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Dolomitization of Upper Cambrian Bonneterre Formation, Southeast Missouri

The Bonneterre Formation of southeast Missouri contains a wide variety of dolomites and dolomite textures which are the results of multiple episodes of dolomite formation. The Bonneterre Formation crops out near the St. Francois Mountains at the core of the Ozark dome and is host for several large Mississippi Valley-type Pb-Zn deposits. The Bonneterre is predominantly a dolomite where it crops out, but contains limestone in the subsurface.

The Bonneterre was deposited by a series of shoaling-upward depositional cycles. A complete cycle was terminated by a tidal-flat complex which prograded basinward. The top of a completed cycle is a disconformity. Recognition of major transgressions which begin some of the larger cycles provides a basis for correlating the Bonneterre throughout southeast Missouri.

Several cores from diamond-drill holes drilled for Pb-Zn ore were logged and sampled for thin sections and trace-element geochemistry. Based on petrographic and stratigraphic relationships observed in the cores, the dolomites of the Bonneterre Formation can be separated into six types. (1) Tidal-flat dolomites are light gray and fine crystalline. These rocks are finely laminated and contain features indicative of evaporitic environments. (2) White-rock dolomites are coarse crystalline and very light gray. Individual crystals of this rock usually have sweeping or undulose extinction when viewed under crossed nicols. (3) Brown-rock dolomites are generally brownish gray to olive gray and fine to medium crystalline. Sedimentary features are well preserved in some of the fine-crystalline examples of this lithology. (4) Clear rims or zones of dolomite that are epitaxial overgrowths on other dolomite crystals are another type of dolomite found in the Bonneterre. This dolomite contains ferroan zones (as determined by staining with potassium ferrocyanide), and is associated with stylolites. (5) Saddle dolomite was deposited in all types of diagenetic pores. (6) Hydrothermal dolomite is associated with Pb-Zn sulfide minerals.

Stratigraphic and paragenetic relationships combined with trace-element geochemistry provide a basis for interpreting the origins of the Bonneterre dolomites. Tidal-flat and white-rock dolomites formed in the near-surface diagenetic environment. Tidal-flat dolomites formed in evaporitic environments similar to modern sabkha environments. White-rock dolomites formed in freshwater-saline water mixing zones. Clear dolomite rims with ferroan zones are interpreted to have formed in the subsurface diagenetic environment and are the results of pressure solution. The formation of brown-rock dolomites involves both near-surface and subsurface diagenetic environments. Saddle dolomite formed late in the diagenetic history of the Bonneterre formation and may be related to the introduction of basinal brines to the southeast Missouri region.

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Occurrence and Significance of Sedimentary Structures in Limestone Concretions, Greenhorn Formation, Northwestern Black Hills

It is now recognized that depositional environments of shales can be expanded beyond the phrase "quiet-water" deposition. One of the difficulties in delineating different depositional envi-

ronments in fine-grained sediments is that descriptions of sedimentary structures in shales are not common. If the structures are preserved by some diagenetic process, then they can be more readily used in the interpretation of depositional environments. Diagenetic carbonate concretions that formed by the localized precipitation of cement in pore spaces of sediment would be expected to preserve original fabrics. Because of good exposure and greater resistance to weathering, concretions may exhibit features that are difficult to see in the less resistant surrounding shale.

The Greenhorn Formation (Upper Cretaceous) north and west of the Black Hills is predominantly a shale with abundant limestone concretions. The concretions are generally restricted to certain zones. Shale exposures are generally unspectacular. The concretions, which are more resistant to weathering, contain a variety of physical and biogenic sedimentary structures. Commonly the structures are subtle. Polished slabs enhance or reveal structures not apparent in the field. Concretions from a given layer exhibit similar sedimentary structures. Parallel lamination is the most abundant physical sedimentary structure. Laminae range from 0.1 mm (.003 in.) to 1 cm (.4 in.) in thickness. They can be continuous with a constant thickness, continuous with a variable thickness, or discontinuous. Low-angle ripple cross-stratification is present in some laminae. Graded bedding, cut-and-fill structures, and flame structures are also present. Biogenic structures include distinct burrows, burrow-disrupted layering, and thoroughly bioturbated textures.

Depositional textures of the Greenhorn concretions include mudstone, wackestone, and packstone. Major grain types are inoceramid prisms and fragments, foraminifera, quartz, fish debris, and pellets. In some concretions, pellets are deformed indicating compaction occurred prior to cementation.

The range of sedimentary structures, depositional textures, and abundance of quartz in Greenhorn concretions suggests variations in depositional conditions. Some laminae must have been deposited in quiet water with a current velocity close to zero while other laminae must have been deposited by currents of higher velocities. Cross-stratification is evidence that tractive currents were active in depositing and/or reworking the bottom sediments. The biogenic structures provide evidence of infaunal life and bioturbation.

Where shale exposure is good, the same structures are observed in the shale as in the concretions. Therefore, structures in concretions are representative of the surrounding shale at that level. Concretions should not be ignored as a source of information regarding sedimentary structures. They can be valuable in the interpretation of paleoenvironments of shale.

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Cathodoluminescence in Carbonate Petrography: Some Aspects of Geochemical Interpretation

Commonly only Mn^{2+} and Fe^{2+} are considered to be responsible for the luminescence behavior of calcite and dolomite. However, a fairly large number of trace elements interact to produce certain luminescence characteristics in these minerals (as described by Gies in 1975 and 1976). The ions of these elements can be grouped into activators, sensitizers, and quenchers.

Activators are those ions that lead to active luminescence, undergoing excitation (entrapment of energy), temporary storage, and emission. Main activators in carbonates are Mn, Pb, and several rare earth elements. Sensitizers are those ions that undergo excitation and transmit some of this energy to the activators. Main sensitizers in carbonates are Pb and Ce. Quenchers

are those ions that trap excitation energy, but whose outer electron transitions do not result in luminescence. Main quenchers in carbonates are Ni and Fe.

As opposed to visual determination, only a spectral analysis of the emitted radiation paired with a chemical analysis can detect which of all these elements participate in the luminescence of a particular carbonate crystal. A visual observation, such as "bright-orange luminescence," is merely a mixture of wavelengths, and this color can result from different spectral compositions due to correspondingly different trace element contents.

Activators, sensitizers, and quenchers have to be present in certain minimum and below certain maximum concentrations in order to be effective. The minimum concentration for the most important activator in non-hydrothermal carbonates, Mn^{2+} , is well below 100 ppm, and it is even lower if the crystal contains any sensitizers in effective concentrations. Pb^{2+} and Ce^{2+} sensitize Mn-activated luminescence at concentrations as low as perhaps 30 ppm. The most effective quencher is Ni^{2+} , which kills Mn-activated luminescence at concentrations as low as possibly 35 ppm. Fe^{2+} seems to effect initial quenching at about 30 to 60 ppm. Up to about 10,000 ppm, the luminescence behavior of calcite and dolomite depends on the Mn^{2+}/Fe^{2+} ratio. No luminescence occurs above this level, whatever the Mn^{2+} concentration.

Mn^{2+} is the most important activator in carbonates because it leads to the most obvious luminescence; it is relatively abundant. Fe^{2+} is probably the most important, although not most effective, quencher due to its very high and variable abundance. If one attempts to interpret the luminescence behavior of carbonates in terms of the geochemical environment, however, the other activators, sensitizers, and quenchers have to be considered too. In particular, those elements associated with organic matter could be enriched in organic-rich (or even bituminous) carbonates, and elements primarily associated with clay minerals can be expected in impure, argillaceous limestones and dolostones, and their diagenetic carbonate phases.

The luminescence of carbonate cements, thought to result from Mn^{2+} and Fe^{2+} alone, has often been taken as an indicator of the redox-potential of diagenetic fluids. This is only permissible if it can be shown that the other elements are not involved to any significant degree.

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Submarine Cements—The Peloidal Question

The peloidal texture common to submarine substrates lithified by magnesium calcite appears to be the result of the same processes responsible for the deposition of the cement. These peloids do not, as reported earlier, represent the deposition of internal sediment of fecal or unknown origin. Rather, they are the physicochemical product of the precipitation of calcite from seawater, as indicated by: (1) the widespread occurrence of peloidal calcites in a variety of marine environments; (2) the generally limited size range of the peloids; (3) the well-developed zonation of peloidal textures in many cement crusts; (4) the presence of peloids in restricted microcavities; and (5) the chemical similarity of peloids and associated magnesium calcite dentate rim cements.

Although these magnesium calcite peloids resemble aragonite peloids formed by rapid repeated nucleation in experimental precipitation of aragonite from supersaturated seawater, their rates of formation must differ because pore waters are incapable of spontaneously providing the calcium carbonate required for the extensive deposition of magnesium calcite found in restricted submarine settings. Observations of magnesium calcite precipitating on experimental substrates placed on the ceiling of a submarine cave suggest that clotting or nucleation of magnesium

calcites may be a very slow process, perhaps commonly involving the nucleation within an initial submicrocrystalline calcite "dust" precipitate. The final stage consists of the precipitation of dentate microcrystalline rim cements around the peloid centers.

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Diagenesis and Mass Transfer in Sandstone-Shale Sequences

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 (1,000 to 3,000 m) of overburden has 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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Mississippian Carter and Lewis Sandstone Petroleum Geology of Black Warrior Basin of Alabama

The Black Warrior basin of northwestern Alabama is an excellent locality to prospect for combination petroleum traps; to date over 1,000 wells have been drilled in the region and 62 petroleum fields and pools have been discovered. Mississippian sandstone reservoirs presently have the greatest hydrocarbon potential, the Carter and Lewis sandstones being the most economic of these reservoirs. Cumulative production for the Carter includes more than 700,000 bbl of oil and 12 bcf of gas. The Lewis has produced over 5,000 bbl of oil and 12 bcf of gas. The Carter was deposited as part of a high-constructive, elongate to lobate delta which prograded from northwest to southeast into the basin. The Lewis accumulated as a series of elongate, northwest to southeast-trending sand bodies on a shallow marine shelf. Carter distribu-