

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.

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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.

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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 (≤ 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.