

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