

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-

bon exploration will follow from a determination of the system shale/sandstone/organic material. We need to tie in the nature and timing of shale mineral reactions and their control on the fluid and mass transfer from shale to sandstone.

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Clay Mineral Catalysis and Petroleum Generation

Kerogen, the major organic component of sediments and sedimentary rocks, is the immediate precursor of petroleum hydrocarbons. Recent studies of kerogen maturation during burial diagenesis show that decarboxylation of fatty acid constituents and C-C bond cleavage of hydrocarbon groups, both attached to the kerogen polymer, lead ultimately to petroleum-hydrocarbon formation. The low temperature range over which this occurs (60-110°C) has suggested that the clay mineral matrix may play a role in catalyzing these important reactions.

Kinetic studies of clay-organic reactions have demonstrated the effectiveness of clay catalysis in organic acid decarboxylation and cracking reactions and suggest the mechanisms involved.

Kinetic constants deduced for these reactions from the natural maturation of kerogen during diagenesis reveal a further complication in sediments. Because kerogen is a solid, relatively immobile polymer, structural rearrangement is necessary to bring reacting groups in contact with catalytic sites. Mechanical movement plays a role in promoting catalytic activity.

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Brines, Clay Minerals, and Equilibria: Predicting Diagenetic History and Reservoir Quality in Oligocene Frio Formation of Texas

Sandstone reservoirs of good quality, displaying abundant deep secondary porosity, exist on the upper Texas coast, whereas secondary porosity and permeability in sandstones of the lower coast are occluded by authigenic ferroan calcite and chlorite. This difference in regional reservoir quality is controlled by bulk mineralogy, temperature, pressure, and pore-fluid chemistry. Concentrations and activities of major species show depth dependent trends that correspond to pore pressure gradients and associated thermal gradients. Salinities decrease near the base of hydropressure, but increase at intermediate pressure gradients between 0.465 and 0.7 psi/ft (10.5 and 15.8 kPa/m). At higher pressure gradients salinities decrease with depth. The Ca/Na ratio is lowest at top of geopressure. Predictions from solution-mineral equilibria using approximately 130 analyses of Frio brines add new insight on relative mineral stabilities and in-situ pH, and are consistent with the diagenetic sequence developed from petrographic data. Kaolinite is stable in geopressured waters relative to Ca-montmorillonite and plagioclase; it is abundant on the upper coast as a late stage cement. Lower temperature and in-situ pH (high P_{CO_2}) explain the general absence of chlorite on the upper coast; its formation on the lower coast is promoted by higher temperature, a mineralogy rich in volcanic and carbonate detritus, and inferred higher pH. The key to predicting reservoir quality at depth is the deep hydropressured waters. Activity indices are indicators of reservoir quality. Waters of the lower coast plot more deeply into the stability field of chlorite than do those of the upper coast.

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Diagenesis and Mass Transfer in Sandstone-Shale Sequences and the Sedimentary Cycle

An analysis of diagenesis and mass transfer is made drawing on the literature and our work from the Brazilian shelf and Barbados. It is shown (although not unanticipated) that the initial sedimentary mineral composition is a major control of diagenetic products. For example, dioctahedral clay minerals, chlorite, and quartz characterize arkoses, whereas trioctahedral clays and zeolites are most commonly found in lithic sandstone. Dioctahedral smectite-rich shales exhibit the classical smectite/illite to illite burial pattern. However, mafic, trioctahedral clay-rich shales show a burial sequence of saponite to chlorite/saponite mixed layer, a progressive increase of chlorite-rich phases with increasing burial depth. Other compositionally dependent reaction paths are also discussed.

To assess mass transfer between shale and sandstone during burial, all major diagenetic pathways must be known for both rock types. A model for the Brazilian shelf sandstone-shale sequence is used as an example of quantification of mass transfer. Both sands and shales act as nearly isochemical systems; sandstones lose less than 2% K^+ to shales, and gain less than 3% H_2O , H^+ , and CO_2 during burial diagenesis.

It is shown using data from Barbados and the literature that burial diagenetic reactions are essentially irreversible, at least until the stage of weathering. Thus, these reactions can be used to assess the amount of overburden removed. Comparison of the diagenetically produced trend of illite/smectite compositions with depth in Barbados to trends produced in areas which have undergone only subsidence (e.g., Gulf Coast) suggests that about 3,300 to 9,800 ft (2 to 3 km) of overburden have been removed in Barbados.

The irreversible and nearly isochemical nature of burial diagenetic reactions places constraints on the role of diagenesis in the sedimentary rock cycle. An attempt is made to quantify the global importance of these reactions in the rock cycle.

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Permeability of Clay Shales

Coefficient of permeability is the important material property in the Darcy equation of fluid flow through porous media. Coefficient of permeability is determined by the size of pores, tortuosity of flow channels, porosity, and the nature of the fluid. Mineralogy of shales influences permeability primarily through the size and shape of the particles. Small and filmy particles produce small and highly tortuous pores, whereas large and thick plates or equidimensional grains produce large pores with small tortuosity. The contribution of the fluid to the coefficient of permeability is not limited to the effects of its density and viscosity. The nature of the fluid in which the shale is formed or the fluid that flows through the shale can influence the size, shape, and arrangement of the particles. In general, the mechanical or physico-chemical mechanisms that promote aggregation increase permeability and those that cause dispersion tend to decrease it. The interaction and bonding of the fluid or organic and inorganic complexes in the fluid with the surface of pores, through such mechanisms as electro-osmotic back-flow, appear to have a secondary influence on the permeability of clays. The effect of the same factors on the permeability of low porosity materials such as shales are unknown.

The observed values of the coefficient of permeability for