

to 7.5Å XRD band, in a poorly crystalline silicate phase. Concentrations of B in squeezeates, water leachates, and different size fractions closely parallel Si, supporting this hypothesis.

Transition metals show decreases with depth in the $-0.1 \mu\text{m}$ (clay mineral-dominated) fractions and equal or lesser increases in the coarse fractions. This trend becomes more marked as the OPZ is encountered. Comparison of total metal with that freed by reducing and oxidizing leach solutions, plus XRD and petrographic observations, suggests removal of some transition metals from the altering 17A phase and their incorporation into coarser sulfidic and possibly carbonate phases.

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Relation of Illite/Smectite Diagenesis and Development of Structure in the Northern Gulf of Mexico Basin

Water expelled from smectite into the pore system of the host shale during the process of diagenesis may migrate out of the shale early or may be totally or partly trapped and released slowly through time. In areas such as the northern Gulf of Mexico basin, where much of the water is partly trapped, clay diagenesis data indicate a close relation between high fluid pressure buildup and the smectite-illite transformation process.

Abnormal pressures affect, in part, the type and quantity of hydrocarbons accumulated since pressure controls the direction of fluid flow and partly controls the geometry of structures formed in basins where shale tectonism is the primary mechanism for structural development. In basins of these types, contemporaneous faults and related anticlines are the most common types of productive structures found. The depth to which faults can penetrate and the angle of dip that faults assume at depth is dependent largely upon fluid pressure in the sedimentary section at the time of faulting. Some faults formed in the overpressured Tertiary section of Texas have been observed to flatten and become bedding plane types at depths near or above the temperature level required for thermal generation of hydrocarbons. This observation suggests faults of these types play a minor role in draining hydrocarbons from deep shales within basins where thick overpressured sedimentary sections are present at shallow depths and where shale tectonism is the primary mechanism for structural development.

Microfracturing resulting from increased fluid pressure is indicated to be a primary mechanism for flushing fluids from deep basins where thick abnormally pressured sedimentary sections are present. This flushing process would be enhanced by clay diagenesis since water supplied from smectite would cause the process to continue for longer periods of time and to extend to greater depths than could be attained if only remnants of the original pore water were present in the section. Large volumes of diagenetic water present within the microfracturing interval could also act as a vehicle for primary hydrocarbon migration provided hydrocarbons are present in a form and in sufficient quantities to be transported.

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Illite/Smectite Diagenesis and Hydrocarbon Generation in Cretaceous Mowry and Skull Creek Shales of Northern Rocky Mountains-Great Plains Region

The Lower Cretaceous Mowry and Skull Creek Shales and their equivalents are among the major source rocks in the northern Rocky Mountains-Great Plains region. They are the major source of hydrocarbons in the Lower Cretaceous Muddy

Sandstone of the Powder River basin. This sandstone has a geographic distribution similar to that of the Mowry and much of the Skull Creek.

Illite/smectite mixed-layer clay in the Mowry and Skull Creek Shales of eastern Montana and western North Dakota is unaltered. No significant amounts of hydrocarbons have ever been found in the Muddy Sandstone of this area. Hydrocarbons in the Muddy Sandstone occur within or immediately adjacent to areas in which the smectite component of the illite/smectite in the Mowry and Skull Creek Shales has undergone alteration to illite during burial diagenesis. Anomalous decreases in the total organic carbon content of the Mowry and Skull Creek Shales lie within areas of illite/smectite alteration and coincide with the deeper parts of structural basins which developed after deposition of the Mowry and Skull Creek. These regional variations in illite/smectite alteration and total organic carbon content reflect thermal maturation and are not provenance controlled. They are useful indicators of areas where the potential source rocks have been subjected to temperatures adequate to generate hydrocarbons. The degree of illite/smectite diagenesis in the Mowry and Skull Creek of the northern Rocky Mountains-Great Plains region is thus of exploration significance in the search for hydrocarbons in this area.

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Catalytic Effect of Smectitic Clays in Hydrocarbon Generation

Smectites or three-layer expanding clays promote the thermal decomposition of long-chain aliphatic hydrocarbons to produce hydrocarbons of lower molecular weight. Smectites are believed to act as acid catalysts through the dissociation of water, thus promoting carbonium ion reactions. When sedimentary organic matter, isolated as kerogen from suspected petroleum source rocks, is pyrolyzed in the laboratory, long-chain aliphatic hydrocarbons are in the pyrolyzate, commonly in abundance. When the source rock contains smectite and is pyrolyzed, the pyrolyzate has significantly less high molecular weight aliphatic hydrocarbons and more lower molecular weight hydrocarbons.

Mixtures of kerogens with quartz, silica, alumina, calcium carbonate, kaolin, or illites not containing smectite-illite mixed layer clay, yield pyrolyzates more similar to those of the kerogen alone, i.e., the range of hydrocarbons in the pyrolyzates is broad including those of high molecular weight. This is interpreted to be due to a lack of catalytic activity of these minerals as compared with the catalytically active smectite. The catalytic effect of smectite is observed particularly when the concentration of sedimentary organic matter in the source rock is relatively low, amounting to less than about 2% total organic carbon. Smectites in sediments with a modest or low amount of organic matter are critical regarding the type petroleum generated, exemplified by the gas condensates of the northern Gulf of Mexico basin and Indonesia. Consequently, it is concluded that smectitic argillaceous sediments containing less than approximately 2% organic carbon are poor sources of oil, although they may be productive of gas and gas condensate.

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Probable Interactions Between Stevens Sandstone (a Miocene Deep-Water Turbidite) and Surrounding Siliceous Shales in San Joaquin Valley, California

The upper Miocene Stevens Sandstone deep-water turbidite

in the Gulf Poloma oil field, San Joaquin Valley, is an immature, arkosic sandstone overlain and underlain by distal fan siliceous shales. Porosity development in about 100 ft (30 m) of Stevens Sandstone in well U36-28 (present burial depth ~ 11,000 ft, 3,350 m) has followed the stages: (1) reduction of primary porosity due to initial burial compaction to near zero in the finer grained rocks, (2) replacement of silicates and filling of remaining primary porosity with calcite cement reducing the porosity to near zero, (3) dissolution of most calcite cement to produce up to 15% secondary porosity, and (4) reduction of secondary porosity by growth of authigenic clay minerals, mostly chlorite and kaolinite. Thus, major porosity development is contingent on a source of calcium for the calcite cement. The source of the calcium is assumed to be from dissolution of calcite tests in the surrounding siliceous shales, though this is difficult to prove. Calcium is concentrated in stylolites and fractures within the siliceous shales, suggesting the mobilization of calcium. The siliceous shales, equivalent to the siliceous Monterey Formation, are more quartz-rich than the arkosic Stevens Sandstone. The source of the silica in the siliceous shales is inferred to be recrystallized diatom frustules. The < 1 μ m quartz content in the sandstones generally increases toward the contacts with the siliceous shales suggesting invasion of silica from the shales into the sandstones.

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Organic Carbon Content and Fractured Shale Reservoir Evaluation Based on Natural Gamma Ray Spectral Logging

Organic-rich, dark, and highly radioactive shales are encountered worldwide in several geologic sequences. These shales are potential source rocks and frequently owe their significant but localized production potential to natural fracture systems that are concentrated in brittle, calcareous, cherty, or wilty zones interbedded in an otherwise impermeable rock.

Under these circumstances, standard interpretive well logging techniques do not provide satisfactory formation evaluation results. However, such calcareous, silty, and cherty zones, frequently characterized by low concentrations of potassium and thorium but excessively high uranium content, are located easily with natural gamma ray spectral logging techniques. Gamma ray spectral logging, in addition to total gamma ray counts, measures and records the individual contributions of potassium (in percent), and uranium and thorium (both in ppm) in open and/or cased well bores.

The typical log response in organic-rich shales shows high potassium and thorium content plus excessive uranium enrichment. Such logging information correlates with the organic carbon content, as illustrated by field data.

Basic concepts of natural gamma ray spectral logging devices are reviewed, and field experiences in the Cretaceous Niobrara and Pierre Shales in the Rocky Mountains, Woodford Shale of Oklahoma and west Texas, and Devonian shales of the Appalachian basin, etc will be discussed.

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Role of Clay Composition on Extent of Smectite-Illite Diagenesis

Evidence has been presented from the northern Gulf of Mexico which suggests that, over periods of several million years, the smectite-illite transition is largely controlled by temperature. Although kinetics obviously control rates over shorter intervals of time, the progression from smectite to illite with

depth can be viewed largely as a succession of equilibrium states provided source and hence composition have been relatively constant. The abruptness of the transition zone over which this reaction occurs is proportional to the product of reaction enthalpy and geothermal gradient. Arrhenius plots of the log of the equilibrium coefficient versus reciprocal of the absolute temperature yield reaction enthalpies ranging from 26,000 cal/mole along the south Texas coast to as low as 1,800 cal/mole in the Mississippi Delta. It has been found that clays with high reaction enthalpies are typically montmorillonites, derived from volcanic ash, with lattice substitution principally in the octahedral layers. However, low enthalpy smectites found farther east are derived from the Mississippi River provenance and are beidellites with predominant tetrahedral substitution and hence more mica-like in structure.

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Clays as Acid Geocatalysts in Generation and Maturation of Petroleum

Geocatalytic transformations have been proposed to account for the formation of oil under the mild reaction conditions that prevail in most oil-forming sediments. Several key steps in this process can be rationalized as acid reactions catalyzed by sedimentary minerals. The acid catalytic activity of selected clay and other sedimentary minerals has been determined based on the ability of these materials to mediate the decomposition of *t*-butylacetate in a low temperature reaction (100°C). For a given clay, the specific acid catalytic activity per gram clay is strongly dependent on the cationic form. For a series of clay minerals saturated with the same cation, the specific acid catalytic activity is proportional to the cation exchange capacity. The specific acid catalytic activity of a mineral is also proportional to its ability to catalyze such diverse reactions as carbon-carbon bond cleavage, hydrogen disproportionation, epimerization, and decarboxylation. Most petroleum-forming sediments of varying age, origin, and type contain some clay minerals and are found to possess low but measurable acid catalytic activity. These sediments can act as acid active catalysts in the formation and maturation of petroleum.

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Clay Mineral Reactions in Clastic Diagenesis

Studies of clastic sediments have documented the formation and transformation of clay mineral assemblages during burial diagenesis. The transformation of smectite to illite in shale by its reaction with the decomposition products of detrital K-feldspar and mica results in the production of new pore water at depth. The overall reaction mobilizes all the major chemical components in the shale, most of which are consumed in the formation of the diagenetic assemblage illite/smectite + chlorite + quartz. However, part of all the components is undoubtedly transported from the shale to sandstone units and is involved in cementation, replacement, and diagenetic clay mineral formation in these reservoir rocks.

In contrast to burial diagenetic reactions in shale, where the sequence is monotonic and reasonably predictable, diagenetic reactions in sandstone are frequently variable. This variability is probably attributable to the fact that sandstones are open systems in which the reactions that proceed are controlled in part by the influx of new pore water, the chemistry of which is determined by an outside source.

The useful understanding role of clay minerals in hydrocar-