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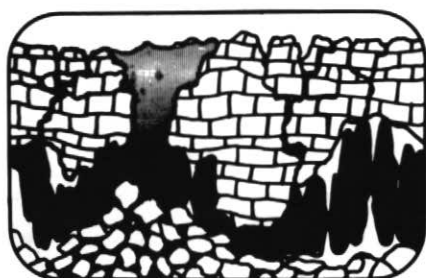
Diagenesis 9 -. Limestones – The Meteoric Diagenetic Environment

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Introduction

Carbonate sediments, born in the sea, remain largely unaltered while bathed in their embryonic fluids of high ionic strength. With time, however, the composition of the pore waters will inevitably change, and if exposed to circulating groundwater, the sediments may undergo profound and geologically rapid diagenesis (Fig. 1).

The meteoric diagenetic environment is one with many apparent contradictions: For example, the main process is carbonate dissolution, yet here is where soft sediment is transformed into hard limestone; the same waters that precipitate $CaCO_3$, when mixed may dissolve $CaCO_3$; while spectacular caves are being excavated, delicate fossils are being preserved.

This environment has been studied more intensively than any other diagenetic realm, yet we are really only reasonably confident about processes and products that occur above the water table.

The wide variety of limestones that result

from meteoric diagenesis – often beginning with the same sediment – are the end result of several reactions, governed by intrinsic and extrinsic factors (Fig. 2) that may proceed at different rates for varying lengths of time. The most important intrinsic factor is *original mineralogy*: sediments composed of several $CaCO_3$ minerals, dominated by aragonite and magnesium-rich calcite (Mg-calcite), which are meta-stable with respect to fresh water, alter most; those sediments composed only of various calcite minerals alter least. *Grain size* controls the rates at which these components change; fine grained sediments, because of their large ratio of surface area to particle size, change most rapidly, whereas large skeletons of the same mineralogy change more slowly. Individual grains will also alter at different rates, depending upon the crystal size and relative amount of organic material. Finally, *porosity and permeability* of the sediment, which govern the rate at which fluids flow

through and the length of time they are in contact with the sediment or rock, affect the speed at which changes take place.

Perhaps the most crucial extrinsic factor is *climate;* in areas of extensive rainfall and warm temperatures diagenesis proceeds quickly and with great vigour, whereas in warm arid regions, because of little water, sediments are often unchanged for long periods, or are virtually unaffected by subaerial exposure. As the dissolving power of fresh water is largely controlled by biologically produced CO_2, the *amount of land vegetation* is also important. Finally, *time* is critical; the longer a sediment is exposed in the meteoric environment, the more intensive the changes will be.

The Meteoric Setting

As outlined in the introduction to this series on limestone diagenesis (James and Choquette, 1983), the meteoric environment can be subdivided in most general terms into vadose and phreatic settings (Fig. 3).

Figure 1 *The shore of Bimini, The Bahamas. The rock on the right is carbonate sediment that* has been cemented by exposure to meteoric waters over the last several thousand years

The water table marks the top of the phreatic zone and represents the level at which hydrostatic pressure is equal to atmospheric pressure. The most common aquifers are *unconfined*, or open to the atmosphere, and the hydrostatic level is within the water-bearing unit. There are two types of gravity-induced flow in this situation (White, 1969). Under conditions of *diffuse flow* there is a well-defined water table and water movement obeys or nearly obeys Darcy's law. The sediment or rock has relatively homogeneous porosity and permeability characteristics, karst landforms are rare and subdued on a generally low relief surface, small cavities are somewhat randomly arranged and flow is relatively deep. In contrast, under *free flow* conditions water moves through integrated conduits which function like a series of three-dimensional subterranean rivers. The water table is discontinuous or difficult to recognize at all, but there is nevertheless a continuous potentiometric surface. Diffuse flow aquifers with a well defined water table are typically developed in newly exposed young carbonate sediments, but with time and diagenesis aquifers evolve into the free flow type characterized by conduit flow and a discontinuous water table. In this paper the focus is on diffuse flow aquifers.

The other entirely different type of flow is *confined*. These aquifers are bounded by aquitards (impermeable layers) and are not connected vertically to the atmosphere. Water flow is by pressure and will rise above the level of the aquifer in wells (artesian flow). Confined aquifers are par-

ticularly important as conduits by which fresh water can flow deep into sedimentary basins and considerable distances out beneath the continental shelf.

Unconfined aquifers characterized by diffuse flow are most usefully divided into

the *vadose* zone, above the water table; the active, shallow, freshwater phreatic zone or *lenticular phreatic zone* (Jakucs, 1977), below the water table; and the *sub-lenticular mixing zone*, also referred to as the transition, mixing, diffusion or dis-
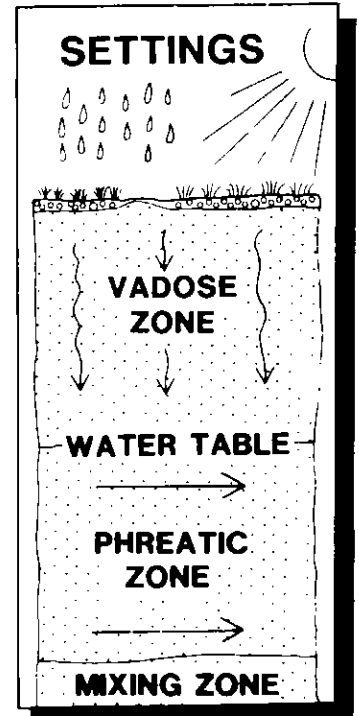
METEORIC DIAGENESIS

CONTROLS

INTRINSIC

MINERALOGY

GRAIN SIZE

POROSITY & PERMEABILITY

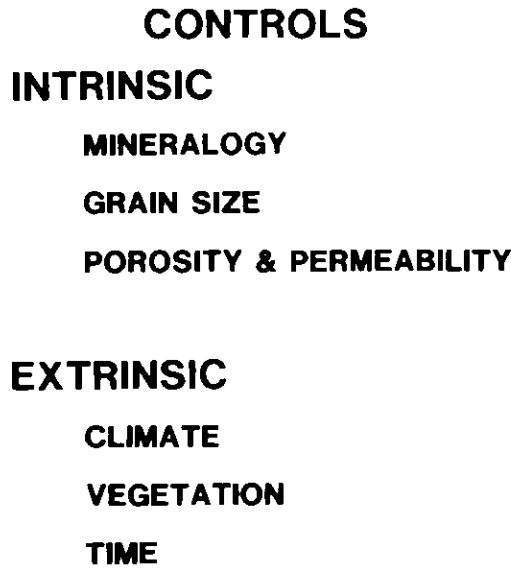## EXTRINSIC

CLIMATE

VEGETATION

TIME

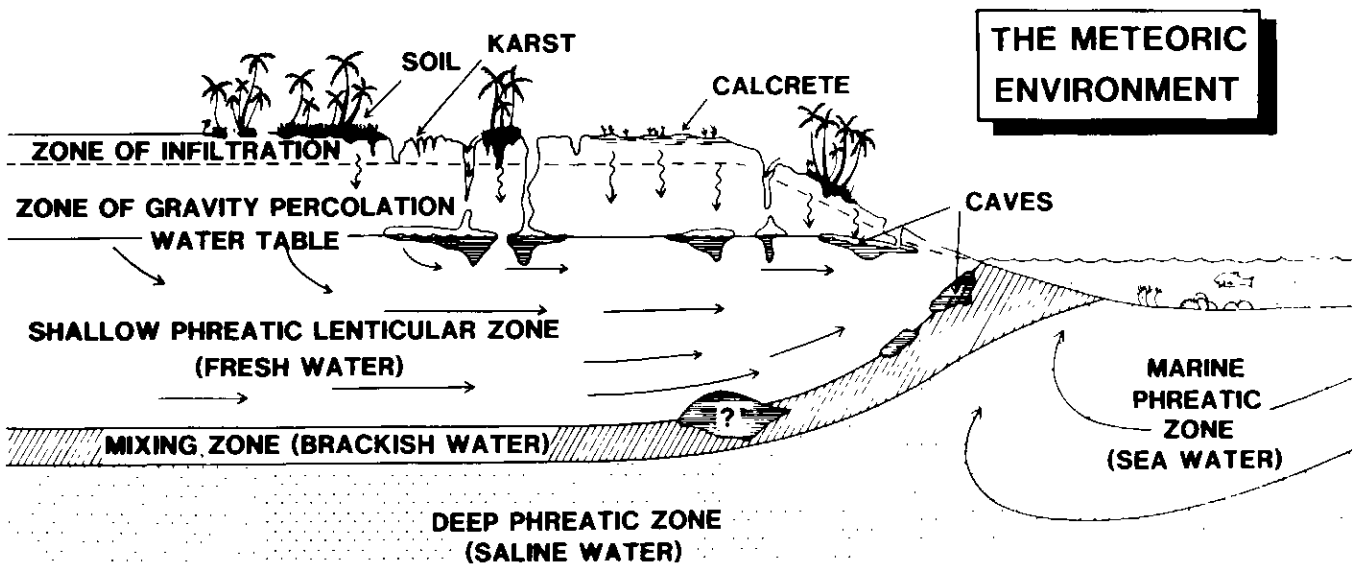**Figure 2** *The principal controls on and settings of meteoric diagenesis*

Figure 3 *A sketch outlining the main zones of the meteoric diagenetic environment*

persion zone. The general relationships of these settings are shown in Figure 3.

The Vadose Zone. Rainwater, meltwater or runoff enters a carbonate sequence either directly on bare rock or through a calcrete or soil. This *zone of infiltration* (Fig. 3) is a realm of complex carbonate-water interaction. Although water may pass directly into the rock, in most situations there is a soil or protosoil on top of bedrock. Biological activity in the soil not only alters the composition of the fresh water but, in many cases, induces carbonate precipitation. This zone is subject also to evaporation or evapotranspiration, especially in the tropics, so that some of the downward percolating waters are drawn back up to the surface, again leading to carbonate precipitation.

The underlying and more extensive *zone of gravity percolation* is characterized by pores variably filled with water and/or air or organically produced gas. Under conditions of *vadose seepage* water trickles through the limestone via a network of tiny fractures or small pores. In contrast, *vadose flow* (Thrailkill, 1968) is the relatively rapid movement of water downward via joints, large fissures and sinkholes, often directly to the water table.

The Water Table. As will be discussed later, the water table is a surface of great importance in carbonate diagenesis. In older, pre-Pleistocene limestones its former presence and position can often only be recognized approximately if at all because of long and complex diagenetic histories. Some criteria that can be helpful in delineating paleo-water tables are presented further on in this article. On relatively small, present-day limestone islands the water table is usually very gently bowed upward toward the island interior, as a rule rising less than a metre per kilometre (Figs. 3 and 4). Beneath widespread carbonate platforms and mainland carbonate plains underlain by flat-lying strata the water table appears to have almost imperceptible relief (Fig. 3). For example, two of the better known karst terrains of North America – the northern Yucatan and the southern peninsula of Florida (Back and Hanshaw, 1970; Back *et al.*, 1976), regions of about 50,000 km² – have water table elevations which reach maxima of only a few metres and mostly less than 20 metres, respectively.

The Lenticular Zone. This zone has as its lower boundary either an aquiclude or a water mass of different composition (Fig. 4). A common situation today is one in which the freshwater lens "floats", iceberg style, balancing on a column of denser marine water beneath it. Early observers (DuCommun, 1828; Ghyben, 1888-89;

Herzberg, 1901, cited by Fetter, 1980) noted in unconfined coastal aquifers that the depth to which the lenticular zone extends below sea level is about forty times the height of the water table above sea level. This relationship is commonly called the Ghyben-Herzberg principle (e.g., Todd, 1980). The precise configuration of the lens is dependent also upon, amongst other things, the permeability of the rock and rate of groundwater recharge. Regardless, the important point is that only minor elevation above sea level can lead to deep penetration of meteoric water and attendant diagenesis.

In this zone, water, which fills the available pore spaces, is actively moving. Except in regions of relatively high elevation,

water movement in the lenticular zone is largely horizontal or subhorizontal (Figs. 3 and 4) and directed toward the local base level of erosion which may be a spring, river or other inland water body, or the ocean.

If the aquifer is very permeable and there is dynamic water movement in the lenticular zone, the interface may be deeper and displaced seaward toward the coast compared to what would be predicted by the Ghyben-Herzberg relationship, because the marine water beneath the lens is actively moving rather than static, as assumed for the relationship. In strongly dynamic systems, "tongues" of freshwater may extend many tens of kilometres seaward beneath the continental shelf in con-

SMALL SAND CAY OR OCEANIC ATOLL
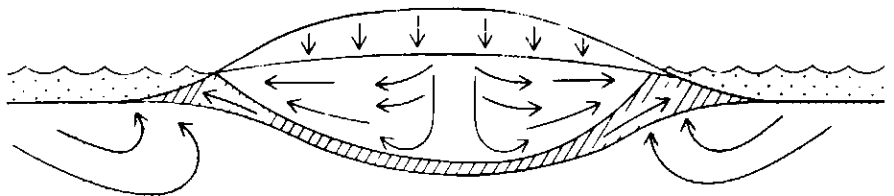
LARGE CARBONATE PLATFORM
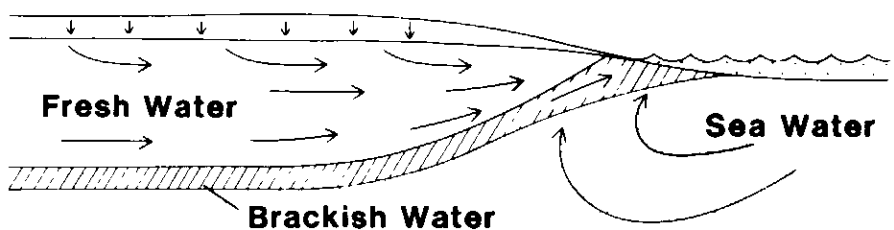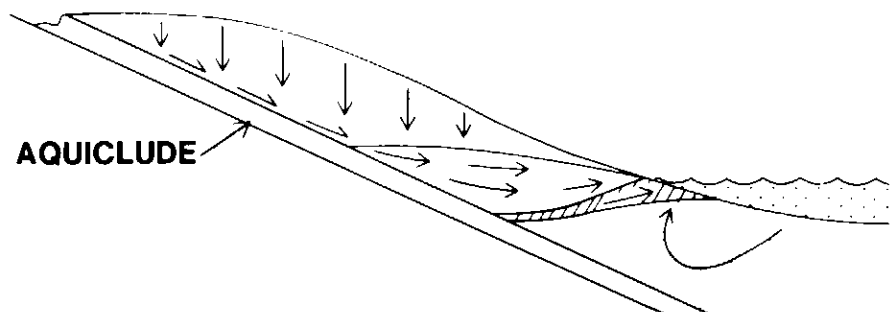

TECTONICALLY UPLIFTED TERRANE

Figure 4 *A sketch showing different scales and configurations of freshwater lenses*

fined aquifers (Manheim, 1967; Johnson, 1983).

The Transition or Mixing Zone. The brackish water zone at the base of the freshwater lens is of great geologic as well as practical interest. It has been suspected since the early 1970s that this zone may be a site where early dolomitization takes place (see Morrow, 1982a,b for an excellent review). Processes that occur in the transition zone are still poorly understood, but its hydrologic and chemical characteristics are becoming better known through studies such as those on which this brief discussion is largely based: Bear and Todd (1960); Back and Hanshaw (1970; Back *et al.*, 1976); Vacher (1974), Plummer *et al.* (1976); Wigley and Plummer (1976); and Back *et al.* (1979, 1984).

In general, the transition zone is a product of physical and diffusive mixing. It is thickest in more permeable strata where these mixing processes are more effective, and also it is thickest toward the coast because of both the higher velocities of groundwater flow near coastal discharge points and the influx of seawater drawn shoreward and upward in the shallow subsurface to replace the discharge.

Salinity profiles in the transition zone – as well as profiles of water velocity, concentrations of single and multiple ion species and such water-dependent mass properties as electrical conductivity – have the form of an s-shaped curve (Fig. 5). Because flow velocity and salinity are inversely related, profiles of the two essentially mirror one another; therefore, flow will be faster and waters more dilute in the upper part of the transition zone. The importance of these relationships here is that both conditions should have a bearing on whether carbonate will dissolve or precipitate.

It is important to be aware that, although the transition zone is often portrayed as being quite thin compared to the freshwater zone above it, the zone can be quite thick in permeable carbonates of oceanic islands. Figure 5 illustrates the variations in transition zone thickness that Vacher (1974) found in the main freshwater lens on Bermuda, where the transition zone is often as thick as or thicker than the freshwater lens itself (as defined by the 1% relative salinity contour). To a close approximation the Ghyben-Herzberg relationship, which assumes no mixing of waters, would apply in effect to the part of the lens bounded

by the 50% relative salinity surface and the water table (Vacher, 1978).

Deep Phreatic. Water in the deeper phreatic zone may be slowly moving or almost stagnant groundwater, or in the case of young exposed carbonate platforms or islands it may be seawater.

An important result of the dominance of vertical, gravity-controlled seepage and flow in the vadose zone, compared with horizontal water movement in the phreatic zone, is that large solution cavities formed in the two zones have different elongation, commonly vertical in the vadose zone, but mostly horizontal along and for a short distance below the water table. Caves that clearly have formed in brackish-water transition zones have been documented along the eastern Yucatan coast (Back *et al.*, 1979), a setting where one would expect them to be elongate parallel to the main flow direction, as suggested in Figure 3. Where dissolution in the phreatic zone is strongly influenced by flow rates, transition-zone caves may tend to be larger and more numerous toward the coast where flow rates are particularly high.

Changes in base level due to tectonic disturbances or worldwide sea level changes must inevitably shift the positions and spatial relationships between the major hydrologic zones of the meteoric environment.

Dissolution and Precipitation

It is well known that limestone dissolves when exposed to fresh water. Although the processes are easily observed and the general theory is well understood, some of the principles governing the dissolution and precipitation of carbonate are still poorly known. This is because we must deal with a multi-component system simultaneously involving all three natural phases – gas, liquid and solid. An additional complicating factor is that in perhaps the most important case, the transformation of sediment into limestone, we must also deal with a suite of several different minerals. Trying to understand all the processes which are happening at once is much like learning to juggle: having finally mastered the art of keeping three objects in the air, you are handed several more and told to put on a good show!

The reaction between carbonate minerals and meteoric waters in general is most simply expressed by the equation

$$CaCO_3 + H_2O + CO_2 = Ca^{\cdot \cdot} + 2HCO_3$$
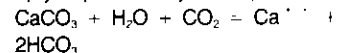
The exact mechanisms of the $CaCO_3$-CO_2-H_2O chemical system are complex, involving a series of reversible and mutually interdependent reactions, all proceeding at different rates and each regulated by different equilibrium constraints. Recent re-

HYDROGEOLOGIC CROSS SECTION
WITH RELATIVE SALINITY CONTOURS THRU
TRANSITION ZONE

TRANSITION ZONE
PROFILES IN 5 WELLS

March 1974
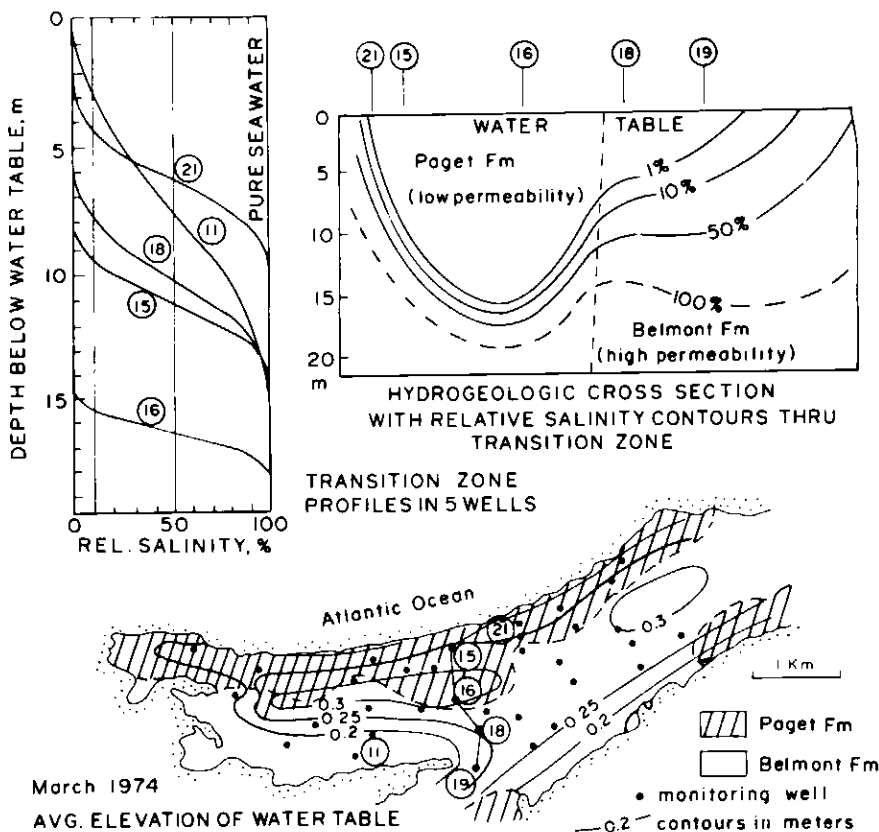AVG. ELEVATION OF WATER TABLE

Figure 5 *A hydrological case study map of the water table and profiles of the transition (mixed-water brackish) zone in the main (Devonshire)* lens on the main island of Bermuda (modified from Vacher, 1974)

views can be found in Bathurst (1975); Plummer et al. (1979); Bögli (1980); and Drever (1982).

Under natural conditions this equilibrium reaction is represented by (1) dissolution of carbonate, (2) oversaturation and (3) precipitation of new carbonate. Diagenetic processes would be relatively simple if this reaction were all that was involved, but dissolution and precipitation rates are often slowed down or halted altogether by kinetic factors. Kinetics are particularly important in slowing down precipitation and thus maintaining supersaturation.

Dissolution (Corrosion)
Dissolution and precipitation of $CaCO_3$ are controlled in most natural situations by the flux of CO_2 in and out of the water. Addition of CO_2 by any means will drive the reaction to the right, resulting in dissolution. The simplest way is to increase pressure or decrease temperature. Kinetic effects do not seem to be significant. In the meteoric environment dissolution (corrosion) is brought about in several ways (Fig. 6), some of which are quite unexpected. The reader is referred to excellent treatments of this topic by Thrailkill (1968) and Bögli (1980).

Simple Corrosion. The amount of CO_2 dissolved in water open to the air depends upon the partial pressure of CO_2 (P_{CO_2}) in the air at the air/water interface. Calcite is soluble to the extent of about 12 to 15 ppm in pure water (depending upon the temperature). Rainwater, however, is in equilibrium with atmospheric CO_2, which averages about 0.03% by volume (P_{CO_2} about $10^{-3.5}$ atm.), and so is in reality an extremely weak acid. Thus simple corrosion is the dissolution brought about by rainfall on bare rock surfaces (Fig. 6).

Biogenic Corrosion. Air in the soil zone has a significantly higher P_{CO_2} than the atmosphere because of plant respiration and decay of organic matter. As rainwater percolates through the soil, addition of biogenic CO_2 increases the CO_2 content, typically to an equivalent P_{CO_2} of about $10^{-1.0}$ atm. Values of 1% to 2% are common, but in some poorly ventilated tropical soils may be as high as 20% to 25% ($P_{CO_2} = 10^{-0.7}$ atm.). Consequently, waters emerging from below the soil are very "aggressive" chemically and can rapidly dissolve orders of magnitude more carbonate than could ordinary rainwater.

Mixing Corrosion. Runnells (1969) has emphasized that mixing of two solutions which are both saturated with respect to a given mineral may lead to a mixture which is either supersaturated or undersaturated depending upon the character of the original solutions and on the minerals in question. These non-linear relations can result in extensive subsurface limestone alteration.

Mixing of waters in the subsurface can be expected to be a common phenomenon in all carbonate terranes. In the simplest cases this may involve (1) mixing of different meteoric waters, (2) mixing of meteoric and deeper subsurface brines, and (3) mixing of meteoric waters and sea water.

When carbonate groundwaters are mixed, the resulting saturation state depends upon (1) the P_{CO_2}, (2) the temperature, (3) the ionic strength (salinity), (4) the degree of calcite saturation, and (5) the pH of the end member solutions prior to mixing.

Chemically, the simplest type of mixing occurs when two bodies of meteoric water, isolated from contact with the atmosphere and each at equilibrium but with different CO_2 contents, come together (Fig. 6). The resulting mixture will lie somewhere along the straight dashed line joining A and B in Figure 7, depending upon the proportions of each. The composition will move up and to the left until the saturation line is reached, with dissolution occurring in the process. This has been called "mixing corrosion" by many authors, but Wigley and Plummer (1976) prefer to call it the P_{CO_2} effect, because there are other types of mixing corrosion as outlined below. This process is most effective when each of the waters mixed is saturated with respect to the calcite. If one of the waters is supersaturated, then the effect is diminished or negligible, as can be seen in Figure 7 by joining waters of composition A and C. In natural systems this mixing can be en-
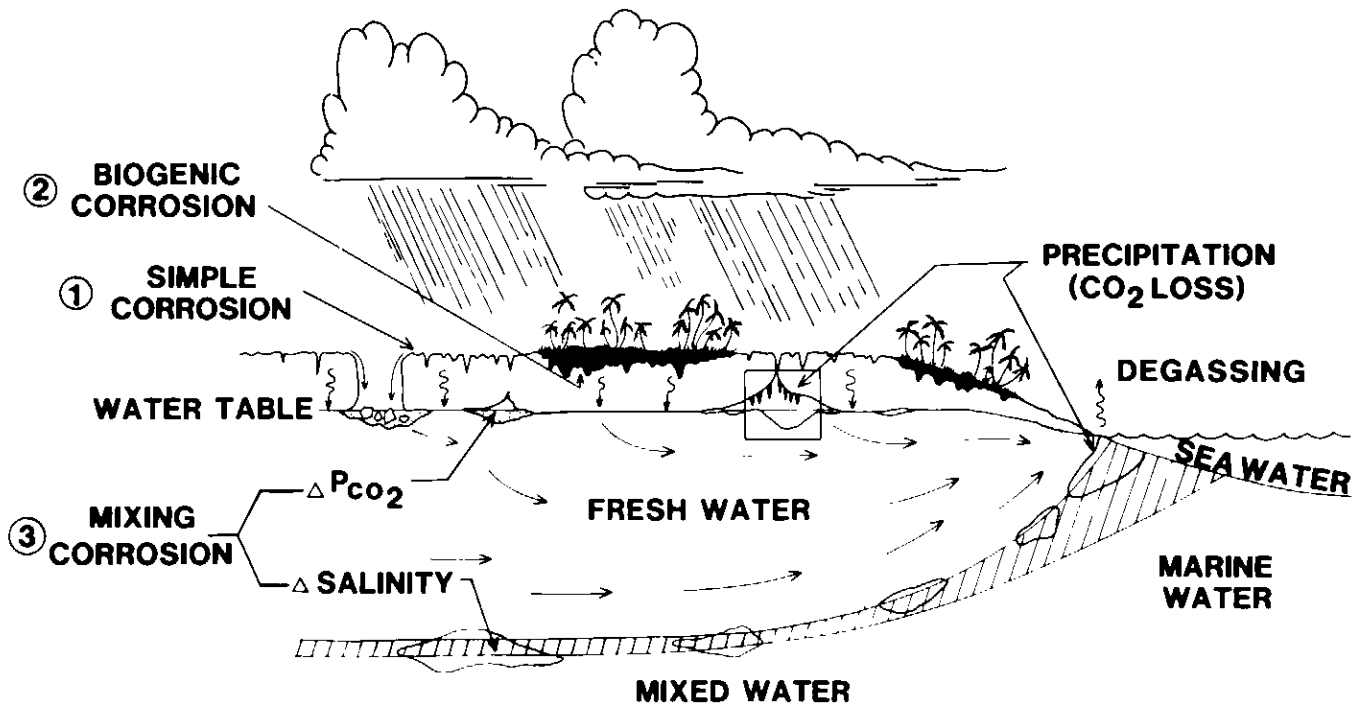

Figure 6 *A sketch illustrating the areas of dissolution (corrosion) and precipitation of carbonate during the exposure of calcite limestone to percolating meteoric waters; surface features are sketched in Figures 12 and 14, detail of square in Figure 21*

visaged as the mixing of high P_{CO_2} vadose water with low P_{CO_2} phreatic water. The effect is much reduced, however, if the vadose water is in equilibrium with a low P_{CO_2} (e.g., vadose flow), the phreatic water is in equilibrium with a high P_{CO_2} (because of slow degassing), or if the vadose seepage or groundwater is supersaturated with respect to calcite.

A similar corrosion effect may be achieved by mixing waters of different temperature. This can occur when vadose seepage is cooled at the water table. If the system is closed to P_{CO_2}, then the effect is minimal; but if it is open to P_{CO_2}, changes as small as 1°C can be significant. In reality, however, in well-ventilated caves, this is more than balanced by precipitation from waters supersaturated with respect to calcite.

When otherwise similarly saturated solutions with differing ionic strengths are mixed, appreciable undersaturation may result. In natural systems, because waters of differing salinity generally have unlike P_{CO_2} and pH values and are at different saturation states when mixed, the results may be quite variable; a spectrum of expected situations has been synthesized by Plummer (1975). Although the precise curves for any given pair of variables are different, the results follow the same general trend (Fig. 8), showing that as seawater mixes with carbonate-bearing groundwater the mixtures initially become increasingly undersaturated with respect to calcite. With continuing addition of seawater undersaturation decreases, so that mixtures containing large amounts of seawater are oversaturated. Once in the field of oversaturation, precipitation should result but is generally inhibited kinetically by high Mg^{+2}, PO_4^{-3} and SO_4^{-2} concentrations. As might be expected, mixing of waters with varying pH may also lead to corrosion with the degree of undersaturation increasing with decreasing pH.

Undersaturation can also result from a decrease in Ca^{+2} concentration in surface streams during times of high flow, which then descend to the water table by vadose flow and mix with groundwater.

Hydrostatic Corrosion. As the hydrostatic head increases in the phreatic zone, so pressure increases, and thus fluids are able to dissolve more carbonate. This process was thought by many European karst workers to be at least as important as mixing corrosion in the subsurface (Jakucs, 1977).

Oversaturation and Precipitation

Under this topic we must consider two reactions: (1) a first-order reaction in which precipitation occurs because of P_{CO_2} variations in the meteoric water, here called

water-controlled precipitation, and/or (2) a second-order reaction in which precipitation is brought about by differences in $CaCO_3$ mineral solubility, here called *mineral-controlled precipitation.*

Water-Controlled Precipitation. Precipitation of calcite (low magnesium calcite, i.e., calcite with less than 4 mole % $MgCO_3$) can only occur under conditions of oversaturation. From the earlier equation it can be seen that this may be achieved by removing some CO_2 from the system, most simply by heating the water or decreasing the pressure. Near the top of the vadose zone this occurs by either evaporation or loss of CO_2. Assimilating plants also can take their CO_2 from the water, causing precipitation. Vadose waters that are at equilibrium with a high P_{CO_2} degas and precipitate carbonate when emerging into a cave or the atmosphere with a lower P_{CO_2}.

If the CO_2 content of the water remains constant as, for example, in the phreatic zone where it is isolated from contact with the atmosphere, then theoretically the subsurface waters should be saturated with respect to calcite. But they should not be oversaturated, because there are calcite nuclei everywhere in the surrounding limestone available for precipitation. In addition, from the previous discussion of dissolution it is clear that if two waters saturated with respect to calcite are mixed, dissolution and not precipitation will occur, and the same situation seems to be true for seawater-freshwater mixing.

Under natural conditions, however, groundwaters are commonly supersaturated. Once the waters are saturated, calcite will precipitate if it can, but is often pre-

vented from doing so by various inhibiting factors. This aspect is poorly understood and several things, such as kinetics of crystal growth, flux of CO_2 and inhibition by other ions, serve to illustrate the problems. It is well known, for example, that more energy is needed to grow a crystal than to dissolve it, and so the rate of crystal growth is slow relative to dissolution. Also, the rate at which CO_2 gas dissolves in water is very fast, but the rate at which a solution evolves CO_2 to the atmosphere is very slow, and the rate of calcite growth is slower still. Finally, ions such as Mg^{-2}, SO_4^{-2} and PO_4^{-3} are all known to inhibit both dissolution and/or precipitation. If precipitation is prevented, then the saturation state will continue to rise, with the solution becoming progressively oversaturated, until a thermodynamic drive is reached that is sufficient to overcome the kinetic problem. As rates are commonly the main problem, given sufficient time precipitation will occur.

At our present level of understanding it seems that the phreatic lens and transition zones in calcite-only systems are zones of dissolution, and if cementation does take place there the process by which it does so is poorly understood. An exception might occur near the shoreline where CO_2 evasion, induced by tidal pumping, is important (Hanor, 1978).

Mineral-Controlled Precipitation. Aragonite, magnesium-calcite and calcite are the $CaCO_3$ minerals that make up most shallow-water carbonate sediments. The processes of dissolution described above are equally applicable to these minerals, but precipitation is another matter. Because
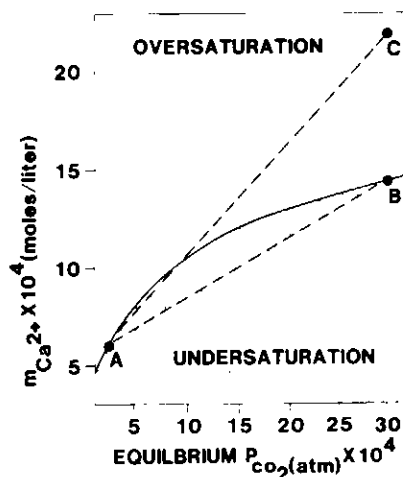
Figure 7 A diagram illustrating the non-linear relationship between equilibrium and dissolved $CaCO_3$. The mixing of waters such as A and B in any proportion will result in undersaturation. The mixing of waters such as A and C will lead mostly to oversaturation (after Thrailkill, 1968)
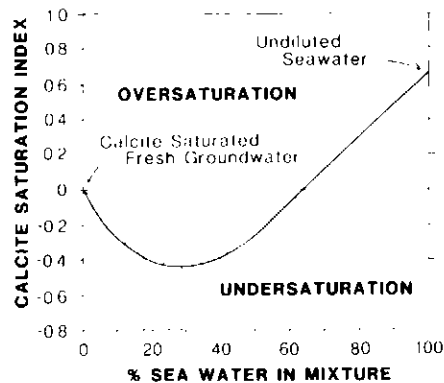
Figure 8 A generalized diagram based on families of curves from Yucatan, Bermuda and Florida illustrating the effect on calcite saturation in groundwater by mixing waters of different ionic strength, in this case seawater and meteoric groundwater. The curve is a spectrum of blends representing the mixing of seawater with a groundwater that is exactly saturated with respect to calcite

we are now dealing with a group of minerals with differing solubilities, the main process is not one of calcite dissolution, but instead (1) dissolution of the more soluble phases (aragonite and magnesium-calcite), (2) resultant oversaturation with respect to calcite, and (3) precipitation of new calcite.

$$\text{CaCO}_3 \xrightleftharpoons[\substack{\text{aragonite} \\ \text{Mg-calcite}}]{\text{calcite}} \text{Ca}^{++} + \text{CO}_3^{=}$$
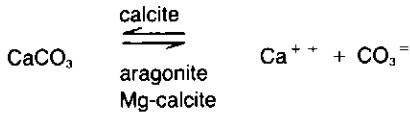
The important point here is that in this process calcite is never dissolved because oversaturation is achieved and maintained by dissolution of aragonite, and to a lesser degree by magnesium-calcite.In addition, this process leads to a wholesale change in mineralogy, from metastable carbonates to calcite.

Aragonite and magnesium-calcite are stable when bathed in sea water because it was from sea water, with its high ionic strength, that they were precipitated. All three minerals, however, are soluble in fresh water, but to differing degrees. Specifically, the solubility of magnesium-calcite progressively increases with increasing magnesium content, as the calcite lattice becomes more and more distorted. Aragonite is also more soluble than calcite and has the same solubility as magnesium-calcite with about 12 mole % $MgCO_3$ (Walter, 1983). Thus, in relative terms, magnesium-calcite components with more than 12 mole % $MgCO_3$ are the most soluble and so alter the most rapidly, followed by aragonite and magnesium calcites with about 12 mole % $MgCO_3$ and then magnesium calcites with less magnesium, the least soluble phase of all being calcite with virtually no magnesium. In addition, many of these components, because they are either biogenic or are precipitated from seawater and have relatively high trace cation contents as well as organic and fluid inclusions, are slightly more soluble than pure minerals.

All of the $CaCO_3$ mineral transformations take place by dissolution of one mineral and precipitation of calcite. What is important in this process is that *large amounts of water are not necessary*, unlike the simple calcite-water interactions described previously. Consider, for example, the aragonite-calcite reaction, which can be envisaged as occurring in a beaker of fresh water (Fig. 9-1) in which two carbonate minerals, a piece of aragonite and a piece of calcite, are immersed. Immediately after immersion (Fig. 9-2) both the calcite and the aragonite begin to dissolve until the water is saturated. As noted in the earlier section, this reaction is almost instantaneous. However, since calcite is less soluble than aragonite, the water becomes

saturated with respect to calcite first, but is still undersaturated with respect to aragonite, so the aragonite continues to dissolve. But now (Fig. 9-3) the water is oversaturated with respect to calcite, and as there is a calcite crystal present, $CaCO_3$ will precipitate as calcite crystal cement. With this precipitation the solution is now undersaturated with respect to aragonite again, and so more aragonite dissolves. Thus the process continues, with aragonite continuing to dissolve but never contributing enough $CaCO_3$ to reach saturation because of continuing calcite precipitation. Eventually (Fig. 9-4) all the aragonite is gone and the process stops, the final product being an original calcite crystal or grain surrounded by newly precipitated calcite.

Quite clearly the same reactions could begin all over again if a new aragonite crystal were introduced. Theoretically, the same beaker of water could be used to alter large amounts of aragonite and magnesium-calcite to calcite. In reality, what would happen is that the ions from the aragonite and magnesium-calcite that do not fit into the new precipitated calcite, especially Mg^{-2} and Sr^{-2}, would become so concentrated in the water as to inhibit the precipitation of calcite. In the intermediate stages, though, because of the rising trace-element concentration in the water and selective absorption on the calcite, these elements would be partitioned into the new calcite in small but ever increasing amounts. An analogous situation exists in nature. Waters at the recharge end of a freshwater aquifer have low trace element concentrations, but by the time they reach the distal, discharge point, because they have taken part in so many reactions along their path, they have relatively high trace element concentrations. Calcites precipitated in the distal parts of the aquifer will therefore have higher trace element concentrations compared to those precipitated in the proximal part (Kinsman, 1969).

An important point that must be remembered in all of this is that once the aragonite and magnesium-calcite have all dissolved to produce new calcite, the process stops. The driving force for calcite precipitation throughout the system is gone, and now, in a monomineralic all-calcite system, precipitation is localized and water-controlled.

Kinetics also are important in this system. Under natural conditions, if the freshwater diagenetic alteration of aragonite and magnesium-calcite to calcite were governed solely by equilibrium processes, then groundwaters would never be very oversaturated with respect to calcite, whereas in reality they are. Also, if the kinetics of the processes were rapid relative to the age of the groundwaters, all water should be in equilibrium with calcite, but it is not. In most instances the waters are oversaturated with respect to calcite and just undersaturated with respect to aragonite (Plummer *et al.*, 1976). Thus non-equilibrium processes, such as dissolution, precipitation and crystal growth as well as the flux of CO_2 in and out of the groundwater are again important. For example, it has been estimated that the rate of aragonite dissolution in "fresh" meteoric water is 100 times faster than the rate of calcite precipitation (Schmalz, 1967). Thus it is important to remember that waters in the meteoric environment, as long as they are still in contact with metastable carbonates, may be several times oversaturated with respect to calcite, not because the nuclei are not there to precipitate on, but because the processes are slow in the time frame of water movement.

In summary, the mineral-controlled processes involve dissolution of aragonite and magnesium-calcite and precipitation of calcite. This new calcite, called *diagenetic calcite* by some workers, can be precipitated in open voids as cement between grains or within grains, or can be precipi-
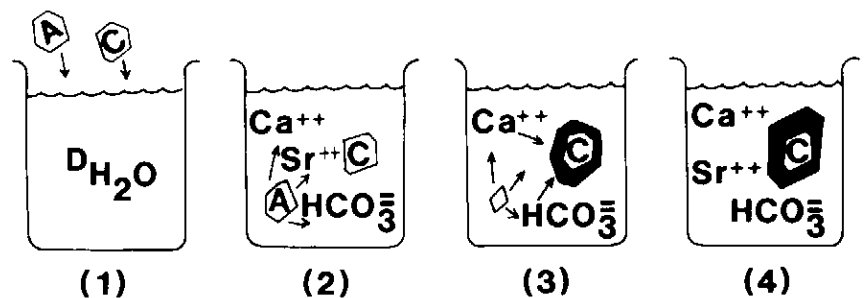
─DISSOLUTION & PRECIPITATION ─→

Figure 9 *A sketch illustrating the simultaneous dissolution of aragonite and precipitation of calcite in a beaker of distilled water*

tated on a microscale inside a particle, replacing the original aragonite or magnesium calcite.

Styles of Diagenesis

From the foregoing, it is clear that meteoric diagenesis is driven by two reactions, one between water and carbonate minerals in general, or *water-controlled alteration*, and one between water and minerals of differing solubilities, or *mineral-controlled alteration*. In a suite of metastable minerals both processes are operative; in calcite sediments or calcite limestones only water-controlled alteration takes place. The difference between these processes is well illustrated in the vadose zone. Water coming into contact with metastable minerals directly beneath the soil profile will dissolve all species until it is saturated, but as the solution percolates downward, alteration will occur because of differing mineral solubilities, not changes in P_{CO_2}. If the waters should subsequently emerge into a cave open to the atmosphere, then precipitation due to degassing and not different solubilities will take place. In contrast, if all the sediments are calcite then dissolution beneath the soil and precipitation in the cave will still occur, but no mineralogical changes will take place in the bulk of the vadose zone.

In water-controlled alteration, reactions and reaction rates are governed by differences in crystal size, grain size, porosity and permeability, or the presence and absence of fissures and cracks. Most of the changes are not controlled by the fabric of the limestone and so will be cross-cutting or "non-fabric selective" (Choquette and Pray, 1970). In contrast, in mineral-

controlled alteration, because each grain is different, changes will be "fabric-selective" and much of the original sediment fabric will be inherited in the new limestone, albeit in an entirely different way.

In the following sections we first outline the processes of water-controlled alteration, because they are applicable to all carbonates. Next we describe processes and products that occur during mineral-controlled alteration or, more specifically, during the change of a metastable suite of $CaCO_3$ minerals to calcite.

Part 1 – Water Controlled Alteration

The Rock-Air Interface

The limestone surface in the meteoric environment, whether open to the air or beneath a soil cover, is the first carbonate to come in contact with acidic waters. Limestone surfaces forming the upper part of the zone of infiltration are often intensively altered and develop features that are easily discerned in outcrops, cores and thin section and so are valuable indicators of subaerial exposure. Esteban and Klappa (1983) have recently synthesized what was previously a very diverse and widespread literature concerning these structures, and much of the section on caliche in this paper is condensed from their article. They concluded that there are really two end-member diagenetic facies here: (1) the *caliche facies* and (2) the *surface karst facies*. These diagenetic facies are not mutually exclusive; karst and caliche

may coexist at any one time and overlap in any one area. Whereas karst can develop under all climatic conditions, caliche is attributable to a generally semi-arid climatic regimen. Before outlining the attributes of these two facies it should be stressed that many subaerial exposure surfaces may not contain any diagenetic features, so the absence of such features in the rock record does not necessarily mean that the limestone was never subaerially exposed.

Caliche

Caliche (or *calcrete* or *duricrust*) is that carbonate-lithified portion of the soil profile developed commonly, but not exclusively, on carbonate sediments and rocks (Figs. 10 and 11). Because caliches are accretionary and thus commonly preserved in the rock record, they have been intensively studied over the last twenty years.

Caliche zones range from centimetres to metres in thickness and may be complex in the extreme, with part of the profile resulting from alteration of the underlying limestone, part from precipitation of new calcite and much from a combination of both sets of processes. Characterized by such features as irregular, often laminated crusts, rhizoids, diagenetic peloids, ooids and pisoids, breccias, clotted micritic and chalky carbonate, leached and vuggy porosity and microborings and iron oxides, these horizons commonly stand out in a sedimentary sequence. Because their features are similar to some formed in the marine environment, however, they are

Figure 10 *Modern hard laminated caliche (C) developed on soft Pleistocene reef limestone, Barbados (scale in cm)*

Figure 11 *Ancient caliche (C – between arrows) illustrating good alveolar texture, developed in the Carboniferous Newman Limestone, Kentucky (scale in cm)*

often overlooked (James, 1972; Read, 1976).

Lithologies. As with other soils, modern caliche is vertically zoned and upward is composed of four rock types: (1) massive chalky carbonate, (2) nodular and crumbly carbonate, (3) irregular plates and sheets, and (4) a compact crust or hardpan. The position and development of these lithologies in a vertical sequence is highly variable (Fig. 12), but massive chalky carbonate most commonly is found at the base grading down into underlying rocks or sediment.

The caliche *hardpan*, commonly cream to brown in colour, may range from 1 mm to over a metre in thickness, is composed of microcrystalline to cryptocrystalline calcite and ranges from structureless to horizontally laminated. Thicker hardpan generally is brecciated and exhibits dissolution and precipitation features, pisoids and rhizoids. The upper surface of the hardpan in semi-arid climates commonly is colonized by lichens which may cause textural and fabric changes as deep as 2 cm below the surface, producing spongy, microscopic or micritic layers composed of organic-rich and organic-poor mm laminations. Thus the fabric of the hardpan may resemble that of a stromatolite and, in fact, Klappa (1979) has called these structures "lichen stromatolites". Criteria that can be used to differentiate calcrete crusts from marine stromatolites have been outlined by Read (1976).

Beneath the hardpan or, if the hardpan is not developed, directly beneath soil cover, there is a series of thin, commonly friable, horizontal to subhorizontal plates or sheets which are separated from one another but join and bifurcate laterally. This zone, which generally grades down into nodular calcrete, may be several metres in thickness.

Caliche nodules (glaebules of soil terminology) range from silt to pebble size and from spherical to irregular or cylindrical in shape, and may be isolated or coalesced in arrangement. These structures, which are commonly concentrically laminated, have been called caliche ooids, pseudo-ooids, ooliths, peloids, pellets, pelletoids, pisolites, coated particles and, more recently, have been included by Peryt (1983) under the term vadoids.

Chalky caliche is often well developed and may be up to one metre in thickness but is generally absent in areas where the rocks have high initial porosity. The white- to cream-coloured uncemented carbonate is composed of silt-sized calcite grains, commonly microspar, with scattered nodules.

The *transition* zone down into the host carbonate is characterized by strong evi-

dence of in-place alteration and replacement of the original carbonate. Fossils, for example, are often preserved but embedded in calcified host material, or coated with calcite laminations. If developed on bedded carbonate, alteration takes place preferentially along bedding and joint planes. This basal zone may be absent or metres in thickness.

Because roots may penetrate any of the zones, *rhyzoids* - features formed by the precipitation around or replacement of roots by calcite in the form of root molds, casts of tubules, concretions or actual petrification - are a diagnostic fabric of the caliche profile. Roots both contribute to the formation of platy calcrete and lead to brecciation. This brecciation, which also may be due to expansive crystallization, results in teepee and pseudo-anticline structures.

Included in many calcrete profiles are black pebbles. The blackening may be due either to trapped organics within crystals (Ward *et al.*, 1970) or metallic oxides precipitated on fungal hyphae (Esteban and Klappa, 1983).

Petrography. The petrographic appearance of caliche is best described as messy. The predominant fabric is a clotted peloidal micrite with microspar-filled channels and cracks. Grains and fragments of limestone are separated from the surrounding matrix by circumgranular cracks due to shrinkage and expansion. Fragments of original limestone, or individual grains if a relatively young carbonate sediment, may be coated with micrite laminations, which in turn may be connected by thin laminations bridging grains. A complete spectrum of partly replaced (micritized) particles to completely altered grains may be visible. Replacement of some grains and not others commonly results in a "floating texture"

of particles in a micrite matrix.

Voids in the caliche profile often display an alveolar texture (Fig. 11), or a network of anastomosing micrite walls 100 to 150 μm across inside cylindrical to irregular holes. Some open voids may be floored with geopetal crystal silt (Dunham, 1969) which filters into cavities from the chalky zone. In other instances the rock has a more vermicular texture, or dense networks of micrite tubules and rods in a micrite matrix yielding a spaghetti-like texture.

In addition to micrite, needle fibres of calcite a few microns to tens of microns long are common. They may be a randomly oriented mesh (the "lublinite" of soil science) and occur in voids within the hardpan, they may form platy horizons or nodules, or they may be tangential with the needle-shaped crystals arranged in a band.

Another distinctive caliche precipitate is *Microcodium* or elongated to petal-shaped calcite prisms or ellipsoids or bell-shaped clusters which Klappa (1978) proved to be calcified mycorrihizae (soil fungi and cortical cells of higher plant roots).

Variations. Depending upon length of exposure and climate, the caliche profile will change with time. Following the development of weathered detritus and a protosoil by the colonization by lower plants (lichen, fungi, algae, bacteria), the caliche profile becomes differentiated into two separate horizons; water percolation and plant roots generate the upper transition zone; precipitation of calcite forms the chalk zone. As accumulation of $CaCO_3$ continues, a point is reached where soil-forming organisms can no longer maintain viability so that soil-forming processes decrease and cementation and hardpan formation increase, fossilizing the profile. Finally, the profile is so lithified that it is just another limestone and the process begins again, a protosoil forms

VARIATIONS

CALICHE PROFILE

HARDPAN
PLATES &
CRUSTS
NODULES
CHALKY
                    0.5
                    to
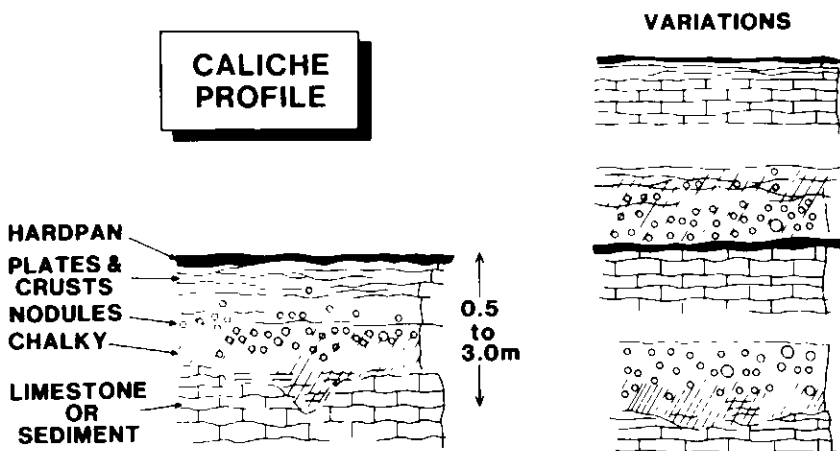   3.0m
LIMESTONE
OR
SEDIMENT

Figure 12 *Sketch of a caliche (calcrete) profile showing all the elements (left) and some of*

the observed variations from various modern examples (right)

and plant roots penetrate the hardpan, leading to brecciation and rhyzoconcretions.

As with the other features described in this article, there is a gradation from the wholly meteoric formation of caliche inland to a transition zone along the shoreline. It is common to find the hardest crusts developed in the supratidal zone and just above because there the sea spray supplies carbonate to the crust, enabling precipitation to continue at a more rapid rate; as would be expected, the calcite there has a higher $MgCO_3$ content (James, 1972). In some areas, such as the shoreline along the southern Persian Gulf where virtually the only source of water is sea spray, caliche crusts and pisolites develop but are composed of Mg-calcite and aragonite (Scholle and Kinsman, 1974).

In summary, the caliche zone is a diagenetic soil profile which involves alteration of original limestone or sediment and precipitation of new carbonate, both of which are modified or partly controlled by plants of various types. This assemblage, which changes character with time, is probably the most messy and confusing of all diagenetic zones.

Ancient Caliche. There are few well documented examples of caliche in the rock record (Esteban and Klappa, 1983), and none from the Early Paleozoic.

Surface Karst

Surface karst or exokarst, because it is a dissolution and not an accretionary phenomenon, is much more difficult to recognize in the rock record. In vertical section it is represented only by irregular bedding contacts, and so only on well exposed bedding planes can the style be determined with any confidence. Paleokarst has rarely been recognized by sedimentologists, although there is a wealth of information about modern karst in the geomorphological literature (Jennings, 1971; Sweeting, 1972; Jakucs, 1977; Ritter, 1978). It occurs in all modern climates, is the result of normal and biogenic corrosion and is slow under arctic conditions but extremely rapid in the tropics. The process of dissolution takes place both on bare rock and beneath soil, but generates somewhat different features under the two conditions. Corrosion is especially active beneath soil and intensive in the humid tropics because of high temperature and increased vegetal litter and soil. Although biogenic corrosion by carbonic acid is the most important process beneath tropical soils, dissolution due to other acids, such as fulvic, crenic, sulphuric and nitric, is also significant, but unlike the reactions associated with carbonic acid, many of these reactions are irreversible. The style of development also
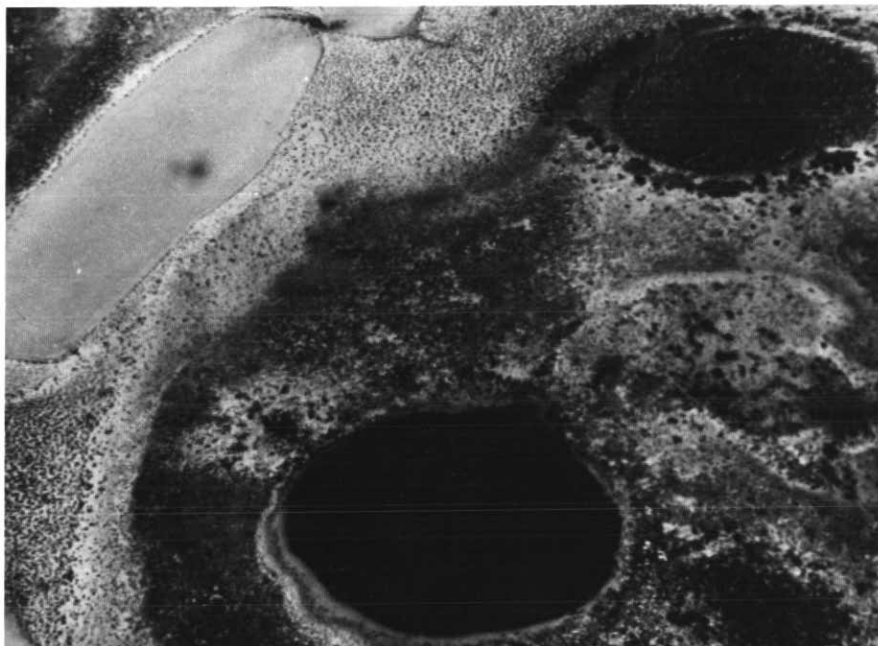

Figure 13 *Large sinkholes, several hundred metres in diameter, developed in Pleistocene limestone, Andros Island, The Bahamas, and now filled with water or vegetation*
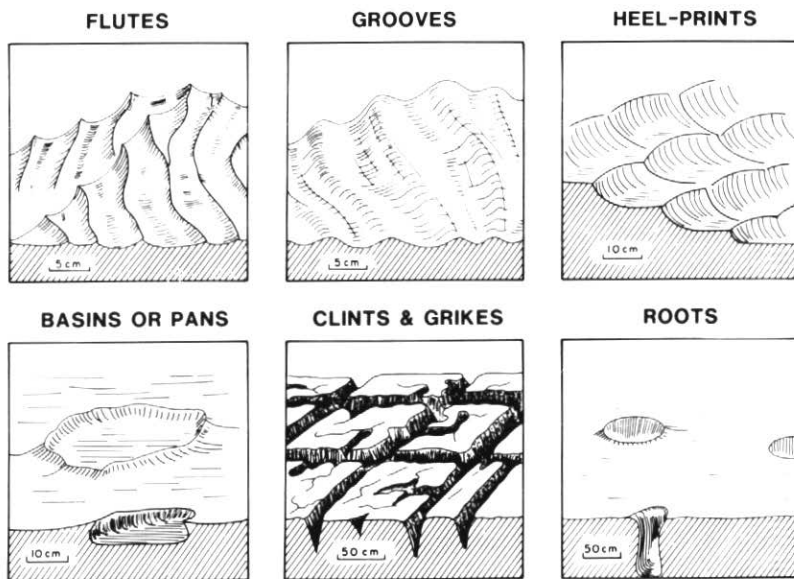
SURFACE SOLUTION SCULPTURE (KARREN)

Figure 14 *Sketches of different types of surface solution sculpture*

depends a great deal on the porosity and permeability of the limestone itself, with surface features developed best on well lithified limestones.

Regardless, it is clear that climate is a major controlling factor in the development of karst. Surface alteration at high latitudes or altitudes is restricted to slowly developing karst. In temperate or Mediterranean-type climates, karst and calcrete are common but their development is seasonal. In general, deserts display poor karst and in semi-arid regions caliche is common. But in regions of high rainfall karst forms a fantastic array of towers, jagged ridges, hogbacks, canyons and sinkholes which, together with extensive vegetation, make such regions practically impenetrable to surface travel and poorly known.

Even though surface karst is most intense in the humid tropics in areas of substantial relief, in the past most carbonate platforms were exposed as vast flat plains, just above sea level with little relief. Such a platform today is the Nullabore Plain in southern Australia (one of the world's largest karsts, ca. 200,000 km^2) which, because of the semi-arid climate, is heavily mantled with calcrete, exhibits minimal solution sculpture and contains less than a score of caves that reach to the water table and relatively few shallow caves (Jennings, 1971). Other level karst plateaus, such as the Yucatan Peninsula (Stringfield and LeGrand, 1974) or Bahama Banks, because they are in a rainy climate, look like Swiss cheese from the air, with innumerable dolines or sinkholes (Fig. 13). On the ground the limestone is fluted or pitted by solution sculpture and dotted with small, solution basins (Bourrouilh, 1974).

Surface karst features, from a practical standpoint, can be subdivided into small-scale solution sculpture or features smaller than a metre in size which can be seen in outcrop-size exposures, and large-scale features tens of metres to kilometres in size which, although sometimes seen in outcrop, are better thought of as karst landforms.

Solution Sculpture. These dissolution or corrosion features, developed either beneath a soil or on bare rock, are generally called "karren" in the English and German literature, or "lapies" in the French and eastern European literature. These features have a wide variety of shapes, and as Bögli (1980, p. 53) succinctly states, "the multiplicity of possible karren forms makes a morphological system endless". Nevertheless, there are a number of common, recurring forms which are outlined below and diagrammed in Figure 14. As a general rule the sculptures tend to be sharp and jagged on exposed rock, but rounded if below a soil cover.

Figure 15 *Syngenetic phytokarst characterized by sharp irregular cockling and numerous irregular pores in Pleistocene limestone, Andros Island, The Bahamas (arrow points to hammer for scale)*
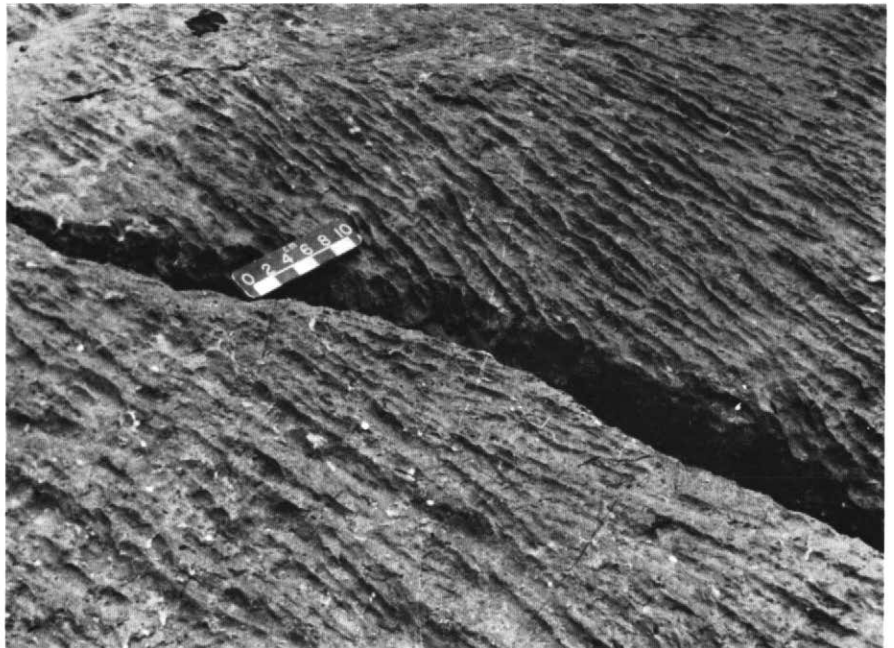

Figure 16 *Ancient rillenkarst (Late Devonian – Early Mississippian) developed on Ordovician limestone, Western Newfoundland (scale in cm)*

(a) *Small karren:* In temperate climates bare limestone surfaces are generally smooth (although the larger-scale sculptures may be sharp edged), but in tropical climates or where there is rain-splash and mist the rock surface is textured by tiny, slightly elongate, cup-like pits generally less than 3 cm in diameter called "cockling", which intersect at knife-sharp edges and give the rock a crinkly or cindery appearance (Fig. 15). In tropical regions a similar texture of black-coated, jagged pinnacles, marked by delicate, lacy dissection, has been called "phytokarst" (Folk *et al.,* 1973) because of the intensive activity of endolithic microflora in its formation. These smallest of features can form very quickly, in as little as four years. They are especially characteristic of limestones with good intergranular porosity and are well developed in the intertidal and supratidal zones.

(b) *Medium-sized karren:* These slightly larger features on bare rock develop in the form of solution runnels and solution pans. Two of the most distinctive forms are *solution flutes* (rillenkarren) or razor-sharp, finely chiselled runnels (Fig. 16) and *solution grooves* (rinnenkarren) or slightly larger runnels with rounded furrows, both of which develop on slopes of well-cemented, hard limestones. All of these forms develop quickly and may reach lengths of metres in the tropics. These may be straight on steep surfaces or meandering on flattish surfaces. On more horizontal surfaces *heel-print karren* (frittenkarren) in the form of crescentic steps are more common.

Solution basins (*kamenitza* or *kamenica*) are small, flat-bottomed pans or basins often exhibiting overhanging edges which characteristically develop on horizontal limestone surfaces (Fig. 17). They can develop as rainwater collects in small depressions, beneath humus patches or in the intertidal zone through the combined action of mixing corrosion and bioerosion.

(c) *Large karren:* Once covered by soil, increased corrosion tends to smooth all edges and points, remove small karren forms and widen and deepen pre-existing features (Fig. 18). The general term *rundkarren* is applied to these features, which range from wavekarren or wavy surfaces like corrugated tin in temperate climates to cavernous karren in the tropics.

Forms that seem to develop best under these conditions are *clints* and *grikes* (*flachkarren*) or flat-topped blocks (clints) bounded on all sides by solution-widened joints (grikes) which are rectangular to diamond-shape in plan. While most workers (e.g., Sweeting, 1972; Bögli, 1980) think that these develop beneath soil, Purdy (1974) suggests that they may also develop on bare rock surfaces. At joint intersections cylindrical pits several metres deep may

Figure 17 *Modern solution pans, (kamenitza) developed on Pleistocene limestones, Bermuda (scale in cm)*
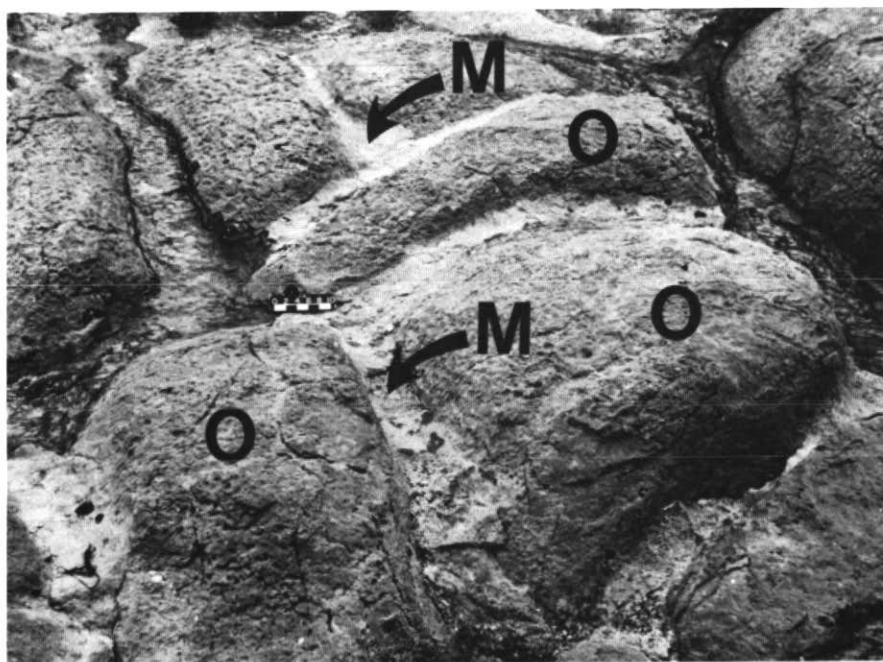

Figure 18 *Ancient rundkarst developed on Ordovician limestone (0); the depressions are filled by Mississippian limestone (M – light grey), Western Newfoundland (scale in cm)*

be produced, which may evolve into solution pipes or potholes. As the grikes widen with time, the surface passes through a phase referred to as *kluftkarren* to a stage of solution pinnacles (*spitzkarren*) or assemblies of upward-pointing pyramidal or projectile-shaped bodies of rock separated by interconnected clefts or basins. While these pinnacles may develop beneath soil-cover inland, they also form on bare rock and on coastal carbonate rocks in the intertidal zone and higher.

In addition to the soil, the roots of plants and trees in the tropics etch tortuous single and branching channels in the rock that may reach depths of 25 metres. Locally the channels may criss-cross the limestone so densely as to turn it into something resembling a sponge, in places with more

than 75% pore space. In four to ten years, for example, a hairline crack can be turned into a rock channel of arm or thigh thickness (Jennings, 1972). In Pleistocene carbonates the complex interrelationship between karst and caliche is well demonstrated by common pipes which owe their origin to root corrosion but are lined by calcrete and filled with rhyzoids, formed by organically-induced precipitation.

Karst Landforms. The most widespread of these larger features are *dolines* or sinkholes which may be funnel- to bowl- to flat, dish-shaped structures, metres to kilometres in diameter and up to 100 metres deep (Fig. 13). They owe their origin to dissolution beneath a soil cover or subsurface dissolution and either gradual subsid-

ence or collapse. Breccias that fill collapse dolines are characterized by mixed soils and speleothems together with the v-shape of fallen overlying beds.

The other large-scale features, such as cenotes, cockpits, magotes, uvalas, karst vallies and poljes, are more in the realm of geomorphology, and excellent summaries of these landscapes can be found in general texts on karst (e.g., Jennings, 1971; Sweeting, 1972; Jakucs, 1977; Bögli, 1980).

Subsurface Karst

The Vadose Zone
The zone of infiltration is dominated by processes of intensive physicochemical and biological corrosion related to intensive organic activity (Esteban and Klappa, 1983).
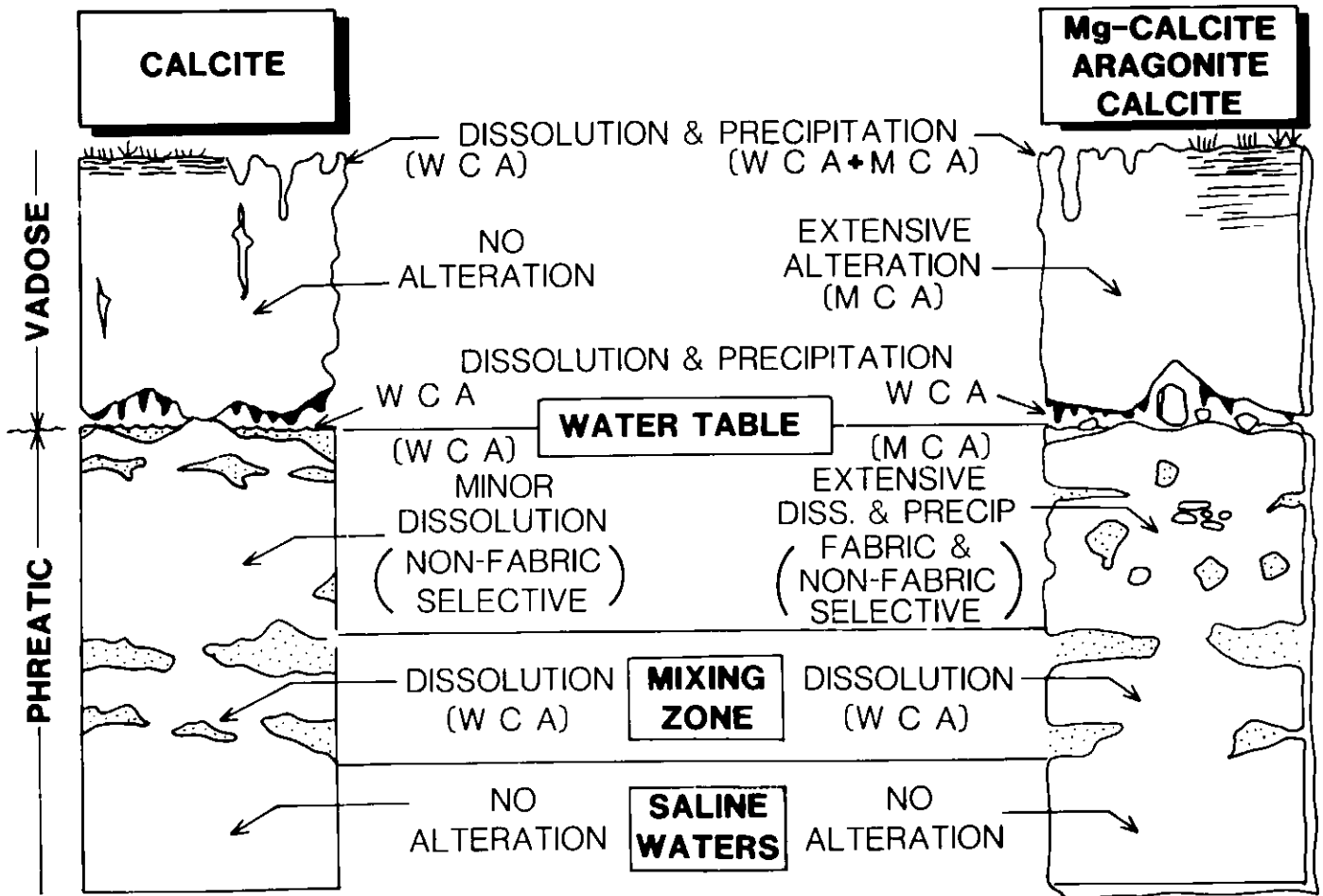

Figure 19 A sketch illustrating the different diagenetic processes that affect a carbonate composed of calcite (sediment or limestone), versus one composed of a mixture of magnesium – calcite, aragonite and calcite. Water-controlled alteration (WCA) is driven by evasion and inva- sion of CO_2 while mineral-controlled alteration (MCA) is driven by differences in $CaCO_3$ mineral solubility

Vertical caves are pronounced here, and collapse breccias may be common. Precipitates are usually fine grained (moonmilk) and/or globulites (popcorn).

As the CO_2-rich acidic waters emerge from below the soil they dissolve carbonate quickly, become saturated, and lose their aggressiveness within a few decimeters of the soil zone. Once the waters are saturated in an all-calcite carbonate host rock, no further dissolution or precipitation takes place. Consequently, this zone is relatively "inactive". Reaction does take place, however, if the limestone grains are extremely small and so reactive, or if mixing of vadose seepage and vadose flow occurs, or if large cavities open to the atmosphere are encountered, or if there are changes in temperature.

Conversely (Fig. 19), if the sediments are composed of a mixture of aragonite, magnesium-calcite and calcite, each with a different solubility, then this is a zone of intensive activity (see part 2 of this discussion).

Under conditions of vadose flow, the system is effectively *open to CO_2* and the aggressiveness of the waters after initial dissolution is governed by the diffusion rate of CO_2 across the water-air interface. If the channels are large, rapidly flowing water may be aggressive to depths of 100 metres or so (Thrailkill, 1968). Dissolution also occurs, when vadose seepage and vadose flow meet, by mixing corrosion.

Many caves found in the vadose zone are due to dissolution at perched water tables or are relic water-table caves abandoned when the water level dropped. It is clear that some caves, however, particularly those strongly elongated vertically, form in the vadose zone itself, either to survive unchanged or to be modified by phreatic processes.

The Water Table
This realm, including the base of the vadose zone, the water table surface and the upper part of the phreatic zone, is one of intense chemical activity, perhaps more intense than anywhere else in the shallow subsurface.

Dissolution. Most dissolution occurs at or below the water table, in the phreatic part of this realm.

(a) *Processes:* If the system is entirely subterranean, closed to outside air, then this region where vadose and phreatic waters mix is a level of intense corrosion. It is here that many caves are formed. Phreatic water movement is generally horizontal and the origin of the waters may be allochthonous, from outside the local area. Since the level of the water table varies seasonally, the water table may rise into the vadose zone during times of flood,

resulting in a whole zone of caves at this level.

(b) *Features:* There are a wide variety of dissolution features, such as passages, channels and shafts (Fig. 20), which can be related to both the type of water flow and lithology (Bögli, 1980). Smaller cave karren are superimposed on the larger cavities. The walls and ceilings may be smooth or pockmarked with corrosion pockets, dimples and pits, or textured by rills and grooves similar to surface karst and especially common where vadose waters emerge. Pendants of relic limestone in the form of cones of rock may hang down from the ceiling or protrude up from the floor.

Scallops or crescentic, shell-shaped dissolution features can form on the surface where a stream flows over limestone, but are particularly common in caves. The crests in these features lie transverse to flow and the steeper slopes face downstream.

Precipitation. Most precipitation, but not all, takes place in the meteoric part of this realm, in the upper parts of caves and cavities above the water table.

(a) *Processes:* Regardless of the mineralogy of the sediment or rock, if the system is ventilated with atmospheric air, the reverse occurs. High P_{CO_2} vadose waters entering the top of water-table caves equilibrate with low-P_{CO_2} atmospheric air, degas and precipitate carbonate. Exactly the same phenomenon occurs as springs emerging from a hillside precipitate travertine (Julia, 1983; Chafetz and Folk, 1984).

Flowing waters in the cave are also at equilibrium with atmospheric air, and so precipitation only occurs because of variations in temperature and turbulence.

It is a paradox that once caves are open and can be visited by geologists, the processes which formed them largely have ceased, and they are in the process of being decorated by various precipitates (Moore and Sullivan, 1978; Thrailkill, 1976).

(b) *Features:* Subterranean precipitates can be subdivided into two types: (1) calcareous *tufa* – soft porous rock to which plants contribute significantly, and (2) calcareous *sinter* (speleothems) – nonporous, crystalline, hard limestone.

The most common tufa is *moonmilk*, which is composed of microscopic carbonate crystallites or lublinite (random needle crystals); although plastic and containing from 35% to 75% water when precipitated, upon drying the deposit turns to a powder. Plants play a significant role in the precipitation by removing CO_2 from the water, and the resulting crystallites are enmeshed in a net of filaments from bacteria, actinomycetes and algae.

Sinter is precipitated either from thin films of water flowing over the rock or in pools of water. Precipitation from water films results in crystals that grow outward from the rock surface for only a short distance, with growth terminated at the air-water interface (Fig. 21). As a result, the outer surface of the calcite is smooth, with scalenohedral terminations never developing. This style of precipitation is typical of the vadose part of the cave, and forms flowstone and dripstone (Fig. 22).
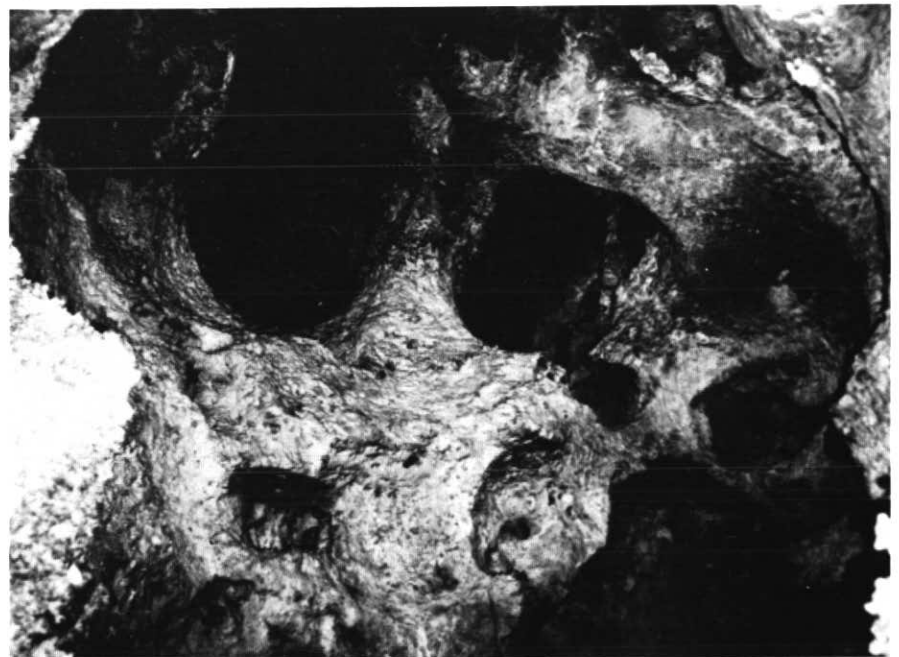

Figure 20 *Large dissolution cavities (ca. 1.5 m in diameter) excavated into Permian carbonates,* Carlsbad Caverns, New Mexico – note the lack of decoration
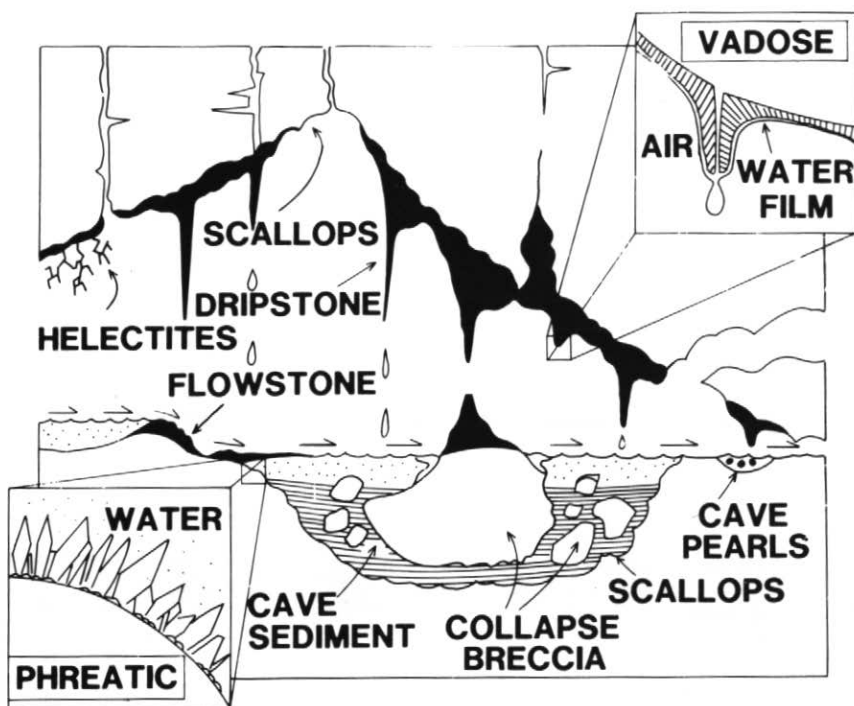
Figure 21 *A sketch illustrating the styles of precipitates (sinter) formed above and below the water table in a cave open to the atmosphere*
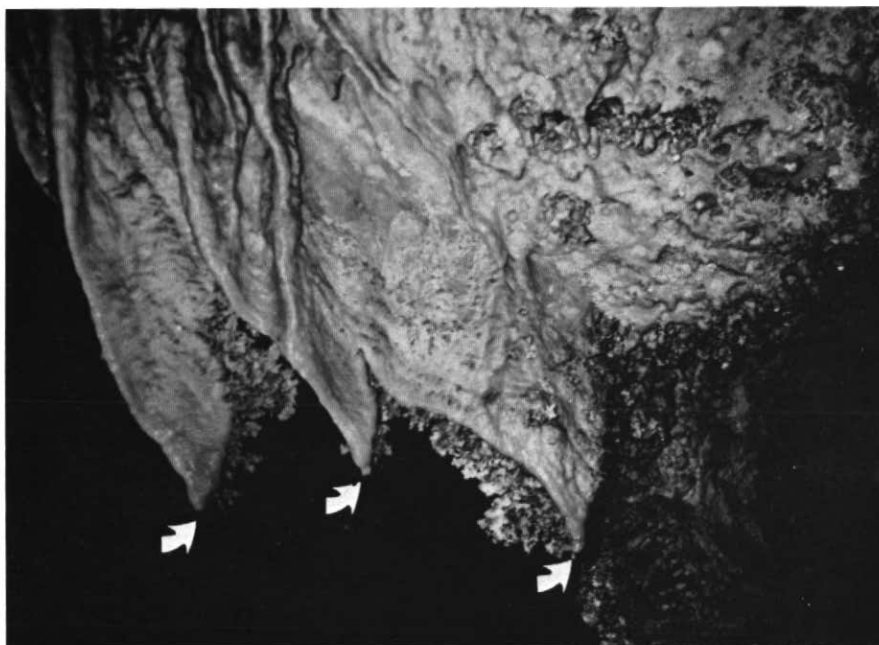

Figure 22 *Dripstone curtains about 1 m in length decorated by cave popcorn, Carlsbad Caverns, New Mexico – arrows point to water droplets*

Dripstone ranges from draperies to "soda-straws" to stalagmites and stalactites to helectites. Deposition begins from a drop of water on the ceiling, with precipitation beginning at the area of attachment. Since CO_2 is given off from the surface of the drop, precipitation starts there, causing a ring of calcite. Ring is added to ring to form a tubular structure – the "soda straw". Water flowing as a film over the exterior surface of the soda straw deposits a second type of calcite which constructs the familiar conical or candle-shaped form. This outer coating is most commonly composed of elongate calcite crystals which, in sections cut normal to the stalactite long axis, have their long and optic axes radially disposed. Some of the growth surfaces are discernible by bands which contain abundant impurities. In an effort to reconcile the growth of large crystals with a complex internal fabric from a thin film of water, Kendall and Broughton (1978) suggest that precipitation takes place initially from thin water films in the form of tiny crystallites which grow syntaxially. The columnar crystals form by a process of syntaxial coalescence immediately behind the growing surface. This two-stage process leads to fretted crystal boundaries and not to straight ones, as might be expected from competitive growth of large crystals. Those crystals in speleothems with para-axial boundaries are interpreted to be due to precipitation during episodes of cave flooding.

In addition to these deposits in the vadose part of the cave, bars of sinter called *rimstone* form on the cave floor, where water from a pool flows over an obstruction as a thin film. When it flows over this rim there is an increase in the loss of CO_2 and calcite is precipitated. Most precipitation in pools or beneath the water table in the phreatic part of the zone, however, is different. Because there is no bounding surface, crystals grow out into the water equally in all directions as true crystals with scalenohedral terminations (Fig. 21). The largest crystals grow in the quietest water; the more the water flows, the more numerous the calcite nuclei are and the closer the calcite crystals stand, and in rapidly moving water, rounded surfaces like cauliflower, composed of innumerable tiny crystals, can form. The seed crystals for precipitation are thought to form at the water surface because of CO_2 diffusion into the air. These may sink or may aggregate into small rafts. Cave pearls (concentrically laminated pisoids) form in pools of moving water or splash pools.

Plant life in caves has important geological implications. As caves lack light, heterotrophic bacteria (including actinomycetes or mold-like filamentous bacteria), algae and fungi as well as chemo-autotrophic

bacteria are the most common forms. In addition to their contribution to the formation of moonmilk, these organisms result in the precipitation of other minerals. The black, sooty coating on cave walls and pebbles is a variety of manganese minerals whose precipitation is aided by specialized bacteria. On the other hand, chemautotrophic iron bacteria, which obtain N_2 from the air and carbon from iron carbonates, liberate ferrous iron, which is oxidized to give a red colour to cave sediments.

The Lenticular Zone

Carbonate-water interaction in this shallow phreatic setting is poorly understood because it is inaccessible, and conclusions must be drawn from theoretical calculations and laboratory experimentation (Plummer, 1975) and data from wells (Back et al., 1979).

Dissolution. There is a brackish zone of mixing at the base of the fresh-water lens. Theoretical calculations and observations, especially near the shoreline, from Yucatan (Back et al., 1979; Hanshaw and Back, 1980), Florida (Back and Hanshaw, 1970) and Bermuda (Palmer, 1984) indicate that this mixing zone between fresh and marine waters is dominantly one of corrosion and porosity formation. It is significant to note that corrosion becomes more intensive when fresh and hypersaline waters mix (Plummer, 1975). Since the saturation state is dependent upon so many factors, however, in some areas of the Florida aquifer mixing does not result in undersaturation.

In areas far removed from the effect of sea water, Jakucs (1977) has noted that caves are common at the base of the lenticular zone (see Vernon, 1969, for examples in the Florida aquifer) and has ascribed their formation to hydrostatic corrosion, but some of this may be due to mixing of fresh waters from the upper phreatic and more stagnant and saline waters from the lower phreatic.

Precipitation. There is considerable confusion about calcite precipitation in the lenticular zone. From the above, it appears that corrosion is the dominant process in calcite limestones. Hanor (1978) has proposed several processes to promote degassing and so precipitation near the area of outflow, but there does not seem to be much suggestion of widespread precipitation.

Syngenetic Karst

The rock-air interface in metastable carbonates is particularly susceptible to alteration because of the generally porous nature of the sediments. The sediment surface hardens almost instantaneously, as a thin, millimetre-thick crust of altered grains ce-

mented by calcite. This grey crust also contains algae and fungi and develops within months to years in quarries and new road cuts. The porous nature of the sediments also aids in the rapid and deep development of caliche, particularly in semi-arid climates.

In spite of the often poorly consolidated nature of metastable sediments during early phases of meteoric diagenesis, karst processes are ongoing. The products have been called syngenetic karst (Jennings, 1971) because they develop during lithification. Not all karst features develop, however. Solution sculpture is minor, except where calcrete is exposed directly to rainwater. Solution pipes are common, especially those associated with roots, but the familiar solution features along joint intersections are missing. Caves are well developed, generally due to lateral dissolution at the water table and minor vertical dissolution. Because excavation accompanies lithification and the surrounding poorly lithified sediments are inherently weak, roof collapse dominates more of their history than is characteristic in consolidated limestone and is a distinctive trait of these early caves. Once well lithified into calcite limestone, the full spectrum of karst features may develop.

Ancient Karst

Since karst is a dissolution phenomenon, a major problem is recognizing when dissolution occurred (Wright, 1982), i.e., whether the features observed were formed soon after deposition, or are the result of present processes, or were formed at some un-

known intervening time. Particularly troublesome is intrastratal or subjacent corrosion, which forms in the subsurface along lithological boundaries and creates features that resemble surface karst and could be mistaken for such. The surest way of confirming that the feature is fossil is to find skeletons or calcretes cemented onto, or borings penetrating into, the paleosurface. Other criteria that might be useful in certain cases are suggested by Read and Grover (1977) and Wright (1982). On a smaller scale there is a problem in the differentiation of paleokarst surfaces and stylolites (Walkden, 1974).

PART 2 – MINERAL CONTROLLED ALTERATION

This diagenesis can be seen going on today or, at least, inferred to have taken place recently in Holocene and Pleistocene carbonates in numerous warm, sunny places, and so is exceptionally well documented. The reader is referred to excellent recent reviews by Bathurst (1980), Longman (1980) and Flügel (1982) for additional information.

The Process

The common stages by which metastable carbonate components alter to calcite are now well known (Friedman, 1964; Land, 1967; Purdy, 1968; Matthews, 1974). Soon after meteoric waters begin percolating through a sediment, small elongate or equidimensional calcite crystals precipitate as cement on grain surfaces. They grow equally on magnesium-calcite or aragonite particles and earlier submarine cements,
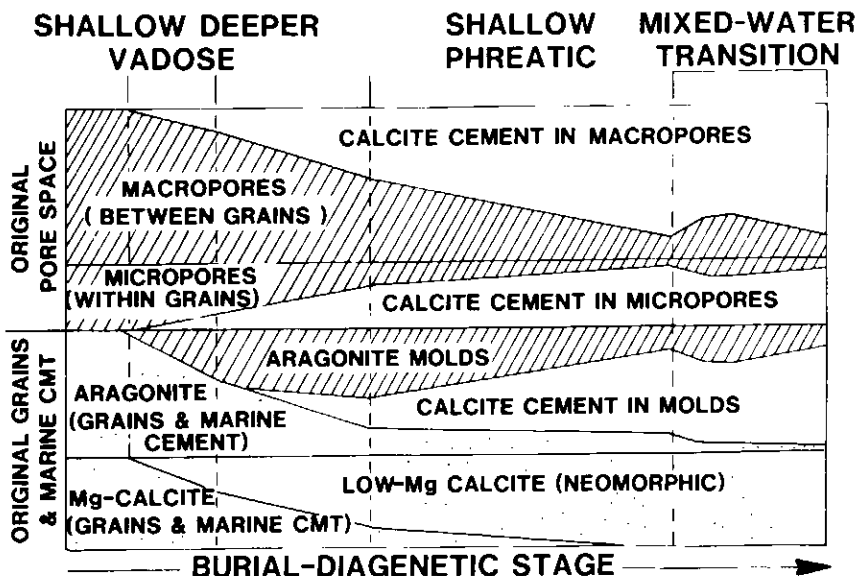
Figure 23 Idealized diagenetic evolution of an aragonite and magnesium-calcite sediment as it passes through meteoric diagenetic zones, in a terrain of low to moderate rainfall. Inferred changes in the transition at the base of the lenticular zone are based on calcite saturation relationships suggested in Figure 7

giving the sediment some coherence. The next step, which occurs as more cement is being precipitated, is the start of alteration of magnesium-calcite components to calcite, by dissolution of Mg-calcite and reprecipitation of calcite on a microscale (Oti and Muller, 1984). By now, most particles are coated with a rind of calcite cement which may constitute up to one quarter of the rock volume. It is only now that aragonite changes, either dissolving to form molds or altering to calcite across an alteration front with much textural preservation. Dissolution of aragonite produces copious quantities of $CaCO_3$ to be precipitated locally as cement both inside and between particles and in new holes created by aragonite dissolution. By the time all aragonite has gone, the sediment has generally been transformed into hard calcite limestone (Fig. 23). In this system it seems that almost all the cement needed for lithification can be derived locally from aragonite dissolution. So in spite of wholesale fabric rearrangement, there may be only minor net loss of carbonate and just a change in the style of porosity, from intergranular to moldic.

Cementation

By the term "cement" we mean here the growth of precipitated calcite into open pore space, either between grains, or inside grains, or into holes newly created by the dissolution of aragonite. Techniques for differentiating cement from neomorphic or altered pre-existing precipitates are outlined by Bathurst (1975, p. 416-439) and Dickson (1983). Among the more useful criteria, although neither is foolproof, are (1) increase in crystal size away from the substrate and (2) development of scalenohedral terminations directed away from the nucleation surface or substrate. Even these criteria are best checked in fossil limestones by staining and cathodoluminescence for the possibility that the crystals are neomorphic (e.g., Bathurst, 1983).

Vadose and phreatic cements generally have differing morphologies and so can provide a useful guide to the residence of a limestone in different parts of the meteoric diagenetic environment. Many examples of these cements are illustrated in Bricker (1971); their main attributes are outlined below.

Vadose Cements. These precipitates grow from void walls into pores that may at different times be completely filled with either water or air or both, with water just wetting the grain surfaces. This, and the fact that vadose percolation of water is not uniform, results in cements that typically show quite irregular distribution. In outcrops or subsurface cores of Pleisto-

METEORIC CEMENTS
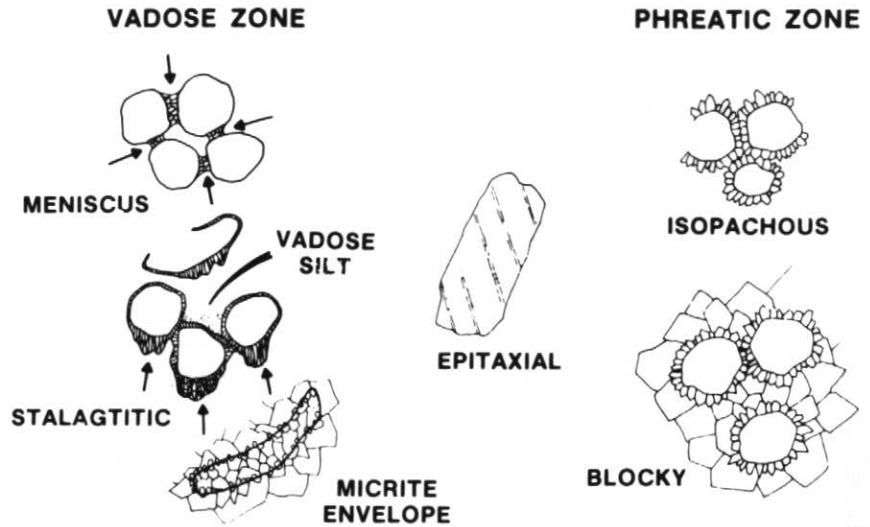
Figure 24 *The different types of cement precipitated in the vadose (left) and phreatic (right) parts of the meteoric diagenetic environment. Epitaxial cements on echinoderm particles may be precipitated in either*
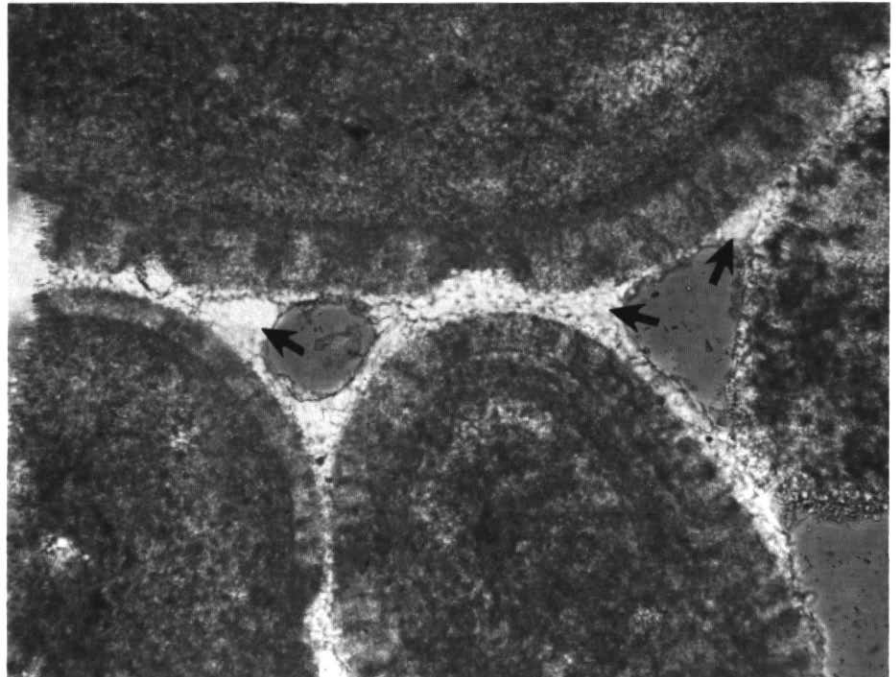
Figure 25 *Pore-rounding cements, probably of vadose origin, in ooid grainstone. The arrows show location of meniscus-style cement bordering partly filled interparticle pores. Ste. Genevieve Formation, Bridgeport field, southeastern Illinois (width of photograph is 0.5 mm)*

cene limestones it is common to see relatively well cemented areas only as millimetres away from areas that are uncemented. Although some cements may be in layers of equal thickness around pore walls (precipitated when the pores are filled with water), more commonly cements reflect growth outward to capillary water-air interfaces of partly filled pores and so have meniscus or pendant shapes (Fig. 24). Crystals in these settings rarely have good terminations (Fig. 25). Meniscus and pendant cements are excellent criteria for vadose precipitation, but if cementation is prolonged and pores are filled, these characteristic shapes are often lost. In our experience, epitaxial overgrowth cements also develop here, particularly on echinoderm grains and some benthic foraminifer tests. It also seems that some early cements in this zone become detached from pore ceilings and fall to the bottom of the pores to form geopetal layers of vadose crystal silt (Dunham, 1969).

Phreatic Cements. Pores in the phreatic zone, unlike those in the vadose, are always filled with water, and so crystals can grow unimpeded except by intercrystalline competition. Thus cement rinds formed here, at least in the shallow lenticular phreatic, are either well developed isopachous layers of calcite crystals around pore walls (Fig. 24) or blocky calcite (Fig. 26). As a general rule, crystals are somewhat larger than in the vadose zone and epitaxial growth on echinoderm particles is more rapid.

Staining. A useful technique for differentiating separate stages of cement precipitation and determining cement morphologies is staining with an acid solution of potassium ferricyanide, which imparts a blue stain to iron-rich calcites (Dickson, 1966; Lindholm and Finkleman, 1972). Since the vadose zone is an air-water system, conditions there are generally oxidizing, so that any iron is in the ferric state (Fe^{+3}) and cannot be incorporated into calcite. As a result, vadose calcite cements are iron-poor. On the other hand, phreatic waters are often reducing, and so iron is in the ferrous state (Fe^{+2}) and can be incorporated easily into the calcite lattice, with the result that phreatic cements are commonly slightly iron-rich. There are, however, some caveats to this concept: first, a source of iron must be present; second, perched water tables are common in the vadose zone; third, not all phreatic waters are reducing; and fourth, many ferroan calcite (and dolomite) cements form in the deep subsurface, below the lenticular zone. Consequently, the interpretation of the stain should be used with caution, remembering that the lack of an iron-rich calcite cement

does not preclude the possibility that it is phreatic in origin.

Cement Stratigraphy. Identification of stages of cement precipitation can be a powerful tool in ascertaining the sequence of diagenetic environments through which a limestone has passed (Fig. 27). In some areas such stages have been found to be systematically arranged and correlatable over tens of kilometres through tens to hundreds of metres of limestones (Meyers

and Lohmann, 1984). This "cement stratigraphy" (Meyers, 1974) can be best unravelled by using a combination of staining and cathodoluminescence.

Alteration of Magnesium-Calcite Components
On the modern sea floor particles and cements are composed of micritic and fibrous magnesium-calcite crystallites (Folk and Land, 1975). As outlined above, magnesium-calcite, because of its generally

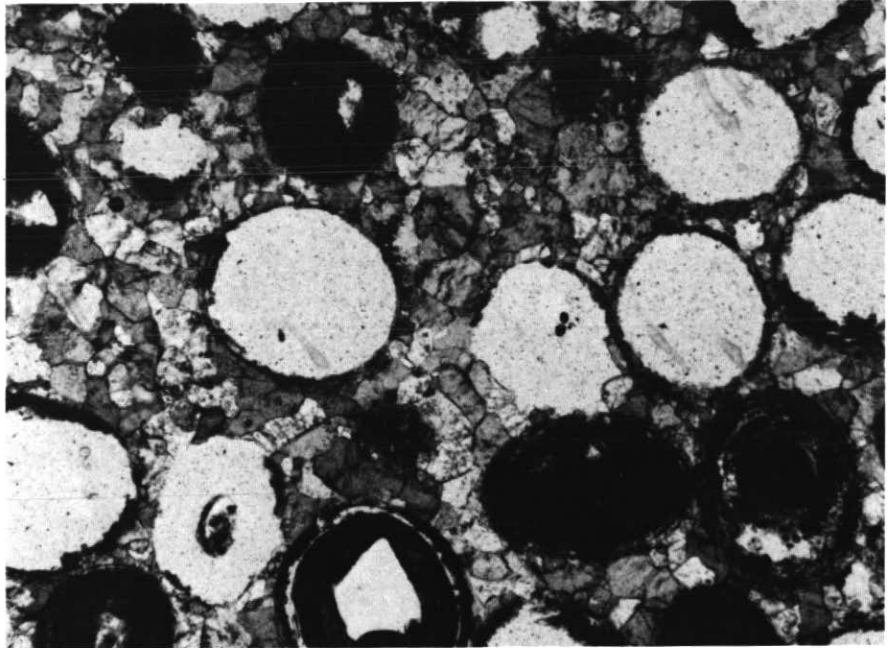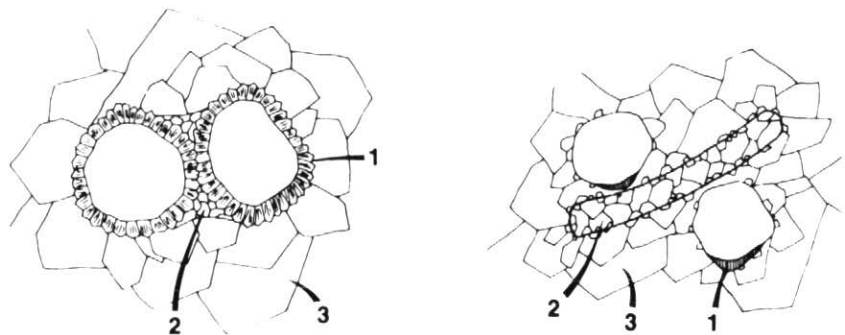Figure 26 *Partially to completely dissolved ooids with some aragonite remaining surrounded by medium crystalline phreatic calcite cement* (photomicrograph, partially polarized light, is 2.5 mm across)

CEMENT STRATIGRAPHY

1. MARINE	1. BEACHROCK
2. VADOSE	2. VADOSE
3. DEEP PHREATIC	3. DEEP BURIAL

Figure 27 *A sketch illustrating two different examples of cement stratigraphy*

greater solubility in dilute waters, begins to alter to calcite before aragonite, very soon after percolating waters have entered the sediment. Because the change does not involve a modification of the original crystal habit, textural changes that accompany alteration to calcite are invisible with the light microscope (Fig. 28). There is, however, dissolution-reprecipitation, and under the SEM it is clear that micron-size crystallites undergo slight enlargement (Towe and Hemleben, 1976; Oti and Muller, 1984). Regardless, the precise crystal orientation of crystals is preserved, which is especially evident in echinoderm tests.

Skeletal magnesium-calcite is heterogeneous, divided into domains having different levels of $MgCO_3$ (Moberly, 1970). Although the replacement process is not precisely known, magnesium calcites do dissolve incongruently, probably reflecting the greater solubility of the $MgCO_3$ phases (Schroeder, 1969). Thus, it is probable that the $MgCO_3$-rich domains dissolve first and calcite is simultaneously precipitated. Under the SEM the new calcite can be seen to have grown epitaxially on adjacent calcite surfaces, preserving the original crystallographic orientation (Benson and Matthews, 1971). Consequently, the resultant calcite component is partly original and partly diagenetic. Most particles, however, are somewhat porous, and it appears that even before the skeleton loses much $MgCO_3$, calcite cement is precipitated into these small intragranular pores.

A potentially useful technique for differentiating between original magnesium-calcite and calcite components in the fossil record, since both display excellent microstructure, has been suggested by Richter and Füchtbauer (1978). Since calcite precipitated from seawater contains negligible iron, grains with excellent fabric preservation but composed of iron-rich calcites must, at some stage, have altered in contact with phreatic or deep subsurface waters. As calcite is stable and should not alter, these iron-rich calcite grains must have been magnesium-calcite originally. The converse, however, is not true, as magnesium-calcite grains altered in the vadose zone would also be iron-free calcite. In addition, some aragonites calcitize with considerable iron incorporation (Sandberg and Hudson, 1983), but the replacement textures are coarsely crystalline.

Alteration of Aragonite Components
Aragonite is volumetrically more abundant than magnesium-calcite in most modern shallow-water, low-latitude carbonate sediments (e.g., most ooids, gastropods, codiacean algae, dasyclad algae and corals are aragonite). Particle and cement habits range from microcrystalline to platy to acicular to fibrous (James and Choquette,
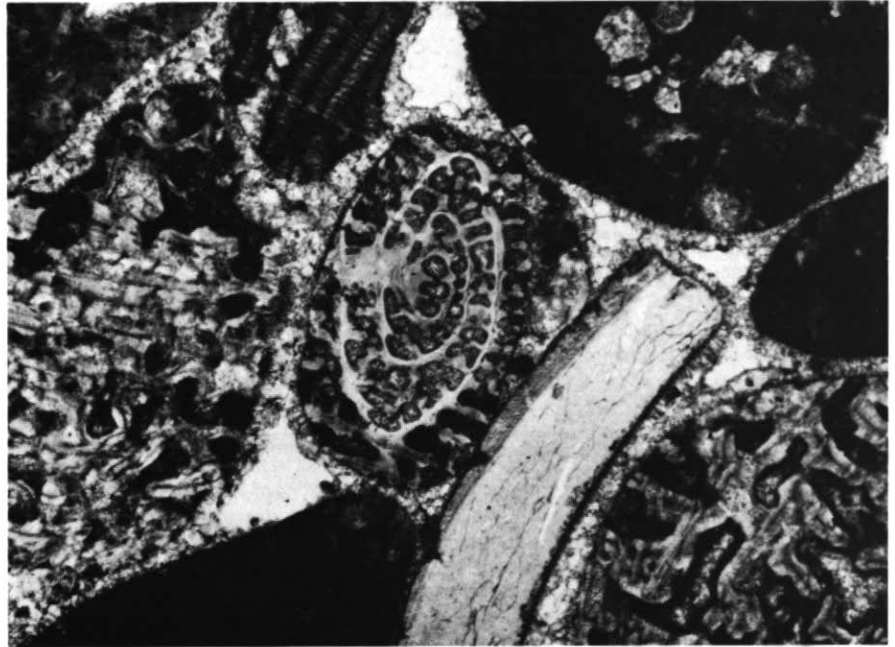
Figure 28 *Pleistocene limestone (Bermuda) in which the Mg-calcite grains (Foraminifera – left, lower right, centre) are now calcite while the mollusc (centre) is still aragonite; the isopachous cement rind is probably phreatic (photomicrograph, partially polarized light, is 2.0 mm across)*
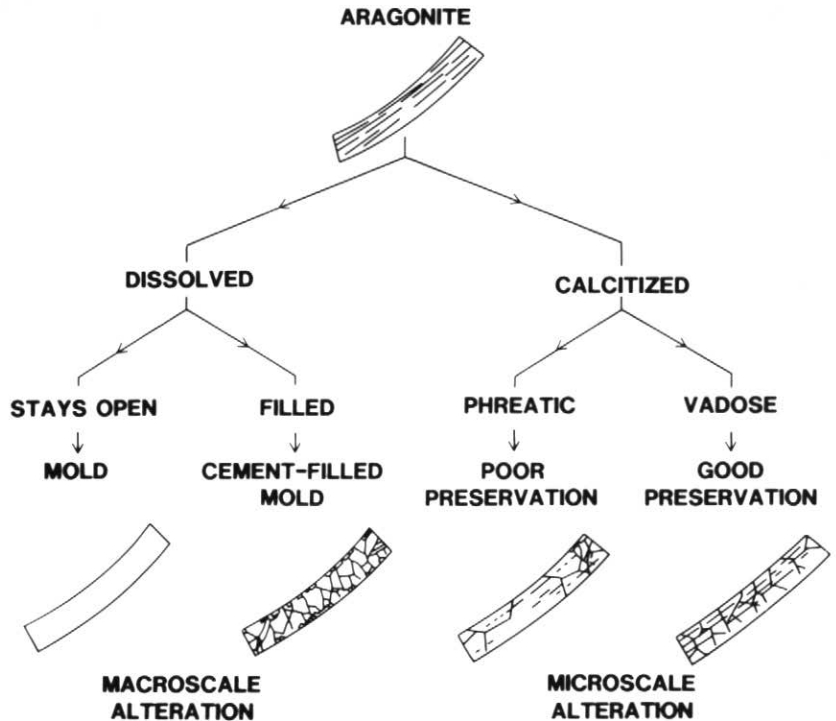
Figure 29 *A sketch illustrating the different ways in which an original aragonite skeleton may be changed during meteoric diagenesis. If dissolved, a mold is formed which may later be filled by cement. If calcitized, some relics of shell structure (often including aragonite relics) remain in the replacement calcite. The best preservation generally occurs in the vadose zone*

1983), though most modern marine cement may be acicular. Unlike magnesium-calcite, the change from aragonite to calcite involves a wholesale crystallographic change from orthorhombic to hexagonal and the resultant process is one of complete dissolution of aragonite and precipitation of calcite.

Aragonite dissolution is controlled by the microfabric of the particle, skeleton or cement. It begins in areas with the highest organic content or smallest crystal size, then proceeds to etch along intercrystalline boundaries commonly yielding a "chalky" aragonite, and finally dissolves the crystals altogether (James, 1974). This dissolution may begin at one point and expand outward or it may proceed from numerous starting points.

From a geological viewpoint, it is the way in which the subsequent calcite precipitation takes place that is important, and two styles are common (Fig. 29):

(1) *Macroscale:* In some cases the whole component – grain, fossil or cement – dissolves away, leaving a hole that may or may not be filled with calcite cement (Fig. 26). This is probably the single most important process creating small-scale porosity in the meteoric environment. The mold may be filled quickly by cement in the meteoric zone or may remain open during burial to be filled much later by deep subsurface cements, brines or even hydrocarbons.

A note of caution! In our experience, magnesium-calcite grains in the meteoric environment do not generally dissolve to form molds (but see Schroeder, 1979, for such an example). Recent studies of pre-Pleistocene limestones, however, suggest that under deep burial conditions and/or later flushing by waters in near-surface environments, some original low-magnesium calcites may dissolve selectively, leaving molds (Donath et al., 1980, James and Klappa, 1983; Sandberg, 1983). This may be due to subtle differences in crystal size, contained organic matter or domains of unreplaced calcite of low, but not lowest, magnesium content (e.g., 4 to 10 mole %).

(2) *Microscale:* In other examples, dissolution of aragonite takes place simultaneously with precipitation of calcite on the opposite side of a water film nanno-metres to micrometres in thickness (Wardlaw et al., 1978), and the basic structure of the original component is partially retained (Fig. 30) – that is, the resulting "calcitized" aragonite is generally a mosaic of calcite crystals which cross-cut original fabric, with the former structure outlined by relics of organic matter and other insoluble material (James, 1974; Pingitore, 1976). This process generally is called neomorphism. In some instances replacement is incomplete and tiny crystallites of aragonite remain as relics entombed in the new calcite (Sandberg et al., 1973; Sandberg and Hudson, 1983). Also, because of the fine scale and the microenvironment in which alteration takes place, the concentration of Sr^{+2} may quickly rise in this water film and so be partitioned back into the new calcite in relatively large amounts (rarely, up to almost 1%; Davies, 1977).

Because fine-scale replacement results in calcitized components that clearly resemble their aragonitic precursors, interpretation of original aragonite mineralogy in ancient limestones is often difficult. Sandberg (1983) suggests a range of criteria that may be used with increasing levels of
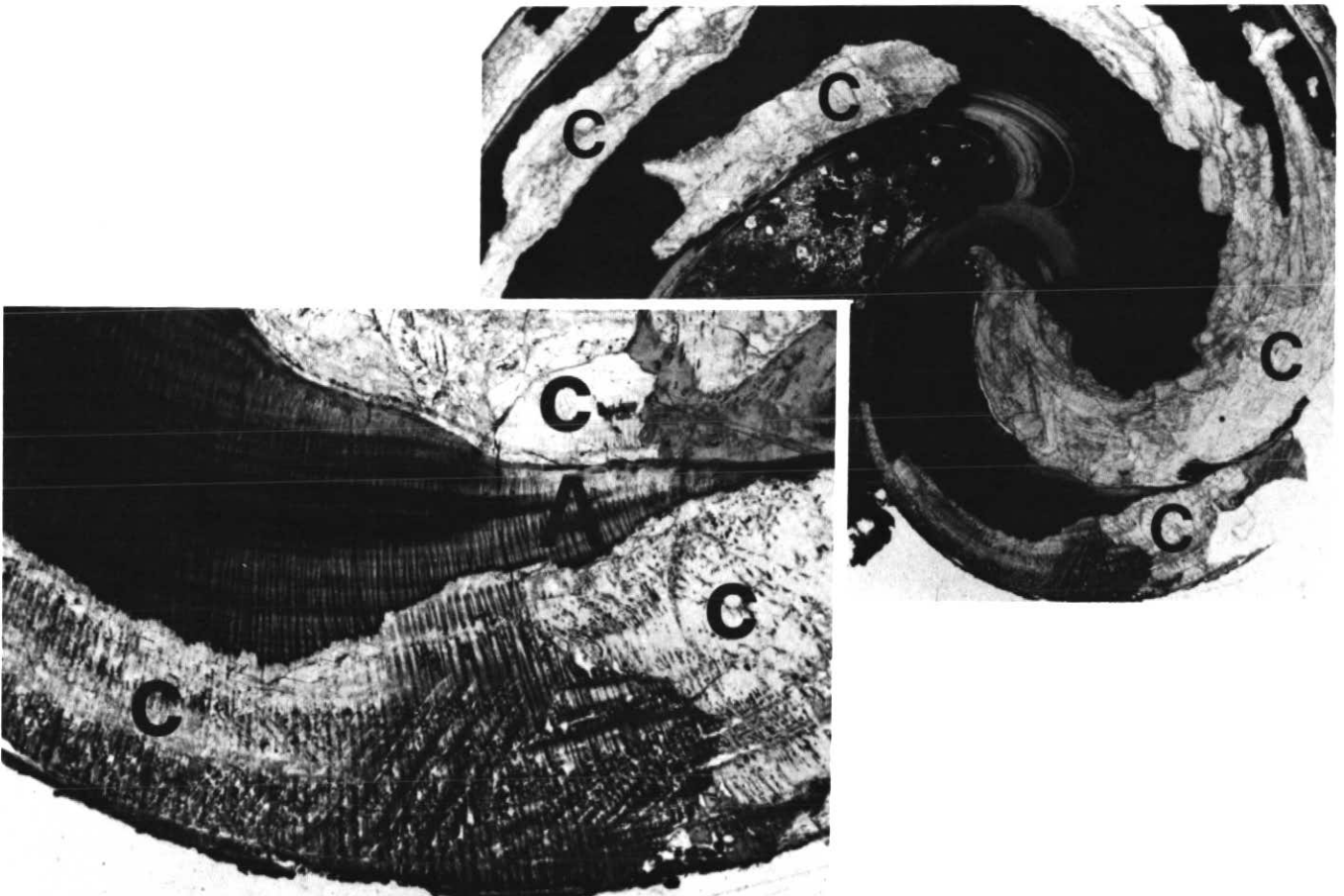

Figure 30 *A Pleistocene gastropod in cross-section* (Strombus gigas) *which is partially aragonite and partially altered to calcite (C); the lower part of the photograph is enlarged at the left illustrating excellent replacement by calcite (C) with the original fabric now entombed in new calcite as relic organic material and inclusions*

confidence to confirm original aragonite mineralogy (Table I).

It appears possible that this process may operate in slightly different ways in the vadose and phreatic zones (Pingitore, 1976). Aragonitic components altered in the vadose zone tend to have fabric-selective mosaics with relatively small crystal sizes, show excellent replacement, and contain some organic residue. The resulting calcites have a relatively low Mg^{+2} and high Sr^{+2} content. Aragonite components that have changed in the phreatic zone reportedly show poor preservation in coarse, cross-cutting mosaics and have relatively high Mg^{+2} contents and low Sr^{+2} values. These differences are thought to result from alteration across a film of water microns thick in the vadose zone but across a chalky zone several millimetres wide in the phreatic zone. In the phreatic, because the skeleton is surrounded by water, calcite continues to grow into a void, whereas in the vadose zone the voids may be filled with air. These changes imply that alteration in the vadose zone can be viewed as somewhat closed, whereas phreatic calcitization takes place in a more open system.

This process is also viewed as occurring in a "two-water system" (Pingitore, 1982), with (1) a small amount of slow-moving water at the dissolution-reprecipitation interface which exchanges with (2) a large volume of faster-moving water percolating or flowing through the rock or sediment. Water at the interface can be considered an almost closed system which is, in turn, connected by diffusion to a large open reservoir.

The alteration of aragonite skeletons to calcite also results in changed petrophysical characteristics. In corals, for example, calcitization leads to an overall decrease in porosity, mainly because of precipitation of calcite cement into pores, but an increase in permeability because of changes in pore-aperture size (Pittman, 1974).

Importance of Grain Size

Most of the processes and products outlined above have been worked out from Pleistocene and Holocene calcarenites because of their convenient grain size and pore diameters. Likewise, grainy rocks should be looked at first in ancient limestones to establish the general diagenetic sequence. When considering the full spectrum of carbonate sediments, however, it is clear that grain size plays an important role. Mudstones, for example, because of their small grain size alter much more rapidly than do contemporaneous calcarenites.

The alteration of polymineralic muds in the meteoric environment is difficult to study because of their small grain size and propensity for rapid alteration. Recent studies utilizing SEM (Steinen, 1978, 1982; Lasemi and Sandberg, 1984) indicate that the same processes occur as in calcarenites. Plio-Pleistocene mudstones formed from aragonite-rich muds are composed of both micrite and microspar (sensu Folk, 1965) and appear to be the end result of concurrent aragonite calcitization and pore-filling cementation. The neomorphic calcite exhibits aragonite pits and relics on polished and etched surfaces and the rocks have been called ADP (aragonite-dominated precursor) mudstones by Lasemi and Sandberg (1984). The cement regions are commonly composed of several crystals which each continue into adjacent relic-rich neomorphic calcite as minute examples of "cross-cutting mosaics" observed by Pingitore (1976) in calcitized corals. This process transforms carbonate mud with 50% to 70% porosity into mudstone with commonly less than 5% porosity.

These mudstones contrast with CDP (calcite-dominated precursor) mudstones, which are mostly micrite composed of crystals with no relics or pits, and are from more ancient limestones.

The importance of grain size or crystal size is well illustrated in the common phenomenon of micrite envelopes (Bathurst, 1966; Alexandersson, 1972). On the sea floor the outsides of carbonate particles, such as bivalve shells, commonly are bored by endolithic algae whose vacated microborings are filled by microcrystalline aragonite or magnesium-calcite cement, forming an "envelope" of finely crystalline carbonate. When these grains come in contact with meteoric waters the small crystals in the envelope, because of their tiny size, alter quickly to calcite (more quickly if magnesium-calcite than if aragonite), before the aragonite of the bivalve begins to dissolve. So for a time the bivalve is still aragonite while the envelope is calcite. Eventually the shell may be leached away and only a thin microcrystalline rind is left outlining the bivalve mold. This mold is then filled with calcite cement (Fig. 24). If it were not for the difference in grain size, mineralogy, or relative resistance to dissolution (if both aragonite), and thus different alteration rates, all would have been dissolved together and there would be no record of the presence of bivalve shells.

At the other end of the spectrum, large, whole aragonitic fossils (gastropods, bivalves, corals) alter more slowly than sand-size aragonite particles, and it is not uncommon to see partly altered corals surrounded by well-cemented but porous calcite limestone containing molds of smaller aragonite grains.

Diagenesis In Vadose versus Phreatic Settings

The style of and relative rates of sediment alteration in the vadose and phreatic zones have been studied on relatively large oceanic islands mantled by Pleistocene carbonates (Bermuda: Land, 1970; Plummer et al., 1975; Jamaica: Land, 1973b; Barbados: Steinen and Matthews, 1973). These results can be used in a general way to approximate conditions on larger carbonate platforms. Studies on small Holocene sand cays (e.g., Joulters Cay: Halley and Harris, 1979) probably better reflect conditions of ephemeral exposure of small portions of platforms. Two examples of vadose versus phreatic alteration are outlined in Figures 31 and 32.

Suspicion that sediments continuously in contact with meteoric waters in the phreatic zone alter more quickly than those in the vadose zone, where water flow is ephem-

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Table I *Aragonite Replacement Criteria*

1. PRESERVATION OF ARAGONITE

2. COARSE* CALCITE MOSAIC, IRREGULAR CROSS-CUTTING STRUCTURE (AS SHOWN BY ORGANIC RELICS OR FLUID INCLUSIONS)

   - a. with aragonite relics
   - b. no aragonite relics but high Sr⁺⁺
   - c. no aragonite relics, and low Sr⁺⁺

   INCREASING RELIABILITY →

3. CEMENT-FILLED MOLDS

   * relative to original aragonite

   n.b. 2b, 2c and 3 are strengthened for cements if external morphology shows large square-ended crystals.

Criteria, in order of increasing reliability, for determining original aragonitic nature of calcitized components (after Sandberg, 1983). Although useful alone, they are best utilized in conjunction with observations on the whole spectrum of preservation styles within a single limestone.

eral, is borne out by studies on the larger islands. Waters in these large phreatic lenses not only percolate down from the vadose zone, but also arrive at the water table directly from lakes, swamps, rivers and via vadose flow through fissures. Because the phreatic waters are from different sources, their chemistries and mineral saturations show considerable temporal variation. In some areas it is estimated that the bulk of the water in the phreatic lens is not from vadose seepage but from vadose flow or lakes, rivers and bogs. Thus the phreatic waters should be of different composition than the overlying vadose waters and, because of mixing, the water table should be a level of considerable chemical activity.

Sediments composed of metastable carbonates appear to alter rapidly in the phreatic zone. Those areas studied to date display both cementation and dissolution that result in extensive lithification in all types of limestones and in abundant aragonitic fossil molds as well as calcitized skeletons. There is not clear information about where in the phreatic zone grains alter most quickly or in what manner, or whether all parts are affected equally. However, Longman (1980) has outlined a hypothetical sequence of alteration for this zone, which remains to be tested.

In any case, because of these differences a common situation in Pleistocene carbonates is for sediments in the vadose zone to be poorly lithified and still mainly metastable, while the same sediments in the phreatic zone are calcite limestone, with a striking mineralogical discontinuity developed at or near the water table.

It is not clear whether dissolution or precipitation will prevail in the phreatic zone during these early stages of diagenesis because the processes depend upon so many factors. If, for example, vadose waters several times oversaturated with respect to calcite because of abundant dissolution of aragonite are mixed with phreatic waters that are just saturated with respect to calcite, and P_{CO_2} levels in the waters are not too different, then cementation can occur at least adjacent to the water table. If, on the other hand, P_{CO_2} levels are very different, then mixing is likely to result in dissolution, as in a wholly calcite system.

Meteoric diagenesis on small islands or sand cays with only local aquifers appears somewhat different. Diagenesis throughout is very rapid in the best studied example, Joulters Cay (Halley and Harris, 1979), but this may be due partly to the high aragonite content of the sediments (almost all ooids). An important difference from large islands is that all the waters pass downward through the vadose zone before they reach the water table and there is little vadose flow, only seepage. Although sediments are only in the initial stages of alteration, several trends are nonetheless evident. The main point is that on small islands the rates of diagenesis above and below the water table do not appear to be much different. In both cementation is patchy, but oolite is more friable below the water table than above because precipitated calcite is a true "cement" in the vadose zone, forming an "onion-skin" on the grains and concentrating as a meniscus at grain contacts. In contrast, calcite in the phreatic zone is precipitated as scattered rhombs all over the grain surfaces and not necessarily at grain contacts. The most intensively cemented zone is right at the water table. Cementation decreases with depth in the phreatic zone as the proportion of sea water increases.

Interestingly, calculations suggest that at the current rate all the sediment will be stabilized to calcite within 10,000 to 20,000 years on this small carbonate sand cay, whereas stabilization will probably take some 100,000 to 1,000,000 years on Bermuda.

The Freshwater-Seawater Mixing Zone

The possibility that dolomite may form in mixing zones has provoked considerable interest in the hydrology, chemistry and mineralogy of such zones (see Morrow, 1982a,b for a good review on the subject).Early reports (e.g., Land, 1973a,b) of dolomite in Middle Pleistocene limestones of northern Jamaica were followed by a search for other occurrences in young Cenozoic carbonates of small to large oceanic islands and coastal regions underlain by extensive limestone aquifers – but with little or no success. Failure to find

PETROGRAPHY

CALICHE

GEOCHEMISTRY
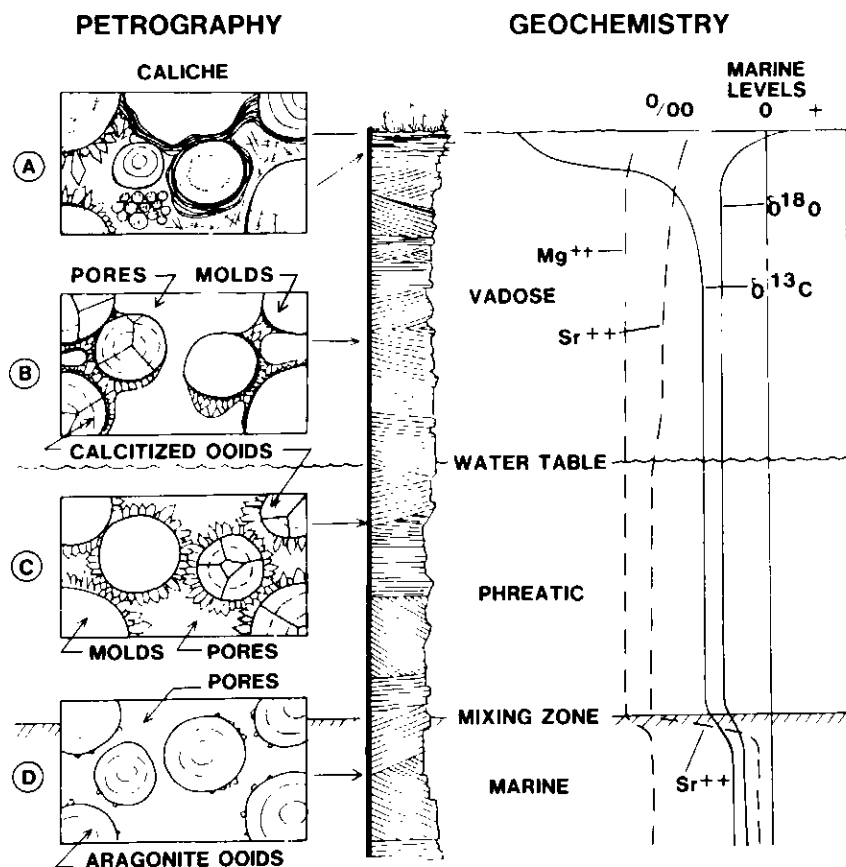
Figure 31 A sketch illustrating a hypothetical core through and ooid grainstone shoal exposed to meteoric diagenesis under semi-arid conditions, resulting in a caliche profile Sediments below the mixing zone are saturated with marine pore waters and essentially uncemented. The geochemical curves are based on results one might obtain from "bulk" analyses. The limestone was originally composed of aragonite ooids, hence the high initial Sr^{+2} and low Mg^{-2} concentrations. Stabilization is essentially complete in the freshwater phreatic zone.

A. Paleoexposure Surface – caliche crust, partial conversion of ooids to calcite micrite, needle and other calcite cements, gravity effects, vadoids. B. Vadose Zone – conversion of ooids to calcite with mostly good preservation, meniscus and gravity calcite cements. C. Freshwater Phreatic Zone – extensive dissolution (fabric selective), calcitization, isopachous calcite cement. D. Mixing Zone – preservation of aragonite ooids, poor induration, some rhombs of low to high magnesium-calcite

dolomite in identifiable mixing zones in Holocene and young Pleistocene limestones has been attributed to undersaturation with respect to dolomite (Bermuda – Plummer et al., 1976) and to slow kinetics of dolomite nucleation and growth (Barbados – Wagner, 1983). Perhaps mixing-zone dolomite is favoured by combinations of high-volume flux of meteoric waters with strong counter-circulation of Mg-rich saline waters into mixing zones, or perhaps by prolonged low stands of sea level with attendant high elevations of recharge areas above grade and correspondingly active vadose and phreatic circulation. That the duration of sea-level stands may be a factor is implied by the widespread dolomitization of Caribbean platform and small island carbonates during the Pliocene and early Pleistocene (e.g., Sibley, 1980; Beach, 1982; Pierson, 1983). In any case, the requirements for dolomitization in mixing zones – although the process is likely in principle (Runnells, 1969) – are far from understood, and the search goes on for significant volumes of dolomite in present-day or former identifiable mixing zones in young Cenozoic limestones where cause and effect can be relatively well established.

Cementation of limestones by $CaCO_3$ in mixing zones may not be extensive. In very young Holocene sediments (ca. 1,000 years old) beneath south Joulters Cay on Northeastern Great Bahama Bank, for example, there is virtually no cementation at all below the freshwater phreatic lens. Minor amounts of low-Mg calcite cement have been found in paleo-mixing zones on Barbados (Benson, 1973; Steinen, 1974), northern Jamaica (Land, 1973a,b) and a coastal area of Grand Cayman Island (Moore, 1973). Coastal mixing zones are, in a sense, involved in the formation of beachrock (discussion in James and Choquette, 1983), but CO_2 degassing in these zones, rather than mixing effects, may be mainly responsible for $CaCO_3$ cements there (Hanor, 1978).

There is considerably more evidence that dissolution is important in mixing zones. Non-fabric selective dissolution occurs along some 150 kilometres of the northeastern Yucatan coast, apparently in a coastal mixing zone (Back et al., 1978, 1979, 1984), producing a striking scalloped morphology and related collapse features (Fig. 33). Mixing corrosion on a large scale has probably occurred along the base of the vast freshwater lens in parts of the south Florida aquifer (Vernon, 1969), and distributions of caves in limestones beneath large oceanic islands, such as Bermuda, suggest that brackish waters may have had a part in their origin (Palmer, 1984).

Where CO_2 is not a major factor and freshwater and seawater mix according to the error function relationship described earlier, it seems likely that dissolution is favoured in the upper, more dilute reaches of the mixing zone (see Fig. 3), as might be expected from Figure 8, and that $CaCO_3$ precipitation (and dolomite formation?), if significant, should take place in the lower reaches of this zone. Where calcite is the cement precipitated, in metastable limestones it might be expected to become more Mg-rich downward in the mixing zone. This Mg-rich fingerprint should not be preserved long or deeply into the sub-lenticular phreatic realm, however, unless by such features as microdolomite inclusions (Meyers and Lohmann, 1978). It is attractive to interpret as products of mixing-zone precipitation those calcite cements which have these inclusions, are clearly not synsedimentary marine in origin, and are spatially associated with identifiable phreatic cements. Meyers and Lohmann (1984) argue persuasively for precipitation of these inclusion-rich cements from regionally extensive transition zones, and it is true that modern brackish mixed-water zones with comparable distributions and geographic extent have been documented in some widespread continental-coastal aquifers (e.g., the South Florida aquifer – Back and Hanshaw, 1970).

It is likely that the rock record will be found to contain more examples of cement stratigraphies imprinted by local and regional mixing zones.
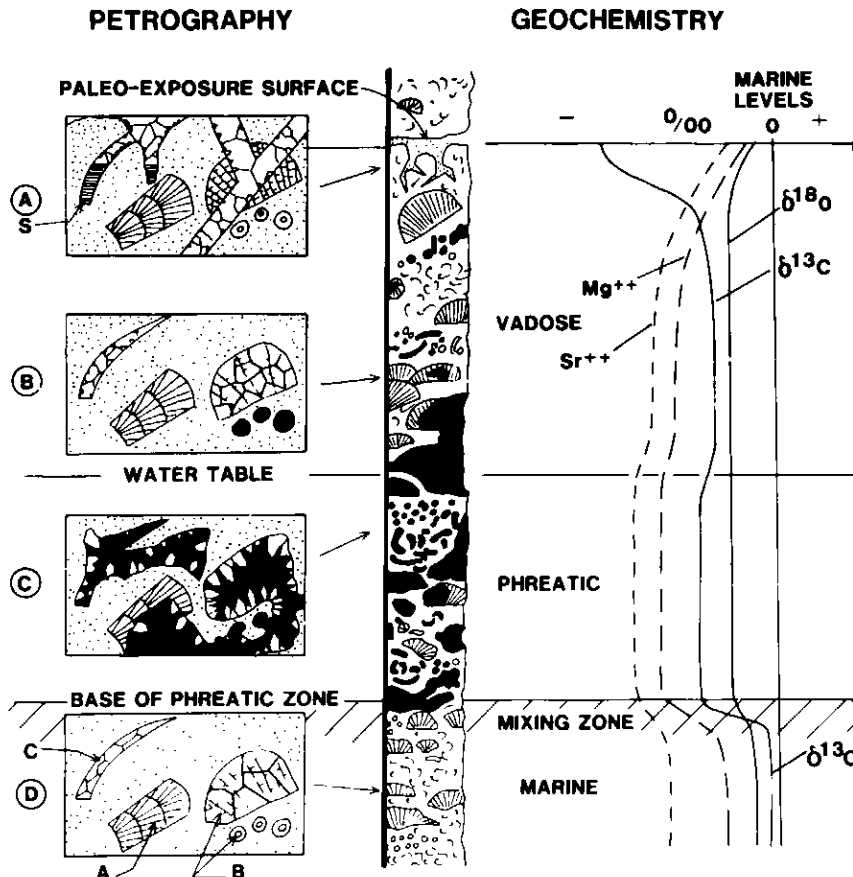
PETROGRAPHY

GEOCHEMISTRY

Figure 32 A sketch illustrating a hypothetical core through a reef limestone exposed to meteoric diagenesis in a warm, moderately humid climate. Subaerial exposure produced a corroded fractured surface karst. Sediments below the mixing zone are saturated with marine pore waters. The geochemical curves are based on results one might obtain from "bulk" analyses. The limestone was originally composed of coralline algae (A – magnesium-calcite), bivalves and corals (B and C – aragonite). Stabilization is mostly complete in the freshwater phreatic and the offset of the $\delta^{13}C$ profile at the water table is due mostly to precipitation of diagenetic calcite cement. A. Paleoexposure Surface – dissolution and fracturing, geopetal vadose sediments, good skeletal preservation. B. Vadose Zone – mostly good preservation though skeletal aragonite is calcitized, minor development of molds and matrix vugs. C. Freshwater Phreatic Zone – extensive dissolution, prolonged flushing, non-fabric selective voids, some calcitization and calcite cement precipitation (black = porosity), D. Mixing Zone – not exposed to meteoric waters, aragonitic fossils may be calcitized, magnesium content of coralline algae high in lower part, dissolution likely in upper part (dilute pore waters)

Geochemical Aspects of Meteoric Diagenesis

Minor Elements. Dissolution of aragonite (at whatever scale from micro to macro) releases strontium (Sr^{+2}) and other less abundant trace cations to the surrounding pore waters; incongruent dissolution of Mg-calcite releases Mg^{+2}. The result in the carbonates is a net *decrease* in both Sr^{+2} and Mg^{+2} either with accompanying passage through the vadose and freshwater phreatic zones, or during continued residence in either zone (Figs. 16 and 17). This loss in Sr^{+2} and Mg^{+2} is apparently reversed with passage through the mixing zone (Wagner, 1983), which appears to be particularly well defined by downward increases in Mg^{+2} content.

Below the water table, beyond the reach of oxygenated water, metals that can exist in lower oxidation states such as Mn^{+2} and Fe^{+2} become available for incorporation into diagenetic calcite (CO^{+2} and Ni^{+2} also may play a role here), resulting in an overall net *increase* in these elements with progressive burial. Meyers and Lohmann (1984) and others have suggested this overall trend, which is discussed in detail in the third review article in this series on deep-burial diagenetic environments (Choquette and James, in prep.).

The level of cathodoluminescence (CL) varies sharply among growth zones in crystals of carbonate cement. As illustrated in Figure 34, vadose cements show little or no CL because vadose waters normally are well oxygenated, so that neither Fe^{+2} or Mn^{+2} can exist. Below the water table oxygenation and Eh decrease rapidly, so in the shallow lenticular phreatic zone CL is both present and highly variable but is essentially nil (dark) in the deeper phreatic zone. Variability can best be attributed to fluctuations in supply of activator ions (mainly Mn^{+2}) and suppressor ions (mainly Fe^{+2}) and to variations in water flux in response to either seasonal or longer cycles; these fluctuations are greatest in near-surface hydrologic regimes, particularly the vadose. Phreatic-zone CL, first identified by Meyers (1974) in a landmark study, has since been described in many parts of the Phanerozoic (e.g., Grover and Read, 1983; James and Klappa, 1983; Meyers and Lohmann, 1984). Cathodoluminescence is a powerful tool for deciphering often-complex cementation histories, particularly where CL zones can be calibrated with minor-cation compositional data.

Although the tempo of research on minor elements in carbonate diagenesis is increasing (see discussions by Brand and Veizer, 1980 and Lohmann, 1983), our understanding of the behaviour of these elements even in the near-surface meteoric environment is still fragmentary and evolving. In general terms, however, the profiles in Figures 31 and 32 appear to be reasonable.

Stable Isotopes. Considerably more is understood about the distribution and diagenetic "behaviour" in carbonates of stable-carbon and oxygen isotopes within the near-surface meteoric. At present, our knowledge of carbonate-ion isotopic compositions diminishes with increasing depth below subaerial exposure surfaces, even in Holocene and Pleistocene carbonates. The profiles in Figures 31 and 32 typify fairly well the kinds of stratigraphic distributions of carbonate $\delta^{13}C$ and $\delta^{18}O$ in young Pleistocene sequences. In these profiles the *patterns* are emphasized rather than absolute values, and it is clear that with variations in absolute composition these patterns are valid for many if not most limestones subjected to near-surface meteoric diagenesis at least as far back in geologic time as Late Paleozoic. The profiles are based on a series of recent studies (e.g., Magaritz, 1975, 1983; Allan and Matthews, 1977, 1982; Salomons et al., 1978; Videtich and Matthews, 1980; Wagner, 1983). The general subject of $\delta^{13}C$ and $\delta^{18}O$ isotopic compositions and isotope geochemistry has been ably summarized by others (e.g., Bathurst, 1975; Hudson, 1977; Veizer, 1983) and a lucid view of principles has been provided by Lohmann (1983).

With sound petrographic work it is possible to interpret the isotopic signatures of meteoric diagenesis with a high degree of accuracy, *provided that one can get an estimate of the original marine $\delta^{13}C$ and $\delta^{18}O$ of a limestone or limestone sequence prior to alteration.* This can be done, as numerous studies have shown, and Lohmann (1984) has convincingly demonstrated, by taking the "heaviest" compositions in a linear, covariant series of values determined for those marine components that show the least evidence of alteration. Such components might be well preserved brachiopods (calcite originally) or marine radiaxial cement, or originally
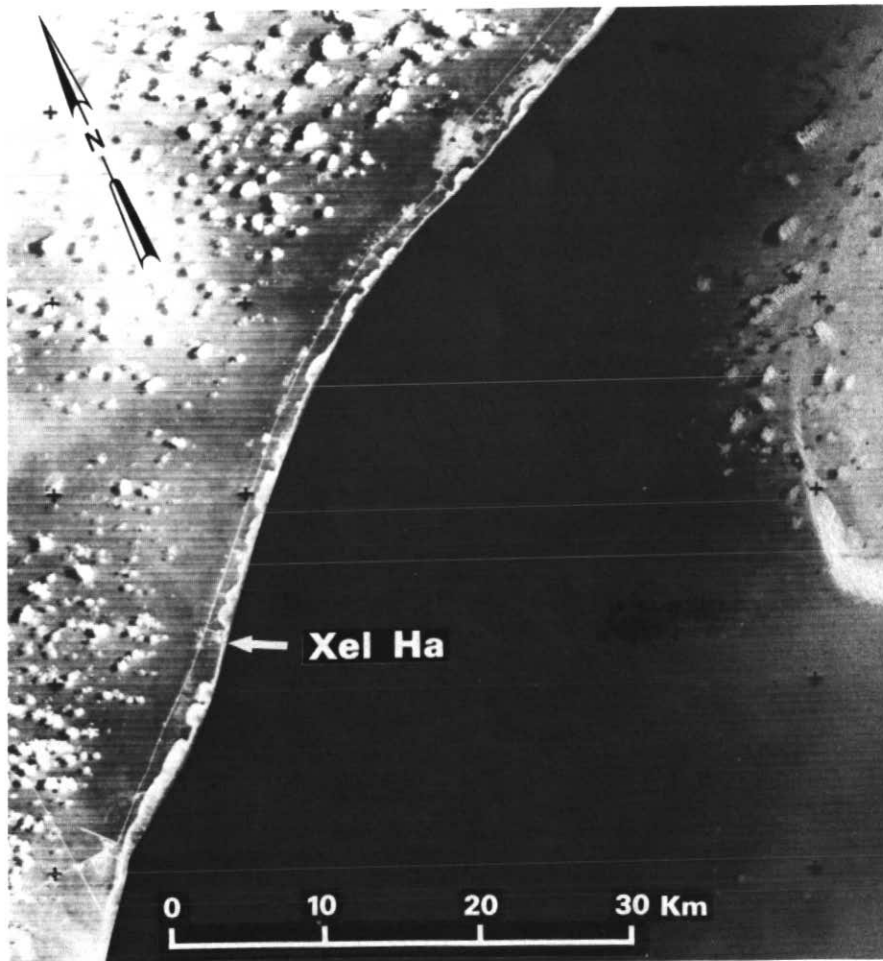
Figure 33 *Part of a satellite photo of the northeastern coastline of Yucatan, Mexico showing the scalloped morphology produced by solution-collapse and enlargement along coast-parallel-ing fracture zones. Studies by Back et al. (1979, 1984) at Xel Ha have shown that dissolution is taking place in brackish groundwaters in a coastal mixing zone. The land area at right is the island of Cozumel. Photo courtesy of William Back, U.S. Geological Survey*

aragonitic rudists in which criteria from Table I indicate good preservation following Sandberg (1983). The covariant trend approach, illustrated in Figure 35, has been used by Lohmann (1983) and others to estimate original marine $CaCO_3$ compositions with apparent accuracy. These graphs were presented in the first of this series of reviews (see James and Choquette, 1983 for references). The need for a "marine baseline" is critical in older Paleozoic limestones – and possibly Cretaceous limestones – where original $\delta^{18}O$ and $\delta^{13}C$ of marine sediments and cements appear to have been several per mille "lighter" than in the present-day ocean (James and Choquette, 1983, Figs. 20 and 21). Contrary to earlier ideas that this isotopic "lightness" was the result of more prolonged diagenetic alteration in older Pleistocene limestones, it now appears that real, non-linear variations in the composition of seawater through Phanerozoic time are represented.

The range, and more significantly the *pattern*, of carbon and oxygen isotope compositions found in many Cenozoic limestones in shallow meteoric settings – where limits of present day or former vadose zones, phreatic lenses and even mixing zones can be determined with increasing confidence – also occur in many Phanerozoic limestones. Ranges in fossil limestones are often smaller because of the damping effects of later burial cements or other forms of alteration, but patterns are similar.

The general tendency in stratigraphic profiles through young metastable carbonate sequences in near-surface meteoric environments is for carbon-isotope compositions to vary considerably down through the vadose, particularly within short dis-

tances (metres or less) of subaerial exposure surfaces; then to stabilize and remain relatively constant through the shallow phreatic; and finally to change through the mixing zone toward marine or nearly marine values. Oxygen-isotope compositions show little variation through the vadose and shallow phreatic except in the mixing zone where they become heavier, enriched in ^{18}O because of preferential loss of ^{16}O by surface evaporation. These general relationships are shown in Figures 31 and 32. Although the relationships were recognized first in Pleistocene sequences, they are often preserved in Phanerozoic limestones (Allan and Matthews, 1982) where they may have value for signalling the presence of ancient subaerial surfaces.

In the $CaCO_3$-H_2O-CO_2 system carbon comes almost wholly from the original carbonate and CO_2 gas. Carbon-isotope variability in near-surface vadose zones is due mainly to the influence of isotopically "light" (^{13}C-poor) carbon. Calcites precipitated in caliche and soil profiles – in hardpans, nodules and associated vadoids – are typically 7‰ to – 13‰ in Recent and Pleistocene profiles, changing downward within a few centimetres to metres at most to values of – 2‰ to – 4‰, which are typical for the rest of the vadose. The "light" compositions reflect contributions of CO_2 from decaying organic matter to vadose pore waters seeping downward or being drawn upward by evaporation throughout the caliche/soil profiles (for discussion of these effects see Rightmire and Hanshaw, 1973; Hudson, 1977; Allan and Matthews, 1982; Lohmann, 1983). Deeper in the vadose, dissolved CO_2 in pore water rapidly equilibrates isotopically with the marine carbonate sediment through which it is percolating.

Oxygen in the $CaCO_3$-H_2O-CO_2 system can come from the minerals, the water and/or the gas, but in reality contributions dissolved CO_2 are miniscule compared to contributions from the water and from host sediment or limestone. Thus oxygen-isotope compositions through the meteoric are much less variable than carbon-isotope values. The $\delta^{18}O$ values of carbonates in caliche and soil profiles are much like those of carbonates in the rest of the vadose zone and the lenticular phreatic (except for the evaporation effect mentioned earlier), generally – 2‰ to – 6‰ in young Cenozoic carbonates.

Covariant trends of $\delta^{13}C$ and $\delta^{18}O$ should also be displayed by $CaCO_3$ cements precipitated from mixtures of marine and fresh meteoric waters, as in a mixing zone. The "end members" can be identified most clearly if they are original marine $CaCO_3$ and carbonate precipitated in a caliche or soil profile (Fig. 35). In progressively more altered carbonates below profiles of this kind (Figs. 31 and 32) one often sees an inverted "J" or "L" shaped trend, as pointed out by Lohmann (1982, 1983) and Magaritz (1983). This kind of trend on cross plots is a result of the extremely "light", $\delta^{13}C$-impoverished CO_2 supplied to near-surface pore waters by decaying organic matter, as noted earlier, and the differences in rates at which pore waters equilibrate isotopically with the host $CaCO_3$ sediments and rocks through which they pass. Where organic matter did not exist or was very sparse at the surface, so that a caliche or soil profile did not develop, a "J" shaped trend will not be expected to develop.

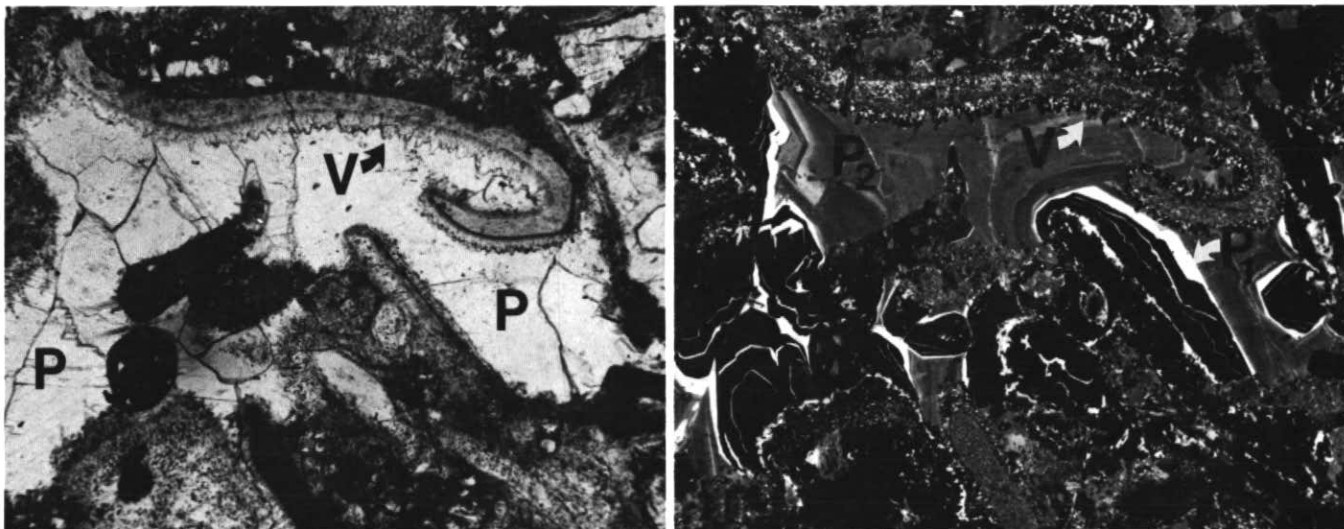Figure 34 Left – two stages of cementation in an Early Cambrian grainstone; V = vadose pendulous cement (plane polarized light), P = phreatic blocky calcite. Right – cathodoluminescence, vadose cement has irregular trace element content, phreatic cement is two-staged; P_1, dark and bright luminescent zones, probably shallow phreatic; P_2, dull luminescence, probably deep phreatic (photo width is 5 mm)

Diagenesis of Stable Carbonate (Calcite) Sediments

It is clear that the extensive alteration and cementation of metastable carbonate sediments is driven by the coexistence of different minerals with different solubilities. But what about carbonate sediments that are mostly calcite? We cannot, unfortunately, make a direct comparison because shallow-water Neogene carbonate sediments are usually a mixture of minerals, but we can look at deep-water chalks (Cretaceous – Recent) to gain some insights. These sediments are, or were, composed almost entirely of calcite skeletal elements originally, with relatively few aragonite bioclasts. Exposures of Cretaceous chalk are widespread in northwest Europe. Where these sediments have not been affected by deep burial or percolation of hot waters they are extremely soft, with over 40% porosity, and have altered relatively little despite 70 to 90 m.y. of shallow burial and prolonged exposure. The chief alteration is the loss of organic matter, aragonite and opaline silica. Calcite fossils are exceptionally well preserved. There is some

calcite cement, precipitated mostly as epitaxial overgrowths on coccoliths and echinoids. This minor cement is likely derived from the very smallest, supersoluble particles. Compared to the metastable suites just described, these sediments are virtually unaltered! The contrast is probably nowhere better displayed than on the island of Barbados where soft Oligocene chalks directly underlie hard, Pleistocene reef limestones and, even though the permeability of the chalk is much less than that of the reef limestone, both have been exposed to percolating fresh waters for nearly the same length of time, about 500,000 years (Fig. 36). It is important, however, to note that in spite of the fact that the chalks are soft they commonly exhibit deep surficial weathering and solution cavities, to an extent reminiscent of calcite limestones.

This striking difference becomes extremely important if the composition of carbonate sediments in the past was at times different from those of today, and dominated by calcite constituents (see discussion by James and Choquette, 1983). If meteoric diagenesis, or more properly, the lack of meteoric diagenesis of chalk, is any guide, then the subaerial exposure of sediments in the lower and middle Paleozoic, for example, should leave little discernible evidence in the form of diagnostic cement, signs of fabric-selective dissolution, or geochemical signature. Since there were likely some aragonitic components in these calcite sediments, there was prob-

ably a little cementation, but very little. Instead, the signature would be more in the form of surficial karst, etc. These conclusions have yet to be tested against the rock record.

Criteria for Recognition of the Products of Meteoric Diagenesis

In summary, it is often possible to reconstruct whether a given stratigraphic unit has resided in a vadose or phreatic zone (or both), either from field relationships, from petrographic features seen at scales ranging from hand specimen to the light and scanning-electron microscopes or, in some cases, from geochemical information. Careful petrographic observation, aided by analysis of cathodoluminescent zonation and cement chemistry, can make possible detailed reconstructions of residence in a succession of diagenetic environments. Many of the petrographic criteria have been distinguished in very young Holocene and Pleistocene carbonates, but are commonly preserved in the older stratigraphic record. Large-scale features of karst terrains are being applied with increasing success to the fossil record, and a great deal is now known about the kinds, if not always the origins, of features formed in the vadose zone. The criteria outlined in Table II are often helpful in both distinguishing and helping identify the interface or transition zone between vadose and phreatic zones in the fossil record. Many of these criteria are quite reliable. Others are less so, either because they may be
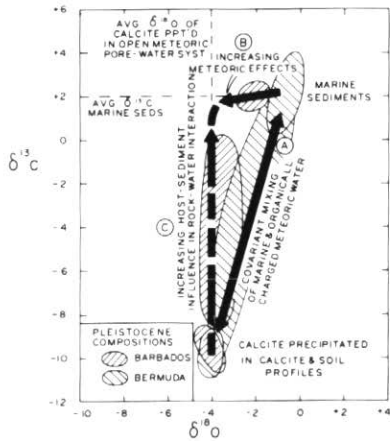

Figure 35 A diagram showing isotopic compositions and trends in metastable carbonates where mineral-controlled alteration takes place in a meteoric system capped by a caliche-soil profile. The covariant trend (A) has as end member marine sediments (seawater) and ^{12}C-enriched pore waters; diagenetic calcites precipitated in a marine-meteoric mixing zone might have compositions along such a trend. If no caliche-soil profile existed, alteration of marine sediments might follow the trend shown by the top arrow gently down to the left (B). The long vertical trend (C) would apply to rock-water interaction beneath a caliche-soil profile in the shallow vadose, where $\delta^{13}C$ becomes heavier downward as "rock" CO_3^{-2} overpowers soil CO_2 while $\delta^{18}O$ remains the same, as shown in Figures 31 and 32. the data fields are from Gross (1964) and Allan and Matthews (1977, 1982). The trends are in part based on interpretations by Hudson (1977), Lohmann (1982, 1983), and Magaritz (1983)

Figure 36 Hard Pleistocene reef limestones overlying soft Oligocene chalks, Barbados. The Pleistocene limestone hardened quickly in the meteoric environment because it was composed of metastable minerals. The chalk remained soft because it was originally, and still is. composed of calcite

produced in both zones near the water table, or because they may originate in other depositional-diagenetic settings, such as beachrock where gravity cements are well known.

The Effect of Climate

Since water and temperature are the two most important extrinsic factors in the processes of meteoric diagenesis, climate – particularly the availability of meteoric water – influences both the intensity and rate of carbonate alteration (Fig. 37). The effects are strongest in the vadose zone.

Under hot, arid desert conditions both karst and calcrete may develop, but slowly and in the form of thin profiles; likewise, alteration in the vadose zone is slow. Thus carbonates exposed for extended periods under these conditions may show little or no effect of meteoric diagenesis. In the phreatic zone, alteration may be more extensive. Water flow in the phreatic is likely to be slow because of limited re-charge. Cementation may be limited and porosity and permeability high. There are few case studies, however, and so clear information is lacking.

If the climate is warm and semi-arid, caliche should be both thick and extensive, with surface karst also present locally. Alteration in the vadose zone is relatively rapid and is dominantly mineral-controlled, if the mineralogies are metastable. Alteration is most generally fabric-selective, and replacement of original aragonite textures is good. Mineralogical changes have been discussed earlier and diagrammed in Figure 23. Geochemical changes, also discussed earlier and outlined in part in Figures 31 and 32, seem to follow the general direction shown, with slight abrupt offsets at the water table if the phreatic and vadose zones behave as somewhat separate systems (Wagner, 1983). Changes are rapid in the vadose and very subdued or essentially nil in the phreatic. Caves are rare and small, and movement of groundwater in the vadose is mostly by vadose seepage.

Under warm and rainy conditions (sub-tropical to tropical), although modern di-agenetic changes are difficult to determine because of extensive vegetation and rug-ged karst topography, surface and subsur-face karst should be extensive, dissolution should prevail over precipitation, and both fabric-selective and non fabric-selective fabrics should occur. Caves and solution-enlarged fractures should be very extensive (Fig. 37), stabilization to calcite limestone rapid, and vadose flow dominant over seepage. Water-controlled alteration is dominant.

Geochemical profiles in metastable lime-stone beneath a karsted surface, outlined in part in Figure 32, ideally may resemble

Table II *Some Features Helpful in Identifying Former Vadose and Phreatic Diagenetic Zones*

	VADOSE OR PHREATIC	RELIABILITY *
MEGASCOPIC		
Calcrete, soil-zone features, root casts, often-complex travertine-filled fractures	V	1
Speleothems	V	1
Stratified/laminated sediment in larger cavities (vadose sediment often inclined)	P	2
Trains of horizontally elongate large solution cavities (may cross-cut structural dip)	P	2
Doninantly vertical solution cavities	P	2
MICROSCOPIC		
Preserved needle-fibres, flower spar, fungal sheath & related near-surface cements	V	1
Meniscus cement	V	1
Gravity cements (micro-stalactite, -stalagmite)	V	1
Isopachous cements**	P	2

* 1 is more reliable than 2.
** May be difficult or impossible to distinguish from isopachous cements of submarine, sea-floor origin (see James and Choquette, 1983).

CLIMATE & METEORIC DIAGENESIS
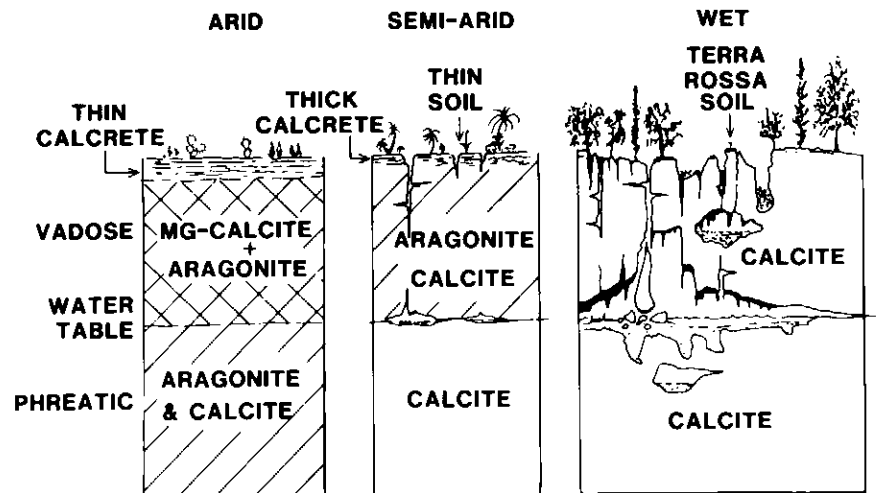

Figure 37 *A diagram illustrating the effects of different climates on a series of metastable carbonates of the same age and composition.* The geochemical profiles in Figure 38 apply largely to semi-arid and wet (high rainfall) situations

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those in the right portion of Figure 38. Because of high-volume flow in the phreatic zone, substantial effects can be seen in compositional profiles. For the $\delta^{13}C$ and $\delta^{18}O$ profiles in the phreatic there may be an offset toward heavier compositions if cementation by calcite has been slight, or offset toward lighter values if meteoric calcite cementation has been extensive. Dissolution of aragonite and magnesium alteration of Mg-calcite may be so extensive in the vadose zone that greatly enriched pore waters lead to enrichment of Sr^{+2} and Mg^{+2} in diagenetic calcite.

In summary, in warm climates the supply of meteoric water is important in determining the rate, intensity and even direction of diagenetic alteration. Variations in rainfall may be substantial across the larger oceanic islands that rise some hundreds of metres above sea level because of rain shadow effects and are generally even greater across large land masses.The economic implications are far from trivial in terms of water supplies for today's populations, the style and extent of porosity and permeability in altered limestones, the general characteristics to be expected in ancient limestones, and other ramifications.

Large-Scale Variations Through Geologic Time

It is common practice to extrapolate the processes and products of meteoric diagenesis observed today to the fossil record. As emphasized by James and Choquette (1983), however, there have been changes in the nature of the atmosphere and biosphere through geologic time which may have profoundly influenced the style of meteoric diagenesis (Fig. 39).

Changes in the Atmosphere. It now seems probable that there have been variations in atmospheric P_{CO_2} through the Phanerozoic. The atmosphere seems to have oscillated between a "greenhouse" mode when P_{CO_2} levels were higher than those today, and an "icehouse" mode when they were more like the modern atmosphere (Fischer, 1981). During the greenhouse mode meteoric waters, with increased P_{CO_2}, would have been more aggressive than they are today. How this would be reflected in the rock record is difficult to assess. In areas of thin soil cover, or at times when soils were poorly developed, increased simple corrosion would lead to more extensive surface karst. Intuitively, one feels that there should be more extensive karst development during these times, yet most extensive dissolution occurs beneath a soil and not on bare rock. So the effect should be most noticeable in areas where there is little soil development, or at times when soils were poorly developed.

Changes in the Biosphere.

Terrestrial: Weathering effects and the generation of CO_2-charged waters are heavily dependent upon the presence and evolution of higher plants. Although land plant fossils are known from the early Paleozoic, they were not a significant part of the terrestrial landscape until Devonian time, but were widespread by the early Mississippian. Thus, even though soils may have existed in the early and middle Paleozoic, they would have been closer to the protosoils of today, dominated by algae and lichens, and unlike the complex biogenic profiles in true soils.

Marine: of equal importance is the mineralogy of carbonate sediments that were available to be altered. As pointed out by Lowenstam (1963) and Wilkinson (1979), the mineralogical composition of shallow-water skeletons has varied through geologic time. Although the trends are not yet firmly established, first-order variations seem clear (Fig. 39). In general, sediments on modern and Cenozoic shallow platforms are or were mostly aragonite and magnesium-calcite, whereas those in similar Mesozoic settings were about equally aragonite and calcite (either high-magnesium or low-magnesium). In contrast, sediments in the middle and early Paleozoic were mostly calcite (except perhaps for the earliest Cambrian). The history of the mineralogy of non-skeletal particles seems more complex (Sandberg, 1983), and varied in an oscillating fashion. Because the

style of diagenesis is partly dependent upon sedimentary mineralogy, those sediments with abundant aragonite will have undergone the most extensive alteration and have been cemented most in the meteoric environment. Conversely, those predominantly calcite and Mg-calcite sediments will be little affected and illustrate features because of water-controlled alteration. These differences are well demonstrated by anyone who has marvelled at the superb preservation of early Paleozoic fossils, yet struggled to discern the nature of the numerous recrystallized and partially dissolved skeletons in Cenozoic limestones (Fig. 40). It often seems that the older the limestone, the better the preservation!

Synthesis. By integrating these variables in a general way, we can speculate on potential variations in diagenesis. The Phanerozoic could be subdivided into five periods when the effects of meteoric diagenesis were probably different (Fig. 39).

1. OLIGOCENE – PRESENT. Since conditions were similar to those today and in the recent past, the present meteoric environment is a good guide to rocks of this age.

2. LATE TRIASSIC – EOCENE. A period when sediments had less aragonite, atmospheric CO_2 was higher and there were no terrestrial grasses, although plant cover in general was extensive. The spectrum of textures and fabrics described in this article should be expected for rocks of this
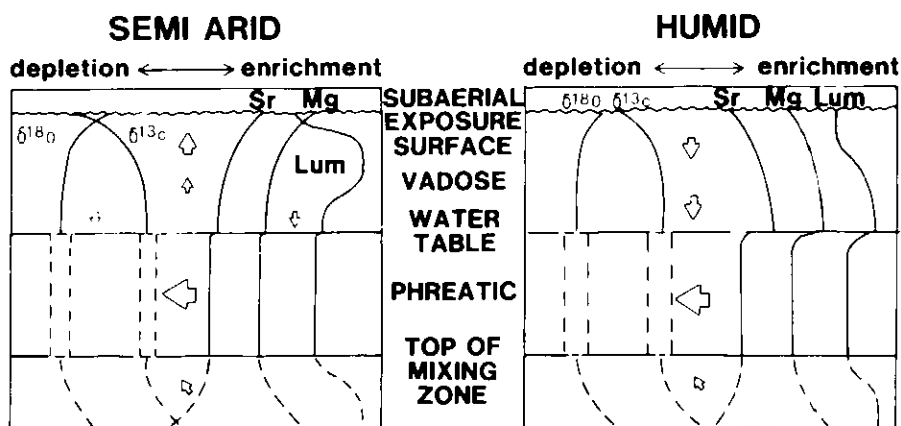
SEMI ARID

depletion ←——→ enrichment

HUMID

depletion ←——→ enrichment

Figure 38 *Stratigraphic patterns of geochemical profiles in a sequence of initially aragonite and magnesium-calcite limestones beneath a subaerial exposure surface, under arid or semi-arid conditions (left) and humid conditions (right). Open arrows show dominant directions of ground-water movement. Offsets in isotopic composition, cation concentrations and cathodoluminescence (Lum, mainly reflecting Mn^{+2} if Fe^{+2} is not excessive) occur at the water table because the vadose and phreatic zones behave as more or less separate hydrologic systems, particularly in the humid setting where water is greater in the phreatic and water chemistry is affected by*

other recharge sources as well. In the arid-semi-arid setting there is upward enrichment in Sr^{+2}, Mg^{+2}, and ^{18}O in the shallow vadose due in part to upward movement of vadose pore waters in response to high surface evaporation "wicking effect". Profiles for the phreatic and mixing zone are similar in both situations. The profiles are somewhat modified from Wagner (1983). They were developed from data from boreholes in the Pleistocene of Barbados (see text) and from profiles of various ancient stratigraphic sequences beneath subaerial exposure surfaces (Allan and Matthews, 1982; Wagner, 1983)

age, with perhaps more obvious surface karst.

3. LATE DEVONIAN/EARLY CARBONI-FEROUS – MID TRIASSIC. During these times the atmospheric pCO_2 was similar to that of today, plant cover was potentially extensive, and sedimentary mineralogy was roughly the same as in younger rocks (less skeletal aragonite). Both surface karst and calcretes probably developed commonly at this time, with somewhat less cementation and dissolution and so less fabric-selective diagenesis than in younger rocks.

4. MID CAMBRIAN – MID DEVONIAN. A time quite different from the recent past; atmospheric P_{CO2} was relatively high. There were no true land plants, so soils were poorly developed. Carbonate sediments were composed mostly of calcite. The effects of meteoric diagenesis at this time were probably minimal and confined to surface and subsurface karst, non-fabric-selective alteration, little cementation, little or no caliche and much fabric retention.

5. LATE PRECAMBRIAN? – EARLY CAMBRIAN. Scant evidence suggests that the atmosphere was like that of today in terms of P_{CO2} and sedimentary mineralogy was like that in the middle Paleozoic, but that there were poor soils. Again much karst, and little or no caliche were developed, but some fabric-selective alteration. Cementation would have been the most significant results of meteoric diagenesis.

It must be remembered that this scheme is a generalization, a background against which to consider meteoric diagenesis, realizing that local conditions may completely overprint the general trends. Conversely, where lack of alteration or absence of meteoric diagenetic features has in the past been interpreted as lack of exposure, it is also clear that exposure may have

taken place without any significant signature.

Summary
Carbonate sediments commonly are exposed to percolating meteoric waters at various times during their history. Since they are mostly deposited in shallow waters, small changes in sea level, whatever the cause, will result in subaerial exposure early in their history, either immediately after deposition or after shallow burial. Once they are exposed, a predictable hydrologic regimen is established, with only minor surficial exposure resulting in relatively deep percolation of fresh water and accompanying diagenesis. Although the occurrence of meteoric diagenesis can be established from textural and fabric criteria, pinpointing specific zones of alteration is difficult because, with time and

fluctuating sea level, the zones migrate through the rock. Stages of alteration are thereby superimposed or early stages of diagenesis are obliterated by later ones.

Although many reactions take place in this setting, in terms of carbonate diagenesis two are critical: (1) a first-order reaction controlling dissolution and precipitation in general by invasion and evasion of CO_2 from meteoric waters; all $CaCO_3$ minerals including calcite are dissolved, but only calcite is precipitated; (2) a second-order reaction that occurs under uniform P_{CO2} conditions but affects minerals of different solubilities; aragonite and Mg-calcite, but not calcite, are dissolved and new diagenetic calcite is precipitated. Both reactions occur concurrently when metastable carbonates are flushed by meteoric waters, but once the minerals have all changed to calcite, only the first-order re-

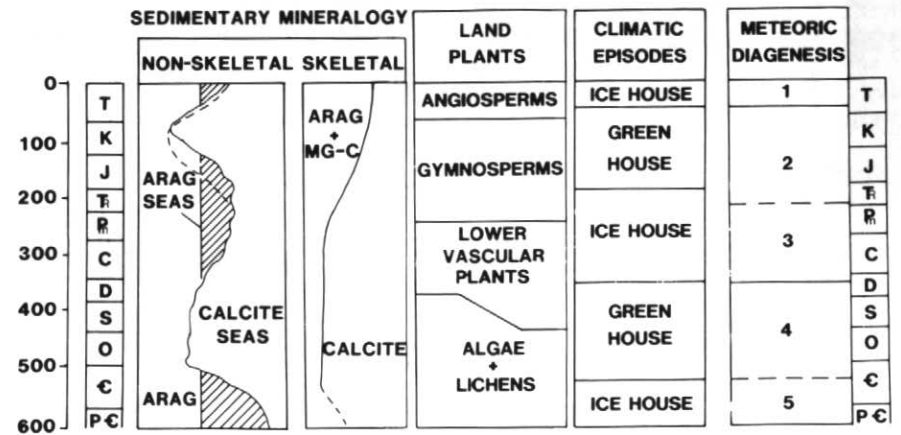| SEDIMENTARY MINERALOGY		LAND PLANTS	CLIMATIC EPISODES	METEORIC DIAGENESIS	
NON-SKELETAL	SKELETAL				
0 — T		ANGIOSPERMS	ICE HOUSE	1	T
100 — K	ARAG + MG-C		GREEN HOUSE	2	K
— J		GYMNOSPERMS			J
200 — Tr	ARAG SEAS				Tr
— P					P
300 — C		LOWER VASCULAR PLANTS	ICE HOUSE	3	C
— D					D
400 — S	CALCITE SEAS		GREEN HOUSE	4	S
— O		CALCITE			O
500 — €		ALGAE + LICHENS			€
600 — PC	ARAG		ICE HOUSE	5	PC

Figure 39 A plot of variations in non-skeletal mineralogy (James and Choquette, 1983; Sandberg, 1983), skeletal mineralogy (approximated from Lowenstam, 1963; Wilkinson, 1979), terrestrial vegetation and atmospheric P_{CO2} (Fischer, 1981) throughout Phanerozoic time. Numbers at right indicate approximate intervals when the combined effects of these variables probably resulted in different styles of meteoric, particularly vadose, diagenesis

Figure 40 Left – Ordovician limestone with all the fossils, trilobites (T), brachiopods (B), and bryzoans (C), preserved because they were originally calcite. Right – Pleistocene limestone illustrating porosity developed by dissolving stick-corals (C) and gastropods (G)

action continues and much of the meteoric environment becomes diagenetically inactive.

Regardless of which reaction is prevalent and what carbonate minerals are present, there is a net loss of carbonate from the system. This is best reflected in a variety of karst-related features. At the same time soil-related processes form a variety of very distinctive caliche carbonates which, because they are accretionary, are preserved and are extremely useful as criteria of subaerial exposure. If the exposed sediments are composed of metastable carbonates, a specific, predictable series of changes takes place, and lithification is achieved by precipitation of cements with distinctive structures which are preserved in ancient limestones. Concomitantly, because the process of alteration involves dissolution and precipitation, there is important cation and isotopic exchange with meteoric waters, leading generally to lower Mg^{+2} and Sr^{+2} contents and higher Fe^{+2}, Ca^{+2} and Mn^{+2}, as well as depletion in both ^{13}C and ^{18}O, compared to the original sediments.

The intensity of meteoric diagenesis is dependent not only upon where in the environment changes have taken place, but also upon the residence time in any particular zone. Climate is also an important factor in vadose alteration.

The processes and products of meteoric diagenesis described in this article cannot be applied equally to carbonates of all ages. Changes in the biosphere (varying skeletal mineralogy and changes in terrestrial vegetation) and the atmosphere (varying P_{CO2}) through geologic time will have had a profound but as yet uncertain effect on the style and intensity of fresh water diagenesis.

Finally, when examining any limestone outcrop it should be remembered that this rock is now in the meteoric environment and many of the fabrics and textures present may be the result of very recent processes!

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