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Noel P. James and Philip W. Choquette

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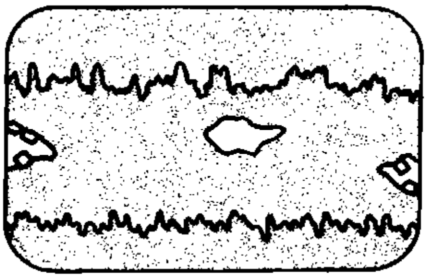

Diagenesis 6. Limestones—The Sea Floor Diagenetic Environment

Noel P. James
Department of Earth Sciences
Memorial University
St. John's, Newfoundland, A1B 3X5

Philip W. Choquette
Denver Research Center
Marathon Oil Company
Littleton, Colorado 80160

Introduction

Diagenesis of carbonate sediments in the marine environment often begins as soon as they are formed: foraminifer skeletons settling onto the deep sea floor gradually dissolve; living bivalves are infested with boring sponges; cement precipitates in coral pores just below those still occupied by the growing organism. In many ways these changes that occur on the sea floor are the most critical in the history of a limestone because they may not only modify depositional facies patterns but also direct future diagenetic pathways. If, for example, crusts should sporadically develop on the surface of a carbonate sand shoal through the precipitation of intergranular cement, a new hard substrate suitable for colonization by a variety of skeletal invertebrates will have been created where none existed before. The new community of organisms may in turn build reefs—thus in a very short time a sand shoal facies has been replaced by a reef facies with no change in the environment except partial lithification of the sediment. The effect of this sporadic cementation will continue as the carbonate sands pass through subsequent diagenetic environments—the unlithified and porous parts of the sands will be flushed first by new diagenetic fluids, while the cemented, nonporous parts will be affected more slowly. Finally, if the relative intensity of sea floor diagenesis can be tied to depositional facies, this knowledge is a powerful tool when attempting to predict trends in reservoir lithologies in subsurface carbonates.

As might be expected, carbonates are affected by a variety of chemical and biological processes as they lie on the sea floor. Precipitation of $CaCO_3$ predominates in shallow tropical marine environments, whereas dissolution is important at high latitudes and in deep water. Because of the preoccupation with lithification among those studying limestones, *any* pore-lining or pore-filling carbonate precipitate is commonly called "cement", regardless of whether it actually acts as a binding agent or simply fills a pore inside a grain. To date, recrystallization or neomorphism do not appear to be significant processes on the sea floor.

The most important biological process is infestation of carbonate hosts by a spectrum of large and small boring organisms.

Because both carbonate genesis and diagenesis occur within the environment of deposition and often under identical conditions, the line between the two is commonly blurred. For the purposes of this essay we have arbitrarily considered all processes outside direct biomineralization as being diagenetic, even though in some instances these processes involve actual particle formation. In the following pages we first give an overview of our current understanding of the diagenesis of carbonate sediments on the modern sea floor, and then we assess the applicability of these observations to the rock record.

Zones of Seafloor Diagenesis

There are two realms of carbonate deposition in the modern ocean: (1) shallow water, characterized by rapidly accumulating sediments (*ca* 100 cm/1000 years) which form mainly in warm tropical and subtropical environments; and (2) deep-water, typified by slowly accumulating sediments (*ca* 10 cm/1000 years) from the fallout of calcareous plankton occurring in oceans worldwide. Sediments on the slopes of shelves and platforms are mixtures of shallow-water and pelagic components. Whereas the shallow-water deposits accumulate quickly and form impressively thick carbonate bodies, comparatively thin pelagic carbonates, because of their enormous extent covering more than a quarter of the Earth's surface, account for over two-thirds of the carbonate currently being extracted from seawater (Hay *et al.*, 1976). Current estimates indicate that between 75 and 95 percent of pelagic carbonate is subsequently dissolved (Broecker, 1974) at the sediment-water interface in the deep sea (Adelseck and Berger, 1975).

In the perspective of geologic time it is important to recall that carbonate sediments made up of pelagic organisms are largely a Mesozoic and Cenozoic phenomenon and insignificant in Paleozoic and Precambrian strata (James, in press).

Vertical Zonation. The general patterns of carbonate accumulation have been known for over a century (Murray and Renard, 1891; Murray and Hjort, 1912). The primary controls on carbonate precipitation and dissolution are pCO_2 and water temperature and pressure. Although water pressure increases in a linear fashion with depth, water temperature does not. Seawater at low latitudes is temperature stratified and comprises three layers (Fig. 1): a warm, homogeneous, near-surface *mixed layer* below which is the *thermocline*, a zone of rapid temperature decrease with depth to around 5°C, and below this point the temperature of the *deep water* is more or less constant to abyssal depths.

The precise determination of the solubility of calcite and aragonite in sea water, however, has proved to be one of the more elusive quests of low-temperature geochemists, and as Morse and Berner (1979, p. 531) point out, "after 100 years of study the major problem of determination of the saturation state of the deep ocean remains largely unresolved". At present our understanding rests on the often conflicting results of laboratory experimentation, mapping of bottom sediments and field observations of particles hung in open containers at various depths in the ocean. These data most recently have been synthesized by Morse and Berner (1979) and Broecker and Takahashi (1978).

In general, near-surface tropical and subtropical seawater appears to be supersaturated with respect to both aragonite and calcite to depths of about 500 metres in the Pacific and 2,000 metres in the Atlantic (Takahashi, 1975). Below this supersaturated water, sediments on the sea floor are exposed to more and more undersaturated water with increasing depth because of increasing pressure and to a lesser extent decreasing temperature. Thus sediments are subjected to faster and faster dissolution rates until finally a depth is reached where the rate of dissolution is equal to the rate of sediment supply from above. Below this depth, called the *carbonate compensation depth* (Fig. 1; Bramlette, 1961) calcite disappears due to dissolution. In regions where carbonate productivity and resulting sedimentation rates are high, such as those near the equator, the CCD is depressed. Oceanic CCD for calcite is now at about 3,500 m in the Pacific and 5,500 m in the Atlantic, and is at its shallowest in the North Pacific and at its deepest in the North Atlantic. Variations of the CCD in the world oceans are discussed in detail by Kennett (1982).

Hills that rise from abyssal depths up through the CCD can be pictured as "the snow-capped mountains of the deep sea" (Berger, 1975), their lower slopes, below the CCD, covered by red clays and siliceous ooze while their tops above the CCD are mantled with white carbonate sediment.

Evidence for dissolution, however, can be seen at depths considerably shallower than the CCD. This gives rise to the concept of the *lysocline* (Berger, 1968), or depth where evidence of considerable (selective) dissolution is first encountered. The lysocline is in general 1,000 m shallower than the CCD and most dissolution takes place within this 1,000 m interval. Broecker and Takahashi (1978) have demonstrated that to within ± 200 m the depth of the calcite lysocline can be explained in terms of carbonate ion concentration in deep waters: the lysocline lies at greatest depth where waters with high carbonate ion concentrations extend to the bottom.

It should be noted that there is often a difference between the "hydrographic lysocline", that zone determined by field experiments in the water column, and the "sedimentary lysocline", marking an increase in the amount of dissolution on the sea floor (Berger, 1975). In fertile regions, near the continental margins in particular, the sedimentary lysocline may rise toward the surface and become diffuse.

But what of sediments on the sea floor in the several thousand metres between the shallow saturated waters and the lysocline? Why, if water pressure is the main control, is there not a gradual but steady increase in dissolution with depth, and why do the particles that lie on the sea floor show only scant evidence of corrosion? The answer appears to be a complex interplay between rates of carbonate accumulation, kinds and sizes of sedimentary particles and, perhaps most important, the kinetics of dissolution (Morse and Berner, 1979). In addition, orthophosphate, present as strongly adsorbed coatings on grain surfaces, is an inhibitor of calcite and Mg-calcite (but not aragonite) dissolution (Berner and Morse, 1974).

The CCD is the depth at which calcite dissolution balances deposition; the other two common sedimentary carbonate minerals, Mg-calcite and aragonite, likewise have compensation depths. Because there are no significant Mg-calcite plankton the Mg-calcite lysocline and compensation depth are poorly known, but they appear to be near those of calcite. A good practical measure of aragonite saturation, however, is the dissolution behaviour of pteropods, small pelagic gastropods with an aragonite shell (Berger, 1978). In marginal seas with antiestuarine circulation, such as the Mediterannean Sea, Red Sea and Persian Gulf, pteropods are common in sediments at all depths, indicating aragonite saturation of these waters. In low latitudes of the open ocean, however, pteropods disappear below about 1,500 m with depth values shoaling towards the higher latitudes. On average, the aragonite compensation depth (ACD) (Fig. 1) is shallower by 3 kilometres than the CCD, but this may vary. As with the CCD, the ACD is deeper in the Atlantic than in the Pacific because Atlantic waters are closer to being saturated for calcite and aragonite due to different overall patterns of deep water circulation. In the northeast Pacific and eastern tropical Pacific aragonite dissolution begins right below the mixed layer (500 m) within an oxygen minimum layer.

Zonation with Latitude. There is a much poorer understanding of latitude variations in shallow-water carbonate solubility. Obvious changes in carbonate sediments are complicated or masked by the effects of surface currents, terrigenous sedimentation and climate, as well as by the fact that outside the tropics many of the carbonates are relict (Emery, 1968; Ginsburg and James, 1975).

In general, *rapid* fixation of biogenic and inorganic carbonate in shallow water appears to be limited to the tropics and subtropics and rarely extends north or south of 30° latitude. Although a complete spectrum of carbonate skeletons is produced in these environments, they are distinguished by abundant production of corals and green algae, both of which are aragonite. Lees and Buller (1972) have, as a result, designated this the *Chlorozoan assemblage* to differentiate it from the *Foramol assemblage* of temperate and polar seas. The principal contributors to the cooler water carbonate assemblages are molluscs, foraminifers and bryozoans with echinoids, barnacles and coralline algae often present. The bulk of these higher-latitude carbonates are Mg-calcite or calcite with rare aragonite, and in mixed-layer mineralogies there are lower amounts of aragonite in colder climates (Milliman, 1974). Non-skeletal grains (ooids, peloids and lumps) and marine cements do not generally occur in these cooler waters and are restricted to the tropical zone, although Alexandersson (1974) has found aragonite and Mg-calcite cements *inside* coralline algae nodules in the North Sea where waters are undersaturated, suggesting strong biological influence.

Even though rates of carbonate production are much lower in cooler latitudes than in the tropics, carbonates may locally constitute up to 50% of the sediment. Observing the high productivity and lack of terrigenous material in such areas, however, the amount of carbonate is somewhat lower than might be predicted—suggesting removal of some portion (Milliman, 1974; p. 105). It is common to observe the effects of dissolution in both calcite and aragonite skeletons from latitudes above 40° (Alexandersson, 1978). Although the actual removal of carbonate is thought to be mostly by physical abrasion aided by maceration (Alexandersson, 1979) dissolution "opens-up" the grains and aids in these processes. There is no clear evidence of dissolution on a large scale.

Thus, in shallow-water environments north and south of the tropics conditions seem to be similar to those below zone of

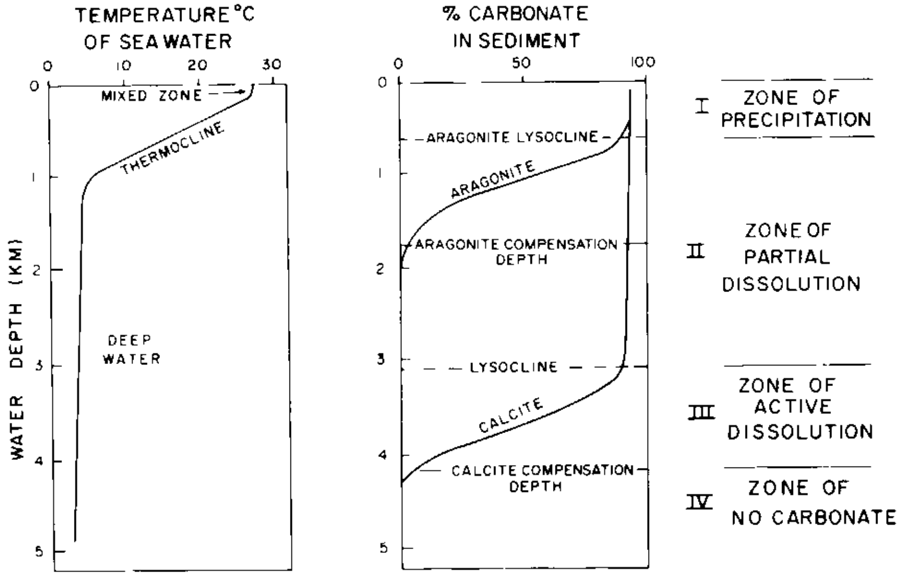

Figure 1 *Generalized diagrams illustrating the relative positions of calcite and aragonite solubility profiles in the modern tropical ocean and the variation in temperature with depth. The major zones of diagenesis are plotted to the right.*

saturation and above the lysocline in the deep tropical ocean.

Taken on balance we can roughly differentiate four zones in the modern ocean in which the conditions for carbonate diagenesis are the same (Figs. 1 and 2).

I. *Zone of Precipitation.* Shallow tropical to subtropical settings in which a complete spectrum of skeletal and non-skeletal particles of aragonite, Mg-calcite and/or calcite occur, as well as aragonite and Mg-calcite cements. The lower limit of this zone where seawater becomes undersaturated with respect to aragonite is about 1,000 m (varying between 500 m and 2,000 m depending on the ocean) in the tropics and shoals to the surface around 30°N and 30°S latitude.

II. *Zone of Partial Dissolution.* Deep-sea settings from the base of Zone I to the calcite lysocline and shallow water settings north and south of about 30° latitude to the polar regions; characterized by wholly biogenic carbonate accumulation (mainly Mg-calcite and calcite), minor dissolution, possible neomorphism and no significant inorganic precipitation of aragonite or Mg-calcite.

III. *Zone of Active Dissolution.* Deep-sea settings between the calcite lysocline and the CCD which may shallow to near the surface in polar seas, distinguished by wholly biogenic calcite accumulation showing abundant evidence of corrosion.

IV. *Zone of No Carbonate.* Wholly deep-sea settings, below the CCD where no carbonate is accumulating.

It should be stressed that this is a generalized zonation and applies chiefly to the open ocean and to associated shelf-slope and platform-slope systems. The major part of the following discussion on sea floor diagenesis is focused on Zone I. We understand very little about alteration in the lower parts of this zone, partly because of lack of study but also because we do not know the lower limit of aragonite saturation with precision (see later discussion on neomorphism).

Basinal Environments. For deep-water environments numerous studies confirm that very little dissolution occurs as particles settle through the water column; most carbonate is dissolved at the sediment-water interface.

If the sea floor is overlain by well oxygenated water, as is the case in most of the well aerated modern oceans, then burrowing allows mixing of interstitial and overlying waters, and so if bottom waters are undersaturated dissolution may take place some centimetres below the sediment surface.

If, on the other hand, euxinic conditions prevail and the overlying waters are CO_2 rich, then corrosion may take place on the sediment surface. Once the carbonate is buried just below the surface, however, dissolution ceases because within the sediment an increase in alkalinity is brought about by bacterial sulphate reduction (Berner, 1971). Carbonates may not suffer extensive dissolution in euxinic basins or on slopes where the oxygen-minimum zone impinges on the sea floor. In fact, although corrosion surfaces have been reported in limestones of basins interpreted as rather restricted (e.g., Lindstrom, 1979), signs of dissolution beneath such surfaces appear to be extremely rare.

Sea Floor Carbonate Precipitates

Mineralogy. Sedimentary particles on the modern sea floor consist of aragonite or calcite or magnesium-enriched calcite (Mg-calcite). Although some organisms precipitate skeletons of calcite, to date only Mg-calcite and aragonite appear to precipitate directly from shallow tropical seawater.

It is unclear what controls this mineralogy or why both Mg-calcite and aragonite are so common (see Bathurst, 1980 for recent summary). From a thermodynamic standpoint calcite with from 2 to 7 mole % $MgCO_3$ is the preferred stable phase in seawater (Berner, 1975). It has been suggested that the presence of strongly hydrated Mg^{2+} ions adsorbed onto the crystal surface (the Mg/Ca ratio in seawater is *ca* 5/1) inhibit the growth of calcite and the Gibbs free energy needed to dehydrate the ions and form aragonite is lower (Bathurst, 1968). On the other hand, it is also known that calcite crystals may precipitate and absorb large quantities of Mg^{2+} as they grow (Berner, 1966). The Mg-calcites so formed are in non-exchange kinetic equilibrium with sea-water. Chave *et al.* (1982) found that in distilled water aragonite has about the same solubility as Mg-calcite with *ca.* 8.5 mole % $MgCO_3$. In seawater, however, since Mg-calcite is in non-exchange kinetic equilibrium, it appears that aragonite solubility coincides with the solubility of Mg-calcite containing 12 to 14 mole % $MgCO_3$ (Berner, 1975; Fuchtbauer and Hardie, 1976) or even 25 mole % $MgCO_3$. Interestingly, Walter (1983) has recently restudied relative solubilities and concluded that, in distilled water, aragonite has the same solubility as 12.5 mole % Mg-calcite.

Whatever the controls, it is clear that they are subtle indeed. In general there does seem to be a preference for a specific mineralogy to be precipitated on a substrate of that same mineralogy (Glover and Pray, 1971) at least in internal pores through which water circulation is slow. For example, it is not uncommon in modern reefs to find aragonite cement within aragonite corals and Mg-calcite cements nearby in the chambers of the Mg-calcite foraminfer *Homotrema*. There are, however, numerous exceptions to the rule of "substrate mineralogy control", and the cements are often interlaminated in pores of reef limestone on a microscale (James and Ginsburg, 1979).

Seawater has been described as "a dilute electrolytic organic soup" so that prediction of any reactions that lead to precipitation must also take into account the large amount of organic material. That organics affect precipitation is clear, but their role is ambiguous. In the first place, all particles are coated with layers of organic molecules which may inhibit nucleation, allowing seawater to maintain supersaturation (Suess, 1970, 1973). At the same time, extracts of organic matter from ooids similar in composition to that found in skeletons (Mitterer, 1971), and the presence of more ^{13}C in marine cements than should be there if they were completely inorganic precipitates (Milliman and Muller, 1977) both point to some sort of involvement by organics.

Although in general Mg-calcite appears

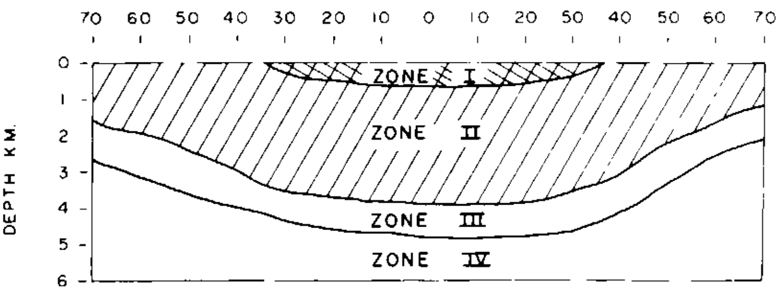

Figure 2 *Variations in the different zones of seafloor diagenesis in the modern ocean.*

to be the most widespread marine cement (James and Ginsburg, 1979), aragonite is common in waters of slightly elevated salinity. Finally, in ooids it appears that the degree of agitation may favour the precipitation of one mineral over another (Davies *et al.*, 1978).

Petrography and Geochemistry.
Magnesium Calcite (Fig. 3)

Magnesium-enriched calcite precipitates generally contain a range of between 12 and 19 mole % $MgCO_3$. The crystals (trigonal $CaCO_3$) generally precipitate either as tiny rhombs less than 4µm across (micrite-size) or as fibres a few tens of µm long. Although iron can be accomodated in the calcite crystal lattice, microprobe analysis of these cements reveals no detectable Fe^2. Probably this is because there is very little iron in seawater and most precipitation takes place under oxidizing conditions where any iron present is in the Fe^{3+} state, and the partition coefficient is close to one (Richter and Fuchtbauer, 1978). Strontium fits uneasily into the calcite lattice because of its relatively large ionic radius and so Mg-calcite rarely contains more than a thousand ppm Sr^{++} (Kinsman, 1969).

Micrite-size crystals. This is the most common type of Mg-calcite cement and it occurs in a wide variety of sediments. It ranges from thin rinds only tens of microns thick around particles and algal filaments to complete fillings of pore spaces. Although micrite is easily seen as cement when encircling particles or lining voids, if the pores are entirely filled it is impossible to differentiate from lime mud. Thus the addition of Mg-calcite micrite cement may, in the process of lithification, change the texture of a grainy sediment from a grainstone to packstone.

Of interest here is the ubiquitous association of micro-peloids, ranging in size from 20 to 100 µm on average, with micrite cement. These are aggregates of Mg-calcite rhombs. The texture of the resulting fine-grained material is reminiscent of the *texture grumuleuse* of Cayeux (1935), a fabric of numerous clots or vague small peloids surrounded by micrite and microspar. While these may well be sedimentary particles of uncertain origin, the persistent association has led some workers (Macintyre, 1977, 1983; Marshall, in press) to suggest that they may be the result of spontaneous nucleation and precipitation of Mg-calcite in the water column and may then settle out of suspension. This precipitation may be either direct or organically induced.

Fibrous crystals. This cement (Fig. 3) is generally found as isopachous encrustations up to several hundred microns thick. The elongate crystals are either nucleated picket-fence style on the substrate (Ginsburg and Schroeder, 1973) or are located at intervals and grow as small spherulites which quickly interfere with one another as they develop (James and Ginsburg, 1979). These spherulites are often arranged in tiers in the cement rind.

Epitaxial crystals. It is interesting that although particles of echinoderm skeletons, composed generally of a single crystal of Mg-calcite, are common elements in many modern carbonate sediments, there has not yet been reported the development of marine epitaxial Mg-calcite cement on these grains. The closest occurrence is the presence of epitaxial crystallites developed on cores of echinoderms in ooid cortexes (Marshall and Davies, 1975).

Aragonite. Aragonite (orthorhombic $CaCO_3$) precipitates are either microcrystalline or needles a few µm or tens of µm long. Loreau (1982) separates these nannocrystals, from largest to smallest, into needles (generally cements), baguettes (generally in the ooid cortex) and nannograins with increasing turbulence favouring needle formation and increasing organics favouring nannograins. Strontium is the major trace element in aragonite whose orthorhombic structure accomodates it easily and cement crystals usually carry about 8,000 to 9,000 ppm, as do most aragonite skeletons (Kinsman, 1969; Bathurst, 1975). The major exceptions are aragonite molluscs which contain between 4,000 and 1,000 ppm.

The needles occur in variety of different habits (Fig. 3):

(1) *Isopachous rinds* are particularly common in ooid and skeletal sands and as epitaxial growths on aragonite substrates such as corals, green algae and gastropods.

(2) *An intergranular mesh* of crystals nucleated randomly on grain surfaces and growing in a variety of directions into a void until it is completely filled by an irregular growth of crystals or crystallites.

(3) *Botryoids* which range in diameter from tens of µm to centimetres, sometimes developed in sands but most spectacular in reef cavities.

Isotopic Composition. When $CaCO_3$ is precipitated from seawater—whether in calcareous skeletons, non-skeletal grains such as ooids, or marine cements—it acquires characteristic chemical "signatures" in the form of $^{18}O/^{16}O$ and $^{13}O/^{12}O$ isotopic ratios as well as minor-cation (e.g., Sr^{+2}, Mg^{+2}, Na^{+}) concentrations. Large numbers of analyses have been done on carbonate sediments and on many of their more common constituents, such as ooids, calcareous green and red algae, corals, brachiopods, mollusks, lime mud, etc. (Fig. 4). Milliman (1974) and Bathurst (1975) have summarized many of these isotopic data on Recent marine carbonate sediments, including the pioneering work of Gross (1964). Progressing from a largely empirical approach of collecting and comparing isotopic analyses, this branch of low-temperature geochemistry is rapidly evolving toward a better understanding of processes, particularly diagenetic processes, operating in carbonates (e.g., Brand and Veizer, 1981; Lohmann, 1982a; 1982b).

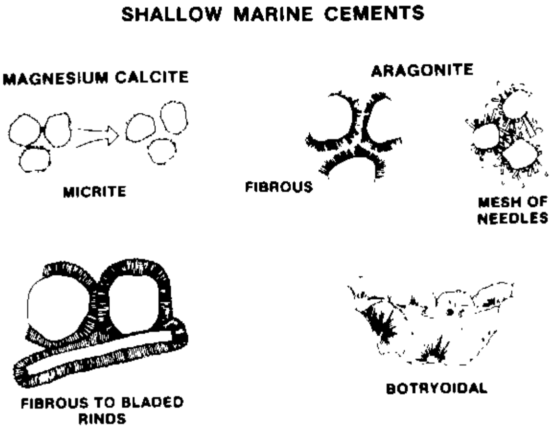

Figure 3 *Different types of modern seafloor carbonate cements.*

Warm-Water Cements. Though much of the spectrum of marine cements and cementation processes is poorly understood, enough information has been gathered about the isotopic compositions of these cements to suggest some general relationships. We know the most about cements being precipitated in modern sediments and reefs at low latitudes, in warm shallow-shelf and platform settings. These cements have relatively heavy, ^{18}O-enriched oxygen-isotopic compositions of 0 to +3 ‰ (Gross, 1964; Shinn, 1969; Milliman, 1974; James and Ginsburg, 1979), and their $\delta^{13}C$'s are heavier (*ca* +2 to +5 ‰) than would be expected had they been precipitated in isotopic equilibrium with seawater +2.0 to +2.5‰ at 25°C; Lloyd, 1971). Because the aragonitic thalli of calcareous green algae and the Mg-calcite of micrite rims produced by endolithic blue-green algae also have heavy $\delta^{13}C$'s dominantly of +2 to +6 ‰, several workers have proposed that these groups of algae are "involved" if not directly responsible for the origin of marine $CaCO_3$ cements (Lloyd, 1971; Schroeder, 1972; Moore, 1973; Milliman and Muller, 1974). A genetic relationship may be difficult to establish firmly until it becomes possible to determine accurately the isotopic compositions of ultra-small samples on the order of, for instance, 10^{-2} mg or less. Also, some marine cements such as aragonite botryoids (James and Ginsburg, 1979) lack signs of endolithic algae or other bioalteration apart from macroborings.

In any event, marine cements in modern warm/shallow environments can be clearly differentiated isotopically from Late Cenozoic meteoric vadose to shallow-phreatic cements (e.g., Allan and Matthews, 1977), and the evidence is accumulating that these differences survive, though often much reduced, in the face of complex diagenetic histories spanning tens to hundreds of millions of years.

Cold-Water and/or Deep-Water Cements. Isotpic studies of $CaCO_3$ cements in modern cold-water shelf carbonates have only recently begun (e.g., Rao, 1981; Nelson *et al.*, 1982), but our understanding of diagenetic changes taking place in deep-sea environments has grown significantly in the past few years due to studies of deep-water carbonates in DSDP cores (Hsu and Jenkyns, 1974) and elsewhere (Schlager and James, 1978). In one deep intra-platform basin, Tongue of the Ocean, pelagic sediments exposed for thousands of years in erosional cuts on the seafloor are undergoing diagenetic alteration along the same course typical of meteoric diagenesis (Schlager and James, 1978): these sediments, composed of aragonite, calcite and Mg-calcite when deposited, lithify within 100,000 years by conversion to calcite micrite with 3.5-5 mole % $MgCO_3$. With increasing content of calcite micrite their $\delta^{13}C$ and $\delta^{18}O$ both decrease, shifting toward lighter, equilibrium values characteristic of the marine "diagenetic trend" proposed by Milliman and Muller (1974). Data for European and oceanbasin (DSDP) chalks of Cretaceous and Tertiary age (Scholle, 1974; Scholle and Arthur, 1980) indicate that the isotopic differences between such modern deepsea hardgrounds and their precursor sediments are largely preserved in the fossil record.

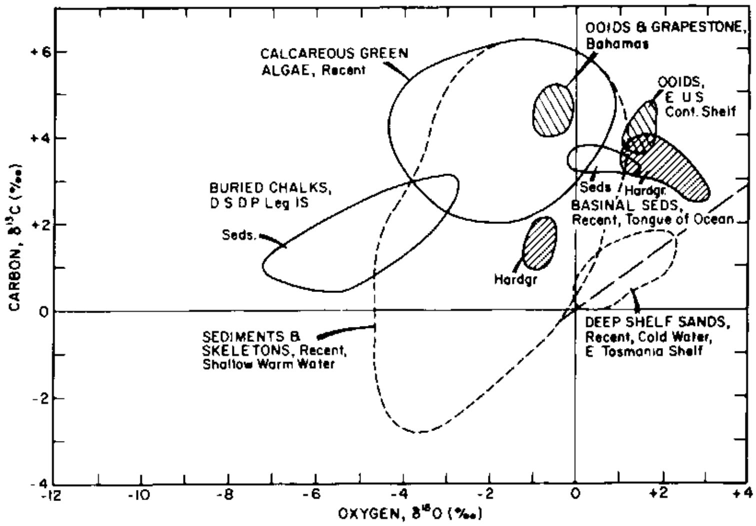

Figure 4 *Crossplot of carbon vs. oxygen isotopic compositions for recent sediments and component particles, and for buried chalks. PDB-1 is the isotopic standard in this diagram. Data are from Gross (1964), Anderson and Schneidermann (1973), Milliman and Muller (1977), Schlager and James (1978) and Rao and Green (1982).*

Habitat of Sea Floor Precipitates

Particles. Ooids are perhaps the most important precipitates in terms of the amount of $CaCO_3$ removed from shallow seawater. They may have a cortex of tangentially or radially oriented crystallites and in the modern ocean the overwhelming majority are aragonite (Simone, 1980; Loreau, 1982), although Mg-calcite forms have been found (Marshall and Davies, 1975).

Although there is compelling evidence that the lime mud found in many shallow-marine settings is mostly biogenic in origin (Stockman *et al.*, 1967; Neumann and Land, 1975), some may indeed be due to direct precipitation. The clouds of aragonite crystallites or 'whitings' seen in many shallow tropical environments are commonly thought to be mud derived from benthic sources stirred up by feeding fish—yet in some cases they may be products of spontaneous precipitation. In the Persian Gulf, for example, there are few aragonitic algae, yet numerous whitings and much mud, but also many fish. Loreau (1982) has recently demonstrated that on the basis of Sr^{++} and Mg^{++} contents both Persian Gulf and Bahamian aragonite needle muds are likely inorganic precipitates.

While most readers will agree that we are stretching the concept of diagenesis by including these sediments, we have done so to place the whole topic in context.

Inside Grains and Skeletons. This type of precipitate, found inside particles and or skeletons, is the most widespread $CaCO_3$ "cement", occurring even in grains that are still rolling around on the sea floor. The cements occur between silt-size particles inside peloids to precipitates lining, chambers and other pores inside skeletal elements (Alexandersson, 1978; James *et al.*, 1976) to precipitates in micro and macroborings. Thus it is not unusual in the fossil record to find grains exhibiting good evidence of internal sea-floor $CaCO_3$ precipitation, yet showing little or no indication that they were actually cemented together in the sea-floor environment.

Between Particles. This type of precipitation is the least common but most important geologically because it is 'rock-making' cement. Thus limestones may be formed soon after deposition in tens to thousands of years, if conditions are right, in the environment of accumulation (Fig. 5).

Platform deposits. The most desirable conditions for interparticle cementation appear to be water turbulence and stabilized sediment. The best site's appear to be

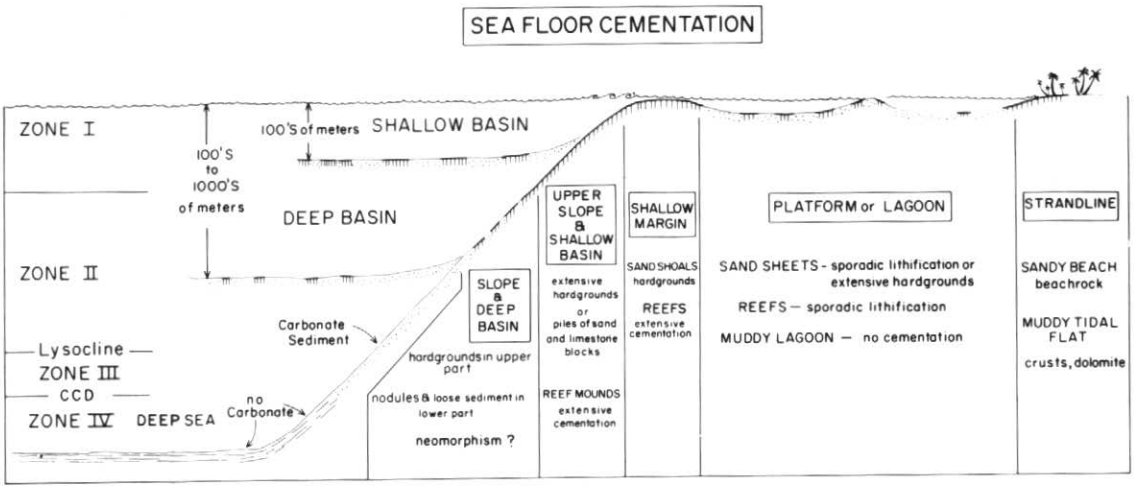

Figure 5 *The locations of seafloor precipitation on a shallow carbonate platform and in adjacent deep-water settings. In all of these habitats, most sediments are unlithified.*

the insides of reefs, especially at or near the platform margin (Ginsburg and Schroeder, 1973; James *et al.*, 1976; Macintyre, 1977) where both conditions are met. Likewise, sand shoals near the platform edge are likely locales, but here most lithification takes place when the sediments are at rest inside the sand shoals or bound by algae (Dravis, 1979). In contrast, muddy lagoonal sediments are rarely lithified, probably because of sluggish water movement, continuous bioturbation and general reducing conditions. Strandline sands also are commonly cemented but this may not be entirely due to reaction with seawater. When viewed in total, even though the majority of sediments on shallow carbonate platforms are not cemented, there appears to be a facies preference for precipitation.

While this generalization may hold true for muddy shelves and platforms, cemented crusts or hardgrounds (Fig. 6) are common in extensive sand sheets on parts of the Bahama Banks (Taft *et al.*, 1968), wide gently dipping shelves such as off the Trucial coast in the Persian Gulf (Shinn, 1969) and in partially enclosed embayments such as Shark Bay (Read, 1974). Lithification is most intense at the surface and decreases in intensity downward, generally ceasing within tens of centimetres of the sediment-water interface. As Wilkinson *et al.* (1982) point out, the processes of lithification may be quite different between platform-margin reefs which have large cavities and are subject to strong currents and waves moving large volumes of normal seawater and non-reefal sands where current velocities are reduced, pore volumes small and communication with surrounding waters limited.

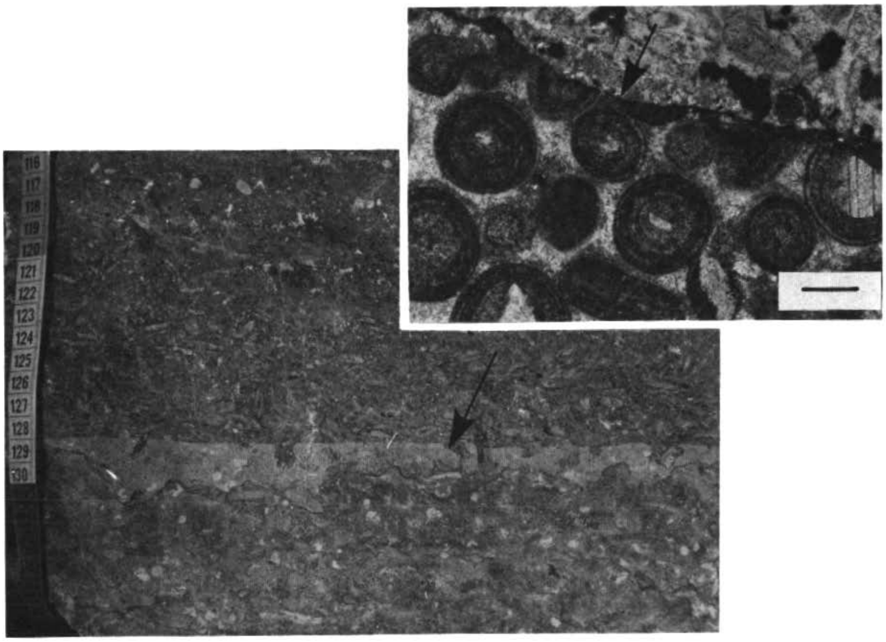

Figure 6 *An irregular submarine hardground (between 129 and 128 cm. on the tape) developed in Lower Cambrian ooid limestones of the Forteau Formation, western Newfoundland. The photomicrograph illustrates the truncated ooids and cements at the hardground surface (arrow indicates location; scale bar 0.5 mm).*

Shallow enclosed basins. In relatively shallow basins such as the eastern Mediterranean and the Red Sea, where there is anti-estuarine circulation and warm waters extend to the sea floor (Fig. 5), basin-floor sediments are locally cemented to form crusts (Gevirtz and Friedman, 1969; Milliman and Müller, 1977) by Mg-calcite generally and occasionally aragonite.

Slope and deep basin deposits. The ocean-facing slopes of shelves and platforms illustrate a range of lithified sediments. The top of the slope, which generally comprises deep portions of the marginal reef and forereef, locally exhibits extensive cementation (Land and Moore, 1980; James and Ginsburg, 1979). Cementation seems to die out with increasing water depth so that below 300 m or so hardgrounds give way first to nodules and then to unlithified sediment (James and Schlager, pers. obs., 1979; Mullins *et al.*, 1980). These partly to completely lithified slope sediments are commonly subject to failure and become clasts in gravity flow deposits (Fig. 7).

Hardgrounds are common on the sea floor swept by the Gulf Stream off the western Bahama Banks, and here in depths of 600 m or so lithified mounds (lithoherms) formed by numerous superimposed crusts and populated by deep-sea ahermatypic corals and crinoids rise 50 m or more above the bottom (Neumann *et al.*, 1977). The cement in these structures is Mg-calcite.

Below these depths is the transition zone where water temperatures decrease rapidly in the thermocline and waters at the sea floor pass from Zone I (precipitation) to Zone II (partial dissolution). Here there is evidence of the alteration of aragonite and Mg-calcite to calcite (see following section on neomorphism).

Neomorphism

In Zone I, on the shallow tropical sea floor, when aragonite and Mg-calcite are precipitated they appear to remain largely unchanged until affected by waters of a radically different character. Nevertheless, there are some reports of recrystallization: Mg-calcite foraminifers and coralline algae altering to aragonite (Murray, 1966; Kendall and Skipwith, 1969; Purdy, 1968); aragonite cements partially replacing aragonitic mollusc shells (Shinn, 1969); parts of aragonitic cements and skeletons changing to Mg-calcite (Alexandersson, 1972; Scherer, 1974; Land and Moore, 1980). These occurrences seem to be rare but they do point out again the subtleties governing precipitation of different $CaC0_3$ phases and tell us that the possibilities for neomorphism do exist, but it may not be common in today's shallow seas.

In deeper water, however, things appear to be somewhat different, and here there is strong evidence for alteration of Mg-calcite and aragonite to calcite (Milliman, 1966; Gomberg and Bonatti, 1970; Schlager and James, 1978). In all of these examples, from the tops of seamounts and the slopes of platforms, arrested sedimentation and prolonged exposure to open seawater appear to be prime requisites. Schlager and James (1978) have shown that this neomorphism may be related to water temperature because while Mg-calcite cements are the norm in the thermocline layer they contain progressively less magnesium in cooler waters, as suggested experimentally by Füchtbauer and Hardie (1976). Below the thermocline the polymineralic muds have altered to calcite, Mg-calcite components have changed to calcite with 3 to 5 mole % MgC0, and aragonite elements have dissolved with the resultant voids sometimes filled by calcite cement. Interestingly, calcite cement is precipitated as epitaxial overgrowths on neomorphosed calcite echinoderm plates. All of this new calcite is in isotopic equilibrium with the cooler seawater.

This deeper water neomorphism is probably rare in the modern ocean because of continuous sedimentation due to the ongoing fallout of calcareous planktonic microfossils. But in the Paleozoic when there were virtually no planktonics and all deep-water carbonate sediments including lime mud came episodically from nearby platforms or shelves, the times between sedimentation events could have been periods of recrystallization and cementation by calcite on the sea floor.

Biological Diagenesis

Even though neomorphism *sensu strictu* is not a common process in shallow-water carbonates, sedimentary particles and rocks do undergo drastic alteration to micrite or mudstone through a combination of biological and chemical processes. The mechanism involves infestation of the carbonate host by one of a variety of boring or endolithic organisms and filling of their holes once they die by fine sediment and/or cement.

Particle Alteration. On a microscale this process involves boring by endolithic algae or fungi into sand-sized particles. Algae, mostly blue-green and green, appear to be most effective in the upper part of the photic zone to depths of about 70 m (Budd and Perkins, 1980). Fungi extend to depths of 500 m and more, whereas heterotrophic algae and bacteria occur to abyssal depths (Friedman *et al.*, 1971). Infestation appears to be most active (Kobluk and Risk, 1977) when grains are at rest in lagoonal or on-shelf settings.

In shallow tropical environments where precipitation is dominant (Zone I) the vacated holes of the endoliths are filled by Mg-calcite and/or aragonite cement (Margolis and Rex, 1971; Alexandersson, 1972). If the numerous generations of boring endoliths are restricted to the grain margin, then a rind of microcrystalline Mg-calcite or aragonite called a "micrite envelope" (Bathurst, 1966) develops. The development of these envelopes is often critical in grain preservation as the sediments go through later diagenetic environments.

If infestation is intense and prolonged the entire grain may be transformed to microcrystalline Mg-calcite or aragonite, with little trace left of the original structure (Kendall and Skipwith, 1969). This pervasive micritization is particularly common in grapestone lumps (Bathurst, 1975) and in stromatolites (Logan, 1974). These "diagenetic peloids" are difficult if not impossible to distinguish from fecal pellets or Mg-calcite cement aggregates in some instances. As a result, it should be stressed

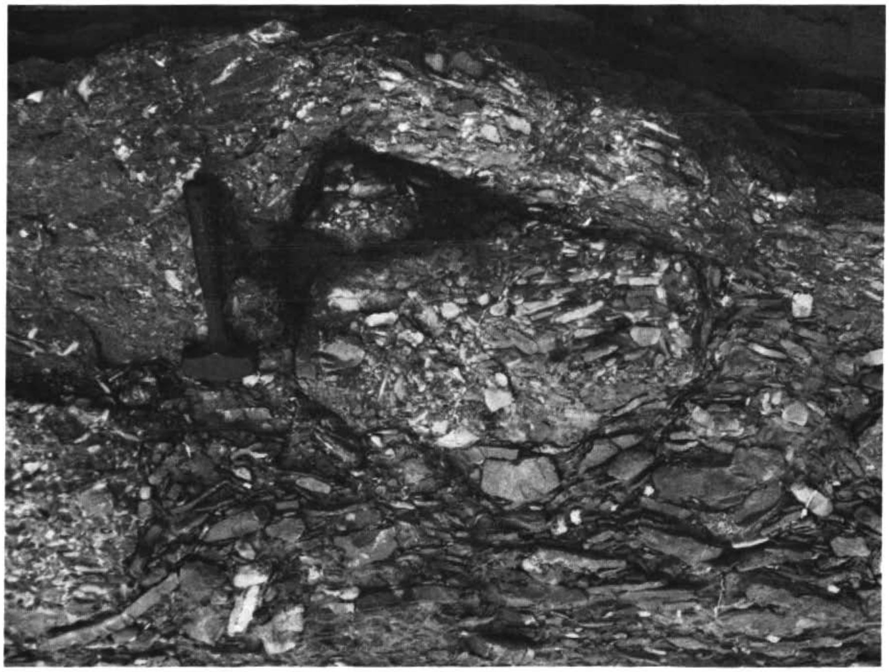

Figure 7 *A debris flow from the Ordovician part of the Cow Head Group, a carbonate slope deposit in western Newfoundland, illustrating the effects of multigeneration seafloor cementation. The tabular clasts are fragmented thin-bedded lime mudstones that were lithified on the slope before being eroded and incorporated into the flow. The boulders of tabular clast breccia to the left of the hammer and at upper right were debris flow deposits lithified on the sea floor before being incorporated into yet another flow. Photograph, M. Coniglio.*

that the term "peloid" applies to grains that may have had very different origins but look the same.

Outside the tropics and in deeper water (Zone II) infestation is often just as intense but because of the lack of precipitation the holes are not filled and so the grains are gradually broken down into finer grained particles (Alexandersson, 1979).

Limestone Alteration. Boring also occurs on a macroscale with sponges, bivalves and polychaete worms being the excavating organisms. Particularly common in reefs and on hardground surfaces, the cavities created by these larger excavating invertebrates may be filled with fine sand to silt-sized sediment and/or cement (Zankl and Schroeder, 1972; James and Ginsburg, 1979). The end result, however, is the same: a skeletal-rich rock is transformed by several generations of alteration into a muddy limestone and much of the original texture is lost.

Strandline Diagenesis

Diagenetic processes that characterize the shallow tropical sea floor also predominate in the intertidal and supratidal zones. Here, however, the environment is more complex because (1) instead of a simple rock-water system the setting is three-phase, rock-water-air; (2) fresh-water flow from land extends seaward out underneath the shore, with the water table at or just below the strandline sediment surface; and (3) the waters themselves are commonly mixtures of marine and meteoric fluids.

Beaches. The most common manifestation of strandline precipitation is *beachrock* - layers of cemented beach calcarenite (Fig. 8) that dip seaward at the same attitude as beach sediments and are composed of the same grains as the beach sand, which can be anything from carbonate to quartz to volcanics; good reviews are to be found in Stoddart and Cann (1965) and Milliman (1974). Some tropical intertidal zones are all beachrock, others have only scattered layers, and many are without it. Strata generally are localized to the intertidal zone up into the zone of wave splash and disappear seaward, landward, and with depth into unconsolidated sediment. The beachrock may be present as scattered nodules, isolated slab-like layers, or whole thicknesses of beach sediment, generally developing a few centimetres below the sediment surface.

The surface of the beachrock is often pitted and bored and exhibits dissolution basins or potholes. In cross-section beachrock is well-laminated and the base of each layer is sharp. The rock is characteristically jointed into blocks and textured by cracks and channels. Erosion of rock slabs and reworking during intense storms leads to conglomerates or ramparts of beachrock clasts. The grain-size of the sediment ranges from sand to boulders.

Induration varies from loosely cemented sand that can be disaggregated by rubbing to well-lithified rock that can be broken only with a hammer. Commonly the surface is hard and the inside soft. Cements are aragonite or Mg-calcite with the same spectrum of fabrics as on the sea floor, but microcrystalline aragonite cement is particularly common (see numerous articles in Bricker, 1971). In some localities these cements have a pendulous or mini-stalactite orientation, signifying vadose precipitation in an air-filled void.

Beachrock forms at surprisingly rapid rates on the order of years to tens of years, so that today coins, bottles, skeletons and other artifacts are commonly found in beachrock. Most workers now seem to agree that precipitation of beachrock cement is from seawater by evaporation in the intertidal zone during low tide (Bricker, 1971), although the composition of the water may be modified greatly by meteoric mixing (Moore, 1983). Other alternatives are by degassing of CO_2-rich carbonate-saturated groundwaters which have migrated into shore areas (Hanor, 1978), or by biologically induced precipitation.

Aragonite Crusts. Aragonite crusts up to 20 mm thick and called "coniatites" (Purser and Loreau, 1973) often coat beachrock, carbonate grains and exposed bedrock in the splash zone. These coatings, which resemble grey to cream-coloured enamel paint, range from smooth encrustations to porous surfaces that resemble tufa or travertine. Beneath overhangs or in beachrock they have dripstone morphologies. These crusts appear to develop only when the substrate is impermeable. In the fossil record such crusts could easily be mistaken for seafloor precipitates.

Tidal Flats. Diagenesis of carbonate sediments on wide, muddy tidal flats is discussed in part in other articles in *Geoscience Canada* (James, 1977; Kendall, 1978; Morrow, 1982). The diagenetic processes are complex and involve not only $CaCO_3$ precipitation but also the formation of dolomite and evaporite minerals.

In terms of limestone formation in particular, however, the same processes seen on beaches predominate, but the rate and intensity of peritidal diagenesis appear to be a function of climate. On humid tidal flats, as typified by the Bahamas, cemented crusts are relatively rare. Only a few centimetres thick (Fig. 9), they are found just above the normal high-tide mark. In the inland marshes the crusts are composed of algal filament molds encrusted with Mg-calcite. In the more seaward channel belt, crusts are peloidal sediment without filaments cemented by Mg-calcite micrite (and often containing dolomite) in which cracks and fenestrae are filled with acicular to bladed aragonite (Hardie, 1977).

On arid tidal flats, such as those along the Trucial Coast of the Persian Gulf (Taylor and Illing, 1969) and around Shark Bay, (Logan 1974), cementation is more extensive and crusts extend over the whole

Figure 8 *A group of geologists walking on the black, algal infested surface of beachrock composed of ooid and grapestone particles cemented by aragonite on the shore of Cockroach Bay, Berry Islands, Bahamas. The white sand near the trees (right) and the sediments beneath the water (left) are unlithified.*

tidal range. Cryptocrystalline aragonite is the most common cement, quickly lithifying intertidal stromatolites and algal-bound sediment. In Shark Bay this grades seaward into acicular aragonite cementing hardgrounds offshore. In some instances the aragonite cement forms pendant growths from the ceilings of large voids and fenestrae.

Perhaps most useful as signatures of shoreline precipitation are the large-scale structures produced. Rapid intergranular precipitation at or near the sediment surface produces expansion fractures and arcuate to polygonal ridges and tepees. These broken crusts may in turn be reworked by storms to produce pavements of tabular clasts.

In many of these crusts micritization of skeletal and ooid grains is intensive so that the peloidal sediment is in part depositional and in part diagenetic.

The Fossil Record

The products of sea floor diagenesis can be recognized in carbonates of all ages. Almost all of the information, however, comes from the Phanerozoic, with little information on Precambrian limestones.

Biological Alteration.

Microborings. Endolithic algae are known in carbonates as old as Precambrian (Campbell, 1982) and micritized grains are an integral part of most shallow-water limestone suites.

Macroborings. Macroboring ichnofossils are known in limestones as old as Lower Cambrian (James *et al.*, 1977) but only one, *Trypanites* (a probable siphonculid worm trace), is found until Middle Ordovician reefs develop and then there is a rapid diversification of forms (Kobluk *et al.*, 1978). The borings of various small bivalves, sponges and echinoids have been found in reefs, reef-mounds and hardgrounds of later Paleozoic and particularly Mesozoic and Cenozoic age (Warme, 1975).

Sea Floor Precipitation. Confident recognition of sea floor cementation and its spectrum of products is a critical part of any study in carbonate petrogenesis, yet two problems bedevil this seemingly simple task: (1) what precisely are the fabrics of the aragonite and Mg-calcite cements once they undergo neomorphism to calcite in another diagenetic environment and (2) were aragonite and Mg-calcite always the normal precipitates on shallow carbonate platforms in the past?

In our experience marine cementation is *not* a common or widespread feature of ancient limestones. It is most commonly documented from fossil reefs (Fig. 10), especially from reef-mounds (James, 1978; 1983) and reef blocks in fore-reef deposits (Fig. 11), where marine cement may make up 50% or more of the rock volume. It is commonly inferred to be present from field evidence of hardgrounds yet rarely is demonstrated there on the petrographic level, possibly because micrite-size cements are the norm and cannot be resolved microscopically. Fibrous cements are rarely seen in marine-shelf grainstones but have been described from fossil beachrocks (Purser, 1969; Choquette and Steinen, 1980).

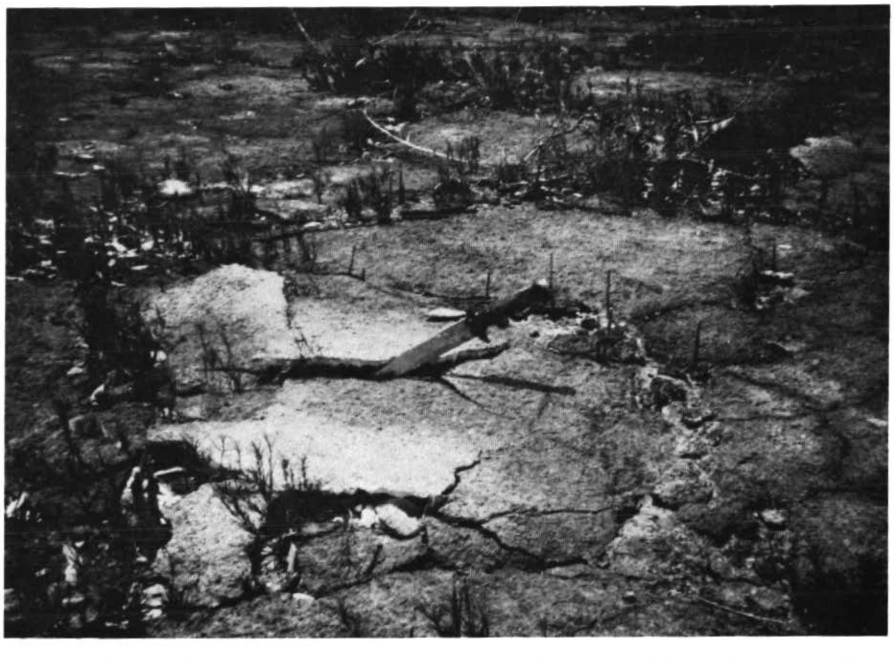

Figure 9 *Brecciated crusts composed of peloids and algal tubules, cemented by Mg-calcite and containing minor dolomite in the supratidal zone of the muddy tidal flats along the western side of Andros Island, Bahamas (handle of the dive knife is 10 cm long).*

Recognition of seafloor lithification. Prior to any analysis of sea floor cement fabrics *per se* the following criteria are useful in establishing early lithification on the sea floor (Fig. 12):

(1) If in bedded sediments, are the lithologic contacts knife-sharp, and if grains are present are they truncated (e.g., Fig. 6)? If cements are present are they truncated?
(2) Is the surface stained by iron or manganese salts or phosphate minerals?
(3) Are there cobbles or pebbles of limestone or sand-grade lithoclasts similar in composition to the matrix, and if so are they encrusted with organisms?
(4) Is the surface encrusted by organisms that require a solid substrate?
(5) Is the rock surface bored and, in thin section, if cements are present, are they bored as well?
(6) If in reefs, is the first-stage cement localized to the reefs?
(7) If in reefs or hardgrounds, is the first-stage cement interlayered with marine sediment in cavities (Fig. 13)?
(8) If in reefs, are there neptunian dykes?
(9) In reef talus are there clasts with first-stage cement or clasts of the cement (Fig. 11)?
(10) If in bedded sediments, are expansion ridges and polygons present?

While these features point to early lithification, many alone may be the result of a short-lived period of subaerial exposure.

In the fossil record beachrock can be differentiated from sea floor hardgrounds only with difficulty, but this may be facilitated by the observation of features such as (1) associated edgewise conglomerates, (2) intertidal erosion features (3) jointing, (4) keystone vugs, (5) pendulous cements and (6) associated facies (Donaldson and Ricketts, 1979; Read and Grover, 1977; Figs. 14 & 15).

A helpful guide is the petrographic nature of the cements themselves. Although by no means always the case, accumulated evidence from the fossil record suggests that most "fibrous" cements as well as many "spherulitic" or mammillary cements were marine though they are common in speleothems. Although it is unquestionable that microcrystalline calcite (or Mg-calcite and possibly aragonite) was precipitated from sea water in the past as it is today, the small size of the crystals, their similarity to carbonate mud and their susceptibility to rapid recrystallization all make the identification of these cements difficult (Mountjoy and Riding, 1981).

Fibrous calcites. These cements (Fig. 16) fall into two general groups:(1) *Fascicular-optic* (Fig. 17) cones of fibrous calcite with divergent optic axes (Kendall, 1977) and (2) *Radiaxial-fibrous* crystals (Fig. 18) with consertal boundaries and convergent optic axes (Bathurst, 1959). It seems certain that most of these fibrous calcites are neomorphic products of one or more precursors (Kendall and Tucker, 1973). At present it is not known with certainty what these precursors were. There is accumulating evidence, however, that fibrous Mg-calcites are the most likely candidates. Important in this regard is the discovery of tiny rhombs of dolomite, 1 to 10 μm in size in both calcite skeletons (Macqueen and Ghent, 1970) and fibrous calcite cements (Lohmann and Meyers, 1977) thought, on the basis of other evidence, to have been originally Mg-calcite.

These fibrous calcites are often preferentially enriched in Mg^{2+} and have $\delta^{13}C$ values consistent with precipitation from seawater (e.g., Davies, 1977; Walls *et al.*, 1979).

Stromatactis. An important structure in fossil carbonates, especially mud mounds, is *stromatactis,* loosely defined as irregular masses of fibrous calcite spar often displaying a flat base. These features originally were thought to be the recrystallized remains of a mound-forming organism, but since the work of Bathurst (1959) are now known to be sediment-floored cavities filled with fibrous, radiaxial calcite cement. Furthermore, Bathurst (1982) thinks that the whole structure is marine in origin and forms by a complex history of multigeneration sea floor cementation and cavity formation.

Epitaxial cement. In contrast to the modern sea floor, there seems to be abundant evidence from the fossil record that syntaxial overgrowths of Mg-calcite cement on echinoderm particles were common phenomena in the shallow marine environment (Myers, 1974; Lohmann and Myers, 1977).

Spherulitic calcite. There are numerous instances of spherulitic calcite (Fig. 19) which mimic the geometry of Holocene aragonite sea floor cements, especially in reefs. Like former aragonite skeletons, the fabric in these botryoids is preserved either as a mosaic of tiny crystals or as paramorphic replacement (Assereto and Folk, 1980; Mazzullo, 1980). In this regard, actual aragonite cement crystallites preserved in calcite have been discovered in rocks as old as Pennsylvanian (Sandberg and Popp, 1981). These replaced aragonite spherulites are sometimes still enriched in Sr and again have a $\delta^{13}C$ content consistent with marine precipitation.

Microcrystalline calcite. Lasemi and Sandberg (1982) have discovered that

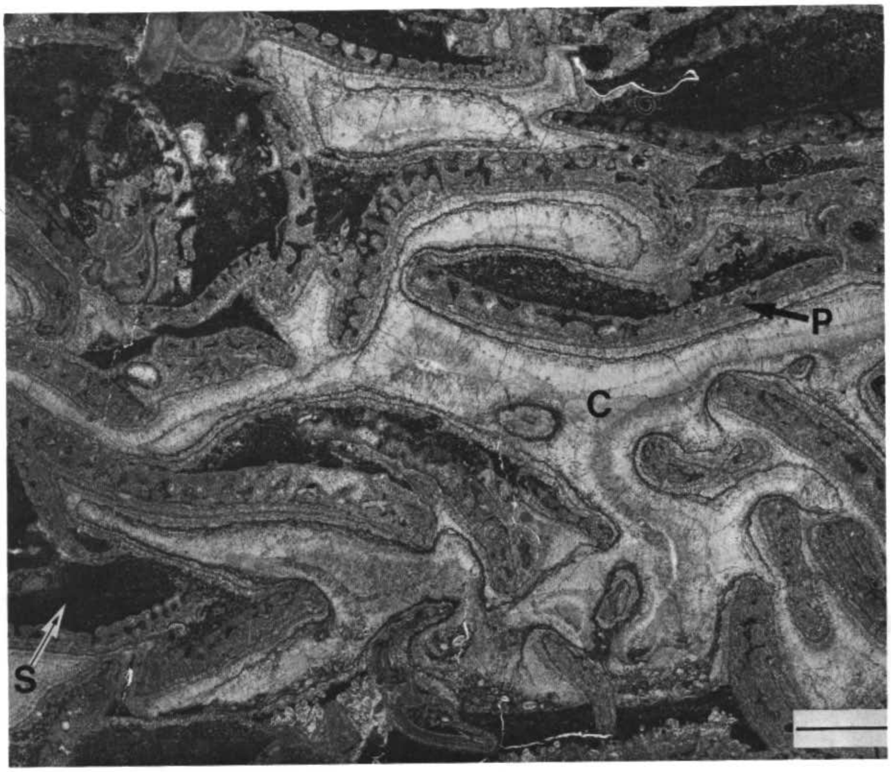

Figure 10 *Photomicrograph of reef mound limestone composed of the ? phylloid alga* Palaeoaplysina *(P) surrounded by several generations of fibrous calcite submarine cement (C) (interpreted to have been Mg-calcite originally) and internal sediment (S); Lower Permian Nansen Formation, Ellesmere Island, N. W. T. (scale 0.5 cm)—photograph, G. Davies.*

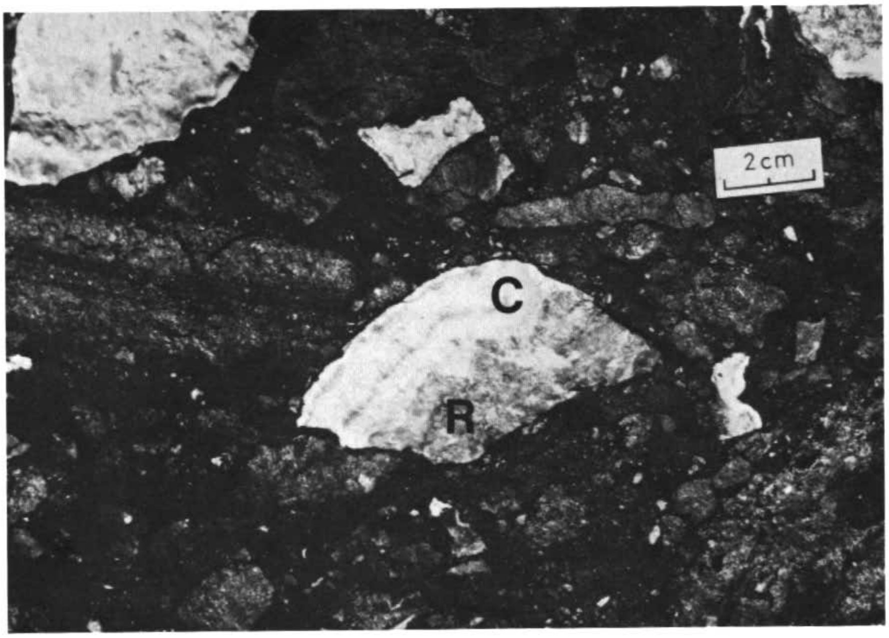

Figure 11 *Fore-reef debris from an Upper Devonian reef, Canning Basin, Western Australia. The clast at centre is composed of reef limestone (R) (mostly the alga* Renalcis *and small stromatoporoids) and fibrous calcite (C). This cement is abundant in contemporaneous reef deposits. Such clasts are often good evidence that the reef itself was subject to seafloor cementation.*

those micrites and microspars with apparently aragonite-dominated lime mud precursors have neomorphic calcite crystals which show pitted surfaces and/or relic aragonite inclusions in polished and etched sections. In contrast, micrite with apparent calcite-dominated precursors are characterized by finely crystalline <4 μm textures, lack any inclusions and have unpitted crystal surfaces.

Isotopic Signature of Fossil Marine Cements. From a number of careful studies involving selectively sampled cements and other components of limestones (e.g., Choquette, 1968; Hudson, 1977; Dickson and Coleman, 1980; Brand and Veizer, 1981; Moldovani and Lohmann, 1982; Given and Lohmann, 1982; Lohmann, 1983a, b) it is clear that marine and other $CaC0_3$ cements in the fossil record have by and large preserved enough of their original signature to be distinguishable from one another (Fig. 20). In general, the marine cements (isopachous, radiaxial fibrous, micritic and botryoidal) contain isotopically heavier carbon and oxygen than near-surface meteoric or burial-diagenetic cements. Compared with co-existing skeletal debris believed to have been low-Mg calcite originally and thus relatively stable (e.g., brachipopods, bryozoa, trilobites), marine cements have roughly the same $\delta^{13}C$ but $\delta^{18}0$'s which may be lighter or heavier. It now seems clear that these cements, along with all other $CaC0_3$ components of limestones, undergo varying degrees of geochemical alteration from slight to extensive (Brand and Veizer, 1980, 1981; Lohmann, 1983b) depending in part upon whether the majority of their diagenesis took place in closed, partly closed or open systems with respect to pore water. Lohmann (1983b) has argued, using both cathodoluminescence petrography and a large body of isotopic analyses, that closed-system diagenesis operates on a microscale to preserve the isotopic signatures of many marine cements.

As will be discussed in more detail in a later essay, the prevailing trend isotopically in limestones undergoing burial diagenesis and acquiring a succession of cements has been toward lighter $\delta^{18}0$ values, generally but not necessarily accompanied by smaller change toward lighter $\delta^{13}C$. This general diagenetic trend has been documented by several workers (e.g., Choquette, 1968; Hudson, 1977; Dickson and Coleman, 1977; Mattes and Mountjoy, 1980; Sears and Lucia, 1980; Lohmann, 1982, 1983b) and can be explained by "exposure" to and reequilibration with

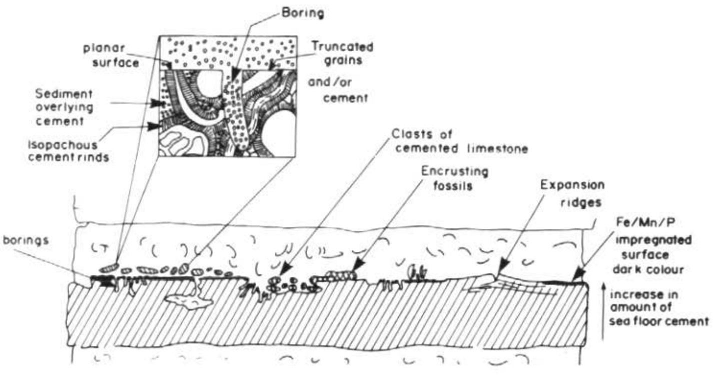

Figure 12 *Criteria for the recognition of seafloor cementation.*

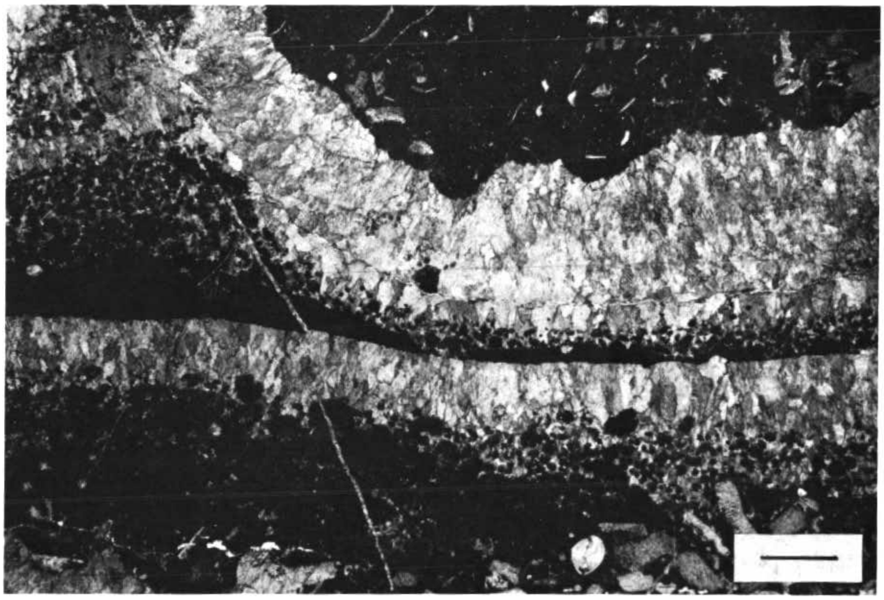

Figure 13 *Photomicrograph of interlayered marine sediment and radiaxial fibrous calcite cement in laminar cavities from a Middle Ordovician reef mound at Meiklejohn Peak, Nevada (scale 1 mm).*

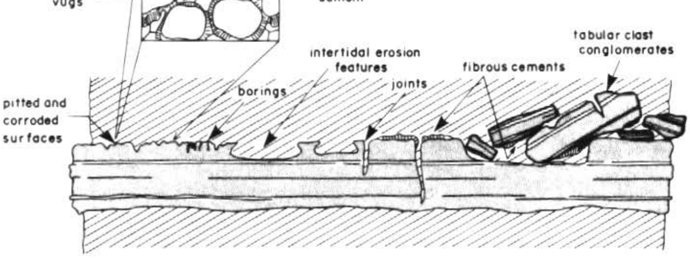

Figure 14 *Criteria for the recognition of fossil beachrock.*

waters of increasing temperature and/or dilution by meteoric water.

There is growing evidence that isotopic compositions of botryoidal (former aragonite) and radiaxial-fibrous calcite (formerly Mg-calcite) cements show systematic variations through the Phanerozoic which seem to transcend regional differences in diagenetic history (Figs. 20 & 21). These variations are consistent overall with the variability of isotopic compositions through Phanerozoic time for whole-rock limestones (e.g., Weber and Keith, 1965; Veizer and Hoefs, 1976) and for brachiopods (Pigott, 1981). Isotopic variations of this magnitude can be explained in a number of ways, including differences in degree of diagenetic alteration and reequilibration (e.g., Dickson and Coleman, 1980). There is a growing basis for believing, however, that the oxygen isotopic composition of seawater itself has varied since Precambrian time (Brand and Veizer, 1981; Popp *et. al.*, 1981). Differences in $\delta^{18}O$ between present-day and past seawater up to 5.5‰ have been postulated by Brand and Veizer (1981), and differences in $\delta^{13}C$ may have been nearly as great (Fig. 21).

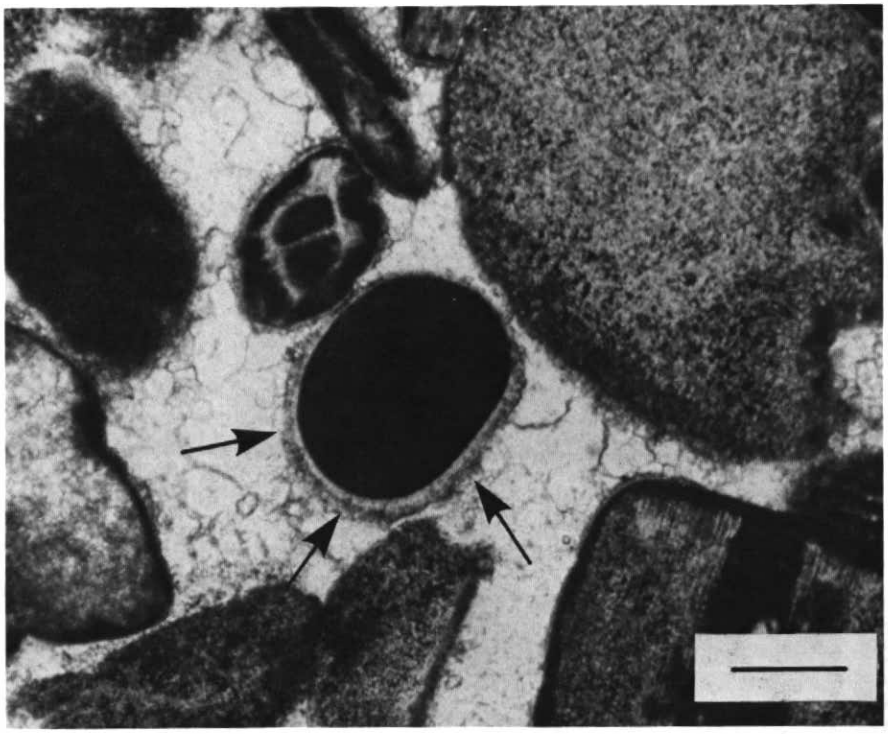

Figure 15 *Photomicrograph of a bioclastic grainstone from the Ste. Genevieve Formation (Mississippian) Bridgeport Field, Illinois Basin, in which the first cement is a fringe of fibrous calcite that is thickest on the undersides of grains (arrows) resembling small stalagtites. This early cement probably developed while the sediment was* beachrock. *(scale 2 mm).*

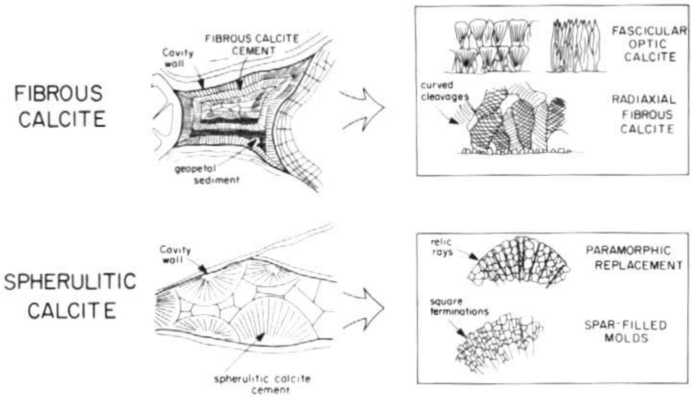

Figure 16 *Fabrics and morphologies of coarse marine cements. Fibrous calcite is generally interpreted as derived from Mg-calcite and spherulitic calcite from botryoidal aragonite.*

Shallow "Calcite" Seas. One of the guiding tenets of carbonate petrology is uniformitarianism, especially the concept that, as in present times, aragonite and Mg-calcite were the most common carbonates forming on shallow sea floors of the past. This axiom has recently been challenged, and it now seems quite likely that an alternative is possible, i.e., that there were times when, instead, calcite was the normal sea floor precipitate (see Sandberg, 1983 and an excellent review by Wilkinson, 1982).

Twenty years ago Lowenstam (1963) pointed out that the composition of marine skeletons apparently had changed during the Phanerozoic: Paleozoic seas were dominated by calcite-secreting invertebrates, Cenozoic and modern seas were characterized by organisms which secreted aragonite and Mg-calcite skeletons, and Mesozoic seas contained roughly equal numbers of each. In the last few years on the basis of new data from fossil skeletons (Wilkinson, 1979; Pigott, 1981), ooids (Sandberg, 1975; Pigott and Mackenzie, 1979), cements (Folk, 1974; Wilkinson, 1982; Sandberg, 1983) and carbonate muds (Folk, 1974; Sandberg, 1975) there is mounting evidence that much of the carbonate in the fossil record may have been deposited or precipitated as calcite. Milliken and Pigott (1977) coined the term "calcite seas" to differentiate these periods from times similar to the "aragonite seas" of today.

An original model of linear change from calcite seas in the early and middle Paleozoic to later aragonite seas has now been replaced by a non-linear model tied to changes in atmospheric pCO_2 (Mackenzie and Pigott, 1981; Pigott, 1981; Sandberg and Popp, 1981; Sandberg, 1983). This most recent model has more universal appeal as it is also related to world-wide sea level fluctuations (Vail *et al.*, 1977) and global tectonics. Fischer (1981) uses the term "greenhouse mode" to label times when the atmosphere contained more CO_2 than it does today and so the surface of the earth was warmer, and the term "icehouse" to characterize times like the present, with lower CO_2, cooler temperatures and continental glaciation. Integrating these concepts, it is postulated that in the past shallow-water carbonate deposition took place under one of the following conditions (Fig. 21):

Calcite Seas. The atmosphere is in the "greenhouse" mode with high pCO_2 because of increased volcanism resulting from rapid and complex convective patterns in the lithosphere. Sea level is high and shallow seas vast because of extension in the length and width of the mid-ocean ridge system.

Aragonite Seas. The atmosphere is in the "icehouse" mode with lower pCO_2 because of the reduced volcanism due to sluggish plate movement and aggregated continents. Sea level is low and shallow seas reduced to narrow strips along continental margins because the mid-ocean ridge system has dropped.

The systematic variations in isotopic composition of fossil marine cements (Figs. 20 & 21) and carbonates in general (Veizer and Hoefs, 1976) tend to support this hypothesis since "aragonite seas" and "calcite seas" should be characterized by heavier and lighter $\delta^{13}C$, respectively. Since marine carbonates show a linear relationship between $\delta^{13}C$ and $\delta^{18}O$ (Milliman and Müller, 1974), we would expect that radiaxial fibrous, botryoidal and other marine CaCO cements also should have had original isotopic signatures which were *heavier* during times of "aragonite seas" and *lighter* during times of "calcite seas". This is exactly the relationship we appear to be seeing in Figure 21, where from groups of analyses the heaviest (most nearly original) isotopic values have been plotted versus geologic time. The departure of the curves for $\delta^{18}O$ and $\delta^{13}C$ in late Carboniferous through Triassic time implies a diagenetic and/or original seawater temperature effect. But the general relationship suggests some consistent non-linear trends in seawater composition through the Phanerozoic which show a close tie with first-order sea level excursions and temperature variations.

The question of whether seawater isotopic composition has, indeed, varied significantly and systematically through time is, of course, critically important in any attempts to interpret the origins of carbonate cements and carbonate rocks using

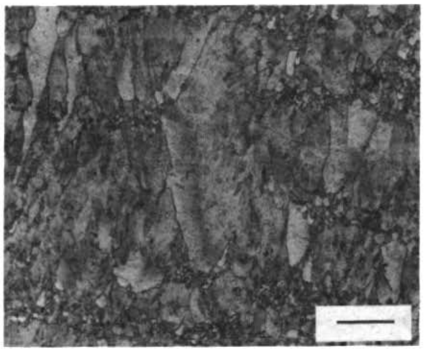
Figure 17 *Photomicrograph in partially polarized light of fascicular optic calcite cement from Lower Cambrian reef mounds in the Forteau Formation, southern Labrador. The numerous nested cones have the same irregular crystal boundaries as radiaxial fibrous calcite but lack the curved twins and have divergent optic axes (scale 0.5 mm).*

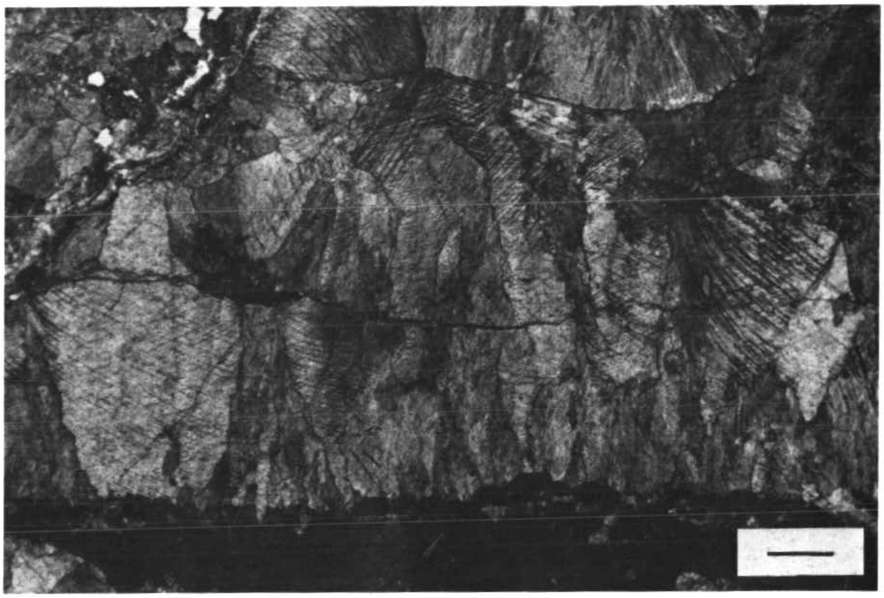
Figure 18 *Photomicrograph in partially polarized light of radiaxial fibrous calcite cements in the Middle Ordovician reef mound at Meikeljohn Peak, Nevada. The crystals characteristically have concertal boundaries, curved twins, convergent optic axes and contain diverging subcrystals. (scale 0.5 mm).*

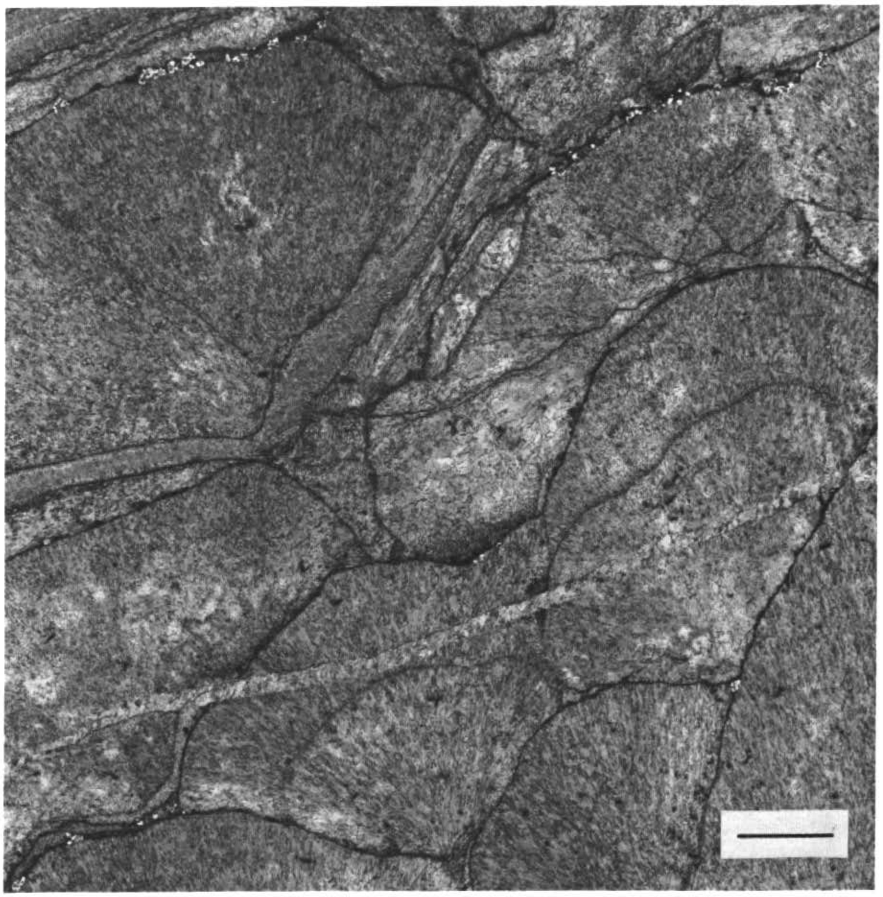
Figure 19 *Photomicrograph of coalesced, strontium-rich calcite botryoids (interpreted to have been aragonite originally) from a reef mound in the Nansen Formation (Lower Permian) Ellesmere Island, N. W. T. (scale 2 mm)—photograph, G. Davies.*

geochemical compositions (Wilkinson *et al.*, in press). The theory outlined above is important and intriguing, but current data only permits speculation—much more data is needed to make it a workable concept. Clarification and testing should be forthcoming from research in progress by Lohmann and Wilkinson and their associates (University of Michigan) and by Sandberg and his associates (University of Illinois). If it is correct, however, then the discussion of carbonate precipitation on the modern sea floor outlined in this essay applies mainly to specific times in the past: (1) late Precambrian and Cambrian, (2) Pennsylvanian to Triassic, possibly Jurassic and (3) Cenozoic. During the early and middle Paleozoic and much of the Mesozoic shallow seas would have been dominated by calcite precipitation.

Another implication is that clear, rhombic calcite cement, characteristic of precipitation from fresh water (see the next article in this series) is not diagnostic alone as evidence of exposure to meteoric fluids, and may be a sea-floor precipitate (Wilkinson *et al.*, 1982).

Conclusion

Marine seafloor cementation appears to be a rare occurrence in both fossil and modern carbonate environments. It is minor in abundance except in very specific settings. These localities of cementation, platform margins and strandlines are extremely important, however, because limestone is created there as the sediments are deposited, thus aiding in the eventual preservation of fabrics and textures.

The initially porous sediments generally undergo rapid porosity and permeability reduction, thus often making these facies, from an economic standpoint, less desirable as reservoirs for hydrocarbons and base metals.

The major prerequisites for early seafloor cementation appear to be an oxidizing environment, a stable substrate and good water exchange. Recognition of submarine cements in the fossil record depends upon a combination of field, petrographic and geochemical techniques, and even then their presence is easily inferred but proven with difficulty.

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This series of articles is an outgrowth of a graduate-level course in carbonate petrogenesis given at Memorial University and a carbonate training seminar presented at Marathon Oil Company. We thank all those willing and unwilling participants who helped shape our ideas. K. C. Lohmann generously allowed us to use some of his unpublished data on the isotopic composition

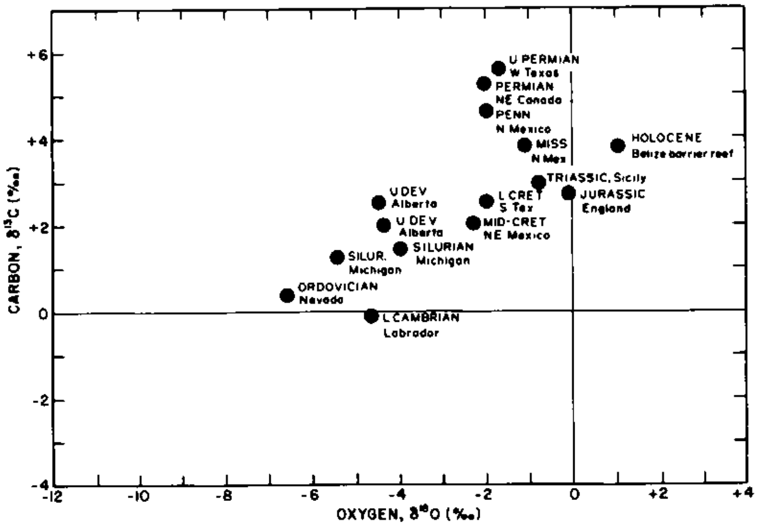

Figure 20 *Crossplot of carbon versus oxygen isotopic compositions of Holocene and ancient fibrous and spherulitic (botryoidal) carbonate cements. The values shown are the "heaviest" compositions from covariate populations of data, believed to approximate most closely the original marine-isotopic compositions of the cements (method of Lohmann, in press). The data are from James and Ginsburg (1979), Moldovanyi and Lohmann (1982), Marshall and Ashton (1980), Given and Lohmann (1983), Davies and Krouse (1975), Lohmann (1983), Meyers and Lohmann (1983), Walls* et al. *(1979), Mattes and Mountjoy (1980), Cercone and Lohmann (1983), Sears and Lucia (1980), Ross* et al. *(1975), and James and Klappa (1983), listed in order of increasing age of the stratigraphic units involved.*

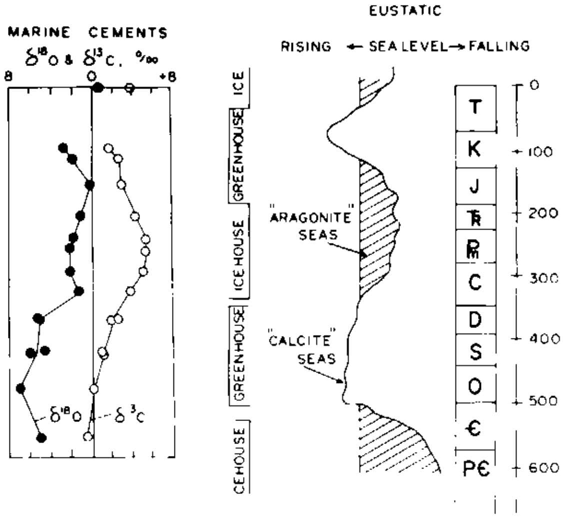

Figure 21 *(Right) The possible distribution of "calcite" and "aragonite" seas in geologic history. Modified from Fischer (1981) and Wilkinson (1982). (Left) Variations in oxygen and carbon isotopic compositions of marine cements through Phanerozoic time. The data are from the sources acknowledged in Figure 20 (caption).*

of fossil cements, thus enabling us to present a much more coherent picture than would otherwise have been possible. This article was critically read by R. G. C. Bathurst, N. Chow, M. Coniglio, P. Sandberg and R. K. Stevens, and its present form owes much to their careful editing. N. P. James acknowledges the Natural Sciences and Engineering Research Council for on-going financial support.

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