

Articles



DIAGENESIS #12. Diagenesis in Limestones - 3. The Deep Burial Environment

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Introduction

Carbonate sediments, or the limestones into which they may have evolved, once buried below the reach of sea-floor processes or below the meteoric environment and the sub-meteoric mixing zone, enter with progressive burial the "deep-phreatic" or subsurface burial-diagenetic realm (Figure 1). It is in this realm that, unless exhumed by tectonic uplift or lowered sea level, the great majority of sedimentary carbonates must inevitably spend most of their geologic existence. It is here, too, that the majority of carbonate sediments which escaped sea-floor lithification or

prolonged meteoric diagenesis undergo most of the changes that lead to their lithification and reduction of porosity.

The importance of deep-burial diagenesis has been recognized more widely in the last fifteen years or so, in considerable part because of the publication of a major synthesis on carbonate diagenesis by Bathurst (1975). Since that time, aspects of the subject have been examined in a number of general or specific studies, most notably the thoughtful works by Bathurst (1975, 1980a, 1980b, 1984, 1985), Schlanger and Douglas (1974), Garrison (1981), Shinn and Robbin (1983), and Scholle and Halley (1985). During this same period, the development and refinement of instruments and techniques for the study of cathodoluminescence, ultraviolet fluorescence, stable-isotope, rare-earth and minor-element compositions, and microscopic fluid inclusions have made possible the acquisition of much new information about the petrologic, mineralogic and chemical changes that take place in the deep-burial realm.

The fundamental importance of diagenesis in this largely occult realm in shaping the porosity, mineralogy, basic fabrics and numerous other features of carbonates is now clear, but many aspects remain to be clarified. The quest for a basic understanding and a general theory of diagenesis in the deep-burial setting has only begun.

The Deep-Burial Setting

Definitions. Burial diagenesis can be defined in general as any change or collection of changes that takes place below the zone of near-surface diagenesis and above the realm of low-grade metamorphism (Figure 1). These limits can vary from one sedimentary basin to another or even within a single basin. By "near-surface processes" we mean the changes caused by processes operating at or very close to the sea floor or in the relatively shallow meteoric environment, within the reach of surface-related processes (Choquette and Pray, 1970). The sub-lenticular mixing zone (see James and Choquette, 1984) is often thought of as part of the meteoric, although its nature and vertical as well as geographic extent are poorly known in all but a few subtropical Cenozoic limestone islands and a few aquifers in Cenozoic and

Mesozoic carbonates. Defined in this way, burial diagenesis is mainly a consequence of overburden due to burial beneath younger strata, and of resulting changes in hydrology, pore-water chemistry, pressure, and temperature. The burial-diagenetic realm would include, for example, the mesogenetic or "deeper burial" realm of Choquette and Pray (1970); the "compactional" and "thermobaric" subsurface regimes suggested by Galloway (1985) for sandstone-shale sequences; the "deep-phreatic" realm of many workers; and for geologists in the petroleum industry the "subsurface" in general. The term phreatic is not very useful because for many it connotes the zone of saturation and water-filled pores anywhere below the water table.

Differences from Near-Surface Processes. The dominant processes, ambient conditions, space and time distributions, and principal products of diagenesis in deep-burial settings are quite different from those in near-surface settings. In the *sea-floor environment*, cementation by aragonite and Mg-calcite is the main inorganic agent of lithification (James and Choquette, 1983) and is highly facies-specific. Lithification in this setting is virtually instantaneous geologically, probably involving time spans on the order of 10^1 to 10^4 years.

In the *meteoric environment*, the main processes of lithification involve the precipitation of calcite, impelled either by dissolution of aragonite and micro-dissolution of Mg-calcite (forms of mineral-controlled alteration as discussed by James and Choquette, 1984), or by more wholesale dissolution and precipitation of calcite (water-controlled alteration). Mineral-controlled alteration redistributes porosity from inter- and intraparticle sedimentary pores to new moldic pores, often with little net change in percent porosity (Harrison, 1975). Water-controlled alteration, on the other hand, creates new, larger, non-selective voids or adds CaCO_3 and reduces porosity. Meteoric-realm diagenesis must involve time intervals which approximate the duration of subaerial exposure at unconformities; in Plio-Pleistocene sequences on modern platforms glacio-eustatic unconformities involve time intervals on the order of 10^3 to 10^5 years (e.g., Steinen and Matthews, 1973;

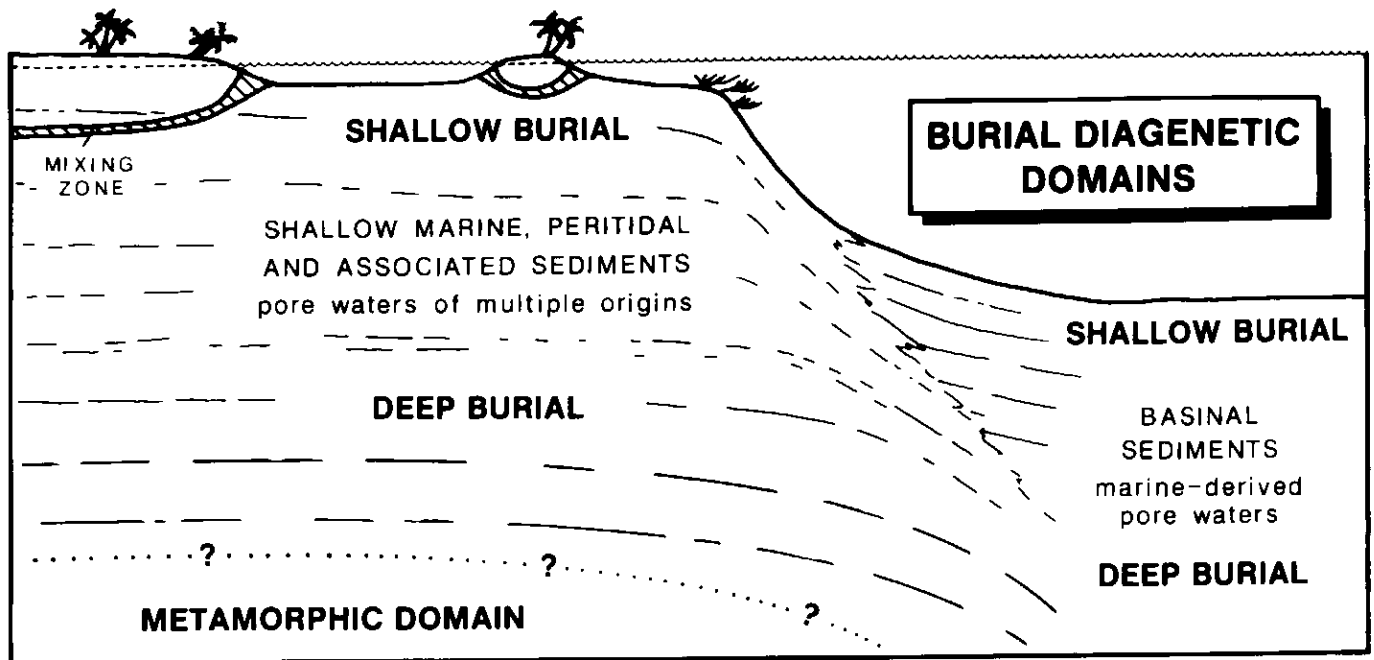


Figure 1 A sketch outlining two general domains of deep-burial diagenesis. The nature and depth range of the boundary with the metamorphic realm are poorly known. The depth is likely to range from a kilometre or less to several kilometres or more.

Table 1 General processes and products in the deep-burial domain.

Processes	Products
Physical compaction	Reduced thickness, porosity and permeability; reoriented and commonly broken allochems; compressed textures and structures
Chemical compaction	Reduced thickness, porosity and permeability; stylolites and other pressure-solution structures; ions for new carbonate cement
Cementation	Mosaic/drusy to very coarse or poikilotopic calcite and saddle dolomite
Burial dolomitization	Anhedral-crystalline dolomite, generally rather coarse
Mineral reactions	Smectite to illite Gypsum to anhydrite Opal A & CT to quartz Fe hydroxides to Fe oxides
Biochemical alteration of organic matter	Kerogen and organic acids
Thermochemical alteration of kerogen	Hydrocarbons and CO ₂
Burial dissolution of Ca carbonate and sulphate	Solution porosity

Table 2 Principal controls in deep-burial diagenesis.

Intrinsic	Extrinsic
Mineralogy	Temperature
Grain size and texture	Pressure
Organic matter, kerogen and hydrocarbons	Time
Early cement or dolomitization	Fluid Flux
Pore-water chemistry	
Porosity and permeability	

Enos and Perkins, 1977; Beach, 1982); older Phanerozoic platforms contain regional and interregional unconformities representing time intervals up to 10^6 to 10^7 years (Sando, 1974, 1985; Sloss, 1984). In the *deep-burial environment* far more complex arrays of processes are operative (Table 1). Dominant among them are physical (mechanical) compaction and dewatering, chemical compaction (pressure solution), cementation, subsurface dolomitization, alteration of hydrous minerals to anhydrous ones, thermally driven mineral stabilization reactions, and alteration and maturation of organic matter with attendant production of organic acids and hydrocarbons. A dominant long-term trend is progressive reduction of porosity by compaction and cementation, at higher and higher temperatures and pressures, in the presence of pore waters that may become increasingly saline. Diagenesis can continue over millions to tens or rarely hundreds of millions of years (10^6 - 10^8 yrs), although rates of diagenetic change fall off rapidly with increasing depth and time.

Factors Influencing Deep-Burial Diagenesis

Intrinsic Factors. Among the most important intrinsic factors (Table 2) are the *mineralogy*, the amount and nature of the *organic fraction*, the presence of introduced *liquid hydrocarbons*, and the *pore-water composition*. A sediment that retains aragonite and Mg-calcite as it goes into the deep-burial environment will have more "diagenetic potential" (Schlanger and Douglas, 1974) to generate calcite cement through dissolution and reprecipitation than will a sediment composed only of calcite. We know relatively little about the mineralogy of platform limestones as they leave the meteoric and sub-meteoric mixing zones and enter the deep-burial realm. Scholle and Halley (1985) have argued that many platform limestones altered in the meteoric zone are calcite and therefore have relatively low diagenetic potential like marine chalks. However, calcite cement of meteoric origin is rarely homogeneous either isotopically or elementally, and therefore must have at least some diagenetic potential (L.S. Land, pers. comm., 1986). In any case, many studies of Recent and Plio-Pleistocene limestones have shown that mineralogical stabilization in meteoric water from aragonite and Mg-calcite to low-Mg calcite can take place quickly, after a few metres to tens of metres of burial (e.g., Steinen and Matthews, 1973; Steinen, 1974; Beach, 1982).

In another kind of "mineralogical" effect, limestones that contain at least a few percent clay minerals or unstable organic matter (in addition to being fine grained) are more susceptible than pure limestones to physical compaction, chemical compaction (pressure solution), and even spaced cleavage due to tectonically induced pressure solution. Furthermore, it is widely thought that the amount

of clay and/or organic matter may be important. Whether clay and silt content is less than or more than about 10% appears influential in determining whether pressure solution produces, respectively, sutured stylolites or non-sutured seams and fitted fabrics (R.G.C. Bathurst, pers. comm., 1986).

Grain size and texture influence the rates at which CaCO_3 components change and sediments compact. Fine-grained and poorly sorted sediments undergo neomorphic and solution-precipitation reactions more rapidly because of their larger reactive surface areas; they also compact more readily than coarse sediments, in marine pore waters at least, because of their greater pore water content and potential for particle rearrangement and reorientation. One consequence of this is that some sediments that were deposited as lime muds undergo so much physical compaction of their fine-grained fraction that they become "diagenetic" wackestone or packstone (Shinn and Robbin, 1983).

Pore-water chemistry has a variety of important effects and roles in burial diagenesis. For one thing, pore waters transmit, by physical fluid flow or ion diffusion, the solute ions produced by dissolution or consumed by cementation and replacement reactions. Moreover, water chemistry seems to have a strong influence on major burial-diagenetic processes. One of the most important of these, pressure-solution (chemical compaction), seems to operate less rapidly in Mg-rich (e.g. marine-derived) pore waters, a factor that may be partly responsible for the retention of high porosity in many chalks (Neugebauer, 1973, 1974).

The introduction of *liquid hydrocarbons* into the pore systems of limestones during burial diagenesis, especially if the pore walls are oil-wet, inhibits pressure-solution and can preclude the formation of stylolites; Dunnington (1967), who first suggested these effects, also noted that the emplacement of oil in some limestone reservoirs of the Middle East might actually have prevented their compaction and created differential-compaction traps for hydrocarbons. Liquid hydrocarbons in pores can also shut off or prevent cementation. This mechanism has been invoked to explain differences in extent of pressure-solution cementation and porosity reduction in some chalk reservoirs in the North Sea (Feazel *et al.*, 1985; Feazel and Schatzinger, 1985).

Early-precipitated cement or early replacement dolomite formed at or not far below the depositional interface will increase the bearing strength of a sediment so that it compacts less readily, at least at relatively shallow depths (< 2 km?).

Finally, the *porosity and permeability* of a sediment or rock, which govern both the volume of contained pore fluid and the rate at which fluids are transmitted, affect the speed at which diagenetic reactions take place. In Holocene sediments, porosity is generally

greater in fine-grained sediments such as lime muds than in coarser carbonate sands (Enos and Sawatsky, 1981). In the geologic record the highest known limestone porosities (up to 80% with very low permeabilities often below 1 md) are found in some Cretaceous and Danian chalks (Scholle, 1977). Permeability in limestones with interparticle porosity, however — other things being equal — is directly related to grain size, so that in general the coarser-grained carbonates will transmit fluids in larger volumes and at higher flow rates.

Extrinsic Factors. Among the many extrinsic factors affecting burial diagenesis (Table 2) it appears that *pressure* and *temperature* are most important. Pressure of at least three kinds is applied to sedimentary sequences being buried: (1) *lithostatic pressure*, transmitted through the solid framework; (2) *hydrostatic pressure*, transmitted only through the pore-system "water column"; and what Bathurst (1975) called (3) *linear or directed pressure*. The first two of these are induced by gravity. The third is really of tectonic origin and has been recognized increasingly in recent years as a major cause of spaced cleavage in tectonized carbonates that yield by brittle fracture. Typical hydrostatic and lithostatic pressure gradients, shown in Figure 2A, give an idea of the pressure ranges ambient over the range of subsurface depths that have been sampled thus far by petroleum exploration drilling. Pore pressure determines the effective stress on a sediment under overburden load, because the effective or net stress is the lithostatic pressure (or total load) less the pore pressure (Terzaghi, 1940). Most subsurface strata at temperatures greater than about 100°C have pore pressures which are higher than "normal hydrostatic" and would lie in the stippled area of Figure 2A. Usually the differences between lithostatic and pore-fluid pressure are small, but under various conditions the pore-fluid pressures can become abnormally high, in which case the strata are said to be overpressured or "geopressed" and the pore-fluid column may support part or all of the overburden load.

Abnormally high pore-fluid pressure can be an important inhibiting factor in burial diagenesis. It can actually "prop up" original pore spaces — either independently or in concert with early near-surface cementation — thereby retarding or preventing physical compaction. It also can slow or shut off the export and import of pore water and prevent any changes in the partial pressure of CO_2 and other dissolved gases, thereby creating a pore-fluid system which is both overpressured and static, in which both pressure solution and cementation may be sharply retarded. Feazel and Schatzinger (1985) also have discussed recently the retarding effects of high pore pressure.

Many processes seem able to cause overpressuring of sedimentary rock pore-fluid

systems, by trapping their fluids. Rapid sedimentation, as in marine parts of major delta systems, can bury sediments more quickly than these can expel connate water. Confinement of porous carbonates beneath stratiform permeability barriers such as compacting shales or evaporites, well-indurated hardgrounds, or limestones having swarms of laterally extensive stylolites, all can cause overpressuring. So also can some diagenetic reactions involving clay, sulphate and silica minerals as discussed next under Temperature, since these reactions add water to the system. The generation of gases such as CO_2 , methane and other hydrocarbons, and H_2S at sites and in strata where the gases cannot escape may cause overpressuring. The abrupt release of overpressure has been proposed as a mechanism for producing certain breccias apparently by dilation, for example in thin-bedded, fine-grained carbonates of basinal origin in the Miocene Monterey Formation of California (e.g. Secor, 1965; Roehl, 1981). Our understanding of and ability to predict the realms and effects of abnormally high pore-fluid pressure in burial diagenesis of carbonates still are primitive.

A very few studies have shown the importance, however, of abnormal pressures as co-agents (with early emplacement of hydrocarbons) in causing the retention of unusually high porosities in some Cretaceous and early Tertiary chalk reservoirs in the central North Sea (Scholle, 1977; van den Bark and Thomas, 1981; Feazel *et al.*, 1985).

Temperature appears to play at least three roles in burial diagenesis and may be of considerable importance.

(1) The solubility of calcite and other carbonates — unlike that of quartz — is 'retrograde' in water having dissolved CO_2 and decreases with increasing temperature (Helgeson, 1969). The decrease is linear up to temperatures as high as 400°C and is substantial, on the order of two orders of magnitude at any one pressure (Bathurst, 1975). This relationship, although complicated by the effects of increasing pressure, indicates that with increasing temperature alone, calcite cement (and by inference, saddle dolomite cement) will be more likely to precipitate.

(2) Increasing burial brings about a series of temperature- and pressure-dependent mineral reactions (Table 1). Some of these release water to the surrounding pore fluids and result in minerals that have higher specific gravities and occupy less space than their precursors. These reactions include the conversion of gypsum to anhydrite at around 1000 m (Murray, 1964; Kendall, 1984), and the conversion in some oceanic sediments of opal-A to opal-CT and finally quartz within a depth range of about 450-2000 m (Isaacs, 1981) which may correspond to temperatures of $40\text{-}100^\circ\text{C}$. These reactions involve changes in crystal-lattice morphology and release water of crystallization. Other reactions which release water along with various cations are the conversion of smectite to mixed-layer clays and finally to illite

commencing at around 2000 m and 60°C in the US Gulf Coast (Burst, 1969; Perry and Hower, 1970; Hower *et al.*, 1976; Boles and Franks, 1979), and the dehydration of various iron hydroxides such as limonite to yield hematite and free water. Still other reactions affecting carbonates, which take place in sandstones, include the conversion of calcic plagioclase to albite, releasing Ca^{2+} and other divalent cations such as Sr^{2+} which have been used as radiogenic tracers of burial reactions (e.g. Steuber and Pushkar, 1983; Moore, 1985; Woronick and Land, 1985).

(3) Increasing temperature together with burial reaction time causes the conversion of sedimentary organic matter from unstable to more stable forms and eventually to hydrocarbons and other organic compounds (see review by Barnes *et al.*, 1984 in this journal). In dirty sandstones the reactions in this complex series are widely thought to release CO_2 which can combine in carboxylic and other organic acids capable of dissolving carbonates (e.g. Schmidt and McDonald, 1979; Hayes, 1979; Bjorlykke, 1984; Surdam *et al.*, 1984). Material-balance calculations have led some workers to suggest, however, that CO_2 produced only by decarboxylation, at least in shales of the Oligocene Frio Formation in the Texas Gulf Coast, cannot account for most of the dissolution porosity found in associated sandstones; other mechanisms and/or long-distance transport of acidic waters must also be responsible (Lundegard *et al.*, 1984; Lundegard, 1985). Dissolution porosity of burial origin is being recognized increasingly

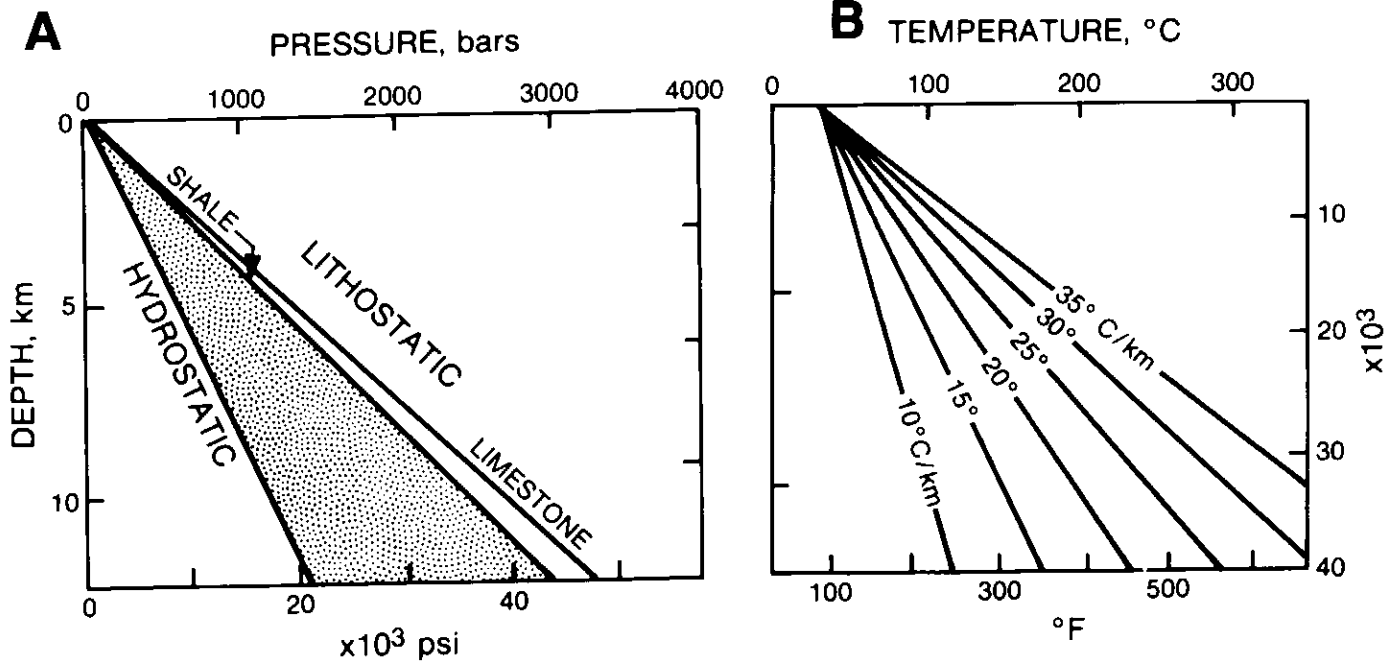


Figure 2 Graphs showing the general ranges of pressure and temperature in the deep-burial diagenetic realm. (A) Static pressure ranges. The position of the hydrostatic pressure curve varies depending on the concentration and density of pore waters. Most pore-fluid pressures in the subsurface would plot on curves in the stippled area. Commonly the change from normal to excessive pore-fluid pressure is a transition marked by more rapid increases in both pressure and (graph B) (B) Temperature ranges assuming different geothermal gradients. Most gradients are $15\text{-}35^\circ\text{C}$, and most are non-linear and commonly steepen (decrease) with increasing depth.

in limestones since its discovery in the early 1980's (Moore and Druckman, 1981; Elliott, 1982; see also Druckman and Moore, 1985; Moore, 1985). Although the mineral and fluid systems must be different, mechanisms like those invoked for sandstones have generally been suggested for the limestones.

Interestingly, the temperature range in which peak generation of hydrocarbons is believed to occur, 60-150°C (Tissot and Welte, 1980), is also the temperature range in which many other burial diagenetic processes involving *inorganic* reactions, pressure solution, cementation, and probably some burial dolomitization and dolomite neomorphism (xenotopic dolomite of Gregg and Sibley (1984)) also take place.

The range of temperatures in sedimentary basins can be great, depending on the thickness of the sedimentary fill and the geothermal gradients (Figure 2B), which in turn depend on ambient heat flow and on thermal conductivity of the sediment. Gradients in most sedimentary basins are in the range of

15-35°C per kilometre of depth and 25°C·km⁻¹ is an often cited normal value (Wood and Hewett, 1984). Gradients can change sharply with uplift and passage of a sedimentary package into a nearer-surface hydrologic regime fed by cooler meteoric waters, as has happened in the Western Canada basin (Hitchon, 1969a, b) and some other basins.

Processes and Products

In the sections that follow, we examine the common sedimentological and geochemical processes and products of burial diagenesis — the records of their passage into the deep subsurface (Table 1).

Physical Compaction

As sediments compact under load they de-water, lose porosity, and decrease in thickness while sedimentary particles and sedimentary structures are modified and/or rearranged, depending on how much porosity they had and whether they were grain-supported or mud-supported initially.

Processes. Physical compaction in marine sediments buried in marine pore waters can be visualized as taking place in three main stages which probably overlap.

Stage 1: Initial particle settling and repacking with resulting dewatering occurs in the first metre or so of burial, where porosities of lime muds may be reduced a small amount, say from 80-75% (Ginsburg, 1957; Brown, 1969; Schlanger and Douglas, 1974; Enos and Sawatsky, 1981).

Stage 2: Particles are rearranged and elongate grains reoriented in grainy sediments, while muddy sediments are compacted with continued dewatering, until a self-supporting "framework" is achieved at porosities of approximately 40%. The relative importance of this stage of compaction is proportional to the original ratio of lime mud to coarse silt size and larger grains. In shallow subtidal sediments this compaction often takes place within a metre or so below the seafloor; one can stand on the sediment rather than sink into it and one can generally core it (L.S. Land, pers. comm., 1986).

Stage 3: Overburden stress is applied at grain contacts, and is accommodated by grain deformation in the form of either ductile squeezing or brittle fracturing and breakage. Lime mud between framework-forming grains, in shelter cavities beneath elongate particles, or within fossils, is generally protected from compaction.

A common conclusion of experiments involving compaction of muddy carbonate sediments is that thickness reductions can be substantial and in some cases greater than porosity reductions, especially in stage 2 compaction (Terzaghi, 1940; Hathaway and Robertson, 1961; Fruth *et al.*, 1966; Robertson, 1967; Ehardt, 1968; Shinn *et al.*, 1977; Bhattacharyya and Friedman, 1979). Shinn and Robbin (1983) compacted modern shallow marine and peritidal muddy carbonate sediments with 47-83% initial porosity down to as little as 27% (mostly 30-65%) of their original thickness, with final porosities reduced to 35-45%. Although some chemical compaction effects were observed in cores subjected to the highest pressures, physical or mechanical compaction was by far the dominant process. At pressures of 66 to almost 1000 kg·cm⁻² (933-13,600 psi), compaction as gauged by thickness reductions essentially ended when porosities were reduced to 35-45%. The results of these experiments indicate that carbonate sediments can compact under as little as 100 m of overburden to one-half their original thickness, with accompanying porosity losses of 50-60% of original pore volume.

Products. Sedimentological products of physical compaction are almost as varied as the constituents of the limestones (Figure 3). In mud-supported or pelleted-mud sediments (mudstone and wackestone) common features include: thinning of laminae between and draping over early concretions (Figures 4

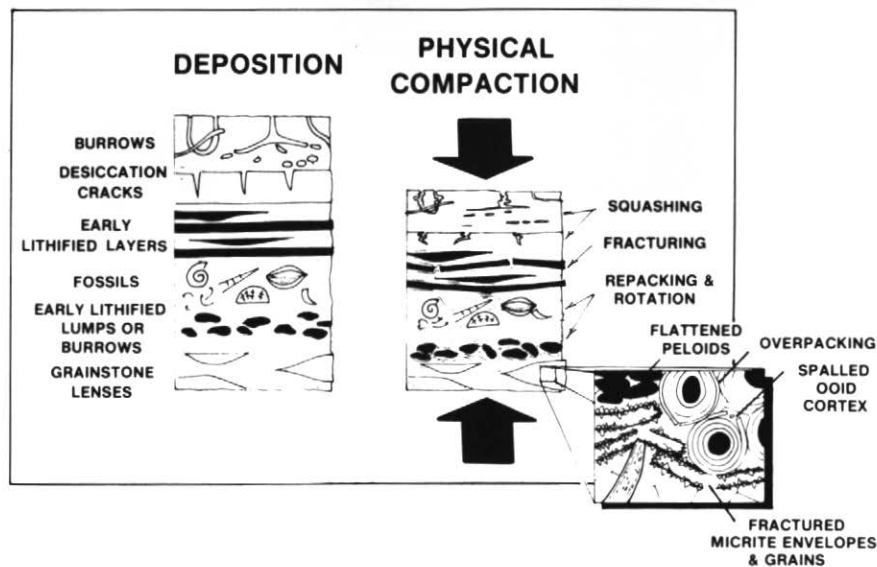


Figure 3 Sketches illustrating features produced by physical (mechanical) compaction.

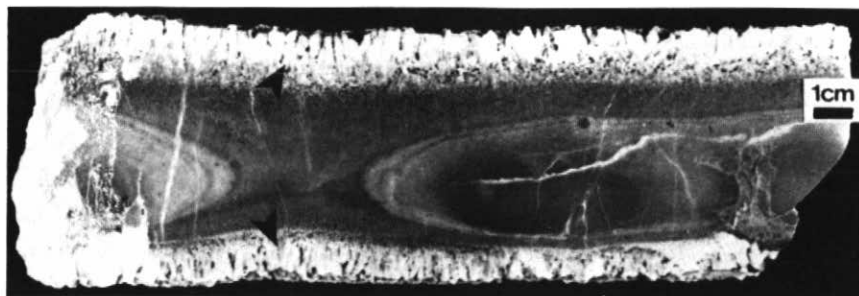


Figure 4 A slab of early burial-diagenetic displacive-fibrous calcite (DFC; arrows) developed on both sides of a mudstone bed that was formed by coalescence of microspar concretions. The bed was thinned a little between concretions by physical compaction prior to formation of the DFC. From Cambro-Ordovician Cow Head Group, western Newfoundland (Coniglio, 1985), photo courtesy of M. Coniglio, published by permission.

and 5), early-lithified layers, and other hard objects; squashed burrows and crumpled fenestrae, gas-escape structures, and desiccation cracks (Figure 6); shells and other elongate grains that have been rotated, packed more closely, or in some instances brought into proximity with other rigid grains against which they have been crushed (Figures 7 and 8); and flattened pellets or other grains (Figure 9).

Physical compaction also produces a variety of swirling structures as well as the textural "telescoping" noted by Shinn and Robbin (1983), converting grain-poor lime mud to wackestone or packstone (Figure 8). Physical compaction can close and obliterate desiccation cracks and fenestrae or birdseyes in peritidal sediments (Figure 6). Organic matter is commonly squashed and deformed into irregular stringers that drape over rigid grains and may look deceptively like stylolites. Relatively brittle laminae and thin mud-cracked beds between layers of plastically compacted mud may fracture and rotate (Figure 8).

In grain-supported clean and muddy carbonate sands (grainstone and packstone), plastic deformation of soft pellets, coated particles and skeletal grains is common (Figure 9). Ubiquitous, however, are fractured and crushed grains of various kinds such as spalled and broken cortical layers of ooids (Figure 10), broken thin rinds of cement around grains that have been squashed, crushed fossils (Figure 11), and fractured micrite envelopes surrounding grain molds. Also typical are planar or curvilinear grain contacts resulting from plastic deformation; care must be taken, however, to be sure these contacts are due to physical compaction and not pressure-solution.

Compaction of lime mud between grains, in sheltered patches either beneath broad particles such as phylloid algal plates and brachiopod valves or inside fossils, is generally very slight, so that original textures and particles are preserved (Figure 12).

Thinning of limestone strata due strictly to physical compaction, though often cited as important, has been well documented in very few published studies. Among the most convincing on a large scale was reported by Beach and Schumacher (1982). They showed that uncompacted pisolitic "island" sediments forming part of the Mission Canyon Formation (Mississippian) in an area of the Williston Basin are surrounded by physically compacted marine sediments. Isopach maps indicate thinning of the marine facies by up to 31%, and abundant crushed fossils and other features in the marine limestones (Figure 11) indicate that the thinning is due mainly or entirely to physical compaction. Differential compaction at smaller scales has been reported by many workers, for example by Byers and Stasko (1978), who calibrated the compaction by *Chondrites* which are alternately little compacted in micritic lenses

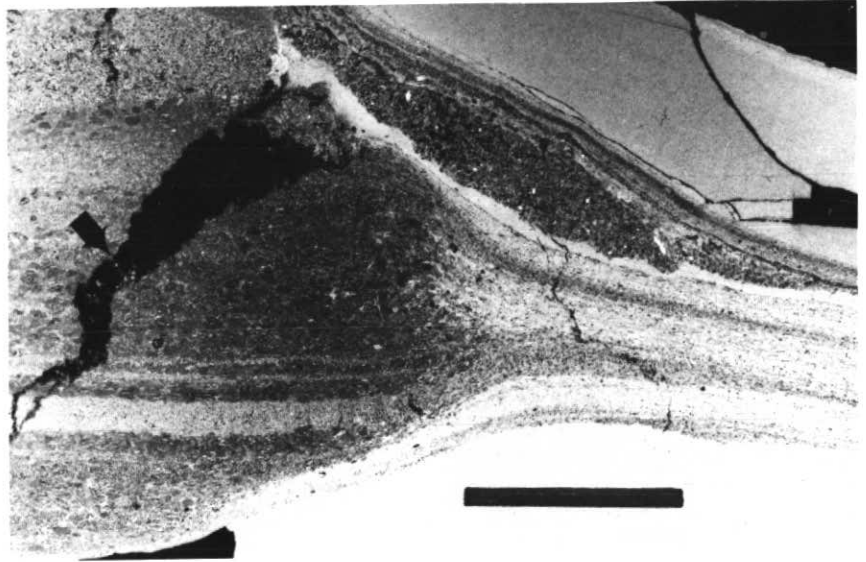


Figure 5 A concretion formed by early-burial microspar cementation of pelloidal wackestone (darker) and grainstone (lighter). The uncemented laminae to right have been compacted to 36% of their thickness as preserved in the concretion. Compaction was probably physical rather than chemical. A dilation crack (arrow), now filled by ferroan calcite spar (black in this picture), opened due to differential compaction of the concretion. Photo is a negative print of a thin-section. Bar scale is 1 cm. From Cambro-Ordovician Cow Head Group, western Newfoundland (Coniglio, 1985), photo courtesy of M. Coniglio, published by permission.

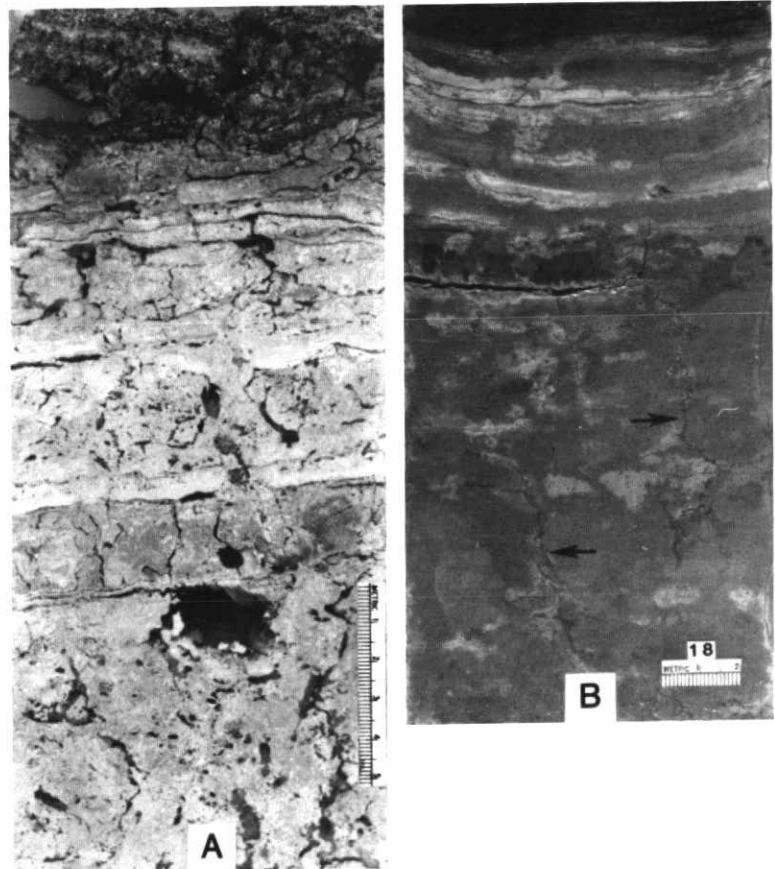


Figure 6 (A) Uncompacted supratidal sediment from the Holocene of south Florida (plastic-impregnated core). The openings are birdseyes or fenestral pores, vertical shrinkage cracks, and burrows, and horizontal cracks and large cavities probably formed artificially. (B) Artificially compacted sediment from the same core. Only the thin storm layers and desiccation cracks in A are clearly preserved. Virtually all the voids have been squeezed shut, and the overall fabric has been strikingly changed. From Shinn and Robbin (1983), photos courtesy of E.A. Shinn, published by permission.

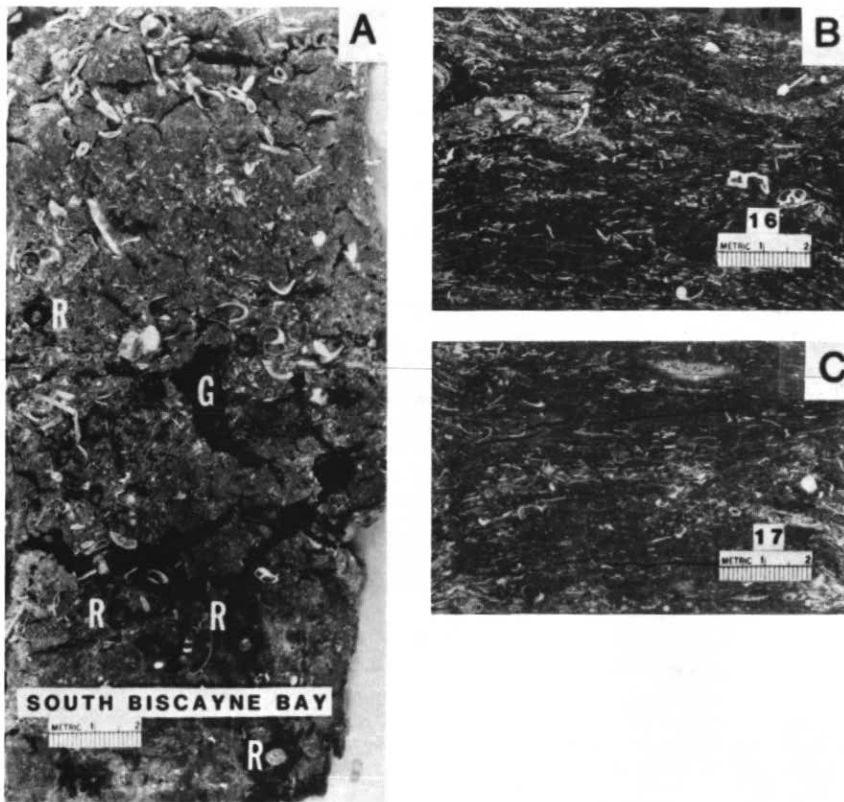


Figure 7 (A) Uncompacted subtidal bioclastic muddy sediment from the Holocene of south Florida (plastic-impregnated core). The mollusk shells and Halimeda plates (white) lack preferred orientation. R = horizontal grass rhizomes, G = marine turtle grass. (B) and (C) Artificially compacted sediments from the same core, under different loads. Mollusk and Halimeda fragments have been reoriented and commonly broken, drape-like swirls have appeared, and all of the "open" and uncalcified structures have been squeezed shut. From Shinn and Robbin (1983), photos courtesy of E.A. Shinn, published by permission.

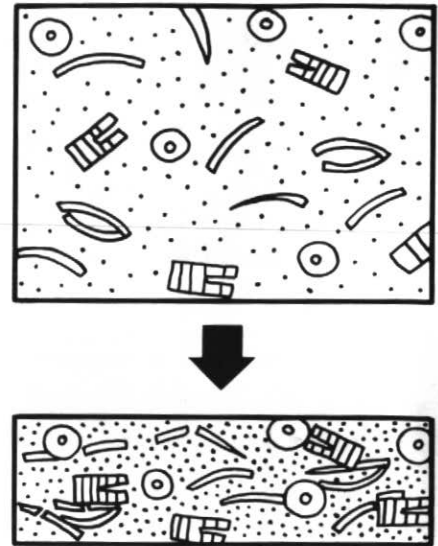


Figure 8 Diagrams illustrating the transformation of lime mud with sparse allochems to lithified, more allochem-rich limestone, as a result of physical compaction alone. Proportions of mud particles to pore space are shown schematically by the dots.

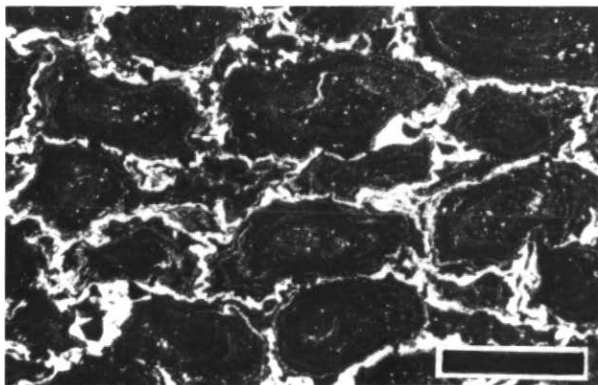


Figure 9 A pisolitic grainstone that has suffered grain flattening by physical compaction, and also pressure-solution interpenetration along microstylolites now marked by dolomite rhombs and voids (white). Bar scale is 1 mm. From the Mission Canyon Formation (Mississippian), Williston Basin, North Dakota (Elliott, 1982), photo courtesy of T.L. Elliott, published by permission.

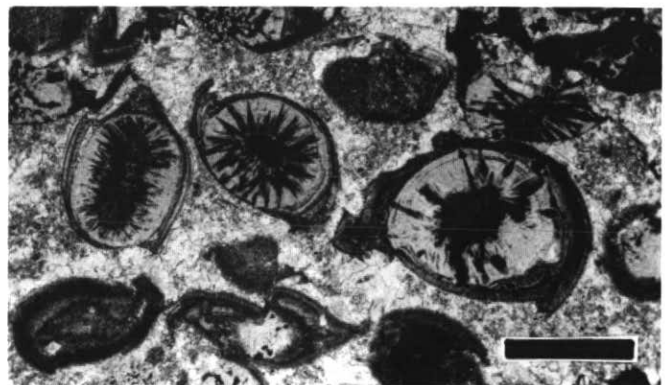


Figure 10 Ooids which have been squashed by physical compaction; outer concentric laminae on the ooids to right and left of centre are fractured and spalled. Some pressure solution also has occurred, embaying outer laminae as in the large ooid to right of centre. Bar scale is 1 mm. Upper Cambrian, Port au Port Peninsula, Western Newfoundland, photo courtesy N. Chow.

and much compacted in shaly partings between the lenses. When considered in light of the experiments by Shinn and Robbin (1983), physical compaction is likely to have been responsible for extensive stratal thinning in the geologic record.

Chemical Compaction (Pressure-Solution)

Chemical compaction or pressure-solution, commonly called pressure-solution compaction, is of great significance in carbonate rocks. It is known to be responsible for reductions of bed and sequence thicknesses in the range of at least 20-35%, thickness reductions that took place after physical compaction. Pressure-solution is also becoming more widely recognized, despite the common difficulty in proving cause and effect, as an important source of carbonate cement in deep-burial diagenesis (e.g. Bathurst, 1975; Hudson, 1975; Wong and Oldershaw, 1981; Scholle and Halley, 1985). Furthermore, it has been demonstrated that spaced cleavage of tectonic origin in folded limestones is in fact a pressure-solution phenomenon, and that space-cleavage surfaces are actually stylolites or non-sutured seams (e.g. Geiser, 1974; Groshong, 1975a, b; Rutter, 1976, 1983; Alvarez *et al.*, 1976; Droxler and Schaer, 1979; Engelder *et al.*, 1981; Geiser and Sansone, 1981; Marshak and Engelder, 1985).

The term "chemical compaction" was proposed by Lloyd (1977) for the loss of porosity and decrease of thickness brought about in limestones by the generation of "autochthonous" carbonate cement internally through pressure solution. Carried to completion, cementation of pores by this process should be capable of completely occluding whatever porosity remains in the wake of physical compaction and near-surface diagenesis. In Bathurst's (1975) words "... a limestone undergoing chemical compaction serves as both a donor and a receptor of carbonate cement".

Pressure-solution and its most obvious products, stylolites, have attracted the attentions of geologists for well over a century, beginning apparently with the inquiries of Thompson (1862) and Sorby (1879, 1908). Quantitative studies of thickness reductions due to stylolites were made more than a half-century ago by Stockdale (1922, 1926), and more recently have been carried out by Dunnington (1954, 1967), Mossop (1972), Playford (1980), Hurley (1986), Bathurst (in prep.) and many others; our experience and discussions with other geologists suggest that major thickness reductions also have been well documented in a large number of unpublished studies. The time and space relationships between pressure-solution, physical compaction and cementation have been examined most recently by Shinn and Robbin (1983), Bathurst (1984), and Scholle and Halley (1985).

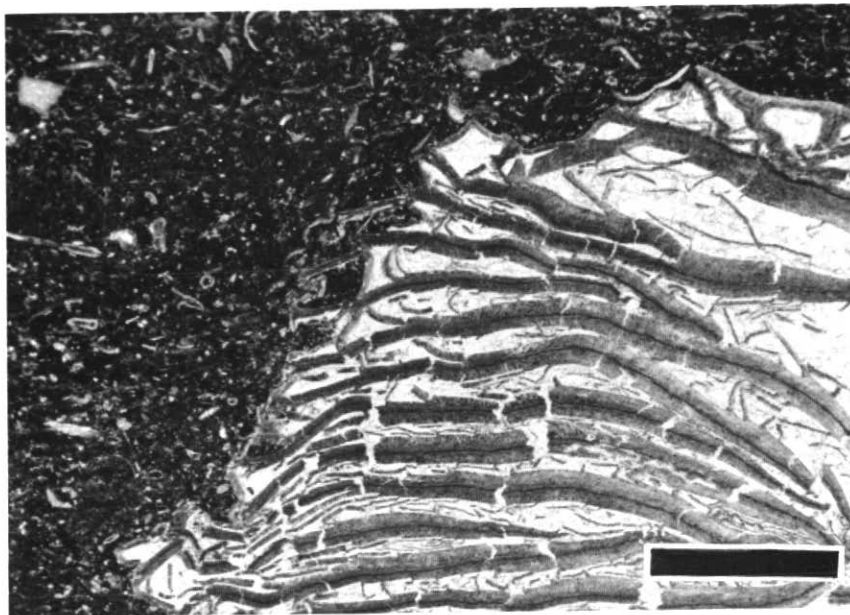


Figure 11 Part of a crushed rugose coral, the victim of physical compaction of the surrounding packstone matrix. Nearshore-marine skeletal limestone from the Mission Canyon Formation (Mississippian), Williston Basin, North Dakota (Beach and Schumacher, 1982a, b). Bar scale is 1 mm. Thin-section loaned by D.K. Beach, photo used by permission.

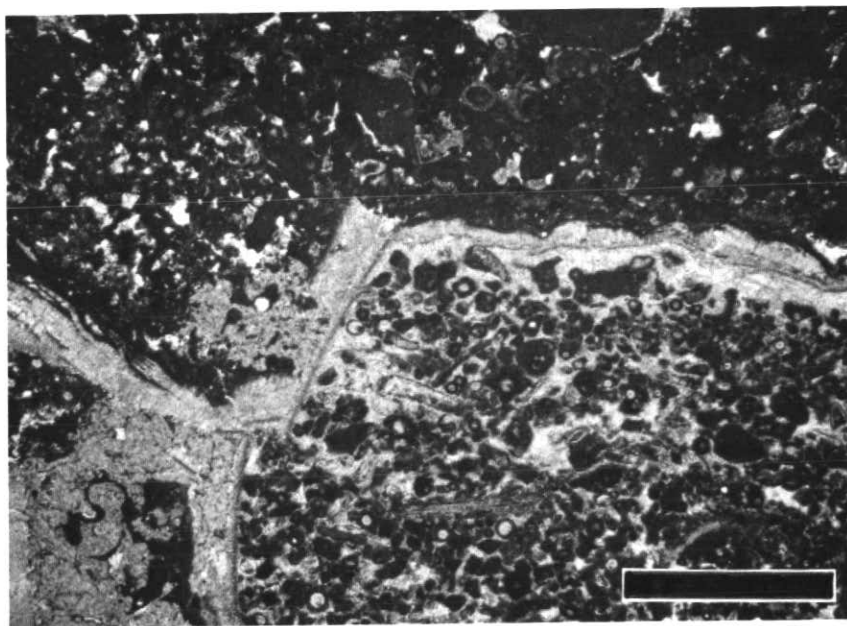


Figure 12 Sheltering effects in compacted shallow-marine foraminiferal-pelloidal limestone. A whole but broken brachiopod shell sheltered the grain-rich sediment inside it from physical compaction, and this sediment is now normally packed grainstone (lower right), while the same sediment outside the shell was compacted and is overly-packed packstone. Bar scale is 1 mm. Mission Canyon Formation, Williston Basin, North Dakota (Beach and Schumacher, 1982b). Thin-section loaned by D.K. Beach, photo used by permission.

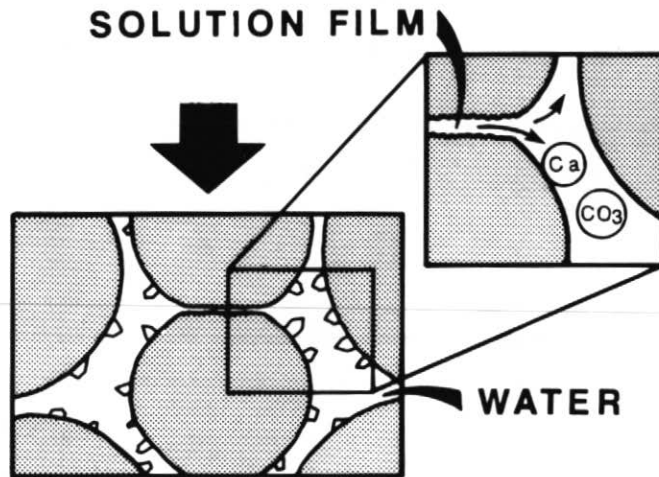


Figure 13 A conceptual sketch of elements on a microscale involved in pressure-solution of two grains pressed together at a sutured contact.

Processes. Pressure-solution is a process wherein pressure due to load or tectonic stress, transmitted to and concentrated at contact points or surfaces between grains, crystals or larger entities (limestone beds, for example), increases the solubility of the stressed mineral(s) due to increasing elastic strain, and causes dissolution at the contact. The phenomenon therefore involves a change of state from solid to liquid, creating a solution film (Weyl, 1959; De Boer, 1977b; Robin, 1978) a few water molecules thick at the contact. This film may or may not be connected with the solution-filled pore system of the rock (Figure 13).

For CaCO_3 , because the solubility-product constant $K_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$ increases at the locus of maximum stress due to increased strain energy, dissolution releases new ions of solute to the solution film. This pressure-induced solubility increase sets up a chemical potential gradient which declines away from the locus toward areas of lower stress. Ions move down this gradient by solution transfer (Durney, 1976) or diffusion, to be either combined and precipitated as new calcite cement at nearby sites where stress and solubility both are lower, or transported in moving pore waters to more distant sites. Each mole of CaCO_3 dissolved by this mechanism will produce a mole of solute ions and therefore, potentially, a mole of CaCO_3 cement. The analogy is nearly exact with ice which is gradually stressed at a contact point, say by a metal-tipped pole: ice dissolves at the contact and a depression forms, with an intervening film of water between metal and ice; when the pressure is released and the metal point removed, provided the air is below the freezing temperature of water, ice forms again in the depression. The main departure from this analogy of course is that in the subsurface the pressure is usually maintained.

Products. Pressure-solution features are amazingly diverse (Figure 14). Even stylolites, the most spectacular products, vary so much in amplitude and in form from one occurrence to another that they have stimulated a series of elaborate classifications (e.g. Stockdale, 1922; Park and Schot, 1968; Wanless, 1979).

The common denominator of stylolites and other sutured seams (Wanless, 1979) is a jagged surface, generally coated by insoluble clays, organic matter and/or other minerals, and made up of interlocking pillars, sockets, and variously shaped "teeth". Sutured seams include stylolites, many microstylolites, and networks of anastomosing microstylolites (the "fitted fabrics" of Logan and Semeniuk (1976) and Buxton and Sibley (1981)). Some stylolites develop selectively at contacts (Figure 15) between beds or nodules of highly contrasting solubilities such as well cemented oolite and microcrystalline dolomite (e.g. Choquette and Steinen, 1980). Often they propagate most extensively in

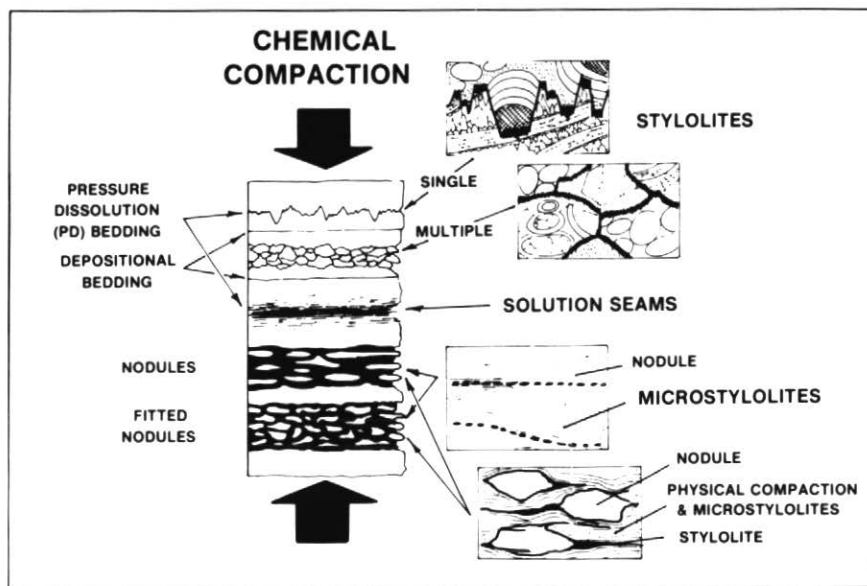


Figure 14 Sketches of features produced by chemical (pressure-solution) compaction.

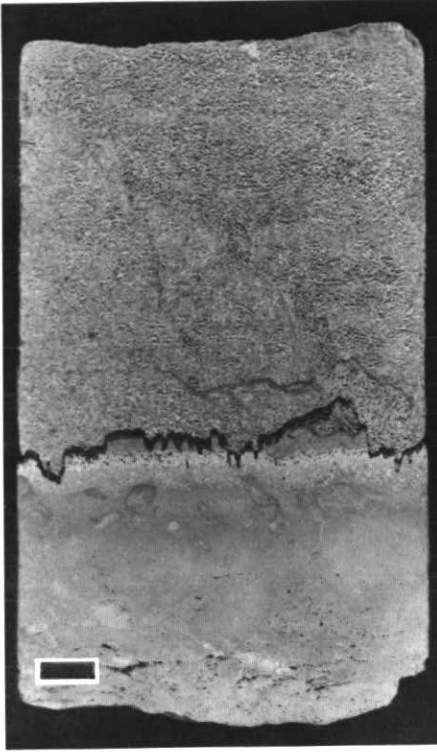


Figure 15 Stylolitic contact between ooid grainstone above and microcrystalline dolomite below. Finely particulate sulphides and pyrobitumen(?) form the dark sutured seam. Core-slab surface, bar scale 1 cm. Ste. Genevieve Formation (Mississippian), Illinois Basin, Illinois.

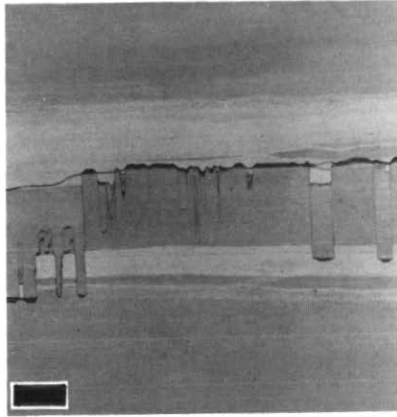


Figure 16 (above) Bedding-parallel stylolites (sutured seams) in thin beds of lime mudstone separated by thin shaly partings (lighter gray). Etched core-slab surface, bar scale 1 cm. Ste. Genevieve Formation (Mississippian), Illinois Basin, Illinois.



Figure 17 (right) Swarms of microstylolites and non-sutured wispy seams in a wackestone with lenticular burrow fillings of grainstone. Bar scale is 1 cm. Bajocian (Jurassic), Lincolnshire, U.K. Photo courtesy of R.G.C. Bathurst, published by permission.



Figure 18 Lower/Left: Outcrop photo of lime wackestones that show "pressure-solution bedding" at fissile partings made up of concentrations of microstylolites. Scale is 0.5 m long.

Upper/Right Inset: Thin-section photo of partings in an area such as that shown by arrow, illustrating a concentration of dissolution seams and microstylolites. Brachiopod shell was broken during physical compaction, then thinned somewhat by pressure solution. Bar scale is 0.25 mm long. Visean (Carboniferous), Clwyd, North Wales, U.K. Photos courtesy of R.G.C. Bathurst, by permission.

relatively clay-free, lime mudstone and wackestone, though they may have been initiated at clay/shale partings between "clean" limestone beds (Figure 16).

On the other hand, non-sutured seams (Wanless, 1979), have been recognized only since the 1970's (e.g. Mossop, 1972) as features probably caused by pressure solution (Figure 17). These are "wispy" surfaces that may extend laterally a few centimetres to hundreds of metres. They are marked, like sutured seams, by concentrations of organic matter, clays, pyrite and detrital silicates, and commonly dolomite of residual or syn-stylo-lite origin. Non-sutured seams develop typically in limestones (and some finely crystalline dolomites) that have significant amounts (more than about 10%) of clay and silt-sized quartz and/or several percent or more of organic matter. Often it is difficult to be sure that these wispy to planar seams are the result of pressure solution rather than physical compaction, and in fact very similar features have been produced experimentally by physical compaction and termed *pseudo-stylo-lites* (Shinn and Robbin, 1983). It can be equally hard to ascertain whether thinning and draping of laminae over and under rigid nodules and other objects, without obvious seams of residues, are due to the "non-seam dissolution" of Wanless (1979) or to purely physical compaction as noted in Shinn and Robbin's (1983) experiments.

In some sequences of stratified limestones the seams are so abundant and closely spaced as to impart a distinct pseudo-bedding strikingly like depositional bedding, as illustrated in Figure 18 (Bathurst, in prep.; Simpson, 1985). Bathurst (in prep.) has reckoned that solution thinning along these non-sutured seams may be comparable to the thinning caused by stylolite-forming dissolution. It would seem, therefore, that there is an important previously unrecognized source of CaCO_3 in addition to obvious stylolites.

Recognition that non-sutured seams (also called clay seams - Barrett, 1964; horsetails - Roehl, 1967, and Mossop, 1972; wispy laminae - Lucia, 1972; wavy laminae - Reinhardt and Hardie, 1976; pseudo-stylolites - Shinn *et al.*, 1977; and "microstylolites" - Wanless, 1979) are pressure-solution features has led to useful new classifications (Garrison and Kennedy, 1977; Wanless, 1979; Buxton and Sibley, 1981; Koepnick, 1984; Scholle and Halley, 1985), as well as a more radical classification and terminology (Logan and Semeniuk, 1976).

The organization of pressure-solution features outlined in Figure 19 is modified from a conceptually simple and useful classification by Wanless (1979). From this way of organizing the observations of many workers and from other considerations, some points of interest emerge as one tries to understand the origins and dynamics of pressure-solution features.

(1) Both sutured and non-sutured seams

can be either bedding-parallel and single or multiple, or reticulate, as implied in Figure 19 by the multiple stylolites and fitted nodules.

(2) Reticulate systems of anastomosing microstylolites (fitted fabrics) and non-sutured seams occur as a rule in limestones made up of abundant rigid entities of sand size or coarser (the "idens" of Logan and Semeniuk, 1976). These may be in grain-to-grain contact, like ooids and skeletal debris in poorly cemented grainstones (Buxton and Sibley, 1981; Meyers and Hill, 1983); or, the entities may be surrounded by more soluble sediment, like burrow-controlled, resistant nodules of chert or carbonate-cemented sediment in a matrix of clayey or organic-rich lime wackestone. Pressure solution presumably starts at grain contacts (often preceded by physical compaction). The microstylolites then propagate irregularly through their host to create a fitted-fabric network. The network style is a result of a high degree of heterogeneity.

(3) Bedding-parallel seams typically develop in well-bedded and/or more homogeneous limestones. The homogeneity commonly exists either because the limestones are lime-mud-rich with few large grains, or because they are grain-rich but have been extensively cemented by calcite and thus have less contrasting solubilities than before cementation. Well-bedded lime mudstones, therefore, tend to have stylolites of fairly uniform amplitudes. Rudstones commonly have stylolites that parallel stratification but vary in their amplitudes because of grain-to-grain solubility contrasts. Sequences in which relatively pure limestones are interlayered with organic-rich and/or clay-rich limestone intervals tend to undergo strong compaction and intense development of stylolites in the less pure intervals (e.g. Figure 18).

(4) Although recent experimental work suggested to Baker *et al.* (1982) that clays reduce the solubility of calcium carbonate with which they are admixed, a large body of field, petrographic and other observations by many other workers indicates the opposite, namely that clays and/or organic matter seem to be required in order for pressure-solution to occur. Furthermore, as just noted, many solution seams show signs of having been initiated along clay partings or clayey zones.

Notwithstanding that many aspects of pressure-solution are poorly understood, still it is useful to try and put together the observations just considered, in a way that may suggest some dynamics for the initiation and propagation of pressure-solution features. As shown diagrammatically in Figure 20, stylolites and microstylolites may begin either as sutures along contacts between rigid grains, nodules and the like, or as non-sutured seams in clay-rich zones and clay partings. Once initiated, the sutures propagate at apparent rates and in patterns that appear to vary in space and time. It was once thought that stylolite geometries are governed in part

by solubility contrasts between grains and other rigid entities (Stockdale, 1922, 1943; Coogan and Manus, 1975). Dunnington (1954) showed, however, that this factor alone cannot be enough because it fails to explain the variations in geometry found among stylolites. A more plausible kinematic control on the development and form of stylolites has been proposed by Guzzetta (1984). This kinematic model of migrating dissolution domains is based on the hypothesis that dissolution can only take place on one side at a time of a pressure-solution contact surface, and will shift from one side to the other through time. Where multiple stylolites are initiated, some propagate parallel as well as normal to the direction of maximum stress, and these then accommodate the stress selectively and continue to grow at the expense of the others.

Does pressure solution end? If it requires only a solution film to proceed, with or without an accompanying fluid-filled pore system, and if metamorphism too involves an inter-crystalline fluid film in which ion diffusion can occur, then pressure solution may not end or be precluded in carbonate rocks that have essentially zero porosity and permeability (R.B. Halley, pers. comm., 1986). Perhaps all that is required is that, in any given set of extrinsic conditions, lithostatic or directed pressure at a contact point or surface must only exceed solution film or pore-fluid pressure by some threshold amount.

Factors that Influence Pressure Solution

The factors that determine when in a sediment's burial history pressure solution will become significant, under what conditions it will slow or cease, and its role relative to physical compaction and cementation, are all poorly understood. What is clear is that a large number of factors can be influential and act together. Among these are the amount of overburden (lithostatic pressure), possibly temperature because of its effects on carbonate mineral solubilities, early cementation and dolomitization, water chemistry, water flow rates, pore-fluid pressure, presence of liquid hydrocarbons, CaCO_3 mineralogy, clay mineral content, content of organic matter, and host-rock porosity and permeability. Many of these factors also influence carbonate cementation, and most of them have been reviewed in detail recently by Feazel and Schatzinger (1985).

Burial Depth. Chemical compaction probably starts in marine sediments within the first few hundred metres of burial. There and until the sediments are firmly cemented, particle-to-particle pressure solution and point-contact cementation (the "spot-welding" of Mapstone, 1975) seems to be the dominant style of pressure solution. Non-sutured and sutured seam pressure-solution features may begin to form toward the lower end of this depth range and certainly become obvious after about a kilometre of burial.

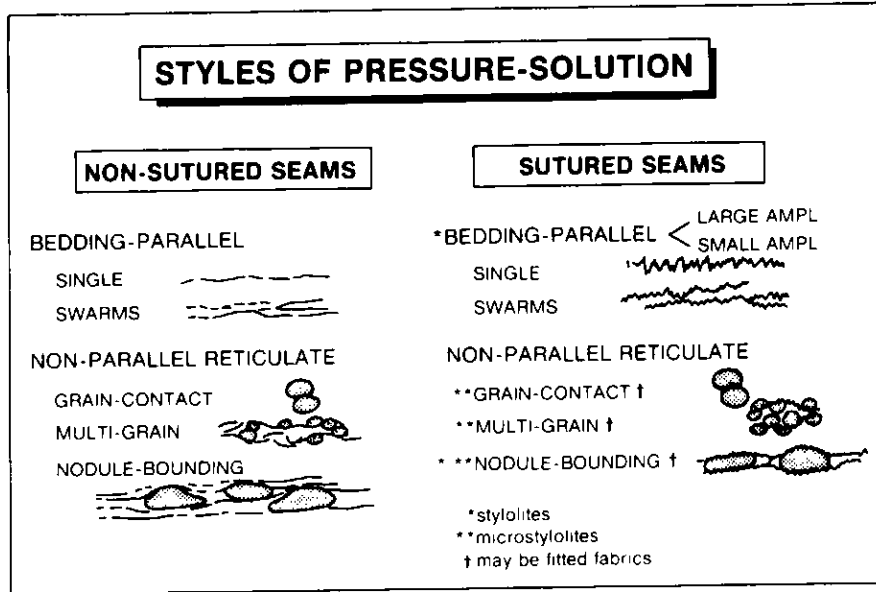


Figure 19 Styles of pressure-solution. Modified from Wanless (1979).

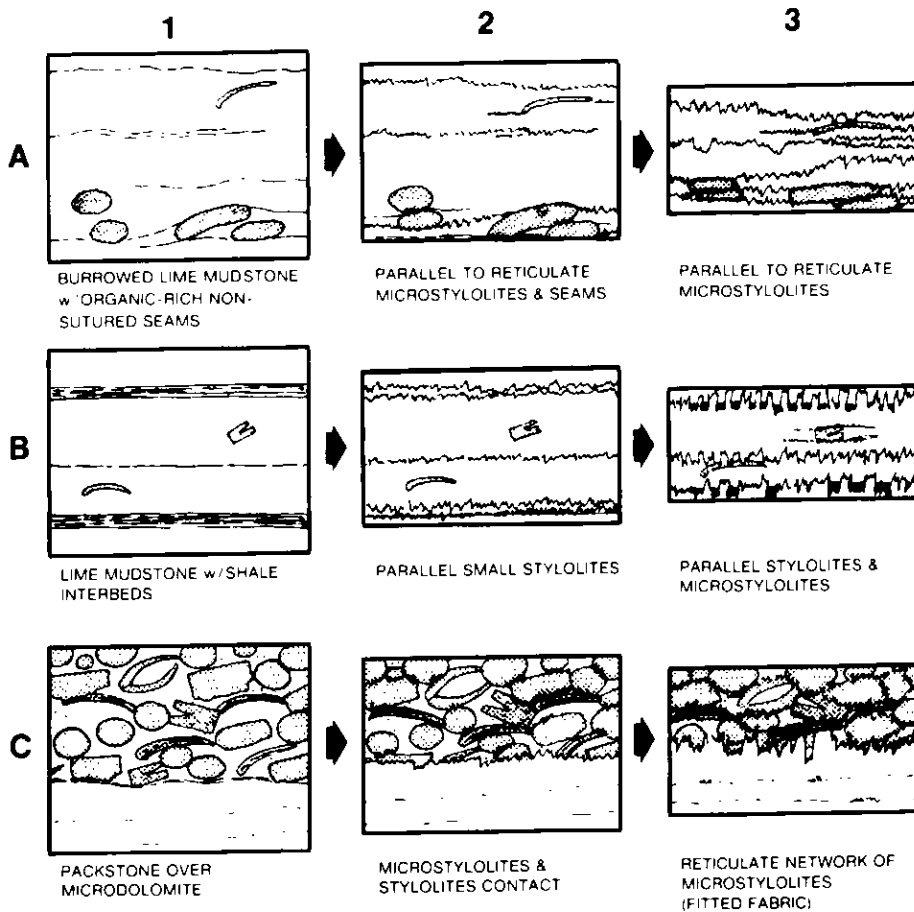


Figure 20 Sketches to suggest pathways along which pressure-solution features may develop and evolve. The initial sediments (stage 1) are assumed to have been physically compacted already, so that further compaction is entirely chemical. The microcrystalline dolomite in C remains essentially uncompactd.

In carbonates being buried in dilute pore waters, the minimum burial depth needed to initiate chemical compaction is likely to be more variable and may often be less. Pressure solution in shallow-marine grainstone and packstone of Mississippian age in south-eastern New Mexico apparently began after "tens to hundreds of metres" of burial (Meyers and Hill, 1983), resulting in fitted fabrics of microstylolites. Stylolites are well developed in Mississippian lime mudstones in the Illinois Basin subsurface, about 150 m below the unconformity separating the Mississippian and Pennsylvanian systems there, and buried now under 550 m of overburden (Choquette and Steinen, 1980). In limestones of the uppermost Madison Group (Mississippian) in parts of western Wyoming, stylolites are intensely developed within a few metres to tens of metres of the post-Madison unconformity, and diminish in intensity downward, suggesting that their distribution may have been influenced by very near-surface meteoric-water diagenesis. Thus, the suggestion of Dunnington (1967) that pressure solution becomes effective and stylolites become abundant after burial to around 600-900 m is probably an oversimplification.

Pore-Water Composition. Pressure solution seems to be accelerated, and physical compaction may be inhibited, by Mg-poor meteoric waters as opposed to marine-derived pore waters. Neugebauer (1973, 1974), drawing on work by Lippmann (1973) and some others, concluded that high Mg^{2+} activities and high Mg^{2+}/Ca^{2+} ratios in North Sea and deep-sea chalks were partly responsible for inhibiting their cementation and porosity reduction by inhibiting pressure solution. The inhibiting effect is apparently due to the high hydration energy of Mg^{2+} , which decreases with rising temperature (Bjorlykke, 1983). These considerations suggest that pressure solution should be favoured in burial settings characterized by meteoric input and should accelerate with rising burial temperature.

Metastable Mineralogy. Wherever aragonite and high-Mg calcite persist into the burial environment they should favour pressure-solution, giving their host limestones a high "diagenetic potential" for alteration (Schlanger and Douglas, 1974). Deep-sea nannofossil-foraminiferal oozes have low diagenetic potentials because their calcium carbonate is all low-Mg calcite. This is a factor in accounting for their slow rates of pressure-solution, cementation, and porosity reduction.

Clay Minerals. On balance, as discussed earlier, clays appear to foster pressure solution. Marshak and Engelder (1985) concluded from petrographic and X-ray diffraction evidence that in order for spaced, pressure-solution cleavage of tectonic origin to develop in limestones, clays must be present between grains or along crystal boundaries to provide "interconnectivity" of

dissolution sites at grain boundaries with the larger-scale, free-fluid system. Bathurst has concluded (pers. comm., 1986) that the amount of clay and associated fines has an influence on the style of pressure solution: Sutured-seam stylolites of the sort illustrated in Figures 15 and 16 are favoured where clay/silt content is significant but less than about 10%, whereas non-sutured seams like those in Figures 17 and 18 tend to develop if clay/silt content exceeds about 10% and/or there is a significant amount (more than a few percent) of organic matter. Where there is neither clay nor organic matter, stylolites are unlikely to develop. Stylolites commonly seem to start developing along clay-shale partings. The observations of Marshak and Engelder (1985) are relevant in this connection. They found that pure lime grainstones deform primarily by twinning, with only isolated tectonic stylolites, and rarely develop tectonic (pressure-solution) cleavage. They also observed that sutured, stylolitic seams develop in relatively clay-poor limestones and non-sutured seams in the more clay-rich limestones.

Early Dolomitization. Early, pre-burial or very shallow-burial dolomitization can inhibit or preclude stylolites from forming. For example, lime mudstones have superbly developed bedding-parallel stylolites in the Ste. Genevieve Formation (Mississippian) in the Illinois Basin, but closely associated microcrystalline dolomites that formed by local alteration of similar precursor lime muds have no stylolites (Choquette and Steinen, 1980). The dolomites acquired a "grain-supported" crystal framework that resisted stylolitic pressure solution.

Liquid Hydrocarbons. Early introduction of oil into the pore systems of limestones still undergoing chemical compaction tends to inhibit or shut off the process, and can entirely prevent the formation of stylolites (Dunnington, 1967) as well as other pressure-solution effects including "autocementation".

Burial Cements

It is now clear that much of the carbonate cement in many well-lithified limestones was emplaced during burial diagenesis. Essentially all cementation in deep-basinal sediments that were never uplifted into the meteoric, chalks included, must be of burial origin (see Schlanger and Douglas (1974) for a thoughtful review of chalk diagenesis in DSDP cores, and Coniglio (1985) for an in-depth study of the petrology of ancient deep-marine limestones). Much of the cement in ancient shallow-marine, peritidal, and platform-margin limestones is of burial-diagenetic origin (Talbot, 1971; Meyers, 1974, 1978; Grover and Read, 1983; Mattes and Mountjoy, 1980; Moore and Druckman, 1981; Elliott, 1982; Frank *et al.*, 1982; James and Klappa, 1983; Burruss *et al.*, 1983; Walkden and Berry, 1984; Choquette and Steinen, 1985; Druckman and Moore, 1985; Mruk, 1985; Brinton, 1986). The importance of burial-

diagenetic cementation has also been forcefully argued on grounds of stable-isotope compositions by Hudson (1975, 1977) and on this and other evidence by Bathurst (e.g. 1975, 1984) and Scholle and Halley (1985).

Shallow Burial "Marine" Cements

Cements of early, shallow burial origin (first few metres to tens of metres) in deeper marine settings include displacive fibrous calcite (also called "beef" and "cone-in-cone"; see Fig. 4), a variety peculiar to highly argillaceous mudstones; and low-Mg calcite cements of micrite, microspar and slightly coarser crystal sizes (ca. 1-200 μ m) found in fine-grained sediments including chalks. Coniglio (1985) has recently documented in detail the sedimentology, petrography and geochemistry of all these shallow-burial cements in Cambro-Ordovician slope and basinal limestones of western Newfoundland.

Deeper-Burial Cements

In chalks the burial cements are micro-to-nanocrystalline, from around 1 to 10 microns except in internal cavities of some skeletal grains, and so have been studied best with the scanning-electron microscope (e.g. Matter, 1974; Scholle, 1977; Feazel *et al.*, 1985). Chalk cements have not yet been investigated in terms of cement zonation and geochemistry because of their ultra-small crystal sizes. The principal types of burial cements found in shallow marine/peritidal limestones include: clear coarse calcite (calc-spar or coarse equant spar); clear-to-turbid coarse dolomite or dolospar ("saddle" dolomite of Radke and Mathis, 1980; "baroque" dolomite of Folk and Assereto, 1974); the xenotopic dolomite of Gregg and Sibley (1984); and coarse anhydrite. Various lines of evidence including aqueous fluid inclusions, oxygen-isotope compositions and cement zonation demonstrate that these burial cements can form over a substantial range of conditions. These include temperatures from around 40-50°C to perhaps 200°C or higher, burial depths from a few hundred metres or less (Meyers, 1980) to kilometres; formation water compositions ranging from brackish to highly saline, from acidic to strongly alkaline pH values, and from moderately to strongly negative Eh values; water flow rates that probably range from almost stagnant to moderately rapid for ground water (order of less than 1-10 $m\cdot yr^{-1}$); and time intervals of anywhere from a few thousand(?) to tens of millions of years.

The general characteristics of coarse burial cements (Figure 21) are now well established. The cements are commonly ferroan (more than 500 ppm ferrous iron) and enriched in Mn^{2+} (more than 100 ppm) but impoverished in Sr^{2+} compared with associated earlier diagenetic cements, and have oxygen-isotope compositions depleted in ^{18}O . Their cathodoluminescence (CL) is characteristically dull and may or may not

show compositional zonation. Aqueous fluid inclusions (generally containing both gas and liquid phases) and hydrocarbon inclusions are common.

The significance of iron and manganese in the 2+ valence state is that they require reducing conditions to exist. Although in theory the waters may have positive Eh values (Frank *et al.*, 1982), in actuality those deep formation waters for which analyses have been made (e.g. White, 1975; Collins, 1975; Drever, 1982) have at least moderately negative Eh. Consequently, ferroan and manganous carbonate cements must precipitate from at least moderately reducing pore waters (Oglesby, 1976; Pierson, 1981; Frank *et al.*, 1982). Near-surface meteoric ground water is normally well oxygenated (Evamy, 1969), but the distal parts of intermediate and deep carbonate aquifers remote from recharge areas can be anoxic (e.g. Grover and Read, 1983).

Cathodoluminescence (CL) is favoured by the presence of Mn^{2+} but inhibited by Fe^{2+} . The ratio of these two cations seems to be more important than their absolute concentrations in determining CL (Pierson, 1981; Frank *et al.*, 1982; Grover and Read, 1983; Fairchild, 1983; ten Have and Heijnen, 1985). Other cations such as Pb^{2+} and Ce^{2+} may serve as activator ions and Ni^{2+} and Co^{2+} as inhibitor ions (Machel, 1985), though they are clearly subordinate to Mn^{2+} and Fe^{2+} and it is unclear whether they affect primarily CL or photoluminescence.

Bladed-prismatic calcite. This cement consists of elongate scalenohedral crystals, generally found growing directly on grain surfaces or atop earlier, marine cements. Crystals are a few tens of micrometres across and up to a few hundred micrometres long, and have prismatic terminations. CL is typically dark with one or more bright lines (Figure 22). Generally where more than one cement type other than marine occurs,

bladed-prismatic calcite is the oldest. Some of these cements, for example in the Lower Cambrian Forteau Formation of Labrador (Figure 22), have two stages, an older stage rich in fluid inclusions and a younger one essentially free of inclusions (James and Klappa, 1983). Bladed-prismatic cements observed in Jurassic Smackover limestones of the Gulf Coast, on the other hand, were found to contain two-phase fluid inclusions, suggesting to O'Hearn (1985) that they origi-

nated in hot brines. The origins of these interesting cements are unresolved, but the usual position of such cements in paragenetic sequences, and the typically dark-bright cathodoluminescence, argue for an origin somewhere in the meteoric, in part in brackish waters of mixed fresh and marine origins. Isotopic compositions found by Mruk (1985), Brinton (1986) and some others are compatible with this interpretation, but details of the settings responsible remain unclear.

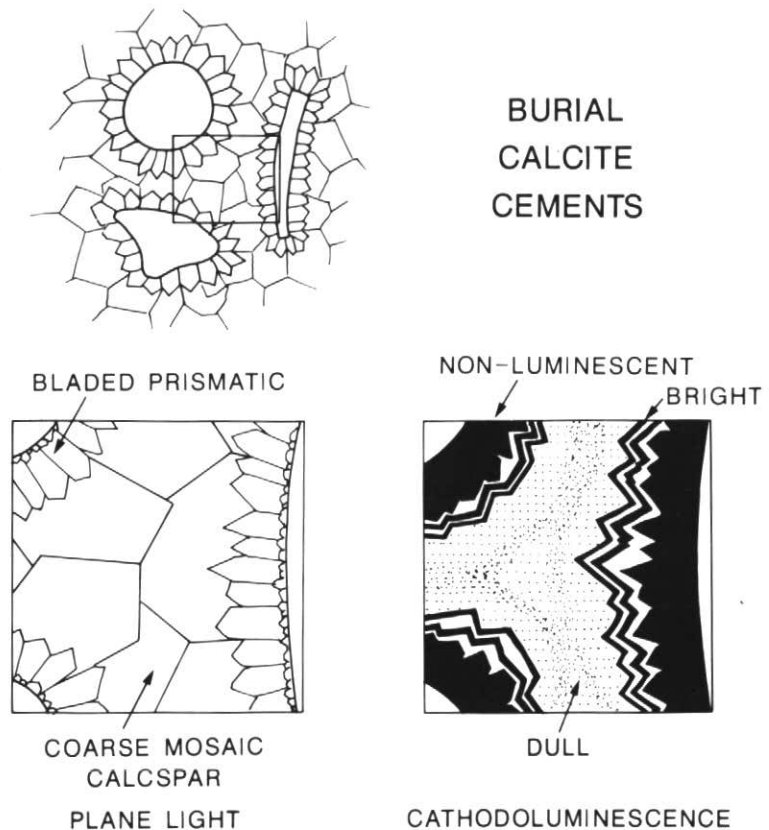


Figure 21 Sketches of burial-digenetic cements as they appear in plane light and cathodoluminescence.

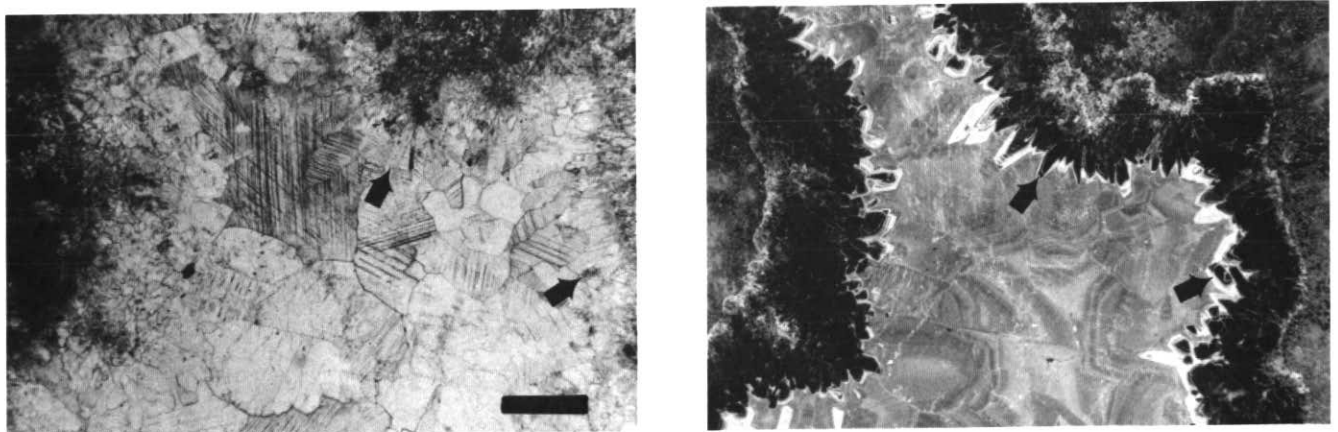


Figure 22 Multiple generations of burial calcite cement in a small reef limestone cavity rimmed by Renalcis and early marine cements.

Left: plane light, illustrating bladed prismatic (arrows) and coarse mosaic calcspar.

Right: cathodoluminescence, illustrating black, non-luminescent prismatic crystals (arrows) with brightly luminescent tips and dull but zoned luminescent coarse mosaic calcspar. Bar scale is 1 mm. Lower Cambrian, Labrador.

Coarse mosaic calcspar. This cement typically consists of plane-sided, equant crystals ranging from tens to hundreds of microns in size, which may or may not be noticeably ferroan and generally have dull, zoned or unzoned CL (Figure 22).

Poikilitic calcite. These crystals can be several millimetres in size and large enough to enclose several depositional grains, and otherwise have dull CL like the coarse mosaic calcspar.

Coarse Dolomite Cement. Saddle or baroque dolomite and xenotopic dolomite are other varieties of burial cement which often are ferroan. Saddle dolomite (Radke and Mathis, 1980) is typified by curved cleavage traces and crystal faces, a peculiar and distinctive sweeping extinction in cross-polarized light caused by a distorted crystal lattice, and often zonation in terms of Fe^{2+} and Mn^{2+} concentrations as well as CL (Figure 23). Xenotopic dolomite (Gregg and Sibley, 1984) is typically of mosaic style and consists of anhedral crystals with irregular or curved boundaries, fine to coarse crystal sizes (ca. 0.1-1 mm) and, as a rule, undulatory extinction. From experimental and geochemical considerations it appears to form at temperatures of about 50°C and higher. Late-stage burial dolomite cements have been reported in limestone and dolomite sequences in many regions (Choquette, 1971; Radke and Mathis, 1980; Mattes and Mountjoy, 1980; Choquette and Steinen, 1985; Moore and Druckman, 1981; Grover and Read, 1983; James and Klappa, 1983; Druckman and Moore, 1985; Prezbindowski, 1985). Commonly the dolomite is closely associated with burial calcspar cement which it either pre- or postdates. Saddle dolomite partly of replacement origin has been discovered recently in grainstones of the Jurassic Smackover Formation in the Louisiana Gulf Coast (D.H. Mruk, pers. comm., 1986). The precipitation of saddle dolomite in preference to calcspar

seems to be favoured by the presence of dolomite-crystal substrates, and at the relatively high temperatures of the burial diagenetic realm can take place in waters with relatively low Mg^{2+}/Ca^{2+} ratios (Rosenberg and Holland, 1964).

Coarse Anhydrite Cement. Large crystals of anhydrite, in some instances poikilitic forms, can be seen in many buried limestones associated with units of anhydrite, often in carbonate-evaporite cycles (Brinton, 1986). Paragenetically, anhydrite cement may predate or postdate the burial carbonate cements (Figure 23). Its presence suggests formation, or conversion from gypsum, at depths of something over 300 m since above that approximate depth gypsum is the more stable form of calcium sulphate (Murray, 1964).

Criteria for Recognition of Burial Cements

Although the characteristics just outlined are generally reliable indicators of deep-burial origin, the surest criteria are those based on determining that cements actually postdate other burial-diagenetic features, such as physical compaction features, stylolites and microstylolites, and hydrocarbons or their alteration products (Figure 24). Generally speaking, cements can be safely dated as "late" if they are involved in one or more of the following kinds of time-space relationships:

- (1) Cement crystals cross-cut stylolites, or microstylolites or pressure-solution seams end at cement crystals.
- (2) Cements heal fractured grains or spalled ooid cortices.
- (3) Cement crystals postdate the physical or chemical compaction of grains (filling "compacted pores"), or enclose or replace compacted grains.
- (4) Cement crystals enclose or postdate hydrocarbon alteration products such as asphalt or pyrobitumen.

(5) Cements fill tectonic fractures or fill dissolution pore spaces which themselves were formed by removal of both grains and early burial cements.

Conditions of Cement Precipitation

Most burial cements, as outlined earlier, formed over a wide range of conditions.

Temperature. Burial calcite and saddle dolomite cements evidently precipitate over a range of temperature from ~40° to 200°C or somewhat higher but most commonly between ~50° and 150°C, and at burial depths between a few hundred metres and several kilometres. Precipitation temperatures have been estimated by three indirect methods, from (1) the temperatures at which primary two-phase fluid inclusions homogenize to a single, vapour phase when heated, (2) stable-oxygen isotope compositions, and (3) inferred geothermal gradients (see Fig. 2) and burial depths at the time of cement precipitation.

Salinity. The aqueous solutions from which burial calcite and dolomite cements precipitate, judging from a large number of determinations of freezing and initial melting temperatures of fluid inclusions, are generally brines of varying salinities. Most of these brines seem to be of Na-Ca-Cl type, and the common salinity range is about 10-100 parts per thousand (‰)(seawater = 35‰). Some of the high salinities are from cement inclusions in sequences associated with evaporites, such as the Jurassic Smackover Formation in the US Gulf Coast (e.g. Klosterman, 1981; O'Hearn, 1985), where the ambient pore waters probably reflect dissolution of evaporites (Collins, 1975; Carpenter, 1978; Moore, 1985). Furthermore, not all cements judged to have formed in burial settings have two-phase aqueous fluid inclusions. Nor does it follow that all pore waters responsible were brines; what we know suggests however, that many were brines.

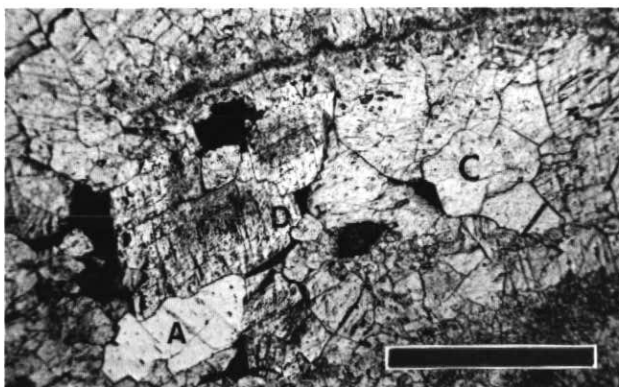


Figure 23 Burial cements in a phylloid-algal mold in skeletal grainstone.

Left: plane light, illustrating mosaic calcspar (C), saddle dolomite (D) with inclusion-rich centres, and anhydrite (A) partly replacing a zoned dolomite rhomb. Dark areas in central part of photo are pore spaces.

Right: cathodoluminescence, illustrating unfilled pore space (black) and outer zones in saddle dolomite cross-cut by non-luminescent anhydrite. Bar scale is 1 mm. Paradox Formation (Pennsylvanian), southeastern Utah (Brinton, 1986). Photos courtesy of L. Brinton, published by permission.

Isotopic Compositions of Cements and Waters. Burial cements typically show a progression, from older to younger cement generations and also within generations, toward lighter and lighter stable-isotope compositions: their $\delta^{13}\text{C}$ values decline only slightly, whereas their $\delta^{18}\text{O}$ compositions decrease sharply, by as much as 10-15‰ (Figure 25). This same progression was observed by Dickson and his co-workers (Dickson and Coleman, 1980; see also Moore, 1985) in a series of compositional zones painstakingly sampled within *single* crystals of burial cement.

Moreover, burial cements are virtually without exception isotopically "lighter" (depleted in the heavier isotopes of C and O) than earlier marine and meteoric cements as well as marine depositional constituents in the same carbonates. These relationships have been observed in a large number of studies both for calcite-dominated cement systems (e.g. Tan and Hudson, 1974; Walls *et al.*, 1979; Meyers and Lohmann, 1985; Prezbindowski, 1985; Moore, 1985; Brinton, 1986), and for systems of multiple dolomite cements in early-diagenetic dolomite and limestone (e.g. Choquette, 1971; Fritz and Jackson, 1972; Mattes and Mountjoy, 1980; Choquette and Steinen, 1980; Brinton, 1986). However, Halley has cautioned that some burial cements may have relatively heavy $\delta^{18}\text{O}$ values and go unrecognized simply because we expect strongly negative values; for example, reservoir water in the Sunniland Field, south Florida has $\delta^{18}\text{O}$ of +10‰ and at present reservoir temperature would make calcite cement with only -2 to -3‰. Land and Prezbindowski (1981) report values of +12 to +29‰ for waters from deeply buried Cretaceous carbonates of south Texas (R.B. Halley, pers. comm., 1986).

The progressive decreases in oxygen-isotope composition primarily reflect increasing temperatures of the precipitating waters. These can be estimated by using assumed or determined values for the oxygen-isotopic compositions of the waters. Graphic charts of the sort published by Prezbindowski (1985) for calcite-water systems based on equilibrium relationships worked out by O'Neil *et al.* (1969), and by Land (1985) for dolomite-water systems can be consulted for this purpose. Using the chart by Prezbindowski (1985) one can get a sense of the temperature ranges involved in individual suites of burial cements. For example, cements with $\delta^{18}\text{O}$ values 8‰ apart would have precipitated at temperatures about 70°C apart, assuming a water of constant isotopic composition. Since progressively younger burial cements commonly have precipitated from progressively more saline and presumably more ^{18}O -enriched waters, temperature ranges like the one just cited must be minimum values.

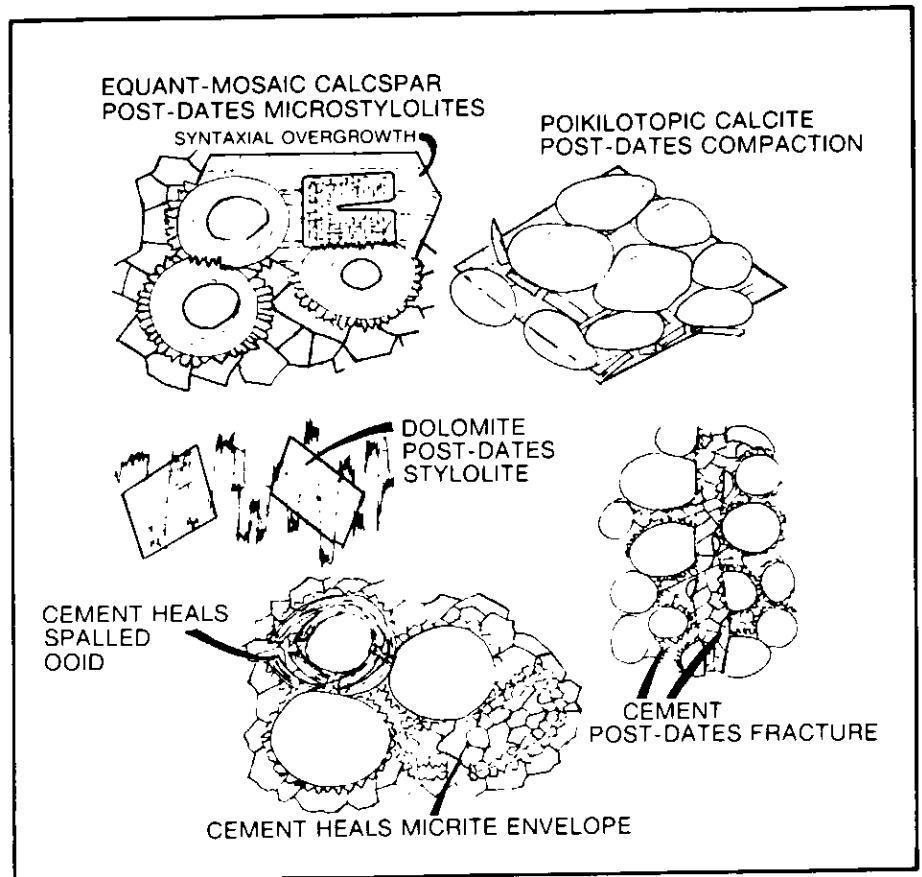


Figure 24 Criteria for interpreting cements as "late" burial features.

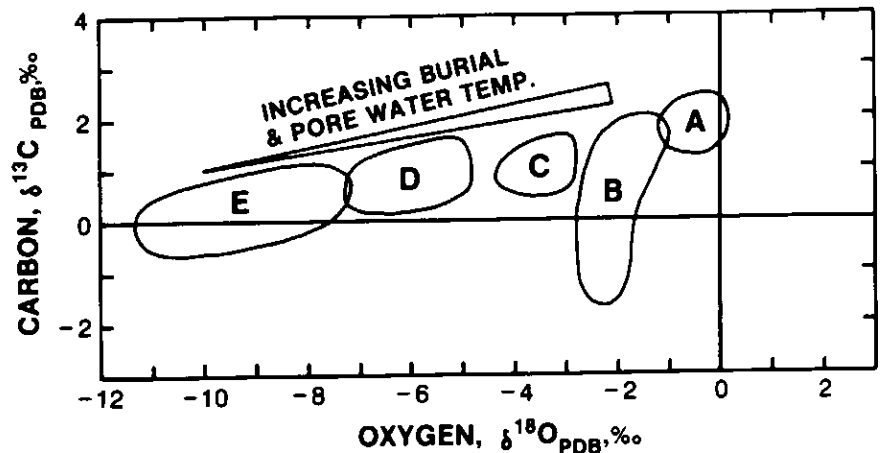


Figure 25 A graph showing the hypothetical trend of systematic changes in isotopic composition which accompany the diagenesis of a marine carbonate sediment (A), first in the meteoric realm (B), then in possibly a mixing zone with precipitation of prismatic cement (C), and finally in successively deeper parts of the burial domain with precipitation of coarse calcspar (D) and saddle dolomite (E). The sequence of cements from B through E was precipitated from progressively hotter waters. This general trend, although hypothetical, has been observed in carbonates — both limestones and dolomites, with both calcite and dolomite cements — from a great many areas and stratigraphic units. It may well be the "normal" trend of cement stratigraphies in the deep-burial domain.

Origin of Burial Cements

Passive Cementation. As in any other carbonate-water system, CaCO_3 dissolved in one place can be transported over large distances before conditions are right for precipitation. It has been shown (e.g. Pray, 1966; Dunham, 1969; Bathurst, 1971, p. 440-441; Scholle and Halley, 1985) that in order to precipitate one volume unit of calcite cement from an imported aqueous solution with reasonable CaCO_3 content, something on the order of 10,000 to 100,000 unit volumes of solution is required. Is water flux likely to be large enough to meet these needs? In relatively shallow aquifers with flow rates of -5-20 metres per year such as the south Florida Tertiary aquifer (Back and Hanshaw, 1971) and the Madison Limestone aquifer of Wyoming, Montana and the Dakotas (Hanshaw *et al.*, 1978), cementation appears to be an active present-day process. But in strata that are buried at depths of several kilometres such as the Smackover in much of the US Gulf Coast, and are unconnected with active aquifers, formation water flow rates are likely to be very small. In the opinion of some workers (e.g. Wood and Hewett, 1984)

no formation waters are likely to be completely static even if overpressured, and some circulation with flow rates of at least 1 metre per year must take place by convection alone.

Autocementation. An increasingly convincing body of evidence points toward the view that in partly closed systems pressure solution may be the main agent for cementation in limestones undergoing burial diagenesis (Hudson, 1975, 1977; Scholle and Halley, 1985). Most studies that have attempted to find cause-effect relationships between stylolites and burial cements, however, have not clearly established such relationships. A few authors have noticed that stylolites commonly occur in intervals of anomalously low porosity (Harms and Choquette, 1965; Dunnington, 1967; Nelson, 1981), but have not established that the cement occluding the porosity was genetically related to the stylolites. The only investigation known to us which demonstrated a *direct* link unequivocally was by Wong and Oldershaw (1981). Those authors showed not only a spatial relationship between stylolites and intervals of low porosity (Figure 26) but a time relationship as well, in which cement zones were found to be genetically related to stages in stylolite growth (Figure 27). The cements are very coarse and the zones, revealed by staining with KFeCN solution, are so spectacular that they can be seen with the unaided eye.

Is it possible that similar time-space relationships exist in other stylolitic and once-porous limestones but have not been identified? To discern them in more finely crystalline cements would require very critical

observations and some measure of luck. Buxton and Sibley (1981) argued that flow rates in limestone aquifers are too high to favour the transport of ions released by pressure-solution solely by diffusion along solution films to nearby precipitation sites. Wherever solution films are connected to water-filled pore systems in which flow is significant, the films should discharge their load of ions into the flow system.

Factors that Promote Burial Cementation.

It is generally accepted that *supersaturation* with respect to both calcite and dolomite prevails in most subsurface pore waters. Exceptions are the shallow "upstream" (up-gradient) parts of aquifers that are being actively recharged, like the Mississippian Madison Formation in the northern US Rocky Mountain and high plains region (Hanshaw *et al.*, 1978) and the confined Biscayne aquifer (Cenozoic) of south Florida (Kohout, 1965, 1967; Back and Hanshaw, 1971); there, undersaturation and dissolution are common. The *general* condition, however, is one of supersaturation. It is likely to be achieved primarily by dissolution of CaCO_3 increasing the activities of Ca^{2+} and CO_3^{2-} in ambient pore waters. Supersaturation is likely to be maintained as long as significant precipitation of carbonate cement or significant dilution of system pore waters by meteoric water do not occur.

Increasing temperature should also work to enable the precipitation of calcite, which is retrograde (Helgeson, 1969). Although increasing pressure partly counters the effects of temperature, experimental work by

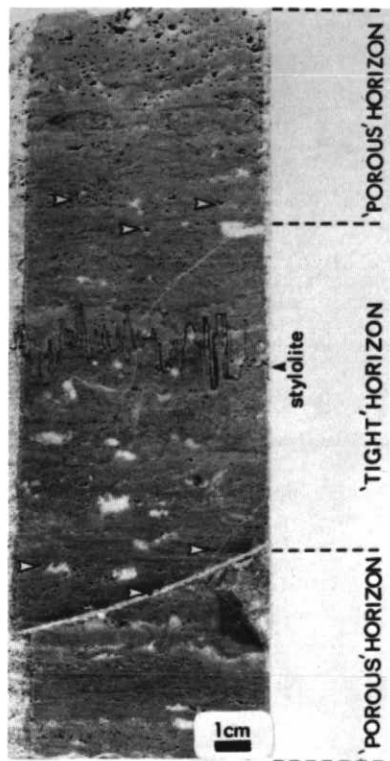


Figure 26 A core-slab surface illustrating the common association of anomalously low porosity (< 6%) with stylolites. Porosities above and below the thin stylolite-related interval are 15-20%. The arrows indicate positions of pores that were used to define the boundaries of the "tight" horizon. Devonian Kaybob reef, Swan Hills Formation, Alberta (Wong and Oldershaw, 1981). Photo courtesy of P.K. Wong, published by permission.

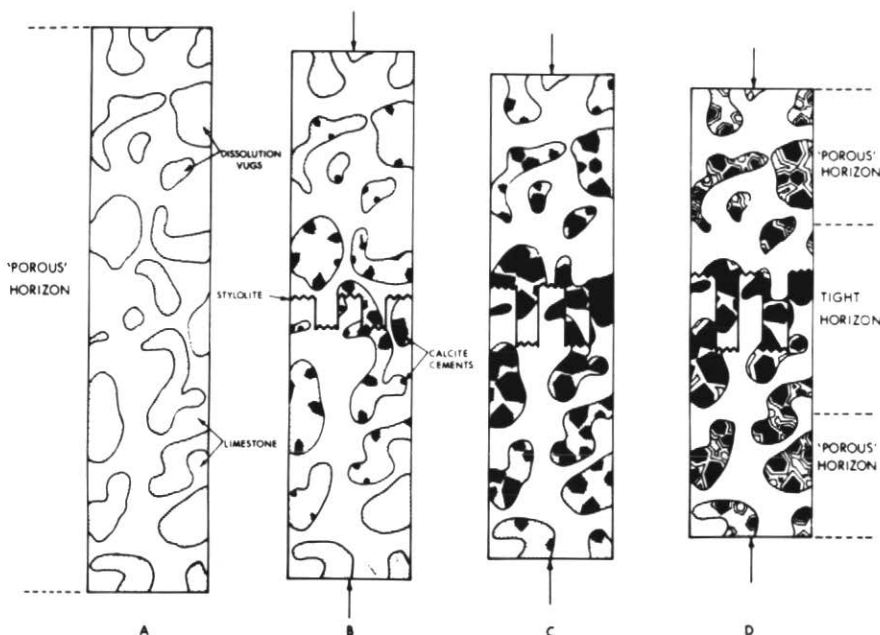


Figure 27 Diagrams showing the development of a stylolite and the concurrent precipitation of coarse, zoned cements with CaCO_3 produced by pressure solution. In its later stages the stylolite grew at the expense of some of the earlier cement. Fe-rich cement is black, Fe-poor cement is white, and pore space is stippled. Devonian Kaybob reef, Swan Hills Formation, Alberta (Wong and Oldershaw, 1981). Diagram courtesy of P.K. Wong, published by permission.

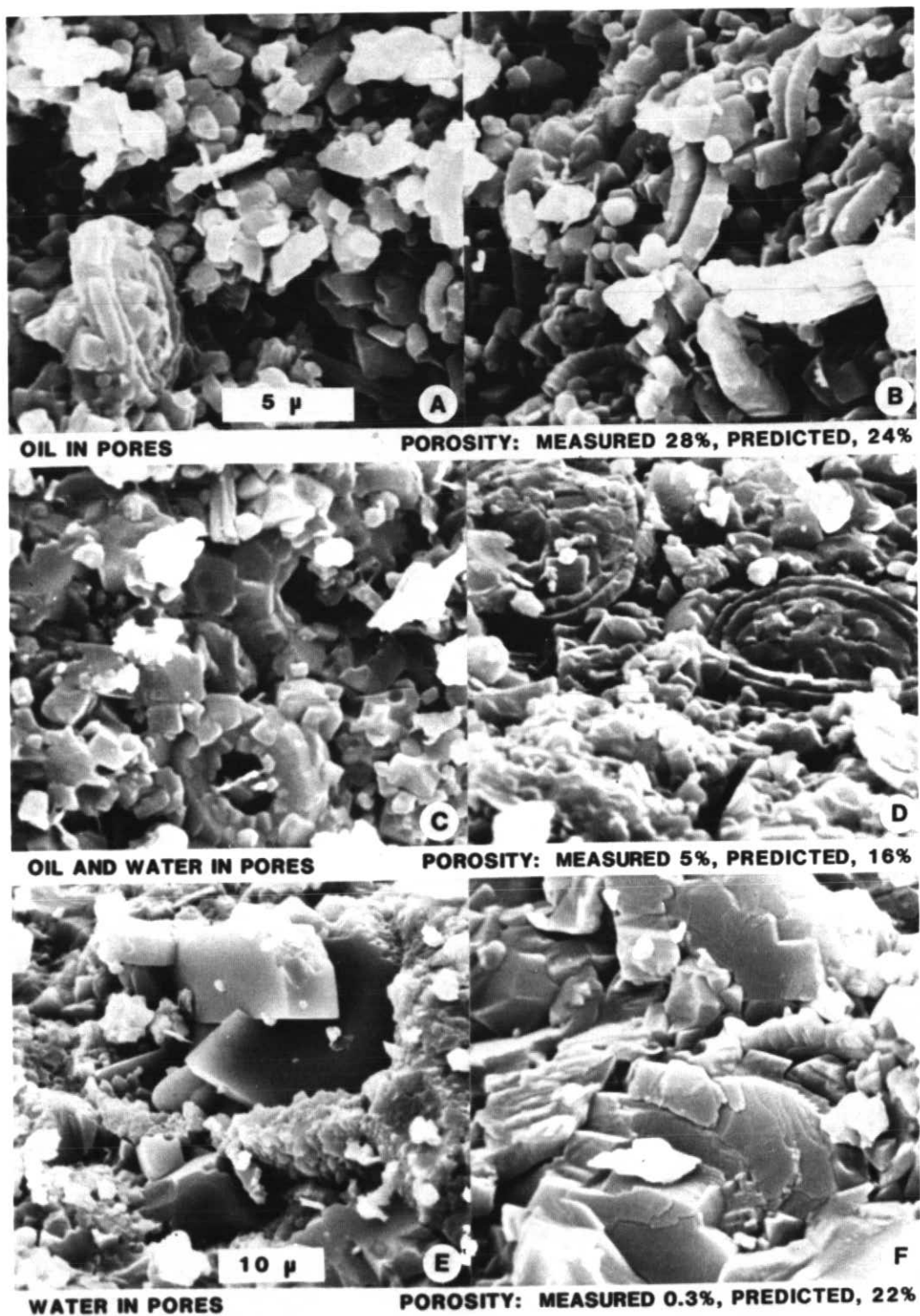


Figure 28 Scanning-electron micrographs of chalk from a well in the Ekofisk area of the North Sea, illustrating the retarding effects of hydrocarbons on burial cementation. Samples **A, B** are from high in, **C, D** from the middle of, and **E, F** from below the hydrocarbon zone. Pore-fluid pressures are believed to be approximately equal in the three intervals. Cementation by calcite was extensive in the lowest, water-saturated zone but was slight in the two zones above, suggesting that it was impeded by hydrocarbons. From Feazel et al. (1985b), courtesy of C.T. Feazel, published by permission.

Sippel and Glover (1964) and Sharp and Kennedy (1965) indicates that over the temperature range from about 25°C to 200°C the solubility of calcite in water decreases by about two orders of magnitude. As much as half of this decrease may be counteracted by increasing pressure, but the change may be significant nevertheless.

Another mechanism that may promote the precipitation of carbonate cements in situations where fracturing and faulting sharply alter the hydrology and pore-fluid pressure of a sequence or basin is *CO₂ outgassing*. Hanshaw *et al.* (1978) suggested this mechanism as a means of precipitating carbonates from meteoric ground water subjected to reduced pressure at the earth's surface. The same process may operate in special situations in the deep subsurface. There, where pore-fluid pressures are likely to be one to two orders of magnitude larger than any in the near-surface meteoric, p_{CO_2} also is likely to be much higher. Any fault or fracture system that suddenly, in terms of geologic time, connects the aqueous pore-fluid column in the deep-burial domain with that in the shallower subsurface will abruptly reduce the pore-fluid pressure of the system connected with the opened fractures, dropping the p_{CO_2} and causing carbonates to precipitate both in the fractures and in the adjoining water-filled pore systems.

Rates of outgassing are highly temperature dependent; a warm bottle of carbonated beverage, for example, loses its CO_2 much more quickly than a cold one. The mechanism is operative where travertine deposits form at the surface vents of hot springs in carbonate terranes. That it may indeed operate in the subsurface is strongly suggested by the fact that dilation fractures and breccias in carbonate rocks, whether of tectonic or other origins, commonly are filled by coarse calcite or dolomite cement for which oxygen-isotope compositions indicate precipitation from hot formation waters; furthermore, these fracture-filling cements often have the same isotopic composition as cements in the

"wallrock" around them (e.g. Murata *et al.*, 1969; Choquette, 1971). Baroque dolomite fillings are common and well known in breccias, fractures and "zebra structures" found in Mississippi Valley-type sulphide-ore gangues and in numerous epigenetic dolomite reservoirs of petroleum. Perhaps CO_2 outgassing through fracture systems was instrumental in their origin.

Factors That Inhibit Cementation. The most clearly identifiable of these (Table 3) have been outlined earlier and are discussed by Feazel and Schatzinger (1985). Entry of hydrocarbons is one of the more important inhibiting factors and has been documented in many limestones, as illustrated in Figure 28.

Dissolution in Burial Diagenesis

The discovery of solution porosity in sandstones, attributed by some to CO_2 and/or H_2S generated during burial diagenesis (Schmidt and McDonald, 1979; Hayes, 1979), led shortly to a successful search for solution porosity of likely deep-burial origin in limestones. Pore space believed to be of this origin was reported by Moore and Druckman (1981; also Druckman and Moore, 1985; Moore, 1985) in deeply buried (> 2-3 km) oolitic and pisolitic limestones of the Upper Jurassic Smackover Formation in the US Gulf Coast. Around that time, solution porosity of presumed burial-diagenetic origin was also reported by Elliott (1982) in limestones of the Mississippian Mission Canyon Formation in the Williston Basin.

The solution pores may be fabric-selective or not (Choquette and Pray, 1970) and include molds, vugs, and solution-enlarged interparticle voids. Fabric-selective pores may be related to previous diagenetic history. A suite of metastable carbonate sediments which is altered and lithified in the meteoric environment may be entirely calcite, but not all its components are the same. Calcite cement is a pure precipitate; calcitized aragonite and Mg-calcite allochems are precipitated calcite with minor embedded organic and mineral relics and high trace element content; original calcite fossils are biogenic

calcite containing organic templates. In the new burial environment, because of differences in crystal size and composition, microporosity, and amount and kinds of original organic matter, the relative solubilities of these components will be subtly different: biogenic calcite > calcitized aragonite or Mg-calcite > calcite cement. Fabric-selective dissolution of biogenic calcite allochems and possibly of calcitized allochems may subsequently take place during burial (Donath *et al.*, 1980; James and Klappa, 1983). This is also manifested by silicification of biogenic calcite and Mg-calcite allochems (bryozoans, brachiopods, echinoderms) in the subsurface, while original aragonite allochems (molluscs, scleractinian corals) are preserved as calcite.

Non-fabric-selective voids may begin as interparticle pores or molds and quickly enlarge. Features that point toward a burial-diagenetic origin of these pore spaces are illustrated in Figure 24, and examples of these types of voids are shown in Figure 29 and 30.

Pores commonly cross-cut both carbonate grains and cements, in situations where the cements are clearly of post-compaction, burial origin. In other cases, solution pores occur along and locally cut across stylolites, which they therefore postdate (Figure 30).

This rather enigmatic, burial-diagenetic porosity has been ascribed by most workers to formation waters with anomalously high concentrations of CO_2 that were supplied by the thermal decarboxylation of organic matter (kerogen). According to Lundegard (1985), however, a more likely source of CO_2 to account for dissolution of carbonate cement in sandstones of the Wilcox Formation (Tertiary) of the Texas Gulf Coast is a series of hydrous pyrolysis reactions between organic carbon and oxygen in water to yield CO_2 or organic acids. These reactions would have occurred in connate waters expelled into the Wilcox sandstones from compacting shales downdip. An alternate mechanism, the production of strongly acidic waters by sulphate reduction (in reaction with methane, for example) to produce CO_2 and H_2S , seems possible in formation waters reducing enough to produce cements, and may have found some support in the discovery of abundant iron sulphides in some Smackover limestones (L.M. Walter, oral comm., 1985).

Whatever the mechanism(s) may be, there is little doubt that (1) solution porosity can be generated in the deep subsurface and may in places be significant, and (2) organic compounds, possibly including liquid hydrocarbons and/or organic acids, are implicated. It is unclear as yet whether solution porosity of this origin is to be found generally in limestones and sandstones situated updip in the flow paths of connate waters being expelled from compacting shales, and the prediction of such late porosity is a difficult challenge.

Table 3 Factors that influence cementation in the deep-burial environment. Based in part on Feazel and Schatzinger (1985).

Inhibiting	Enabling
Stable $CaCO_3$ mineralogy	Metastable $CaCO_3$ mineralogy
Dilute pore waters	Pressure-solution
Hydrocarbons displace pore waters	High-flux hydrology
Low-flux hydrology	Highly oversaturated pore waters (if high flux)
Increase in p_{CO_2} (higher pore pressure)	Increase in temperature
Decrease in temperature	Decrease in p_{CO_2}
Reduced porosity and permeability	

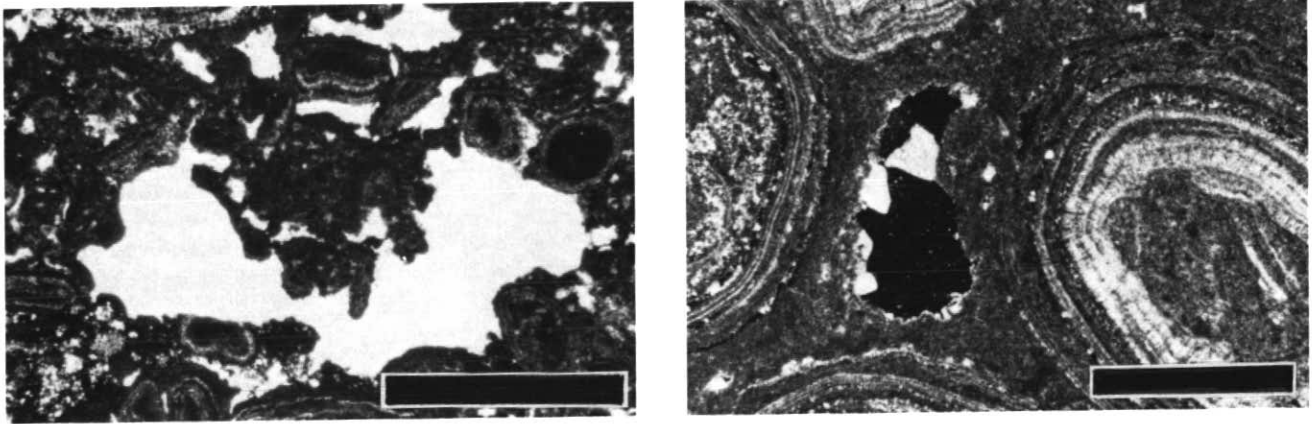


Figure 29 Solution porosity interpreted as burial diagenetic in origin (Elliott, 1982).

Left: Solution vug that cross-cuts both grains and dolomite-lined microstylolites. Most grains are flattened pisolites.

Right: Small vug formed by dissolution of micrite matrix in a pisolite packstone. Calcite crystals interpreted as warm-water precipitates partly line the vug. Bar scales are 1 mm. Mississippian Mission Canyon Formation, Williston Basin, North Dakota. Photos courtesy of T.L. Elliott, published by permission.



Figure 30 Solution pores (P) and calcspar (C) interpreted as burial diagenetic, formed by dissolution along a stylolite. Bar scale is 1 mm. Mississippian Mission Canyon Formation, Williston Basin, North Dakota (Elliott, 1982). Photo courtesy of T.L. Elliott, published by permission.

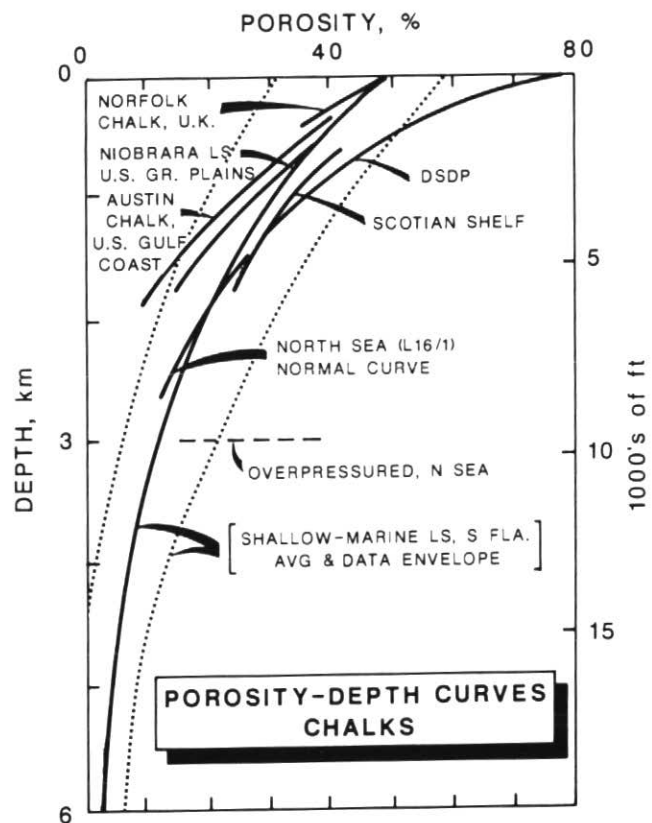


Figure 31 A plot of percent porosity versus depth for various limestone sequences. All but the deepest curve (to 6 km) are for Cretaceous and Tertiary chalks (from Scholle, 1977; Lockridge and Scholle, 1978; Schlanger and Douglas, 1974). Chalk curves other than for DSDP carbonates and chalks from the Scotian Shelf and North Sea well L16/1 probably reflect some diagenesis in the meteoric. The deep curve is for shallow-marine and peritidal limestones from the south Florida shelf; the dotted lines enclose the spread of data for this curve (after Schmoker and Halley, 1982).

Changes in Porosity with Depth

The sum of all these processes and products should be reflected in changes in porosity with depth.

General Trends. Most reliable information comes from Cretaceous and Tertiary chalks in oceanic settings as a result of the Deep-Sea Drilling Project (DSDP), synthesized by Garrison (1981). Data for chalks in the North Sea, adjoining areas in Great Britain, and the US High Plains and Gulf Coast have been developed or synthesized by Scholle (1974, 1977), Lockridge and Scholle (1978), Scholle and Halley (1985). All of the porosity-depth information for the South Florida basin comes from studies by Schmoker and Halley (1982) and Schmoker (1985).

Figure 31 gives most of the porosity *versus* depth curves that have been published to date, and shows a number of important features. The DSDP curve, when combined with data for North Sea chalks (1 well, Scholle, 1977), has an exponential shape: rates of porosity reduction are highest at shallow depths and decrease exponentially with burial depth. The same is true for South Florida

basin limestones, even though they appear to be much more varied lithologically than the chalks and likely spent part of their burial history in the meteoric environment. The exponential aspect was what led Pray (1960) and Schmoker and Halley (1982) respectively to suggest the concept of a porosity "half-life" or "half-depth".

There is a general porosity *versus* depth relationship for oceanic chalks in marine pore-water systems. The right-hand curve in Figure 32 is based on porosity data from a dozen DSDP sites down to about 1.1 km sub-bottom, and on chalks in a North Sea well from about 1.6 to 2.5 km sub-bottom. Building on interpretations by Schlanger and Douglas (1974), the chalk curve has been extrapolated to about 6 km; there it probably converges with a somewhat differently drawn curve for the South Florida limestones. Most Phanerozoic limestones buried to comparable depths lose all but about 5 percent or less of their porosity (Schlanger and Douglas, 1974; Scholle and Halley, 1985). Limestones with that little porosity generally have so little permeability (<0.05 md is typical) that further

throughput or expulsion of pore waters is unlikely and compaction and cementation should be arrested.

This general curve for chalks in a marine pore-water system also traces, albeit in very generalized form, the progressive lithification of pelagic, nannofossil-foraminiferal ooze (unconsolidated) through chalk (poorly consolidated) into lithified limestone. Most deep-sea oozes, and also shallow-marine lime muds (Ginsburg, 1957), lose some porosity in the first metre or so of burial. After this initial reduction from 80 to 75 percent, physical compaction remains dominant down to around 200-250 m, where porosities are reduced to 60 percent and ooze changes into chalk. From 200-250 m to around 1000 m chemical compaction becomes more and more dominant as the smaller nannofossil remains dissolve under load and low-Mg calcite micrite cement precipitates, initially cementing grains at their contacts. From around a kilometre downward, pressure-resolution and "autocementation" clearly must continue to dominate, until diminishing permeabilities end pore-water circulation.

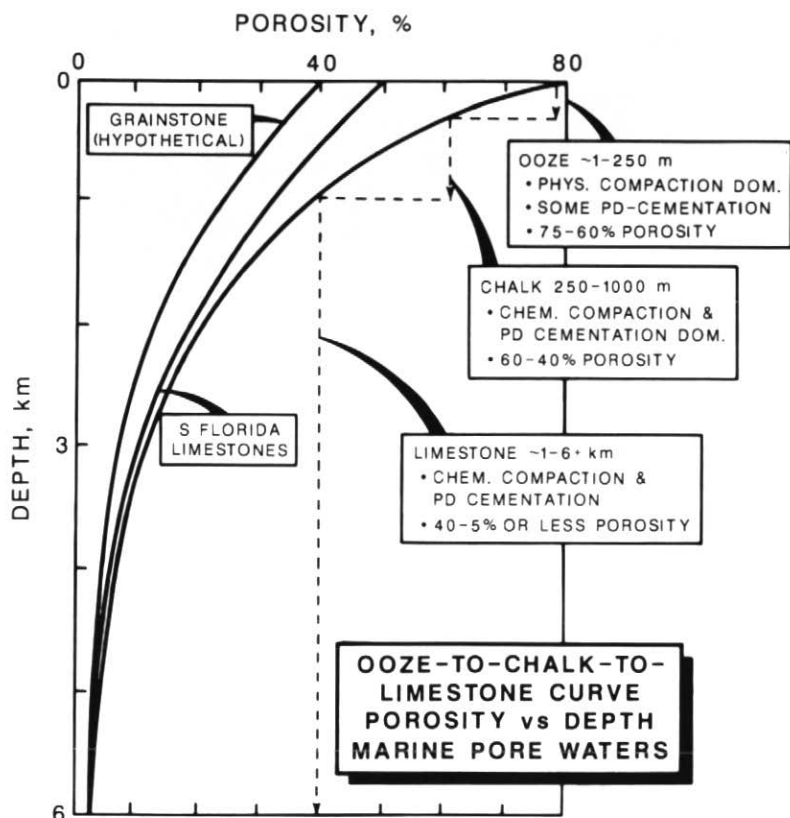


Figure 32 Generalized porosity versus depth curves. The *chalk curve* is for DSDP cores of unlithified nannofossil-foraminiferal ooze, partly lithified chalk, and indurated limestone and represents a general lithification sequence for lime-mud sediments saturated only with marine-derived pore waters. The lithification stages are from Schlanger and Douglas, 1974. The *south Florida curve* is from Schmoker and Halley (1982). The *grainstone curve* is hypothetical and is extrapolated from an average value at "zero depth" for modern sediments (Enos and Sawatsky, 1981).

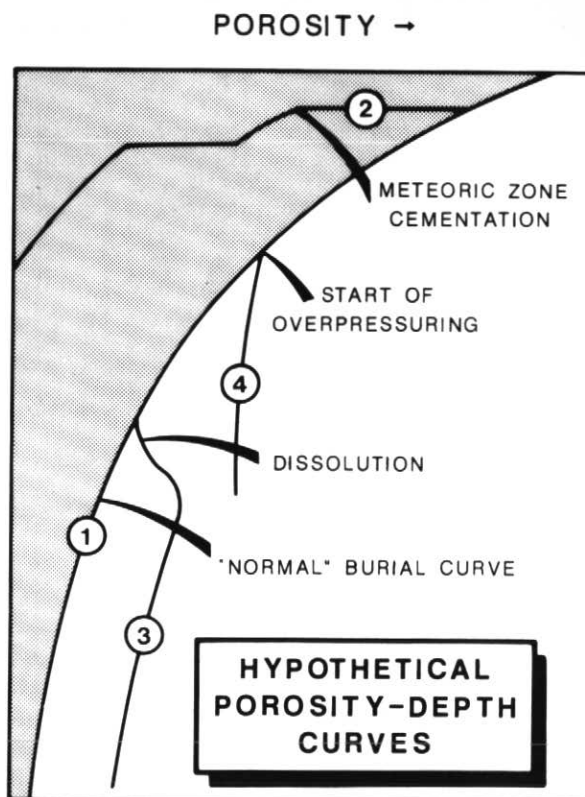


Figure 33 Hypothetical curves of porosity versus depth for four known situations:

1. "normal" burial of fine-grained sediments in marine pore waters;
2. cementation in the meteoric (horizontal segments) alternating with burial in marine pore waters;
3. reversal of normal trend by dissolution in the deep subsurface followed by resumption of normal burial;
4. porosity reduction arrested by build-up of abnormally high pore-fluid pressures.

If we add average values of initial porosity for modern shallow-marine carbonate sediments (Table 4) at the zero-depth level in Figure 32, we can define an envelope which should allow us to predict in very approximate fashion the porosity-depth characteristics of virtually any CaCO₃ sediment buried in a marine pore-water system. This envelope, which assumes convergence at around 5% porosity or less, is in accord with data from compaction experiments that show rates of porosity reduction (compaction) to be lowest for clean carbonate sand (grainstones) and highest for mudstones. It is interesting that the south Florida curve falls within this envelope. The similarity in trends can be interpreted in more than one way, particularly since the data for south Florida limestones show a considerable amount of scatter (Figure 31; Halley and Schmoker, 1982; Schmoker and Halley, 1982).

From published information about the stratigraphic age relationships of the oceanic chalks (Schlanger and Douglas, 1974) and the south Florida shallow-marine limestones (Schmoker and Halley, 1983) one can get a crude picture of the rates at which porosity is reduced in these Cretaceous to Pleistocene sediments. For chalk (Schlanger and Douglas, 1974), reduction from 80% to 75% porosity in the top metre or so is accomplished in around 50,000 years; reduction from 75% to 60% by physical compaction to depths of 200-250 m takes on the order of 10 million years (m.y.); and reduction from 60% to 40% at around 1000 m depth takes as long as 120 m.y. For south Florida limestones the age relationships are less well constrained but point to roughly comparable or slower rates of porosity decrease with depth; the first porosity "half-life" (50-25%) or "half-depth" would be approximately 50 m.y. (1.5 km) and the second and third (25-6%) would be around 150 m.y. (4-6 km).

Rates of porosity reduction appear to be substantially greater in limestone sequences that now reside or in the past resided in the meteoric realm, as pointed out by others (e.g. Bathurst, 1985). Unfortunately there is very little information about porosity variations over depth intervals of more than a few tens or hundreds of metres through meteoric zones. The porosity depth curves in Figure 33, which are qualitative, portray the shapes one might expect for different burial-diagenetic histories: (1) a "normal" curve of the kind shown in Figure 32; (2) a curve for chalk or lime mud that was subjected very early on to meteoric-zone or conceivably marine cementation by imported CaCO₃; (3) a curve of the sort expected if solution porosity were created after burial to considerable depth; and (4) a curve imposed by early build-up-of high pore-fluid pressure. It seems possible that the south Florida data, given its rather wide scatter, could include thin meteoric zone profiles.

Table 4 General porosity ranges of common textural types of modern carbonate sediments. Compiled from Enos and Sawatsky (1981), Schlanger and Douglas (1974), and GRAPE porosity profiles by Harms and Choquette (1965) and by Pray and Choquette (unpublished).

Chalks	70-80%
Lime muds (mudstone texture)	60-70%
Muddy lime sands (wackestone and packstone)	50-60%
Clean lime sands (grainstone)	40-50%

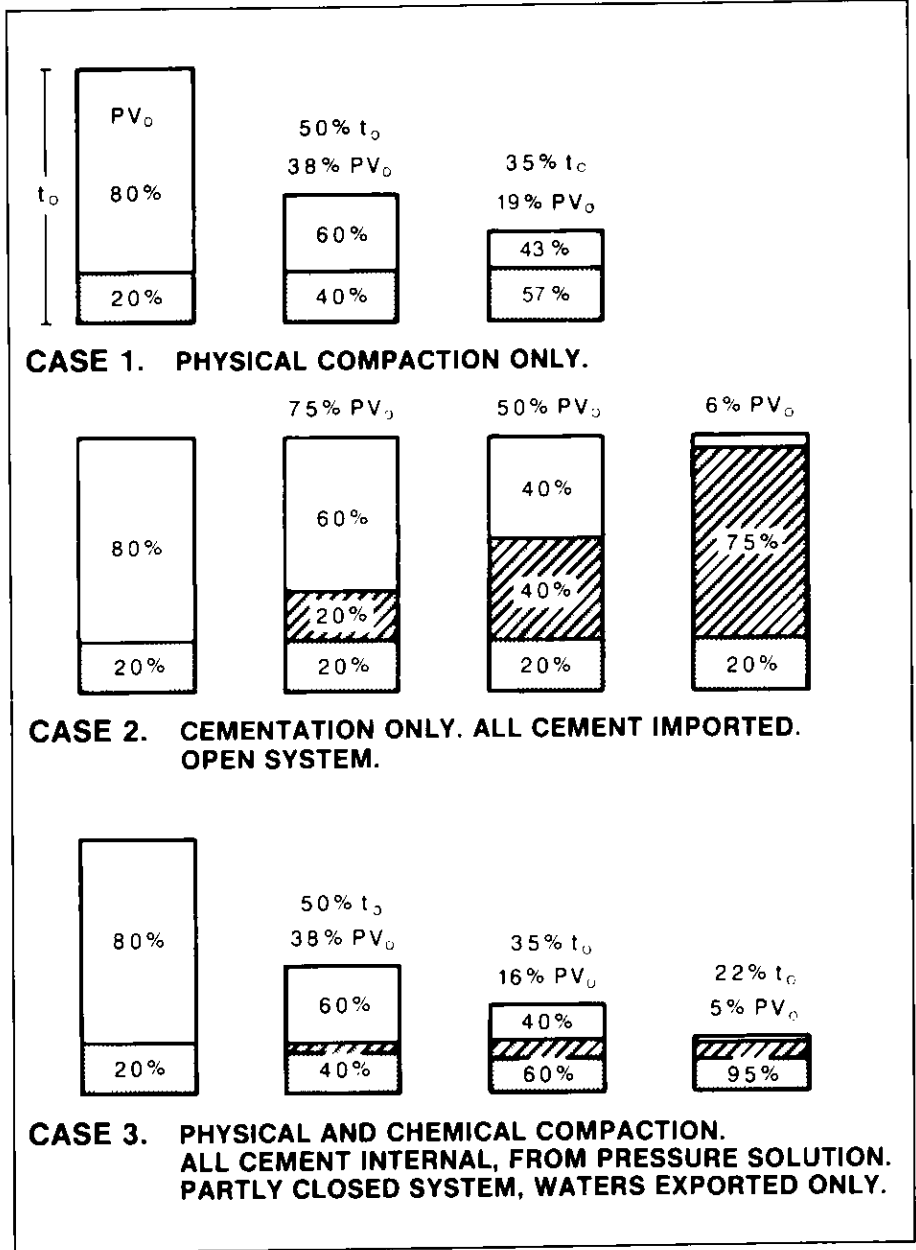


Figure 34 Diagrams showing the changes in pore volume, percent porosity, and thickness for three hypothetical cases of compaction and/or cementation. For purposes of these diagrams, all solid constituents are shown by the shaded/stipple pattern, the cement portion of the solid fraction is indicated by the hachured pattern, and pore space is white.

Volumetric Considerations. At this point it may be helpful to summarize the principal ways, and some of their implications, that initially high pore volumes may be reduced. The simple diagrams in Figure 34 illustrate these points. Initial pore space can be reduced, in principle at least, entirely by physical compaction (case 1), entirely by precipitated cement (case 2), or by combinations of compaction and cementation as suggested in case 3. It is important to distinguish between changes in pore volume and changes in porosity, which is the percent of bulk volume occupied by pore volume. Porosity is the property that is measured whether using wireline logs, standard core-analysis methods, the GRAPE porosity-profiling device (Harms and Choquette, 1965), or various other means.

In case 1 the original thickness (t_0) is reduced to 35% and the original pore volume (PV₀) to 16%, but the measured porosity is reduced from 80% to 40%. The distinctions here are important for what they imply about

the real pore space now available for filling by cement, in this example only 16% of the original pore space. A quite different picture emerges from this way of looking at volume changes than that implied in the idea of a "porosity half-life" suggested by Pray (1960) and later reworded to "porosity half-depth" by Scholle and Halley (1985), for those concepts are based on measured porosities — the only measures of pore-space volume that are normalized and so can be compared between different data sets.

Case 1, based as it is on the work of Shinn and Robbin (1983), should be considered to apply to fine-grained sediments that are subjected to increasing load while saturated with marine pore waters only. It seems likely that if the same sediments had been saturated with meteoric water when subjected to such extreme stress, some cementation would have occurred.

The other extreme example is shown in case 2 of Figure 34. Here the same initial pore volume is assumed, but it is reduced

entirely by precipitated cement unaccompanied by compaction, with no significant change in thickness. As in case 1, the measured porosity at one stage in pore-volume reduction is 40%. In this case also, a true "porosity half-life" is represented, because the real reduction in pore volume is exactly the same as the reduction in measured porosity. The important difference is that the real pore volume filled and remaining to be filled by cement is far greater here than in case 1.

Furthermore, in case 2 all of the cement required is assumed to have been imported from cement donors somewhere else; none is supplied by the sediment or receptor itself. Case 2 may be a fair representation of those shallow-marine, peritidal (e.g. beachrock) and perhaps eolian carbonate sediments that "set up" and/or become partly cemented at the sediment-water or sediment-air/water interface, then during meteoric diagenesis acquire cement quickly enough to withstand a significant (though not predictable) amount of load stress and compaction. Cementation may be mineral-controlled or water-controlled as discussed earlier in this series (James and Choquette, 1984). The sediment is, however, entirely a receptor of cement.

Case 3, in which both physical compaction and cementation produced by pressure solution work to reduce initial porosity, is probably closer to reality than the two preceding, extreme situations. The first three stages shown there probably model closely what happens in chinks and other fine-grained ocean-basin sediments that undergo marine-only burial diagenesis (Schlanger and Douglas, 1974; Garrison, 1981), as discussed in the next section. The fourth stage, with 5% porosity, is assumed from extrapolated porosity *versus* depth curves shown in Figures 31 and 32. Cement, which at the end stage occupies about half of the "rock volume", is internally generated by pressure solution; the sediment is both donor and receptor, and in the sense that pore waters are expelled both from the sediment and through it from underlying sediments, the system is partly closed with respect to ambient pore water.

Burial Diagenetic Models

In spite of obvious deficiencies in our data and understanding, it is nevertheless important to try and summarize what we know or can surmise about burial diagenesis. For this purpose it is useful to envision two general end-member domains (Figure 1, Table 5): (1) a *basinal burial domain* involving relatively deep-marine sediments which are being buried in undiluted, marine pore waters; and (2) a *shelf/platform burial domain* involving shallow-marine and peritidal/coastal sediments which are being buried in varied pore waters ranging from meteoric to marine to occasionally evaporitic, in response to episodes of emergence and

Table 5 Similarities and differences between basinal (B) and shelf/platform (S/P) burial domains.

SIMILARITIES

GENERAL TRENDS with increasing burial include:

- TEMPERATURE & PRESSURE INCREASE
- POROSITY REDUCTION, to less than 5-6% after 5-6 km burial (Many thin, exposed shelf/platform carbonates are cemented tight before entering the shelf/platform burial domain.)
- EXPULSION OF PORE WATERS
- HYDROUS TO LESS HYDROUS OR ANHYDROUS MINERALS
- MORE SALINE PORE WATERS
- PHYSICAL COMPACTION FOLLOWED BY CHEMICAL COMPACTION

CEMENTS: mostly dull CL & ferroan in shelf/platform domain; less well known but finer-crystalline in basinal domain

DIFFERENCES

BURIAL RATES: slow in basinal (B), high in shelf/platform (S/P) with interludes of exposure

STARTING PORE WATERS: B: marine
S/P: meteoric to brackish, marine & hypersaline

STARTING SEDIMENTS: B: mostly stable fine-grained CaCO₃ with low diagenetic potential & high physical compactibility; some metastable CaCO₃ in shelf-derived debris flows; thin lithified intervals; often argillaceous/organic rich
S/P: metastable to stable CaCO₃ & dolomite, fine- to coarse-grained, commonly lithified, with variable diagenetic potential; subtidal muds, evaporites & shales compactible

ACCESS BY METEORIC WATER: B: nil unless uplifted
S/P: usual due to eustatic and/or tectonic uplift

CARBONATE FOR CEMENTS: B: pressure solution dominant source
S/P: meteorically derived water at shallow/proximal depths, pressure solution more important with burial; sulphate cement from dissolution of evaporites.

POROSITY REDUCTION: B: follows exponential curve(s) of type in Fig.32 unless arrested or reversed;
S/P: can follow similar curve(s) but also can go more swiftly in high-flux settings; rates more variable; reduction by physical compaction variable with facies & access of meteoric water

exposure that interrupt their ongoing subsidence and burial. Burial loading may be more or less uninterrupted, as in the deeper marine parts of many sedimentary basins (1 above), or repeatedly interrupted as appears to be the case in many shallow marine carbonate shelf/platform provinces bordering basins (2 above); or initially uninterrupted as a sequence is progressively buried, then arrested or reversed by basin margin or intra-basin uplift.

Although the general course of burial diagenesis seems generally similar in many respects, there are important differences between the two domains which we attempt to summarize in the discussion that follows (Table 5).

Basinal Burial Domain

General Characteristics. Sediments that accumulate in basinal environments, apart from sand-sized and coarser allochthonous debris flows, are dominantly fine-grained. They carry marine pore waters into the subsurface, which are modified only by reactions between pore fluids and the organic and inorganic constituents of the sediments. Meteoric ground water may impinge on sediments of the outer shelf, or on sediments short distances downslope from exposed shelf/platform and ramp margins, but should not interact with basinal sediments even during low sea-level stands. The diagenetic system is partly closed hydrochemically, in the sense that pore waters are being expelled only upward and toward the basin margins (Bonham, 1980) during the phases of major thickness and porosity reduction. There should be no significant transport in counter-current directions, unless by hydrologic convection (Wood and Hewett, 1984).

Sedimentation and burial rates are slow, in the range of 2-15 m·(m.y.)⁻¹. Build-up of abnormal pore-fluid pressure may occur nevertheless, for example beneath hardgrounds or zones of intense stylolite development or physical compaction or beneath zones of abundant carbonate concretions and layers. Geothermal gradients should be low, in the range ~ 15-20°C·km⁻¹.

Nature of Sediments Entering the Burial Realm. Most of these will be unlithified, except for thin hardgrounds. The boundary between shallow (few metres to a few tens of metres?) and deep is somewhat arbitrary and is perhaps the lower limit at which sulphate reduction takes place, biogenic methane is produced, early-burial carbonate concretions and layers form, and chert nodules originate. Some workers place the boundary in the transition from bacterially mediated reactions to thermally mediated reactions, at approximately 60-80°C (L.S. Land, pers. comm, 1986). Carbonate fractions of pelagic sediments will be composed of low-Mg calcite, without aragonite or Mg-calcite, and thus stable, with little or no "diagenetic potential" (Schlanger and Douglas,

1974). Aragonite and Mg-calcite in allochthonous carbonates should survive well past the shallow-burial domain. Displacive- and replacive-fibrous calcite cements such as cone-in-cone may also have formed (see Coniglio (1985) for detailed information about shallow-burial features in fine-grained limestones).

Trends in Diagenesis. These will be dominated in the basinal domain by the expulsion of pore waters (dewatering), physical compaction initially and later pressure-solution compaction, the consequent long-term reduction of thickness and pore volume, the production of carbonate cement by pressure solution, and the thermochemical conversion of organic matter to hydrocarbons.

Burial-Diagenetic Features. Porosity generally decreases sharply in the upper 200-250 metres as outlined in Figure 32, mainly due to physical compaction. Through the first 800-1000 metres(?) of burial the sediments will show decreasing Sr²⁺, Mg²⁺ and bulk δ¹⁸O as some of the finer-grained constituents dissolve initially under grain-contact linear pressure (pressure solution) and low-Mg, low-Sr finely crystalline calcite cements begin to precipitate.

Cementation will start somewhere below 200-250 metres and become dominant below 1000 metres, will be directly due to pressure solution (autocementation), and should be volumetrically proportional to the amount of pressure solution unless flow rates of expelled pore fluids are high enough to move solute ions quickly away from sites of pressure solution. Because Mg²⁺ concentrations and Mg/Ca ratios are relatively high in marine pore waters, stylolites may begin to form at greater depths than they would in shelf/platform burial domains involving more dilute waters. However, pressure-solution "bedding" (Figure 18), due to intervals of closely spaced stylolites and non-sutured seams, should be common in sequences with clay- and/or organic-rich strata.

The cathodoluminescence of cements produced in sub-basin burial diagenesis is speculative. Early-burial displacive fibrous calcite may be dully to rather brightly luminescent (Coniglio, 1985). Later burial calcite microcements should have dull CL with little or no zonation, reflecting the general monotony of basinal pore-water systems. Some burial dolomite may form, especially if the sediments are argillaceous, and should be ferroan, with dull, possibly zoned CL.

Shelf/Platform Burial Domain

General Characteristics. The sediments are far more varied and may include, in various combinations, limestones of mudstone to grainstone texture, reef carbonates, peritidal limestone and dolomite, coastal plain evaporites, and coastal plain to shallow marine sandstones and shales. Because these shallow marine to coastal sediments are commonly exposed intermit-

tently during accretion, they are periodically filled with meteoric groundwater. Consequently, *before* they exit the meteoric environment they may have seen multiple generations of fresh to brackish to marine or even hypersaline waters related to low and high stands of sea level.

Sedimentation and burial rates will vary from low to very high in the case of reef carbonates. The pre-burial diagenetic system will in general be open, since during times of exposure parts of the shelf/platform sequence will be recharge areas and others will be confined or unconfined surface aquifers linked to recharge areas. With burial, diagenetic systems may become partly closed as fluid flow directions become dominantly upward and laterally toward the updip margins of these shelf basins. Build-up of abnormal pore-fluid pressure may occur locally beneath evaporites and compacted shales, early-cemented permeability barriers of various kinds, and zones of intense stylolite development. Geothermal gradients may range from low to quite high.

Nature of Sediments Entering the Burial Realm. The limestones will vary in CaCO₃ mineralogies from metastable to completely stabilized (see James and Choquette, 1984). Because some carbonates will be lithified and others not, their resistance to physical compaction and/or chemical compaction will range from low in marine lime muds and uncemented marine lime sands, for example, to very high for such carbonates as calcrite, beachrock, shallow-marine hardgrounds, lithified reef carbonates, and dolomites of peritidal/supratidal or mixing-zone origin. Porosities also will vary widely. Pore waters will range from fresh to marine, or in evaporitic sequences to hypersaline. Limestones associated with karst terranes will have acquired stable mineralogies and a wide variety of water-controlled alteration features (James and Choquette, 1984) including vugs, caves and solution-enlarged fractures, internal sediment, and a variety of speleothems. Limestones that still retain their metastable mineralogies, or retained them while in the meteoric or shallow-marine setting, may already have undergone mineral-controlled alteration, perhaps in the form of low Mg calcite cements or of selective dissolution of allochems.

It is unclear in any detail what the mineralogies and cements in the carbonates may be when they exit the lenticular mixing zone and enter the sub-lenticular, shallow burial realm. The limestones may have acquired non-luminescent, bladed and prismatic calcite cements with brightly luminescent sub-zones (Figure 22). Early-diagenetic finely crystalline dolomite will probably have formed in some meteoric (mixed-water?) settings, and both the dolomite and some limestone may have acquired some pore-lining limpid dolomite cement.

Trends in Diagenesis. The dominant trends will include the evolution of pore waters from a varied suite to mostly saline to hypersaline brines; greatly varying amounts of physical compaction during relatively shallow burial and of chemical compaction during shallow(?) to deeper burial; cementation with both locally sourced CaCO_3 from pressure solution and more remotely sourced CaCO_3 produced by dissolution beneath exposure surfaces; dehydration of certain minerals such as gypsum and smectite; and long-term reduction of porosity.

Burial-Diagenetic Features. Porosity should vary considerably in the shallow reaches of the burial domain but generally should decrease overall, at rates that will vary, if controlled by cementation, according

to the amount of alteration accomplished earlier in the meteoric realm. The duration and extent of physical compaction must vary considerably too, but cannot be predicted in any but very general terms. Uncemented marine sediments will suffer substantial compaction. Pressure-solution features are widespread in shallow-marine limestones, and include grain-to-grain microstylolites and non-sutured seams, swarms of non-sutured seams in nodular arrays, and bedding parallel stylolites and non-sutured seams. Pressure-solution features in limestones may begin developing at shallower depths than in sub-basin diagenesis — perhaps after as little as a few tens of metres in some cases — because of the more dilute waters with lower Mg/Ca ratios and lower Mg^{2+} concentrations.

Cementation should continue from the lenticular mixing zone downward. Burial cements precipitated either below the reach of fresh meteoric ground water, or in deep aquifers at long distances down-gradient from recharge areas (see Back and Hanshaw, 1971; Hanshaw *et al.*, 1978; Grover and Read, 1983), will by and large have dull cathodoluminescence which may or may not be zoned. These cements will include both coarse calcite spar and saddle or baroque dolomite, and many of them will be ferroan. Older to younger burial cements will vary systematically in oxygen-isotope composition toward lighter $\delta^{18}\text{O}$ values, and in trace-element compositions toward lower concentrations of Sr^{2+} and higher Fe^{2+} and Mn^{2+} . Fluid inclusions will generally record progressively higher temperatures of precipitation from aqueous pore fluids that become more saline with depth and are dominantly of Ca-Na-Cl type.

Cement Sequences and Burial History

Many different burial-history scenarios of course apply in sedimentary basins, and often can be discerned in the intricate "cement stratigraphies" (Meyers, 1974) that result. Many authors (e.g. Meyers, 1974, 1978; Walls *et al.*, 1979; Mattes and Mountjoy, 1980; Dickson and Coleman, 1980; Moore and Druckman, 1981; Grover and Read, 1983; James and Klappa, 1983; Moore, 1985; Walls and Burrows, 1985; Burruss *et al.*, 1983; Mruk, 1985; Brinton, 1986) have used various aspects of cement stratigraphy and geochemistry to reconstruct burial histories.

Figure 35 is an attempt to portray the sequences of carbonate cement types, with CL characteristics, that might be precipitated in various diagenetic realms starting with the seafloor and meteoric settings and progressing into the basinal and shelf/platform burial domains, during three commonly encountered stages: (1) widespread marine transgression (high sea level), (2) lowered sea level with consequent exposure, and (3) continued subsidence and burial, all without tectonic uplift.

Where sedimentary basins, containing a spectrum of facies from shallow-marine/peritidal or continental to shelf basin or basinal, are deformed and their margins exhumed and exposed to recharge by meteoric waters into aquifers, a whole array of major changes must then take place: the hydrology of the system commonly becomes dominated by meteoric waters which are modified with transport into the subsurface; geothermal gradients may be altered, becoming lower in the recharge areas and changing laterally to steeper gradients across the subsurface parts of the deformed basin — changes that may influence the course of carbonate cement precipitation; and the recharge portions of limestone aquifers may then become major donors of cement because of large-scale dissolution.

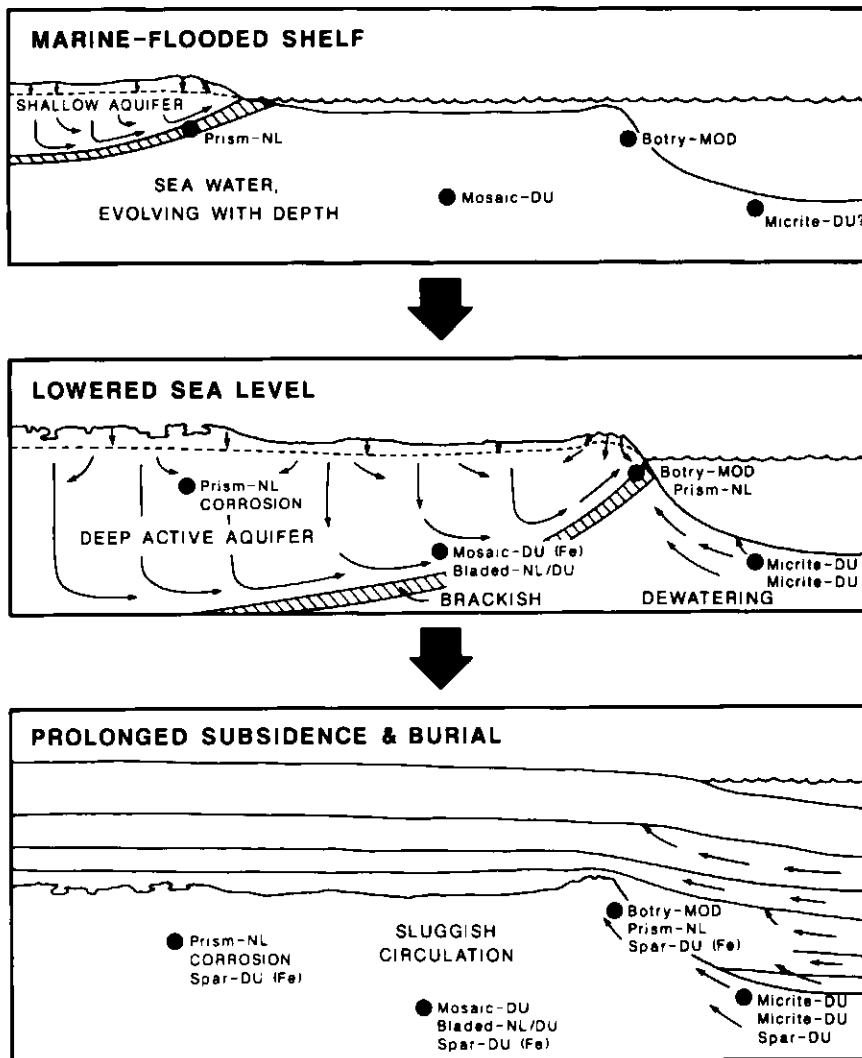


Figure 35 A diagram showing the cement stratigraphies that might develop in different settings with lowered sea level followed by prolonged subsidence and burial of a carbonate sequence. The basinal burial domain is at right and the shelf/platform domain at left. Abbreviations: DU = dull cathodoluminescence, NL = non-luminescent, MOD = moderately luminescent. Prism = prismatic, Botry = botryoidal, Spar = coarse calcspar.

All of these modifications to the basin dynamics will inevitably be recorded in the burial-diagenetic record. Investigations of the present-day and past hydrology and the geochemistry of many basins and deep aquifers, notably the Western Canada or Alberta basin (e.g. Hitchon, 1969a,b; Garven and Freeze, 1984a,b), provided the basis for a model sketched in Figure 36. As in many other basins, the general paleohydrology, hydrochemistry, and burial-diagenetic history of this particular basin have also been intimately bound up in the generation and migration of hydrocarbons in the basin and the origin of lead-zinc sulphide ore deposits and their associated epigenetic dolomite host rocks in the Pine Point and other districts.

Conclusion

Much of what we see when we look at a limestone is the result of its residence in the burial diagenetic environment. The most dramatic changes are brought about through compaction. Physical compaction, occurring first, may transform depositional texture from wackestone to packstone, compress un lithified sediment, squash and obscure critical depositional features, and through plastic and brittle deformation rotate, fracture and crush sedimentary particles. Chemical compaction or pressure-solution, taking place deeper, results in stylolites or non-sutured seams, which can create a new style of *diagenetic* bedding/stratification, pressure-solution pseudo-bedding. Dissolved carbonate is precipitated locally (autocementation) and probably accounts for much burial cementation. The bladed, coarsely crystalline, poikilotopic, commonly ferroan burial cements have distinctive isotopic, cathodoluminescence and fluid-inclusion signatures which point to precipitation from brines, promoted by general carbonate supersaturation and elevated temperature. The dominant, prevailing trend in burial diagenesis, as

pointed out many years ago (e.g. Pray and Choquette, 1966; Choquette and Pray, 1970), is toward complete or nearly complete occlusion of porosity. Some porosity may be retained, however, for a variety of reasons: if the sediments were already low-Mg calcite or dolomite prior to burial; or formation-water flux was sluggish over much of the sediment's burial history, and/or residence time in the burial setting and depth of burial were insufficient for pressure-solution cementation to proceed to completion; or perhaps the geothermal gradient was low and the temperature effect on carbonate solubility was suppressed; or again, perhaps most desirable and serendipitous of all, if the occlusion of porosity was shut off by the influx of hydrocarbons. Dissolution may also take place, though perhaps on a limited scale, through reactions between formation waters and maturing organic matter. Although the processes and general products of burial diagenesis give us an idea of the features and the kinds of limestones to expect in deep-burial settings, the actual fabrics and structures that develop in limestones are largely dependent on differences in the original composition and early diagenetic history of the sediments. Two preliminary diagenetic models representing burial *versus* shelf/platform sediments, respectively removed from or associated with early "exposure" to waters of meteoric origin, are proposed to highlight these differences.

Only with hindsight are we likely to know whether or not in the 1980's we have been on a plateau or a steep climb in the search for unifying principles in the burial diagenesis of sedimentary carbonates. It does seem clear that our understanding of the dynamics and our ability to forecast or even adequately chart the different courses of diagenesis in this largely occult realm are still quite primitive. There is much to learn but we have come a long way; the next steps in the search are sure to be exciting.

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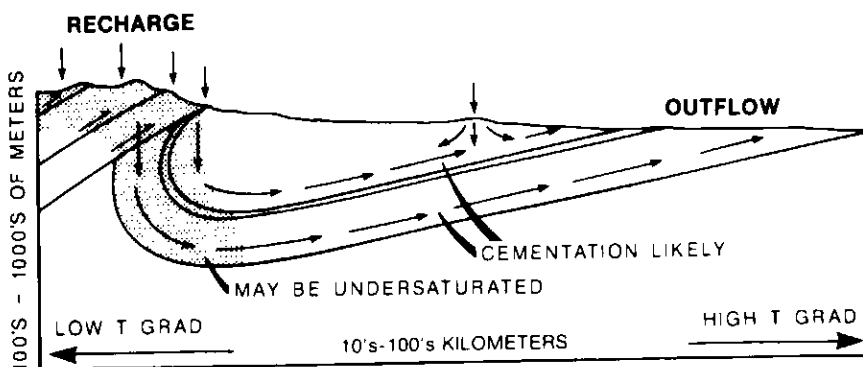


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