

ative position of mean high tide and the lagoon or channel margin at the time of deposition.

WALKER, ANN L., U.S. Geol. Survey and Univ. Washington, Seattle, WA, THANE H. MCCULLOCH\*, U.S. Geol. Survey, Seattle, WA (present address: Mobil Research and Development Co., Dallas, TX), NEIL F. PETERSEN, Superior Oil Co., Houston, TX, and RICHARD J. STEWART, Univ. Washington and U.S. Geol. Survey, Seattle, WA

Discrepancies Between Anomously Low Reflectance of Vitrinite and Other Maturation Indicators from an Upper Miocene Oil Source Rock, Los Angeles Basin, California

In the westernmost Los Angeles basin, the "nodular shale," a distinctive, richly organic bituminous and phosphatic mudstone, occurs just above the unconformable base of the upper Miocene Modelo Formation. This 11.5 m.y. old bathyal oil-source rock is present in wells to burial depths >3,810 m (12,500 ft), and is inferred to be present within the central syncline of the basin beneath about 9 km (5.5 mi) of late Miocene to Holocene clastic cover.

Forty-four subsurface samples of the nodular shale were collected from 14 selected wells located mostly between the Playa del Rey and Crescent Heights oil fields. Sites were selected to give the widest available range of sample depth and temperature where present burial depths are maximal, and where geothermal gradients are firmly established. Median random reflectance (%R<sub>o</sub>) of first-cycle vitrinite is least in the shallowest samples, clusters about 0.24% in the deeper samples, and exceeds 0.30% only in the deepest and hottest samples. Extremes in the range of measured median %R<sub>o</sub> are tabulated below with corresponding extremes of sample temperatures, depths, Time-Temperature Indices (TTI), and calculated %R<sub>o</sub> equivalents of the TTI values.

%R <sub>o</sub> (measured)	Temp. (°C)	Depth (m)	TTI	Calculated %R <sub>o</sub> from TTI
0.12	105	1,664	4	0.4
0.40	153	3,810	70	1.0

All measured values of R<sub>o</sub> are significantly depressed compared to other maturity criteria. Significantly, second-cycle and oxidized vitrinite from these same samples show normally elevated reflectance.

Eight of the samples processed for reflectance measurements were analyzed for total organic carbon content, which ranges from 2.21 to 9.41%. Most of the organic detritus is amorphous degraded algal material; less than 10% is structured vitrinite. Thermal alteration index values for the amorphous material range from 2 to 2<sup>1/2</sup>, corresponding with hypothetical conversion R<sub>o</sub> values between 0.45 and 0.75%, again notably higher than the measured values. The ratios of extractable hydrocarbons to TOC in the 8 samples suggest "mature" levels of thermal evolution, as do carbon preference indices of 0.93 and 1.14 from extracts of 2 samples.

Strikingly similar patterns of vitrinite reflectance values have been described from alginites in some Australian coalfields and oil shales. The data suggest to us that hydrogen-rich organic matter matures at lower temperatures and at a substantially faster rate (and lower TTI values) than detritus dominated by structured organic matter of lower hydrogen content. The depressed R<sub>o</sub> measurements evidently reflect the hydrogen-rich nature of the dominant detritus and thus are not reliable indicators of either paleotemperature or thermal maturity in the most oil-

prone source rocks. In fact, depressed R<sub>o</sub> values may be indicators of ultra-rich source rocks when normalized for other influences.

WALKER, T. R., Univ. Colorado, Boulder, CO

Feldspar Transformations During Sandstone Diagenesis (SEPM Presidential Address)

No abstract.

WALLS, RICHARD A., and GEOFF BURROWES, Petrosec Exploration Co., Houston, Tx

Role of Cementation in Diagenetic History of Devonian Reefs, Western Canada

Devonian (Givetian and Frasnian) reef reservoirs in Alberta and British Columbia contain 60% of the conventional recoverable oil and 20% of the recoverable gas in the Western Canada sedimentary basin. Although the depositional history of these reefs is well understood, it is the diagenetic "overprint" that is often responsible for their reservoir quality.

Frasnian (Woodbend and Beaverhill Lake Group) reefs are characterized by stromatoporoid and coral knoll reef belts deposited near moderately sloping bank edges. Bank margin sediments are composed of skeletal lime grainstones, packstones, rudstones, and rare framestones. In contrast, bank interiors are often extensive (e.g., Redwater, Swan Hills) and characterized by cyclic deposition of lagoonal and tidal flat sediments. Certain Givetian reefs found in evaporate basins (e.g., Rainbow or Zama) usually occur as "pinnacle" reefs with steep (>20°) margins and only minor bank interior development. Frasnian reef complexes range in size from 1 km<sup>2</sup> (0.4 mi<sup>2</sup>) to greater than 600 km<sup>2</sup> (230 mi<sup>2</sup>) with thicknesses from 100 to 400 m (330 to 1,300 ft). Givetian pinnacle reefs are commonly as much as 300 m (984 ft) thick, but with areal extents of less than 1 km<sup>2</sup> (0.4 mi<sup>2</sup>).

Regardless of differences in size, depositional history, and age, most reefs have been subjected to diagenesis in essentially three environments: (1) submarine (marine to hypersaline pore waters), (2) subaerial (fresh to brackish pore waters), and (3) subsurface (below phreatic aquifers, saline to brackish pore waters). Fibrous calcite cements, syndepositional fracturing, displacive calcite cements, micrite cements, and bored hardgrounds are typical submarine diagenetic fabrics, particularly at bank margins in Rainbow reefs and certain Leduc reefs (e.g., Golden Spike, Ricinus). Subaerial disconformities are numerous in most reefs, and associated vadose diagenesis produces localized paleosols, microstalactitic and meniscus cements, and abundant solution porosity. Phreatic or shallow burial cements usually include clear, equant calcite or dolomite that vary in Fe<sup>++</sup> and Mn<sup>++</sup> concentrations. Subsurface cementation produces nonferroan calcites and dolomites which are often related to stylolite formation (e.g., Kaybob, West Pembina D-2, Strachan, Ricinus). Other diagenesis occurring during burial includes dolomite and anhydrite replacement, sulfide mineralization (e.g., Pine Point, Presqu'île barrier reef), and bitumen formation (e.g., Clarke Lake, Rainbow).

Primary porosity and permeability are altered by the "overlapping" processes of cementation and solution (vadose and/or phreatic) that occur early in the diagenetic history. In reef interiors these subaerial processes produce stratified reservoirs with impermeable barriers (cemented beds) to vertical flow (e.g., Golden Spike, Swan Hills, Judy Creek). Submarine cementation is rare in most reefs but can be locally pervasive resulting in occlu-

sion of bank margin and fore-reef porosity. Absence of significant subsurface cementation in many reefs (e.g., Redwater, Golden Spike) aids in preservation of the reservoirs formed during earlier diagenesis.

In summary, it is the early diagenetic history in many Devonian reefs in the Western Canada basin that is responsible for reservoir distribution and quality. Likewise, the knowledge that reef margins and interiors often have different cementation histories is important in both reef exploration and reservoir management.

WALTER, LYNN M., Univ. Miami, Rosenstiel School Marine and Atmospheric Sci., Miami, FL

#### New Data on Relative Stability of Carbonate Minerals: Implications for Diagenesis and Cementation

Redetermination of magnesian calcite solubilities indicates that the constants currently in use overestimate their solubility by 300%. The relative chemical stability of aragonite and magnesian calcite plays a fundamental role in controlling the behavior of these metastable minerals during the diagenetic transformation to stable low-magnesian calcite limestone via dissolution and reprecipitation reactions. Temporal evolution of rock and groundwater geochemistry, as well as development of limestone fabrics, depends on the relative chemical reactivity of carbonate grains during dissolution as well as their receptiveness to cementation in both marine and meteoric diagenetic systems.

Following the laboratory determination of magnesian calcite stabilities by L. N. Plummer and F. T. Mackenzie in 1974, it has been accepted that magnesian calcites containing greater than 7.5 mole %  $MgCO_3$  are more unstable than aragonite, and become progressively more unstable with increasing mole %  $MgCO_3$ . For example, 18 mole % magnesian calcite was thought to be seven times more soluble than aragonite.

The solubilities of several biogenic magnesian calcites (echinoid, 12 mole %  $MgCO_3$ ; red algae, 18 mole %  $MgCO_3$ ) have been redetermined. The new data for the stability of the magnesian calcites indicate that previously determined solubilities for magnesian calcites were significant overestimates. Using the new stability constants from the present study, 12.5 mole % magnesian calcite is equivalent in stability to aragonite, and an 18 mole % magnesian calcite is only twice as soluble as aragonite. Thus, the solubility of magnesian calcites must be reduced by 300% from existing values in the literature.

It is believed that the discrepancy with previous work on magnesian calcite stability is due to sample preparation procedure. In the present study, care was taken both to eliminate submicron fine particles by ultrasonic cleaning and to reduce the crystal strain induced by crushing. Experiments show samples not so treated yield larger magnesian calcite solubilities because of enhanced reactivity and solubility of adhering submicron particles and strained crystal surfaces.

The new stability relations have significant implications for the sequence and pathways of diagenetic reactions. Mineralogical stability and available surface area are the main chemical controls on the rate of diagenetic alteration. Given the reduced solubility offset between aragonite and magnesian calcite, aragonites having more complex microstructures and, hence, more reactive surface area, dissolve more rapidly than coexisting high-magnesian calcites.

The lower solubilities for the magnesian calcites sharply reduce the potential chemical region in ground waters where the incongruent dissolution of magnesian calcite is possible. Since the specific nature of dissolution is closely related to the rate and style of

cementation, these findings prompt the reevaluation of possible pathways which may be taken during early diagenesis.

More work remains to be done to quantify the precise effects of mineralogy and grain microstructure into a complete predictive model for patterns of cementation, but it is clear that the reduced mineralogical stability offset between aragonite and magnesian calcite makes microstructural detail and ground-water geochemistry prime controls over the reaction paths followed during the early diagenetic stabilization of shallow-water carbonate deposits.

WARME, J. E., and N. SCHNEIDERMAN, Colorado School Mines, Golden, CO

#### Patch-Reef Cementation: Holocene of Enewetak Atoll and Jurassic of Morocco

Atoll lagoon patch-reefs in modern (Enewetak, Marshall Islands) and Middle Jurassic (High Atlas Mountains, Morocco) settings exhibit geologically instantaneous cementation.

Three kinds of cements are pervasive in a shallow-water ( $\leq 7$  m, 23 ft) patch-reef in the lagoon at Enewetak, precipitated in skeletal and other voids in samples that radiocarbon date from 700 to 1,800 years B.P. Aragonite, blocky Mg-calcite and nanocrystalline Mg-calcite all are present in the same thin sections. The latter appears as micrite in thin section, but is clearly crystalline cement as seen with the SEM. At least two of the cements commonly occur in the same void, but they never appear intergrown, suggesting that subtle (and not understood) changes in chemical environment control episodes of cementation. The same sequence of cements commonly occurs in adjacent voids (cavities, boring, corallite cavities, intergranular, etc); where a typical sequence is: blocky Mg-calcite rims followed by aragonite sprays (usually nucleated around loose carbonate debris) and/or nanocrystalline Mg-calcite cementing fine-grained loose debris. An important in-situ process involves development of borings which became filled with rapidly cemented debris, converting parts of the reef from skeletal carbonate to cemented debris in situ. Petrographically, the fabric of the reef is converted to packstones and wackestones, with little of the original boundstone preserved for the petrographer.

The exhumed Middle Jurassic atoll near the town of Rich in the Central High Atlas of Morocco exhibits a rim of pinnacle reefs surrounding a lagoon with hundreds of patch reefs, identical with modern atolls. Evidence for pre-burial marine cementation includes multiple episodes of cross-cutting borings that have been filled with debris and cemented in the time between borings; attached epibiotic organisms over cemented reef-and-mud masses; cascaded beds of crinoid, brachiopod, bivalve, etc, debris down the flanks of cemented reef-and-debris mounds; and over-steepened flanks of these mounds. A thorough recrystallization makes determination of cement types difficult in the Moroccan examples. However, by comparison with modern examples, we reinterpret the "mud" fillings of cavities, corallites, etc, as representing original Mg-calcite cement rather than low-energy muds.

At both localities no evidence exists for subaerial cementation. Both are associated with abundant muddy substrates, although well ventilated by tidal currents and choppy waves in the lagoon at Enewetak, and affected to some extent by waves and currents in Morocco. These examples indicate that lagoon reefs can be tightly bound by marine cements, losing porosity before burial, as can reefs in higher energy surf zones as documented in Belize and elsewhere.