

## **Diagenesis 5. Limestones: Introduction**

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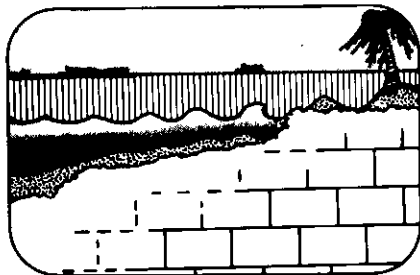
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# Articles



## Diagenesis 5. Limestones: Introduction

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### Introduction

Limestones are among the most capricious of rocks. Mostly born from the sea and generally biogenic in origin, they possess an extremely sensitive record of past life and conditions on earth, yet because they are lime and so easily susceptible to chemical change, this record is often blurred or rendered unreadable by diagenesis. Paradoxically, this same diagenesis is beneficial to society because the holes and voids created during alteration are often filled later by base metals and hydrocarbons. So, to understand limestones for any purpose it is important to decipher the often complex series of processes that have modified their texture and composition through geologic time.

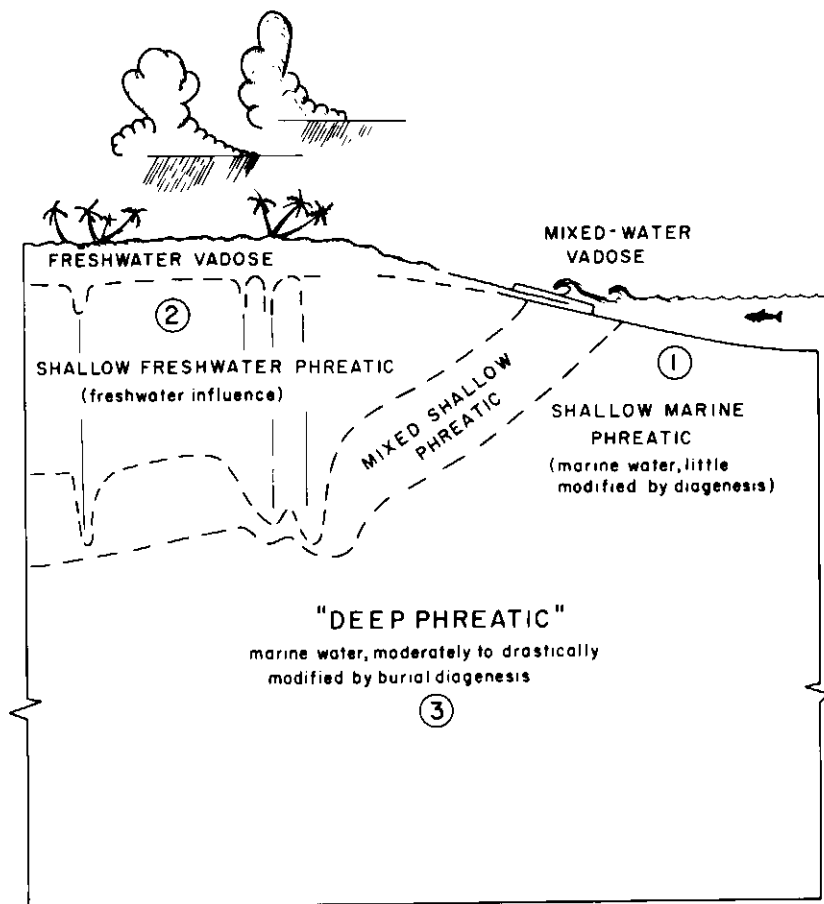
The articles in the forthcoming series on limestone diagenesis are an overview and not an in-depth treatment of the topic; they are intended as a guide to our current understanding and a synthesis of those concepts useful in interpreting the diagenetic evolution of fossil limestones. Since most

fossil limestones are marine, it is to the understanding of these rocks that this series of articles is specifically directed.

### Diagenetic Environments

Since rock-water interaction is the primary driving force in carbonate diagenesis, the

key factor in the diagenetic equation is the composition of surface and subsurface fluids. The waters most commonly in contact with carbonate rocks and sediments are marine, meteoric or deep subsurface in origin. With time, as carbonates are deposited, precipitated, buried, eroded, exposed



**Figure 1** A sketch outlining the main diagenetic environments through which carbonate sediments and rocks pass in geologic history. Depending upon hydrodynamics, configuration of the aquifer and permeability,

the freshwater phreatic waters may underlie only the exposed area as illustrated here or may extend seaward beneath the shelf and underlie a thin shallow marine phreatic zone.

and reburied, they are subject to interaction with these different fluids, each of which reacts with the sediments or rocks in a special way and leaves a unique diagenetic signature. Each region (Fig. 1), characterized by waters of different composition, can be thought of as a separate *diagenetic environment* (Purdy, 1968). In this synthesis we recognize three major diagenetic environments: (1) the *sea floor* and underlying shallow marine phreatic, characterized by marine waters, together with the strandline bathed in mixed marine and fresh waters; (2) the *meteoric*, distinguished by the freshwater vadose and phreatic zones and the shallow phreatic zone of mixed fresh and marine waters; and (3) the *deep subsurface*, where pores are filled with waters that were once marine but have been moderately to drastically modified by burial diagenesis. Changes that take place in each of these settings will be the topic of a separate article in the following series, but to place the whole spectrum in context we first summarize the main attributes of all the realms and outline the diagenetic changes that occur in each (Fig. 1).

*The Sea Floor.* Carbonate precipitation, although not ubiquitous, is the predominant diagenetic process on the modern sea floor. It is manifest in the formation of grains (i.e., ooids), the hardening of soft grains by intragranular precipitation (i.e., peloids) and the lithification of loose carbonate sediments to form sea floor limestone. In contrast, the main biological process in operation is boring, by a variety of macro and microendoliths whose ultimate product is the destruction of much depositional fabric.

Both of these processes, precipitation and boring, take place on the shallow tropical sea floor. With increasing water depth, accompanying increases in pressure and decreases in temperature combine to result in some cases in neomorphism and ultimately in complete dissolution.

*The Meteoric.* If carbonate sediments composed of a variety of minerals precipitated from seawater are—through either uplift, eustatic fluctuations in sea level, or simple accumulation exposed and so flushed by meteoric waters, whole-scale mineralogical changes occur. The original minerals, aragonite and magnesium rich calcite, are transformed to low magnesium calcite and in the process many components undergo alteration of their microstructure, while others are dissolved to create new porosity and permeability. At the same time, it is in this environment of the near-surface aquifer that widespread cementation occurs, for while the original minerals tend to be dis-

solved or transformed, the more stable mineral, low Mg calcite, is being formed concomitantly.

If carbonate sediments remain in this setting long after all the metastable minerals have altered to low-Mg calcite, or if old limestones are exhumed and reexposed, then widespread dissolution is the norm, resulting in a variety of karst features.

The rates at which mineral transformations, dissolution, early cementation and the formation of karst features occur are strongly influenced by local surface temperature and rainfall.

*The Deep Subsurface.* As carbonate sediments undergo progressive burial and are subjected to increasing temperature and pressure during and after lithification, they go through a variety of modifications. The important changes which occur include mechanical and chemical compaction—during which porosities may be sharply reduced; cementation by carbonate, sulfate, and silica silicate minerals; conversion of metastable forms of  $C_3CO_3$  to low-Mg calcite (often accompanied by other changes such as clay and gypsum dehydration); decomposition, as well as biochemical and thermochemical transformation of original organic matter. As has been shown in some detail recently, the dominant trend in burial diagenesis seems to be a long-term reduction of porosity through thousands of metres of burial. Under some conditions, however, porosity appears to be created anew during burial diagenesis through dissolution of carbonate grains and cements. The details of the dissolution process are still unclear, but apparently involve the production of  $CO_2$  by organic compounds undergoing thermo-biochemical reactions in the presence of other pore fluids.

*Diagenetic Pathways.* Most carbonates, because they are formed on the sea floor, have the potential to be altered in that environment and so bear some signature of early diagenesis. Similarly, most fossil limestones have been subjected to burial diagenesis. Carbonates need not, however, ever have been modified by percolating meteoric fluids. It is common though to see some evidence of meteoric diagenesis in limestones, generally because in shallow-marine settings they accumulate rapidly to sea level. This, combined with subtle fluctuations in sea level, commonly leads to subaerial exposure and thus meteoric diagenesis, even if short lived.

In actual experience the different diagenetic processes vary markedly in importance from environment to environment (Table I). Most sediments on the modern seafloor are affected to some degree by

bioerosion, but cementation is facies specific and most deposits are unlithified. Once exposed to percolating nonmarine fluids, all sediments suffer some dissolution together with variable cementation and neomorphism. The effect of organisms is localized to the soil zone with the formation of calcrete and phytokarst. In the deep subsurface compaction and cementation affect all rocks and sediments and are commonly accompanied by neomorphism. Dissolution, however, appears to be restricted to specific situations.

The degree to which any carbonate is altered in any of these settings depends upon (1) the composition and flux of the waters through the sediment or rock, and (2) the length of time the rock or stabilized sediment remains in the environment.

Because cements are progressively added to the rock as it passes from one diagenetic environment to another, the sequence of alteration can often be worked out best by examining the "Cement Stratigraphy" in detail.

*Techniques and Literature.* The indispensable source of information on the topic of carbonate diagenesis is the text by Bathurst (1975) and the followup article in 1980. For a more general treatment of the subject the reader is referred to the books by Friedman and Sanders (1979), Blatt, Middleton and Murray (1980) and Flugel (1982). Good sources for the identification of components are the volumes by Scholle (1978) and Horowitz and Potter (1971). For a parallel treatment of diagenesis with a somewhat different approach the article by Longman (1980) is recommended.

Since the changes that take place are largely chemical, the study of carbonate diagenesis requires both petrographic and geochemical analysis. The basic relationships are seen from stained slabs and thin sections or acetate peels and may be augmented by scanning electron microscopy. Especially useful are the trace-element concentrations of strontium, magnesium, iron and manganese and the concentration ratios of carbon ( $^{13}C/^{12}C$ ), oxygen ( $^{18}O/^{16}O$ ) and, in special cases, sulphur and strontium isotopes. Cathodoluminescence, induced in carbonate minerals mainly by excitation of reduced manganese ( $Mn^{2+}$ ) and allowing differentiation of various zones within carbonate crystals, has become widely used in recent years. Finally, the nature of past fluids themselves may sometimes be ascertained from study of fluid inclusions.

### Selected References

The literature on carbonate diagenesis is vast—the following texts and papers together, give the reader a working overview and introduction to the topic.

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An excellent overview of cathodoluminescence—as applied to carbonates, with good photographs.
- Bathurst, R.G.C., 1975, Carbonate Sediments and Their Diagenesis: Elsevier, New York, 658 p.  
The authoritative text on the subject of carbonate diagenesis—very readable with exhaustive scholarship. Any worker in the field should have this book.
- Bathurst, R.G.C., 1980, Lithification of carbonate sediments: Sci. Prog. Oxf., V. 66, p. 451-471.  
An update on research in limestone diagenesis since 1975.
- Blatt, H., 1982, Sedimentary Petrology: W.H. Freeman, San Francisco, 564 p.  
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- Blatt, H., G. Middleton, and R. Murray, 1980: Origin of Sedimentary Rocks: Prentice-Hall, Englewood Cliffs, N.J., 782 p.  
One overview chapter on carbonate diagenesis.
- Bricker, O.P., 1971, Carbonate Cements: Johns Hopkins Press, Baltimore, 376 p.  
Numerous short articles which together illustrate the spectrum of cements in carbonate rocks, modern and fossil.
- Flügel, E., 1982, Microfacies Analysis of Limestones: Springer-Verlag, New York, 633 p.  
Although this is a general text there are good reviews on diagenesis—and an excellent source of information on Mesozoic—Cenozoic carbonates.
- Flok, R.L., 1965, Some Aspects of Recrystallization in Ancient Limestones: in L.C. Pray, and R.C. Murray, eds., Dolomitization and Limestone Diagenesis, a Symposium: Society of Economic Paleontologists and Mineralogists Special Publication, No. 13, p. 14-48.  
A good introduction to a complex topic.
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Good photomicrographs of a wide variety of limestones.
- Hudson, J.D., 1977, Stable Isotopes and Limestone Lithification: Journal of the Geological Society, V. 133, p. 637-660.  
An excellent overview and good place to start when considering the application of stable isotope analysis to carbonates.
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- Meyers, W.J., 1974, Carbonate Cement Stratigraphy of the Lake Valley Formation (Mississippian) Sacramento Mountains, New Mexico: Journal of Sedimentary Petrology, V. 44, p. 837-861.  
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- Milliman, J.D., 1974, Marine Carbonates: New York, Springer-Verlag, 375 p.  
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- Purdy, E.G., 1968, Carbonate Diagenesis: an Environmental Survey: Geologica romana, V. 7, p. 183-228.  
A beautifully presented, wide ranging paper on diagenetic environments.
- Scholle, P.A., 1978, A Color Illustrated Guide to Carbonate Rock Constituents, Textures, Cements and Porosities: American Association of Petroleum Geologists, Memoir 27, 241 p.  
An excellent reference while doing carbonate petrography with a good bibliography on techniques and classification.

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