

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

shales are in the range of 10^{-7} to 10^{-12} cm/sec. The change in permeability, with void ratio is expressed as $\Delta \log k = \Delta e/C_v$. The parameter C_v is directly related to the void ratio. For clays, values of C_v range from 0.5 to 4. For shales, the C_v values are in the range of 0.02 to 0.5.

Permeability of fissile shales is expected to be highly anisotropic as compared to massive shales that have a more random fabric. However, permeability anisotropy in shales has not been extensively investigated. At shallow depth, the permeability of shale formations is strongly influenced by discontinuities such as fissures and joints.

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Illite/Smectite Diagenesis: Relation to Coal Rank in Tertiary Sediments of Pacific Northwest

Bentonite partings formed by alteration of air-fall tephra interbedded with coal in three Eocene coal basins (Tulameen, British Columbia; Chuckanut and Centralia, Washington) record the nature of arc volcanism and subsequent diagenesis and metamorphism. Euhedral feldspar phenocrysts, embayed quartz, and relict glass shards demonstrate volcanic provenance, whereas the absence of muscovite, microcline, and other nonvolcanic minerals indicates lack of epiclastic detritus. At Tulameen, abundant sanidine and biotite indicate rhyolitic tephra; at Centralia, plagioclase and absence of quartz and K-spar indicate dacite. Absence of K-spar from Chuckanut deposits may be due to its destruction by metamorphism, since quartz phenocrysts are present, suggesting rhyolite.

Alteration of glassy tephra to bentonite has taken place in two or three steps. (1) Leaching (weathering) in the swamp may have formed allophane or halloysite, but much glass remained unaltered. (2) Early diagenesis at temperatures below 60°C (suggested by vitrinite $R_o = 0.40\%$) formed, by reaction of non-phenocrystic components with pore fluids within individual partings, one of five assemblages depending on degree of prior leaching: zeolite-smectite-cristobalite, smectite-cristobalite, smectite, smectite-kaolinite, kaolinite. Na-smectite at Centralia inherited interlayer Na from original glass. Delicate vermicular kaolinite may also have formed during this stage. (3) Thermal metamorphism has transformed smectite in some Tulameen and all Chuckanut partings to regularly interlayered illite/smectite (I/S). At Tulameen ($R = 1$ ordered I/S with 55% I + kaolinite), the source of potassium for the reaction was solution of phenocrystic sanidine and mica; $R_o = 0.9\%$ suggests 130 to 200°C. The Chuckanut bentonites ($R = 1$ and $R \geq 3$ ordered with 65 to 90% I + chlorite) show $R_o = 3\%$ suggesting temperatures exceeded 300°C; some potassium may have been derived from outside the parting, and more complete illitization may have been inhibited by lack of potassium and by calcium released during albitization of plagioclase.

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Combined Natural Gamma Ray Spectral/Litho-Density Measurements Applied to Clay Mineral Identification

The utilization of well log data to provide a lithologic description of complex formation is well-evidenced. Historically, however, most approaches assume fixed, known, and distinct lithologies for analyst-specified zones. The proposed approach attempts to alleviate this restriction by estimating the

"probability of a model" for the most likely models suggested by the reservoir geology. Lithologic variables are then simultaneously estimated from response equations for each model and combined in accordance with the probability of each respective model.

The initial application of the proposed approach has been the recognition of clays in the presence of calcite, quartz, dolomite, feldspar, anhydrite, or salt. This application has been realized through utilization of natural gamma-ray spectra, photoelectric effect, bulk density, and neutron porosity information.

For each specified model, response equations and parameter selections are obtained through utilization of the thorium versus potassium crossplot and the apparent matrix density versus apparent volumetric photoelectric cross-section crossplot. The thorium and potassium response equations are used to estimate the volumes of clay and feldspar. The apparent matrix density and volumetric cross-section response equations can then readily be corrected for the presence of clay and feldspar. However, a test is applied to ensure that the clay correction lies within limits consistent with the assumed lithology model. If inconsistency is detected, either the estimate of clay volume or the lithology model, or both, are changed.

A computer program has been written to test the proposed approach. Initial field testing in the U.S.A. and Canada has been completed and the program appears to recognize, with minimal analyst intervention, illite, chlorite, and a third clay which is considered to be a kaolinite-montmorillonite mixture. Results from the field are presented for an assortment of wells with varying lithologies.

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Al-Hydroxy Smectite: An Intermediate Between Smectite and Mixed-Layer Illite/Smectite Formed in Burial Diagenesis of Pelitic Sediments?

Reaction mechanisms for the reaction smectite → mixed-layer illite/smectite are proposed based on experimental results. Pure smectite (100% expandable) in NaCl-Na₂CO₃ solutions was heated in sealed gold capsules to 180 and 350°C for periods of 7 and 28 days. The solutions used for this initial hydrothermal treatment were kept K^{\pm} free to prevent the formation of non-expanding illite layers, a condition which would have made it difficult to characterize the exchange properties of expanding layers undergoing transition.

A series of cation exchange experiments using chloride solutions of Na⁺, K⁺, and Mg⁺⁺ were carried out at 25°C to determine the effect of the heat treatment described above on K^{\pm} selectivity and total cation exchange capacity. Data obtained from these experiments show that the hydrothermally treated clays become *less selective* for K⁺ with increasing temperature and length of run. Data also show that the total CEC *appears to decrease* with increasing temperature and length of run. We suggest that this apparent decrease in total CEC as well as the difference of K^{\pm} selectivity is caused by the inability of the exchange cation (Ba⁺⁺ in these experiments) to replace tightly held Al, which diffused to exchange sites from tetrahedral and octahedral positions when the clays were heated.

These results lead us to propose that a smectite-interlayer Al-hydroxy complex may be an important intermediate in the smectite → mixed-layer illite/smectite transformation often observed in buried pelitic sediments. Further study of the rate and mechanisms involved in the formation and ultimate destruction of the Al-hydroxy interlayer material should be