

Reaction rates for a wide variety of reactions involving carbonate phases and aqueous solutions have been investigated by monitoring pH changes as the reactions proceed. Rate constants are available for the escape of CO₂ from solution, for the dissolution of a wide range of calcium and calcium-magnesium carbonate minerals, and for growth rates of aragonite and calcite. Preliminary studies of nucleation energy and nucleation induction time have been carried out, but these studies have limited applicability to natural systems where abundant nuclei already are available. In certain cases where carbonate deposition is assumed to occur, tetracycline marking techniques have been employed to test the validity of the kinetic models.

On the basis of the experimental results, kinetic theory allows the following predictions: (1) in the presence of organisms, surface waters will appear oversaturated with respect to both CO₂ and dissolved carbonates during daylight hours; (2) the composition of a solution in contact with mixed carbonate phases will be determined by the more rapid of the simultaneous dissolution and precipitation reactions, with dissolution generally being the controlling process; and (3) in the absence of a continuing supply of metastable phases, equilibration will be approached more rapidly by the removal of metastable phases (either by solution or by replacement) and much more slowly by interstitial carbonate precipitation. Each of these observations is supported by field evidence.

The observations made suggest the need for caution when applying the results of field study of modern carbonate environments to the interpretation of ancient carbonate rocks.

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EARLY POST-DEPOSITIONAL PRESERVATION OF PALEOSALINITY, A MATHEMATICAL APPROACH

Early alteration of interstitial water can appreciably hasten sediment diagenesis; this is especially true for calcareous deposits. Thus, from a theoretical standpoint, it is of interest to determine if "original" interstitial water can be preserved as a paleosalinity in areas where post-depositional bottom-water salinity changes characteristically take place, e.g., coastal swamps and deltas.

A model based on the coastal mangrove swamps of southwest Florida, an area where marine swamps recently have replaced fresh-water swamps, was constructed and an equation derived to evaluate the effect of long-term and short-term salinity variations in swamp water on the salinity of water entrapped in the 1-3 meters of sediment underlying the swamps. The model considers ionic diffusion in a homogeneous sediment column overlying an impervious basement and underlying swamp water that seasonally (short term) fluctuates in salinity and that systematically decreases or increases in mean water salinity over periods measured in years (long term).

The model predicts that, in areas where the bottom water has an annual sinusoidal-salinity fluctuation with an amplitude of 35 ‰ (parts per mil), the interstitial water will be affected significantly (more than 0.2 ‰) in the upper 35 cm. of the underlying sediment. This prediction is borne out by field data. If the mean water salinity about which the short-term fluctuations take place is increased or decreased, most of the effect of the drift in the mean is transmitted to the bottom of the

sediment column within a few hundred years. Normal sedimentation rates in the swamps have little effect on the rate at which the interstitial water is modified.

Preservation of paleosalinities in the coastal swamps of southwest Florida, or in similar environments, evidently requires special condition, e.g., a recent change in mean bottom-water salinity combined with rapid deposition of sediment. Deposition of sediment isolates underlying deposits from diffusion contact with the changed bottom water.

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DIAGENESIS AND GEOCHEMISTRY OF SEDIMENTS IN MARINE ENVIRONMENT

Diagenetic alterations were induced in sediments in a model representing a shallow-marine shelf by injecting synthetic sea water under partial pressure of carbon dioxide. The sediments from the model were then removed and studied under the petrographic microscope. The study included (1) the interrelation of the chemistry of the interstitial fluid and the mineralogy of sediments, (2) the factors controlling the formation of silica and calcite cements, (3) the processes responsible for transforming sediments into hard rocks, and (4) the sequence of these processes.

The precipitation of silica and calcium carbonate as cements in the model sediments was detected under the petrographic microscope and is shown on photomicrographs. The petrographic analyses indicate that during early diagenesis cements formed in intergranular space only. The calcite cement crystallizes as small fibrous crystals around the grains extending into the pore space and subsequently results in rim cement. Silica cement is formed simultaneously both as overgrowths and in optical continuity around sand grains.

The silica and calcite precipitated as cements in the model seem to be derived from the interaction of clays and sea water. Geochemical environments for such reactions and environments which enhance the cementation of sediments were interpreted from the studies.

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OUTLINE OF GEOLOGY OF NIGER DELTA

The coastal sedimentary basin of Nigeria has been the scene of three depositional cycles. The first started in middle Cretaceous time with a marine incursion and was terminated by a mild folding phase during Santonian time. The second began with the growth of a proto-Niger delta during Late Cretaceous time and ended in a major Paleocene marine transgression. The third cycle, lasting from Eocene to Recent, was the continuous growth of the main Niger delta.

A new three-fold lithostratigraphic subdivision is introduced for the Eocene-Recent Niger delta subsurface, comprised of an upper sandy unit called the Benin Formation, an intervening unit of alternating sandstone and shale named the Agbada Formation, and a lower shaly unit called the Akata Formation. These three units extend throughout the delta and each ranges in age from early Tertiary to Recent. A separate member of the Benin Formation is distinguished in the Port Harcourt area. The Afam Member is interpreted as an ancient valley fill formed in Miocene sediments. Subsurface structures are interpreted

as the result of movements under the influence of gravity, and their distribution is related to growth stages of the delta. Rollover anticlines on the down-thrown sides of growth faults form the main targets for oil exploration, the hydrocarbons being found in sandstone reservoirs of the Agbada Formation.

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MUD INTO SHALE: WHEN AND HOW?

Coring of surficial sediments on the sea floor to date has not revealed the presence of indurated, clayey sediments that are worthy of the name mudstone or shale, even though some clay as old as 50 million years has been recovered. In contrast, very young, argillaceous rocks on continental platforms are in many places indurated and cemented. Shale, in the sense of a fissile argillaceous rock, is uncommon in the younger part of the geological record though it is common in older rocks. Therefore, one can conclude that the induration to mudstone and the development of fissility of shale have two different time scales and thus result from two different processes.

The initial process of induration is clearly linked to simple mechanical compaction under load where water can be expelled, as studies of marine sediments have shown. During this stage there is little gross mineralogical or chemical change in the sediment. Later stages include chemical additions that fill pore space and increase bulk density. Chemical additions are restricted to sediments that do not remain buried permanently under deep water; the additions result from ground-water movement through the mud, a movement that is initiated by the bed being raised above sea-level and thus making possible a hydraulic head in the outcrop area. Much of the chemical precipitation in this stage is simply redistribution of carbonate, but small amounts of silica generally are added too.

Fissility, as was noted long ago, is correlated directly with the growth of phyllosilicate minerals in the *ab* plane, parallel with the bedding. It appears that the 10 A.U. micas and the chlorites are the principal causes of fissility. Accompanying this growth is a general increase in cementation that reduces porosity to low levels. However fissility does not always accompany cementation.

Fissility, then, is the result of preferential growth of the 10 A.U. micas and the chlorites under load that is induced by the geochemical environment. That environment may be characterized as one whose K^+/Na^+ , Mg^{2+}/Na^+ , and alkali/ H^+ ratios are relatively high compared with sea water, and whose dissolved silica concentration is close to that in equilibrium with quartz. The environment that has these characteristics is that of concentrated subsurface brines typical of most ancient sedimentary basins. The correspondence of the time scales of the production of fissility in shales and the formation of brines is important support for this hypothesis.

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HISTORY OF OIL DEVELOPMENT IN LIBYA

Concessions were first granted in Libya during late 1955. At that time 14 companies obtained concessions totaling 130 million acres. By November 19, 1959, concession areas had increased to 265 million acres, but they decreased to 174 million acres by September 1, 1965. On July 29, 1965, 98 individual blocks total-

ing 147,589,617 acres were made available for bidding. As of September 1, 1965, no additional acreage had been granted.

Exploration activity has been concentrated in two basins. Of primary interest is the Sirte basin in east-central Libya.

Since drilling activities commenced in 1956, 1,572 wells have been completed in Libya, of which 44 per cent were wildcats. In the Sirte basin 12 per cent of the wildcat wells have been successful, and in the Ghadames basin of western Libya 18 per cent have been successful. No oil has been found in the Murzuck or Cufra basins.

More than 11 million feet of hole has been drilled, 4.84 million feet of which has been wildcat drilling. Eighty-five oil fields, 59 in the Sirte basin and 26 in the Ghadames basin, have been discovered by means of wildcat drilling. It is estimated that more than 9 billion barrels of oil in place have been found. Individual pool reserves range from a few thousand barrels to more than one billion barrels of recoverable oil. The largest reserves are in Eocene and Cretaceous rocks of the Sirte basin.

At the end of 1961, one company was producing at the rate of 40 thousand barrels per day. Today five companies are producing more than 1.25 million barrels per day.

Industry has spent over 1.3 billion dollars in the search for oil, increasing from 33 million dollars in 1957 to more than 270 million dollars in 1964.

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LOW-ANGLE REGIONAL UNCONFORMITIES

Brief periods of erosion without concurrent structural deformation have produced low-angle regional unconformities. These unconformities may provide the environment for stratigraphic traps where hydrocarbons accumulate within the truncated beds. However, the slight amount of erosional stripping (a few feet per mile) and the absence of significant changes in the lithology make the detection of these low-angle regional unconformities difficult. The chances of recognizing and delineating them seem to depend, at least in part, on the selection of a datum.

Low-angle regional unconformities are common in the Western Canada basin. Only three were selected as examples, because they occur in a sequence generally considered to be one continuous depositional unit: (1) beneath the Mississippian Debolt, (2) beneath the Devonian Calmar, and (3) beneath the Devonian Ireton Formations.

Slight variations in local rates of subsidence effect continuous changes in the direction of the depositional dip. These changes from formation to formation generally are minor. When sedimentation resumes after an hiatus, its new depositional dip represents the cumulative shift in regional tilt gradually introduced during the absence of deposition. The new dip direction in many cases relocated individual members of a sedimentary cycle, more especially the occurrence of sand lenses in a clastic province or of reef build-ups in a carbonate-shale sequence.

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GEOLOGY OF ARCTIC ISLANDS

The Arctic Islands present opportunities for study of the most completely undeveloped potential oil basin anywhere in the Western Hemisphere. Strata are