows on the finely crystalline anhydrite nodules. The petroleum seems to have been altered by TSR since there is a correlation between the overall H_2S percentage and both the sulfur content and the sulfur isotope ratio of the liquid petroleum. As H_2S , due to TSR between anhydrite and petroleum, accumulated there was back-reaction of H_2S with remaining liquid phase petroleum and the generation of a suit of dibenzothiophenes. With advancing TSR and increasing H_2S concentration, the oil progressively changed from typical petroleum $\delta^{34}\text{S}$ values ($\geq 0\text{‰}$) to the sulfur isotope ratio of Permian anhydrite (+9‰). TSR in liquid petroleum accumulations thus not only results in the replacement of anhydrite by calcite and petroleum fluids by H_2S , it also results in the generation of new sulfur bearing organic compounds.

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Integrate organic and inorganic geochemical approaches to reconstructing oil-filling history, NW Junggar Basin (NW China)

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Multi-phase oil charge history is usually reconstructed by comparison of molecular signatures of the inclusion oils with reservoir oils, and by inclusion microthermometry. In this study, organic, as well as inorganic geochemical tools were integrated to provide such information in the northwestern Junggar Basin.

EPMA analyses show that the content of typical calcite trace-element (Mn, Mg, Fe) contents range from < 0.5 to > 4.0 wt.%, indicative of hydrocarbon fluid diluted by formation water continuously, suggesting that fluid source changes during the charge for petroleum moves up in oil-gas-water mixing migration phase.

A hump of unresolved hydrocarbons and a full range of unaltered *n*-alkanes present in the gas chromatograms of free and inclusion oils imply that both had been biodegraded firstly, and were charged later. In terms of biomarker parameters, it is suggested that the paleo oil is most likely sourced from all the three Permian source beds, while the current oil mainly derived from the two older source sequences. This provides another evidence for source changes.

The data for the aqueous inclusions accompanying hydrocarbon inclusions in the Permian reservoir rocks show three populations with modes at around 30 - 50°C, 70 - 90°C, and 110°C, while in the Triassic at around 50 - 70°C, and 90 - 110°C.

Combined with the burial and oil generating history, oil-filling history is reconstructed. During Middle-Late Permian, Low-middle mature oil and gas sourced from Jiamuhe Formation (P_{1j}) migrated into Carboniferous and Permian traps. Mature oil and gas accumulation sourced from Fengcheng Formation (P_{1f}) peaked at Late Triassic. From Early Cretaceous on, gas from the Jiamuhe Formation, with mature-overmature oil and gas sourced from Lower Wuerhe Formation (P_{2w}), propelled the pre-existing hydrocarbons to migrate toward the up-dip areas, with a common mixing of the oil and gas from different sources and/or with different maturities.

Hydrogeochemistry of formation water in the Northern Songliao Basin, China

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The Songliao basin is one of the largest Mesozoic continental rifting basins in China, dominated by Cretaceous fluvial and lacustrine strata. Based upon 2433 pressure data and 6270 water sample data around the basin, it is shown that, not only the abnormal pressures exist in the different formations and structural zones, but also the underpressure coexists with the overpressure within a single geological formation. Besides, the pressure coefficients change gradually from 1.02~1.30 in the western Central Depression to 1.05~0.5 in the eastern Central Depression, and then become 0.65~0.9 in the east Uplift zone, especially in the Quantou formation (K2q). The analysis of hydrochemistry data reveals a distinct compositional variation in the different pressured systems. Water composition is dominated by water type of NaHCO₃ but varies greatly in salinity (1.0 ~ 20 g/L) and ionic ratios in the different areas. The origin of formation water may be attributed to the dissolution of silicate minerals and halite, the interplay of clay dehydration due to compaction, topography-driven meteoric water recharge as well as diagenesis alteration such as cation exchange by albitization of plagioclase, the dissolution or precipitation of calcite and gypsum. Their impacts differ greatly in the different hydrochemical and abnormal pressured environments.

Surface geochemical methods for oil and gas prospecting in rice fields – some constraints

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The subsurface occurrence of hydrocarbon produces a number of geochemical anomalies in the near-surface soil/sediment profile. The studies of such geochemical anomalies have proven to be extremely useful in locating potential areas for hydrocarbon exploration and exploitation (Schumacher, 1996). One of the prominent and widespread methods is the diagenetic carbonate technique, which tries to find out the relationship of near-surface diagenetic carbonate and carbonate cements with leakage of hydrocarbons from depth (Donovan, 1974).

In this work the carbon isotope compositions of soil carbonates formed in a vertical profile of about 1m, collected from a rice field near Kondapuram village (17°28'N, 78°42'E) are reported. The $\delta^{13}\text{C}$ values of these soil carbonates range from -7.9 to -43.9% VPDB. While the isotopic compositions close to -8% are generated in response to diffusion-controlled soil $\text{CO}_2\text{-CaCO}_3$ system under isotopic equilibrium condition (Cerling, 1984), those with extremely depleted values are resulted due to methanotrophic bacterial oxidation of methane emitted in the rice field. These isotopically depleted soil carbonates occur below the root zone and are similar in ^{13}C composition to diagenetic carbonates precipitated due to seepage of hydrocarbon from deep thermogenic source. The significance of this study for countries like India and China is enormous because they constitute more than 50% of the global rice growing areas (Mathews et al., 1991). Thus during surface geochemical exploration for oil and gas, the role of methanotroph-induced carbonate precipitation must be evaluated and care should be taken in interpretation of ^{13}C compositions of soil carbonates, particularly when the samples are collected from rice fields.

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Variation in surface energy heterogeneity of crude oil-smectite complexes with different content of organic matter

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Three crude oil-smectite complexes and one pure smectite were prepared and their low-temperature (77.35 K) nitrogen adsorption isotherms in the relative pressure range of 10^{-6} –0.14 were measured, subsequently. Then, surface fractal (D_{SF})^[1] and adsorption energy distribution (AED)^[2] (Fig.1) were calculated. While the content of crude oil in complexes increases from 0 to 6% and 15%, D_{SF} decreases from 2.87 to 2.69 and 2.53, and their AEDs changes evidently from 3 prominent peaks for pure smectite to just big one and trival one. According to the assignment of AED peaks of pure montmorillonite reported by Tournassat et al., it is found that crude oil molecules prefer interacting with the edge surface firstly, and then with the basal surface and interlayer surface orderly. Above results suggests that information of hydrocarbon formation and expulsion in source rocks could be tracked by measuring surface properties of organo-clays.

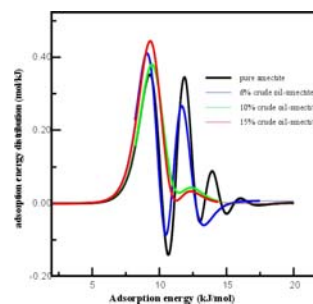


Fig. 1 AEDs of experimental samples

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Carboniferous shales – A probable source of nitrogen in gas accumulations of the North German Basin

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Nitrogen is one of the most abundant non-hydrocarbon gas components in Permian gas reservoirs of the North German Basin (NGB). The eastern part of the NGB, therefore, represents a key study area for the assessment of the behaviour of nitrogen in the sedimentary cycle: i.e. sedimentation, fixation, burial and release of nitrogen. Terrestrial or marine organic matter is the parental source of nitrogen in sedimentary basins. Although most of the organic nitrogen can get lost by de-nitrification, considerable amounts of the remaining nitrogen are incorporated into sediments. Biodegradation of fixed organic nitrogen is the principal process during early diagenesis followed by thermal decomposition during sediment burial. The NH_4^+ released during this process may substitute for K^+ in clay minerals.

In the NGB the natural gas is mainly sourced from coal-bearing strata and organic-rich shales of Carboniferous ages. Open-system, non-isothermal pyrolysis in combination with elemental analysis has been applied to study the thermal liberation of molecular nitrogen from Palaeozoic sedimentary rocks and kerogen concentrates. Heating rates ranged from 0.5 to 2 K/min with final temperatures between 1100 and 1200°C. The N/C_{org} (atomic) ratios of the Palaeozoic shales ranged between 0.035 – 0.108 and were substantially higher than those of the corresponding kerogen concentrates (0.005 to 0.014), the latter representing the range commonly observed for coals. This indicates the presence of significant amounts of inorganic nitrogen in the shales.

Studies of clay mineralogy, vitrinite reflectance, determination of organic and inorganic fixed nitrogen, stable isotopes of nitrogen and carbon yielded indications for potential nitrogen storage in the form of ammonium during diagenesis and deep burial. Calculation of nitrogen loss and isotopic fractionation suggest a release of nitrogen from Upper Carboniferous shales of up to 50 % mainly as ammonia during enhanced thermal conditions and/or fluid-rock interaction. Formation waters and fluid inclusions of this sequence are especially enriched in NH_4^+ . Most of this NH_4^+ can be oxidized to N_2 during upwards migration through the red beds of the Rotliegend section.

TSR and sour gas accumulation: A case study in the Sichuan Basin, SW China

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The enormous sour gas accumulations have recently been discovered in the Lower Triassic oolitic reservoirs from the northeastern Sichuan Basin, SW China. The H_2S contents are generally over 10% and the maximum reaches 17%. Results from 1-D basin modeling indicate that the sour gas accumulations have involved much higher temperature (100–200 °C), and represent the products of both thermal maturation and thermochemical sulfate reduction of early accumulated light oils that had migrated considerable vertical distances. The origins of the gases are supported by their chemical and stable carbon isotope compositions, as well as the occurrence of pyrobitumens in the reservoir. The sour gas is dominated by CH_4 , amounting to about 77% in volume besides 10–17% of H_2S , 6–14% of CO_2 , and less than 0.1% of C_2H_6 . There are almost no heavier hydrocarbons than C_3H_8 . The carbon isotopic composition of methane and ethane shows that the higher the H_2S content is, the heavier the carbon isotopic composition of methane and ethane is. The measured $\delta^{13}\text{C}$ value of methane increases by 1.0–2.5‰ while that of ethane increases more greatly by 4.0–5.0‰. That indicates the preferential participation of C^{12} in TSR. The carbon isotopic compositions of carbonate also indicate an obvious interaction between organic and inorganic carbons in the area studied. The $\delta^{13}\text{C}$ values of the oolitic carbonate rock in the Lower Triassic reservoirs vary from 0.9‰ to 3.7‰ with an average of 2.0‰. However, those of blocky and drusy authigenic calcite crystals are remarkably negative while the minimum is -18.2‰ with average of -14.5‰. This indicates the transfer of organic carbon from hydrocarbons to the secondary calcite (CaCO_3), i.e. $n\text{CaSO}_4 \cdot m\text{H}_2\text{O} + n\text{C}_n\text{H}_{2n+2} \rightarrow n\text{CaCO}_3 + \text{H}_2\text{S} + (n-1)\text{S} + n\text{H}_2\text{O}$, which results in the lighter carbon isotope of the secondary calcite derived from degypsification. The distribution of the gas accumulations is controlled dominantly by the combination of lithologic and structural factors, and the regional variation in the concentrations of H_2S in the gases is closely related to the presence and thickness of anhydrite-bearing evaporitic rocks interbedded/intercalated with oolitic reservoirs.

The roles of inorganic minerals on the oil and gas generating processes

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The laboratory studies previously have show that the activation energies for thermal cracking of macro-organic molecules to light hydrocarbons are much higher than that in nature. These observations have led geologists believe that there must have some catalysts in nature which lower the activation energies for oil and gas generating reactions and make oil and gas generating reactions happened or make them accelerated. In this study, a coal sample was separately heated with kaolin, CaCO₃, Fe₃O₄, FeS, S and without any minerals at temperatures of 250°C to 600°C in closed hydrous pyrolysis systems for 72 h. The results show that inorganic minerals have considerable affects on oil and gas generating processes. The coal can produce much more bitumen "A" when it was heated with kaolin, CaCO₃ and FeS respectively than without any minerals and it can also produce more gas products when it was heated with kaolin, CaCO₃ and S than without any minerals. The carbon isotopic compositions of gas hydrocarbons produced from the coal are also greatly different when the coal was heated with and without minerals. In most cases, the coal produce relatively lighter ethane on carbon isotopic compositions when it was heated with minerals than that of without any minerals.

This study indicates that thermal reaction is a very important factor during the oil and gas generating processes, but mineral catalysis or delay affects also play important roles in those processes. So we should pay more attention on mineral catalysis/delay affects as well as thermal reactions on oil and gas exploration.

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Expulsion of overpressure fluid flow along faults: Geochemical evidence of pore water in the Yinggehai basin, South China Sea

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More than 100 pore water geochemical analyses from 26 wells in the Yinggehai, northern South China Sea margin have been carried out. These samples are collected from Miocene and Pliocene rocks forming in nearshore, neritic, shelf environments. Three kinds of pore water salinity domain could be recognized: non-diapiric area, diapiric area within normally pressured system and overpressured area. Salinity of water in the non-diapiric area ranges from 30g/L to 38g/L, which is equal to or slightly greater than that of normal seawater. In the overpressured system, however, formation water has much lower salinity about 9.9-31.6g/L and ion concentrations (except bicarbonate and carbonate) than normal seawater. The largest variation of salinity ranging from 10.3g/L to 35.9g/L occurs at the diapiric area with normally pressured system, which is related to strong multiple expulsion fluid from overpressured compartments in diapiric structures.

The results indicate that NaHCO₃-dominated water with lower salinity at overpressured strata resulted from the dilution of new-born water from clay transformation, such as the illitization of smectite. High bicarbonate and carbonate concentrations may contribute to mineral dehydration and kerogen-cracking reactions. Strong expulsion of fluid from deep overpressured sediments with low salinity could be explained the variation of salinity in pore water at the top of the overpressured zone in the diapiric structures. The magnitude of TDS and HCO₃ and CO₃ concentrations depend on the distance from the vertical faults connected with the overpressured compartments. The shorter the distance to the vertical faults, the smaller the TDS content is, and the greater the HCO₃ and CO₃ concentrations. Therefore, variation of salinity and ion concentrations in different pressured systems provides a clue to infer the flow pathways and possible diagenetic reactions.

Effects of hydrothermal on organic matters in oil/gas-bearing basins

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Thermal energy is one of the most important factors that control the evolution of sedimentary organic matters and petroleum in the oil/gas-bearing basins. Hydrothermal associated with magma/volcanic activities would carry large amount of heat and could probably accelerate the evolution of sedimentary organic matters from immature to mature or even to overmature and impel the conversion of petroleum to bitumen or even to graphite. A place where magma intruded in a sedimentary basin provides a natural laboratory to examine the above processes in that the intrusion would release a great amount of hydrothermal to its surrounding rocks.

A diabase intrusion of about 60m thick was found intruding into a set of Paleogene black mudstone source rocks in Jiyang Depression, East China. Below the diabase intrusion, sixteen vitrinite Ro values of kerogen in mudstones at intervals of several metres were measured. The results indicate that the source rocks are substantially influenced to some different degrees by the intrusion, and the thickness of influenced source rocks is nearly equal to that of intrusion. The Ro values roar from 1.0% up to as high as 3.8% upwardly within a thickness of about 10m below the intrusion, showing that the organic matters had been highly metamorphosed by hydrothermal.

Another diabase intrusion was found intruding into Silurian sandstone reservoir rocks in the center of Tarim Basin, Northwest China. The pre-existing petroleum in the surrounding sandstones had been extremely altered and completely converted into bitumen and even graphite. The average bitumen reflectance of the hydrothermally altered bitumen is 3.6%, indicating that the bitumen is highly overmatured.

The high heat-potential hydrothermal associated with magma/volcanic activities in oil/gas-bearing basins should be paid more attention with respect to petroleum exploration because it can not only accelerate the maturation and hydrocarbon-generation of hydrocarbon source rocks but also destroy the previously existed petroleum reservoirs.