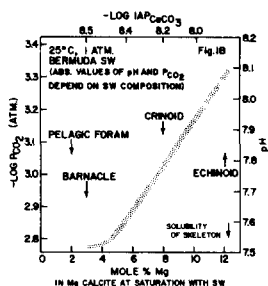
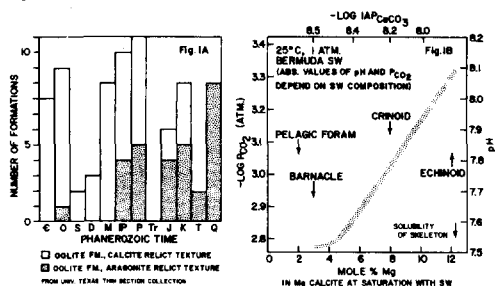


post-Permian fossil assemblages, whereas calcitic forms decline or become extinct. These observations imply a post-Carboniferous change in the chemistry of the earth's surface environment.

To determine the relative importance of factors controlling magnesium calcite solubilities in seawater, saturation experiments were performed. It is important to recognize from these experiments that the composition of a magnesian calcite precipitating at saturation from seawater can be treated as a function of atmospheric CO_2 pressure, at an essentially constant seawater Mg/Ca ratio. Thus, observed trends in the textures of ooids and their interpreted mineralogy through the Phanerozoic may be due to changes in atmospheric CO_2 levels, not necessarily to a major change in the Mg/Ca ratio of seawater. It is possible that pre-Carboniferous CO_2 levels were high favoring precipitation of calcitic ooids and skeletal parts; after the Carboniferous, CO_2 levels fell and aragonite and high magnesian calcites increased in abundance as precipitates.

Diagenetic implications of the time variance in CO_2 pressure are many. Diagenetic patterns based on Holocene models may not be valid for the Paleozoic; solution-precipitation and inversion would be less common than recrystallization prior to the Carboniferous. Reservoir targets of intraparticle porosity in relict aragonite oolitic sands would be less important in pre-Carboniferous rocks. Higher atmospheric CO_2 pressure favors dolomite formation. Finally, the CO_2 content of an environment rather than the Mg/Ca ratio may be the important parameter to consider in many carbonate diagenesis studies.



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Differential Diffusion During Carbonate Diagenesis

Most of the movement of ions during carbonate diagenesis occurs in aqueous pore systems in which the average diameter is too small to permit mass transfer by fluid flow. In such situations, ionic motion proceeds instead by aqueous diffusion. In pore systems of sufficient diameter, ion transport occurs by fluid flow. Water occupies both habitats in typical carbonate sediments. Sediment-water interactions occur predominantly in the diffusion-controlled system, and flushing of the sediments is achieved in the flow-controlled (aquifer) system.

Three parameters control the diffusion of cations

from diagenetic sites to the aquifer (or vice versa): (1) the concentration difference between diagenetic site and aquifer; (2) the diffusion coefficient for the particular cation under ambient conditions; and (3) the length and geometry of the pore path to be traversed. Under the conditions typical of carbonate diagenesis, concentration difference is the dominant variable and pore path plays a secondary role. Concentration differences between diagenetic site and aquifer may be positive or negative; the sign determines the direction of diffusion and the absolute magnitude determines the efficiency of diffusion. At a given moment, cations of different species may travel in different directions and at different rates; hence the concept of differential diffusion. Unlike fluid flow, cation transfer by diffusion is not limited to a single direction and a single velocity. A diagenetic site may thus be relatively open to one cation yet, at the same moment, relatively closed to another. The trace element composition of a limestone is not a simple function of either the aquifer solution or the diagenetic solution, rather it reflects the complex diffusion interaction between the two.

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Diagenetic Mobilization of Uranium and Iron from Red Beds of Catskill Formation in Eastern Pennsylvania

The content of uranium, thorium, lanthanum, and major elements in 272 samples of clastic sedimentary rock from red beds of the Devonian Catskill Formation in eastern Pennsylvania varies with grain size and color (oxidation state). The samples were derived largely from fining-upward cycles in which sandstones, commonly gray to green, were deposited as channel fillings, while overlying shales, commonly red, were deposited as overbank muds. The contents of iron, aluminum, uranium, thorium, titanium, and lanthanum correlate negatively with grain size. Gray to green (reduced) shales and fine-grained sandstones have distinctly lower iron and higher uranium and uranium/thorium content than red (oxidized) sandstones and shales of the same grain size and the same aluminum content. The differences are greatest in shales. Thorium content does not vary with oxidation state.

The levels of uranium, thorium, and iron in green shales are inferred to be approximately the amounts present in the original detritus. Gray sandstones have apparently lost iron and may have locally gained uranium probably by flow of reducing pore waters through the buried channels during early diagenesis. Red muds apparently lost uranium just after deposition because of strong oxidation and at least limited permeation by surface waters. The uranium lost from the red muds furnishes a probable source for uranium in roll-type uranium deposits found in sandstones in the area near Jim Thorpe, Pennsylvania. Recrystallization of amorphous iron oxides to hematite may have promoted the release of adsorbed uranium from the muds.