

7.03

Formation and Diagenesis of Carbonate Sediments

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7.03.1 INTRODUCTION AND BACKGROUND

7.03.1.1 General Overview of Sedimentary Marine Carbonates

Carbonate minerals in modern marine sediments can readily be divided into those found in shoal-to-shallow and deep-water environments. The factors controlling the sources, mineralogy, and diagenesis of carbonates in these environments are very different. Within the shoal-to-shallow water environment, the sources and diagenesis of carbonates differ substantially between carbonate-rich and primarily siliciclastic sediments.

Almost all deep-sea carbonate-rich sediments are composed of calcite low in magnesium (>99% CaCO₃). This material is primarily derived from pelagic skeletal organisms. Coccolithophores

are usually the most important quantitatively, followed by foraminifera. In sediments overlain by waters of intermediate depth such as mid-ocean ridge crests, aragonite derived from pelagic pteropods and heteropods can be found. Calcite cements containing abundant magnesium can also occur in deep-water sediments, but they are relatively rare.

Shallow-water carbonate-rich sediments are largely confined today to the subtropic and tropic climatic zones, but they are found even at high latitudes. Their occurrence is strongly influenced by factors such as water temperature and terrigenous input. These sediments are generally dominated by aragonite, followed by calcites rich in magnesium (>4 mol.%). Low-magnesian calcite is usually a minor component. Dolomite occurs

only in special environments, and even then it is generally not a major component of the sediment. Shallow-water carbonates are primarily produced by the disintegration of the skeletons of benthic organisms, such as corals, echinoids, mollusks, foraminifera, and coralline algae. In some environments, inorganic precipitates such as cements and ooids are also abundant. As discussed later in this chapter, the source of aragonite needle muds remains controversial.

In siliciclastic sediments, the major source of carbonates is also primarily derived from benthic organisms. These include bivalves, other mollusks, sea urchins, and foraminifera. In these sediments there is often a zone of considerable undersaturation produced near the sediment-water interface, where the oxidation of organic matter and bacterially produced sulfides can result in almost complete dissolution of sediment carbonate. Carbonates from organisms that burrow beneath this zone of intense diagenetic activity are often well preserved. In organic-rich siliciclastic sediments sulfate reduction may be very extensive, with the increase in alkalinity outweighing the decrease in pH, resulting in the precipitation of calcium carbonate.

Carbonates in ancient sedimentary rocks are dominantly calcite and dolomite, as predicted by equilibrium thermodynamics. This indicates that metastable shallow-water sedimentary carbonates have undergone major diagenetic changes. The distribution of calcium carbonate in deep-sea sediments indicates that extensive early diagenesis has led to the loss of most carbonate minerals from these sediments. This loss appears to be linked to the saturation state of the overlying waters. However, kinetic and biogeochemical processes also play a major role in controlling the distribution of carbonate minerals. This chapter examines the geochemistry of the early diagenesis of carbonates in marine sediments.

7.03.1.2 Geochemistry of Major Sedimentary Carbonate Minerals

Before proceeding to the “natural world,” a brief commentary on the chemistry of major marine carbonate minerals is offered first. A vast literature exists on this topic: Morse and Mackenzie (1990) can provide an introduction.

Marine carbonate minerals have both biotic (dominant) and abiotic (minor) sources. Their formation is often controlled by kinetic factors or biomediated processes in organisms. Surface seawater is most highly supersaturated (the ion activity product (IAP) is much greater than the solubility product) with respect to dolomite ($\sim 50\times$), followed by pure calcite ($\sim 6\times$), then by aragonite ($\sim 4\times$). It may be close to

equilibrium with respect to high (~ 13 mol.%) magnesian calcites. However, dolomite is rarely found in modern sediments. Sediments containing “recent” dolomite are generally found associated with exceptionally high salinity environments. Aragonite and high-magnesian calcites dominate shoal-to-shallow water carbonate sediments. Seawater must be ~ 22 times or more supersaturated with respect to calcite before pseudo-homogeneous precipitation occurs (e.g., Morse *et al.*, 1997). However, metastable aragonite precipitates, not calcite, due largely to the inhibiting effects of Mg^{2+} on calcite precipitation (Pytkowicz, 1965; Berner, 1975).

Dolomite is one of the most abundant sedimentary carbonate minerals. However, after years of intense study its mode of formation remains controversial, and its properties under Earth surface conditions are less well known than for most other carbonate minerals. The primary reason for this is that its formation is kinetically hindered by its well-ordered structure. Another problem in understanding dolomite may be as stated by Land (1985): “there are dolomites and dolomites and dolomites.” Most recently formed marine dolomites are classified as “protodolomites.” They are far from being perfectly ordered structurally and usually contain a few percent excess calcium. Attempts to measure their solubility have been frustrating, but it does appear that they can be one or two orders of magnitude more soluble than ideal dolomite. Thus, seawater may not be supersaturated with respect to protodolomites.

High-magnesian calcites are common components of shallow marine sediments. They are derived from the skeletons of organisms, such as benthic foraminifera and sea urchins, and by direct precipitation of marine cements. Their solubility is strongly influenced by their magnesium content. The solubilities of biotic and synthetic magnesium calcites differ substantially (Figure 1). In seawater, biogenic magnesian calcite containing ~ 11 mol.% $MgCO_3$ may have about the same solubility as aragonite.

Berner (1976) reviewed the problems of measuring calcite solubility in seawater, and it is these problems, in part, that have led to the use of stoichiometric solubility constants for calcite and aragonite (see Section 7.03.3). The most difficult problem is that, although the solubility of pure calcite is sought in experiments with seawater solutions, extensive magnesium co-precipitation can produce magnesian calcites. The solubility of these magnesian calcites differs from that of pure calcite. Thus, it is not possible to measure the solubility of pure calcite directly in seawater.

Another problem is the determination of aragonite solubility in seawater. A study of the solubility of calcite and aragonite in seawater

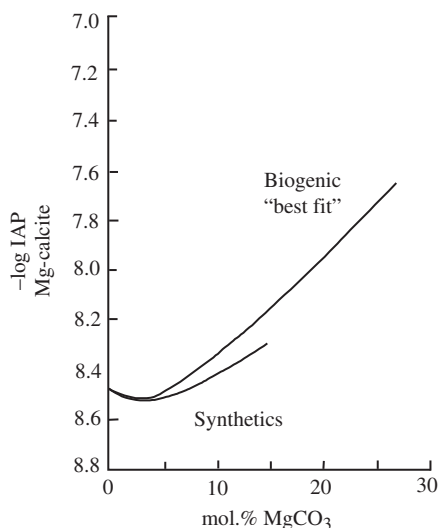


Figure 1 The equilibrium IAP for magnesian calcites of biogenic and synthetic origin versus magnesium concentration (after Morse and Mackenzie, 1990).

was conducted by Morse *et al.* (1980); their results for calcite solubility were in good agreement with earlier work (e.g., Ingle, 1975). However, for aragonite they found a much lower solubility than observed by previous investigators. It was demonstrated that the primary reason for this difference was that earlier investigators had not waited for a sufficiently long period of time to reach equilibrium and that strangely, for equilibration periods of less than about a month, different solubility values can be obtained in a reversible manner. This result points to some type of short-term, solubility controlling surface phase. The value obtained by Morse *et al.* (1980) for aragonite was in good agreement with the value predicted from thermodynamic solubility products and ion activity coefficients in seawater, and the value for the solubility ratio of aragonite to calcite in seawater was 1.51, in good agreement with dilute-solution studies. From these considerations, it appears that the co-precipitation of magnesium (~8 mol.% MgCO_3) with calcite forming slowly from seawater does not change its solubility beyond the uncertainty in the measurements, which is estimated to be less than 10%.

In addition to magnesium, at least trace amounts of many components present in seawater can be incorporated into marine carbonates. Concentrations range from trace (e.g., heavy metals), to minor (e.g., strontium), to major (e.g., magnesium, see previous discussion). This means that there is potentially a large amount of information that can be obtained from the study of carbonate mineral composition. This type of

information allied with stable isotope ratio data, which are influenced by many of the same environmental factors, has become a major area of study in carbonate geochemistry. Much of the research on co-precipitation reactions with calcite and aragonite has been reviewed by Mucci and Morse (1990).

7.03.1.3 The CO_2 System in Oceanic Waters

The chemistry of the carbonic acid system in seawater has been one of the more intensely studied areas of carbonate geochemistry. This is because a very precise and detailed knowledge of this system is necessary to understand carbon dioxide cycling and the deposition of carbonate sediments in the marine environment. A major concept applicable to problems dealing with the behavior of carbonic acid and carbonate minerals in seawater is the idea of a “constant ionic medium.” This concept is based on the observation that the salt in seawater has almost constant composition, i.e., the ratios of the major ions are the same from place to place in the ocean (Marcet’s principle). Possible exceptions can include seawater in evaporative lagoons, pores of marine sediments, and near river mouths. Consequently, the major ion composition of seawater can generally be determined from its salinity. It has been possible, therefore, to develop equations in which the influence of seawater composition on carbonate equilibria is described simply in terms of salinity.

In theory, it should be possible to deal with all carbonate geochemistry in seawater by knowing the appropriate activity coefficients and their response to changes in how salinity, temperature, and pressure affect them. In practice, we are only now beginning to approach the treatment of activity coefficients with sufficient accuracy to be useful for most problems of interest. That is why “apparent” and stoichiometric equilibrium constants, which do not involve the use of activity coefficients, have been in widespread use in the study of marine carbonate chemistry since the early 1970s. The stoichiometric constants, usually designated as K^* , involve only the use of concentrations (m), whereas expressions for apparent equilibrium constants (K') contain both concentrations and apparent hydrogen activities (a_{H^+}) or concentrations. Examples of these different types of constants are

$$\text{stoichiometric constant : } K_{\text{calcite}}^* = m_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}} \quad (1)$$

$$\text{apparent constant : } K_2' = \frac{m_{\text{CO}_3^{2-}} a_{\text{H}^+}}{m_{\text{HCO}_3^-}} \quad (2)$$

It should be noted that in seawater the molality concentration scale (mol kg^{-1} of seawater) is often used, and care must be taken to make certain that stoichiometric and apparent constants are on the same concentration scale as the measured values.

pH values are “apparent” because electrodes do not measure hydrogen ion activity. The surface chemistry of glass electrodes and liquid junction potentials between the reference electrode filling solution and seawater contribute to this complexity. NBS buffer standards have a much lower ionic strength than seawater; this further complicates the problem. One way in which this last problem has been attacked is to make up buffered artificial seawater solutions and very carefully determine the relation between measurements and actual hydrogen ion activities or concentrations (e.g., see review of Millero, 2001). As a practical matter, pH values of seawater are generally measured at $\sim 25^\circ\text{C}$ and atmospheric pressure. These pH measurements must be corrected for pressure and temperature changes for application to *in situ* conditions.

Another practical consideration when dealing with the seawater carbonic acid system is that in addition to carbonate alkalinity, H^+ and OH^- , a number of other components can contribute to the total alkalinity (TA). The seawater constituent that is usually most important is boric acid. Under most conditions, boric acid contributes $\sim 0.1 \text{ mmol L}^{-1}$ alkalinity; it is usually taken into consideration when making calculations. Nutrient compounds, such as ammonium, phosphate, and silica, whose concentrations in seawater are highly variable, can also influence alkalinity. They must be taken into account for very precise work. In anoxic pore waters a number of compounds, such as hydrogen sulfide and dissolved organic matter, can be significant contributors to alkalinity (e.g., see Berner *et al.*, 1970).

One of the primary aims in the study of the geochemistry of carbonates in marine waters is the calculation of the saturation state of the seawater with respect to carbonate minerals. The saturation state of a solution with respect to a given mineral is simply the ratio of the ion activity or concentration product to the thermodynamic or stoichiometric solubility product (Equation (3)). In seawater the latter is generally used and Ω_{mineral} is the symbol used to represent the ratio. If $\Omega = 1$, the solid and solution are in equilibrium; if $\Omega < 1$, the solution is undersaturated and mineral dissolution can occur, and if $\Omega > 1$, the solution is supersaturated and precipitation should occur:

$$\Omega_{\text{calcite}} = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{\text{calcite}}} \quad \text{or} \quad \frac{m_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}}}{K_{\text{calcite}}^*} \quad (3)$$

The calcium concentration in normal seawater can be calculated from the salinity for most purposes (accuracy is almost always better than within 1%). As previously noted, care must be taken in studies of pore waters and in unusual areas such as coastal waters, carbonate banks, and lagoons where significant deviations from normal seawater concentrations can occur.

The apparent constants are not those for standard seawater where seawater composition has been significantly altered. Composition changes can be especially important in anoxic environments where extensive sulfate concentration changes are produced. The carbonate ion concentration can be calculated from any two of the four parameters: pH, total CO_2 (TCO_2), the partial pressure of CO_2 (p_{CO_2}), or TA (e.g., Morse and Mackenzie, 1990).

7.03.2 SOURCES AND DIAGENESIS OF DEEP-SEA CARBONATES

7.03.2.1 Sources and Sedimentation

The primary sources of calcium carbonate in deep-sea sediments are pelagic coccolithophores and foraminifera that grow dominantly in the photic zone. The distribution of calcium carbonate-secreting pelagic organisms is primarily controlled by the fertility and temperature of the near-surface ocean. The fertility of seawater is largely a result of ocean circulation patterns and, in particular, processes leading to upwelling of nutrient-rich waters. In general, coccolithophores are common in temperate waters, but rare in high-latitude cold waters where diatoms dominate. Coccolithophores are numerically much more abundant (usually $\sim 10^4 \times$) than foraminifera. Benthic foraminifera consist either of aragonitic or high-magnesian calcite. Because of their scarcity in deep-sea sediments, aragonitic pelagic organisms have received relatively little attention. Pteropods are the most abundant pelagic aragonitic organisms.

The mechanisms and rates of transfer of biogenic carbonate material from near-surface waters to deep-sea sediments have been investigated intensely. Major studies have dealt with the transition from living organism to carbonate test, rates of sinking, extent of dissolution in the water column and on the sea bottom, and the relation between life and death assemblages. These studies have raised the question of where and when carbonate starts. Formally, diagenesis should probably not be considered to start until the deposition on the seafloor, but pelagic carbonates can be altered considerably between death in the upper water column and deposition on the seafloor

several kilometers below this ocean surface (e.g., Milliman *et al.*, 1999).

Because of their small size, individual coccoliths sink slowly (Lerman and Dacey, 1974; Lerman, 1979) and may spend ~100 yr in the water column. This long residence time should lead to substantial or complete dissolution of coccoliths in the undersaturated part of the water column. The origin of coccolith ooze on portions of the seafloor overlain by undersaturated waters, therefore, is difficult to explain in terms of the settling of individual particles (e.g., Honjo, 1975, 1976). Data obtained from sediment traps have shown that most coccoliths reach the seafloor as aggregates produced by zooplankton grazing and encapsulation in fecal matter.

An extensive investigation of planktonic foraminifera in sediment trap samples from the tropical Pacific and central Atlantic oceans was conducted by Thunell and Honjo (1981). At both study sites, the total foraminiferal flux and the carbonate flux tend to decrease with increasing depth. In addition, the flux of individual species of planktonic foraminifera varies significantly with depth. The number of small, solution-susceptible species decreases with increasing depth. These results indicate that the dissolution of small (<150 μm) foraminifera is significant as they settle through the water column. Mineral collected from the sediment–water interface directly below the Pacific sediment trap array contained no planktonic foraminifera, suggesting that the residence time of an individual skeleton on the seafloor before it dissolves is extremely short (Thunell and Honjo, 1981).

About 12% of the CaCO_3 flux made by Berner and Honjo (1981) consists of aragonite. A study of sedimentation of pteropods and foraminifera in the North Pacific by Betzer *et al.* (1984) using sediment traps confirmed that considerable dissolution of pteropods takes place in the water column. They estimate that ~90% of the aragonite flux was dissolved in the upper 2.2 km of the water column. It should be noted that the depth for total dissolution of carbonates in the water column is considerably more than the aragonite compensation depth (ACD). This is probably due to the short residence time of pteropods in the water column because of their rapid rates of sinking.

7.03.2.2 Distribution of CaCO_3 in Deep-sea Sediments

Diagenesis of carbonates in the deep sea almost exclusively involves the dissolution of calcium carbonate, where only 20–30% of the flux to the seafloor is preserved (Archer, 1996a). As such, it is primarily reflected in large variations in the

weight percent calcium carbonate in deep-sea sediments that can range from 0 wt.% to over 90 wt.%. The distribution of calcium carbonate in sediments with ocean depth has wide variations. In open ocean basins, where rates of detrital sedimentation are moderate to low, sediments above 3,000 m water depth are generally high in calcium carbonate, whereas sediments below 6,000 m generally have a very low calcium carbonate content. Between these depths there is a poor correlation between the weight percent of calcium carbonate and depth (Smith *et al.*, 1968; Archer, 1996a).

Calcium carbonate is more abundant in Atlantic Ocean sediments, and generally occurs in significant amounts to deeper depths than in Pacific Ocean sediments. The major reason for this is that at a given depth Pacific Ocean waters are less saturated with respect to calcium carbonate than Atlantic Ocean waters. A secondary factor leading to greater preservation in Atlantic Ocean sediments is that at approximately the same degree of undersaturation in Atlantic and Pacific Ocean waters, the input of terrigenous material is higher in the Atlantic Ocean. This leads to more rapid burial and to better preservation of carbonates (Archer, 1996b). Higher productivity in overlying waters, often in upwelling areas, can also lead to more rapid carbonate deposition and to higher carbonate concentrations in sediments. A final major factor influencing calcium carbonate preservation is the relative calcium carbonate to organic carbon rain rate ratio. This is important, because oxidation of sedimentary organic matter can decrease the saturation of pore waters with respect to CaCO_3 by increasing $p\text{CO}_2$. This leads to significant carbonate dissolution (for a review of work in this area and recent research, see Mekik *et al.*, 2002). This diagenetic process is discussed in the next section of this chapter.

With increasing water depth, aragonitic pteropods disappear first, followed by the small and fragile types of calcitic foraminifera, until in the deeper parts of the oceans only badly damaged tests of large, thick-shelled foraminifera remain in the surface sediments.

The carbonate compensation depth (CCD) occurs where the rate of calcium carbonate dissolution is balanced by the rate of infall, and the calcium carbonate content of surface sediments is close to 0 wt.% (e.g., Bramlette, 1961). The CCD has been confused with the calcium carbonate *critical* depth (sometimes used interchangeably with the lysocline discussed next), where the carbonate content of the surface sediment drops below 10 wt.%. A similar marker level in deep-sea sediments is the ACD, below

which aragonite is no longer observed to accumulate in sediments.

The name “lysocline” was applied by Berger (1968) to the region of rapid increase in dissolution rate that could be recognized in surface sediments as the level at which small thin-shelled foraminifera disappear or start showing strong signs of dissolution. The foraminiferal lysocline (FL) was defined by Berger (1968) as the depth where the dominant type of foraminifera shifts in surface sediments from “soluble” to “resistant” species ($\sim 50\%$ change in ratio). Berger (1970) also defined another useful marker level in pelagic sediments, which is similarly based on the change in the ratio of “soluble” to “resistant” species of foraminifera. This is the R_0 level at which the first significant ($\sim 10\%$) change in the ratio of these two types of foraminifera is observed in sediments. Laboratory experiments on sediments to determine how much carbonate must be dissolved to produce assemblages of foraminifera that are characteristic of the FL and R_0 levels were conducted by Berger (1968). He found that $\sim 80\%$ dissolution is necessary to produce the FL assemblage and $\sim 50\%$ dissolution is needed to produce the R_0 assemblage. Other attempts to quantify the extent of dissolution required to produce these sedimentary carbonate marker horizons and to relate this to the factors that control dissolution rates are discussed by Mekik *et al.* (2002).

The distribution patterns of coccoliths and foraminifera differ significantly in deep-sea sediments (Schneidermann, 1973; Roth *et al.*, 1975). In most sediments the more easily dissolved coccoliths are missing. Even in areas where the overlying water is supersaturated with respect to calcite (e.g., 3,000 m in the Atlantic Ocean; Schneidermann, 1973), significant dissolution of coccoliths has been observed. Solution-resistant coccoliths, however, may survive in sediments in which all foraminiferal tests have been dissolved. Schneidermann (1973) used these characteristics to create additional subdivisions of the region near the CCD, and Roth *et al.* (1975) emphasized that coccolith and foraminifera solution indices can be used in a complementary manner. Coccoliths are good indicators of dissolution above the lysocline, whereas foraminifera are better indicators of dissolution below the lysocline.

The distribution of aragonite and magnesian calcite derived from shallow-water areas and sediments and deposited in surrounding deep-sea sediments has also been investigated. Notable studies include those of Berner *et al.* (1976) on the Bermuda Pedestal, Land (1979) on the north Jamaican island slope, Droxler *et al.* (1988a) on the Bahama Banks region, and Droxler *et al.* (1988b) on the Nicaragua Rise.

7.03.2.3 CaCO₃ Diagenesis in Deep-sea Sediments

7.03.2.3.1 General relations

One of the most controversial areas of carbonate geochemistry has been the relation between calcium carbonate accumulation in deep-sea sediments and the saturation state of the overlying water. The CCD, FL, R_0 , and ACD have been carefully mapped in many areas. However, with the exception of complete dissolution at the CCD and ACD, the extent of dissolution that has occurred in most sediments is difficult to determine. Consequently, it is generally not possible to make reasonably precise plots of percent dissolution versus depth. In addition, the analytical chemistry of the carbonate system (e.g., GEO-SECS data) and constants used to calculate the saturation states of seawater have been a source of contention. One of the reasons for the controversy regarding the relation between the extent of carbonate dissolution occurring in deep-sea sediments and the saturation state of the overlying water is that models for the processes controlling carbonate deposition depend strongly on this relation. Hypotheses have ranged from a nearly “thermodynamic” ocean where the CCD and ACD are close to coincident with calcite and aragonite saturation levels (e.g., Turekian, 1964; Li *et al.*, 1969), to a strongly kinetically controlled system (e.g., Morse and Berner, 1972) where major differences in the CCD, FL, and saturation depth exist.

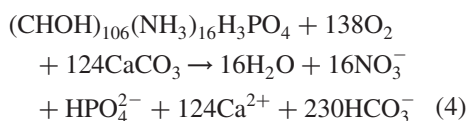
Calculations such as those by Morse and Mackenzie (1990) indicate that the calcite saturation depth is generally ~ 1 km greater than proposed by Berger (1977) and that it is much greater than R_0 . It appears only loosely related to the FL. In the equatorial eastern Atlantic Ocean, FL is ~ 600 m shallower than the saturation depth. If these observations are close to correct, the long cherished idea of a “tight” relation between seawater chemistry and carbonate depositional facies must be reconsidered (Mekik *et al.*, 2002). The influence of near interfacial diagenetic processes on these relationships is discussed in the next section.

7.03.2.3.2 Early diagenetic processes in deep-sea sediments

Numerous models have been proposed for the processes occurring near the sediment–water interface in deep-sea sediments which lead to a balance between dissolution and retention of calcium carbonate in these sediments. A major difficulty in studying and modeling these processes is that many of the most important changes take place over distances of only a few millimeters in a highly dynamic environment.

Early models for the process of calcium carbonate dissolution from deep-sea sediments (e.g., Takahashi and Broecker, 1977) were based on simple diagenetic models, in which calcium carbonate dissolved into the pore waters of the sediments. The alteration of concentrations from an initial saturation state of the overlying water to equilibrium with calcite results in diffusion of the reactants and products and exchange with the overlying waters. The process is governed by the difference between equilibrium concentrations and those found in the overlying waters, the rate of dissolution as a function of disequilibrium diffusion rates, and the thickness of the stagnant benthic boundary layer above the interface. Because the dissolution rate of calcium carbonate is relatively rapid, the depth in the sediment calculated for equilibrium has generally been only a few millimeters.

A major process that had only casually been considered for its potential influence on benthic carbonate accumulation in deep-sea sediments is the oxidation of organic matter. The general reaction for this process is



(Note that this reaction overestimates the oxygen and water content of average organic matter (Hedges *et al.*, 1999).) Although the importance of this reaction in coastal and continental slope sediments that are relatively rich in organic matter was widely recognized, its effect was generally ignored in deep-sea sediments, which usually contain less than 0.2 wt.% organic carbon. With the advent of sediment traps, however, it became apparent that significant amounts of organic matter are reaching the sediment–water interface and that near interfacial oxidation of organic matter is potentially a major diagenetic process even in deep-sea sediments.

A model for the influence of organic matter on carbonate dissolution in deep-sea sediments was introduced by Emerson and Bender (1981). In their model, they emphasized the importance of determining the depth distribution of organic matter oxidation. If organic matter is rapidly oxidized after arrival at the sediment–water interface, the CO_2 generated will have little chance to interact with calcium carbonate, and the influence of the oxidation of organic matter on dissolution will only be of secondary importance. If, alternatively, organic matter is rapidly mixed into the sediment by bioturbation, the oxidation of the organic matter can be very important.

Subsequent to the work of Emerson and Bender (1981), numerous studies have quantified and modeled various aspects of the interaction of

organic matter with deep-sea sedimentary carbonates (e.g., Bender and Heggie, 1984; Emerson *et al.*, 1985; Peterson and Prell, 1985; Jahnke, 1988; Jahnke *et al.*, 1986, 1994, 1997; Martin *et al.*, 1986; Sayles and Curry, 1988; Archer *et al.*, 1989, 2002; Berelson *et al.*, 1990; Emerson and Archer, 1990; Archer, 1991; Hales *et al.*, 1994, 1997; Cai *et al.*, 1995; Hales and Emerson, 1996, 1997a,b; Martin and Sayles, 1996; Wenzhöfer *et al.*, 2001; R. A. Jahnke and D. B. Jahnke, in press). It is beyond the scope of this chapter to present a detailed review of this substantial and often complex body of scientific literature. Only the major concepts and points of contention will be presented here for the discussion of the diagenesis of shoal-water carbonate-rich and siliciclastic sediments where similar processes control carbonate accumulation.

The approach that has generally been used is to estimate carbonate dissolution rates via diagenetic models (e.g., Archer *et al.*, 2002), incorporating organic matter oxidation by oxygen (assuming a C:O ratio) that produces undersaturated conditions. However, in deep sediments that contain more substantial concentrations of metabolizable organic matter, suboxic electron acceptors, such as nitrate and MnO_2 , must also be considered. A relationship is then established between the calcite dissolution rate and pore-water saturation state. The general kinetic equation for calcite introduced by Morse and Berner (1972) for calcite dissolution in seawater has been most commonly used:

$$R(\%/d) = k(\%/d)(1 - \Omega)^n \quad (5)$$

where R is the rate, k the rate constant, Ω the saturation state, and n the reaction order. Several variables influence the relationship between the rate and the saturation state, including temperature and dissolved components that act as reaction inhibitors.

The fundamental parameter in all models for calcium carbonate dissolution in the deep sea is the saturation state of pore waters. In order to determine the saturation state, not only must the composition of the pore waters be known, but also the solubility of the calcium carbonate. Therefore, many studies of carbonate chemistry in deep-sea sediment pore waters have focused on the apparent solubility behavior of carbonates in these sediments.

The results of these studies have shown a surprising degree of variability and have further demonstrated the complexity of calcium carbonate accumulation in deep-sea sediments. Several studies by different groups of investigators appeared at about the same time (Emerson *et al.*, 1980; Murray *et al.*, 1980; Sayles, 1980). The results of Emerson *et al.* (1980) and Sayles (1980)

indicated that, in spite of considerable variability in the pore-water chemistry of sediments at a number of different sites in the Atlantic and Pacific oceans, the pore waters are generally close to equilibrium with calcite. Higher ion concentration products in pore waters where Mn^{2+} was measurable were observed by Emerson *et al.* (1980), indicating possible control by a carbonate phase other than calcite. Subsequently, Sayles (1985) observed similar changes below ~ 20 cm in many sediments and Sayles (1980) also found much higher ion concentration products in one sediment containing aragonite. A similar study in the Guatemala Basin was conducted by Murray *et al.* (1980). There the sediment contained only a few tenths of a weight percent $CaCO_3$. A sharp drop in pH below the sediment–water interface was observed as the result of organic carbon oxidation. The pore waters were undersaturated in the top few centimeters, but came close to the predicted value for saturation at depth. Hales and Emerson (1997a) observed different apparent solubilities in sediments from the Ceara Rise and the Ontong-Java Plateau.

Perhaps no aspect of the diagenesis of deep-sea carbonates has been more controversial than the values of rate constant and reaction order in Equation (5) (Figure 2). Most investigators have modeled rates which demand rate constants to be orders of magnitude less than those measured in the laboratory (e.g., Morse, 1978; Keir, 1980; Morse and Arvidson, 2002). The values for the reaction order have ranged from 1 (Hales and Emerson, 1997b) to 4.5 (e.g., Wenzhöfer *et al.*, 2001). Figure 3 illustrates the difficulty of

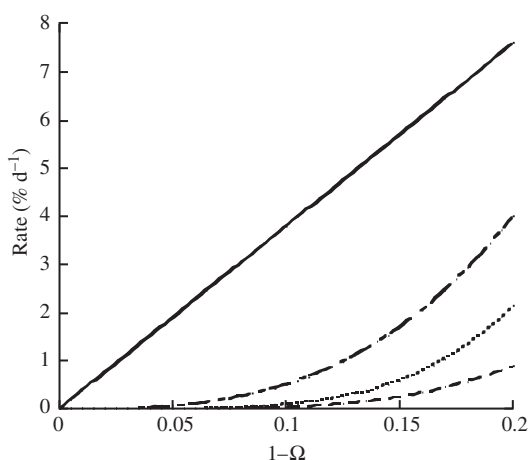


Figure 2 Rate of carbonate dissolution from deep-sea sediment versus $(1 - \Omega)$. Solid line from Hales and Emerson (1996), dotted line from Keir (1980), dashed line from Atlantic Ocean, and dotted and dashed line from Pacific Ocean sediment results of Morse (1978). Note that Hales and Emerson (1996) used a different calcite solubility product.

selecting the proper combination of rate constants and reaction orders for deep-sea sediments. Even within a given study, different values of apparent solubility products and the rate constants have been required (e.g., Hales and Emerson, 1997a; Wenzhöfer *et al.*, 2001). Although there has been a considerable amount of speculation in attempts to explain these large variations in the kinetics of deep-sea carbonate dissolution, our ability to make predictions is still quite limited. A number of parameters may contribute to the variability.

A puzzling observation has recently been made by R. A. Jahnke and D. B. Jahnke (in press). They found that in sediments above the saturation depth that contain high concentrations of calcium carbonate, the ratio of the calcium carbonate dissolution rate to the organic matter remineralization rate was substantially less than at other types of sites. They have suggested that this may be the result of exchange on carbonate particle surfaces coupled with particle mixing, but this process has yet to be clearly substantiated.

In summary, our understanding of the diagenetic factors that control the partial or complete dissolution of deep-sea carbonates can largely be considered to be one of scale. At the scale of the (for differences among) major ocean basins, it is clear that the primary variable is the saturation state of water at a given depth. This is largely controlled by its potential pCO_2 . A secondary influence is the deposition rate of siliciclastic sediments. Within ocean basins, variations in the near-surface primary productivity and the ratio of the rain rate of organic carbon to calcium carbonate to sediments can exert a strong influence and, at least in some areas, lead to substantial dissolution above the saturation depth of the overlying water. This process will be explored further in the discussions of carbonate diagenesis in shoal-water carbonate-rich and shallow-to-intermediate depth siliciclastic sediments, where metabolizable organic matter is at higher concentrations and where it exerts even a greater influence on carbonate diagenesis.

Submarine lithification and precipitation of cements in deep-sea carbonate sediments are relatively rare in typical major ocean basin sediments (Milliman, 1974; Milliman and Müller, 1973, 1977). The cements consist of aragonitic and magnesian calcite mineralogies. They are largely restricted to shallow seas such as the Mediterranean and the Red Sea, and to sediments in the shallower parts of major ocean basins in which biogenic aragonite is also present. Mucci (1987) (see also Garrels and Wollast, 1978) summarized much of the data on the composition of magnesian calcite cements in different environments. He found that many of the shallow-water and

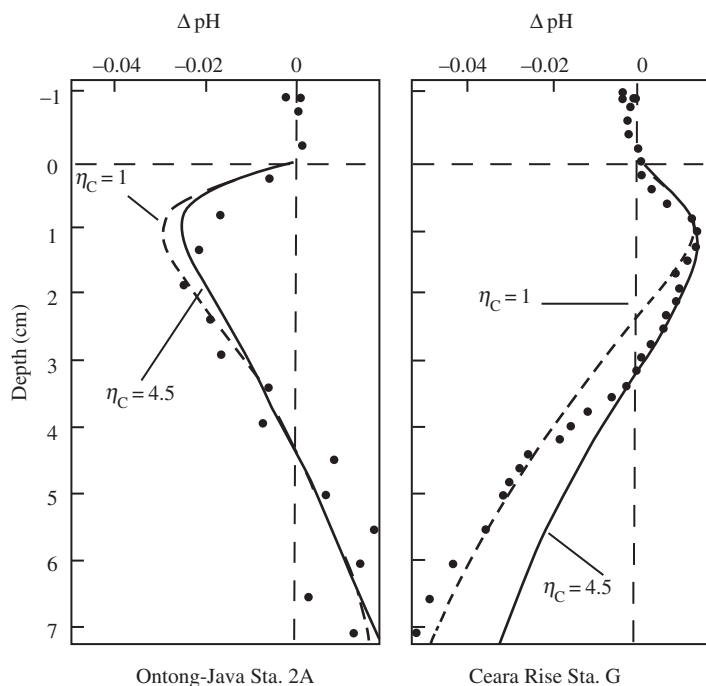


Figure 3 ΔpH versus depth for sediments from the Ontong-Java Plateau and Ceara Rise. n is the reaction order used to fit the data (after Hales and Emerson, 1996).

deep-sea carbonate cements contain 10–15 mol.% magnesium; there is a strong maximum in magnesium abundance at ~ 13 mol.%.

7.03.3 SOURCES AND DIAGENESIS OF SHOAL-WATER CARBONATE-RICH SEDIMENTS

7.03.3.1 Sources of Shoal-water Carbonates

7.03.3.1.1 General considerations

Because shelves in tropical to subtropical environments are capable of producing major quantities of carbonates, they are often referred to as “carbonate factories.” A model in which carbonate production decreases with increasing water depth was produced by Bosscher and Schlager (1992). Others (e.g., Bowman and Vail, 1999) have included the influence of distance from the platform edge as an important factor in carbonate production in shallow-to-shoal water environments.

Carbonate sediments can be subdivided into skeletal and nonskeletal components. Nonskeletal carbonate grains have been divided into five major types: mud, pellets, ooids, lithoclasts, and relict. Carbonate muds are common deposits in low-energy environments, such as tidal flats and subtidal areas. Pellets are formed by the ingestion of sediment by marine organisms and excretion

of fecal material. Ooids are spherical to ovoid, 0.2–1 mm grains with an internal concentric or radial structure. Lithoclasts are fragments of previously deposited, and usually somewhat lithified, carbonate sediment. Relict grains are of older origin, having formed under previous environmental conditions.

The skeletal components of carbonate sediments represent the complete or partial skeleton, or the decomposed and disaggregated skeletal remains, of organisms extant at the time of deposition of the sediment. Sedimentary particles can be produced from calcareous organisms by disaggregation of their skeletons, by mechanical means related to wave and current energy, or by bioerosion of carbonate substrates such as corals, mollusks, and rocks. The wide diversity of shoal-water organisms and their complex composition and morphology, in combination with the varied processes causing their disaggregation, account for the very complex mixture of biogenic carbonate grains in shoal-water sediments.

Seawater in the upper regions of the ocean is strongly supersaturated with respect to calcite, aragonite, and ideal dolomite. Why these minerals fail to precipitate directly from it has been a problem of major interest. In experimental studies (e.g., Pytkowicz, 1965, 1973; Berner, 1975), the magnesium ion has been observed to be a strong inhibitor of calcite precipitation and largely responsible for its failure to precipitate

directly from seawater. The presence of magnesium can also elevate the supersaturation necessary for aragonite precipitation in the absence of nuclei, to a level far beyond that likely to be found in natural waters. Natural organic matter can also strongly inhibit CaCO₃ precipitation (e.g., Berner *et al.*, 1978). It is unlikely, based on this experimental work, that conditions appropriate for direct (homogeneous) nucleation of calcium carbonate will be found in normal modern seawater (Morse and He, 1993). However, these experimental results do not preclude the precipitation of carbonate minerals on pre-existing carbonate mineral nuclei.

7.03.3.1.2 Sources of carbonate muds

The origin of carbonate mud is a long-standing topic of considerable debate and controversy. The three major potential sources generally considered are (e.g., Reid *et al.*, 1992): (i) physicochemical or biochemical precipitation, (ii) postmortem disintegration of calcareous algae, and (iii) physical or biological abrasion of skeletal material. Research has generally focused on either the aragonitic or magnesium calcite mud components. Andrews *et al.* (1997) have found that generally within the silt and clay sizes ($\leq 63 \mu\text{m}$), there is little mineralogic, elemental, or stable isotopic variation.

Fine-grained carbonate-rich sediments that are dominated by small (a few micrometers) needle-shaped aragonite grains are called aragonite needle muds. The two major sources for the aragonite needles are generally considered to be acalcareous algae and abiotic precipitates. Milliman (1974), Bathurst (1975), Scoffin (1987), and Morse and Mackenzie (1990) have reviewed numerous studies of the source of aragonite in calcareous muds. Most of the interpretations of its origin are based on chemical data, although needle morphology has also been used.

Attempts at making budgets of carbonate production and accumulation have also been used in attempts to define the source of aragonite needle muds. In areas such as British Honduras and Florida Bay, the supply of biogenic material appears to be sufficient to provide the sediment for the carbonate muds, although some abiotic precipitation cannot be ruled out. However, in other areas such as the Great Bahama Bank and the Persian Gulf, the biogenic supply appears to be insufficient, and an abiotic source of aragonite needles is needed (e.g., Milliman *et al.*, 1993).

Unfortunately, the precipitation of aragonite from seawater produces needles of a size and morphology that is very similar to those produced by the breakdown of common codiacean green

algae. It is necessary, therefore, to examine the chemistry of the needles to determine their origin. However, even their chemical characteristics are not unambiguously diagnostic (e.g., Lowenstam and Epstein, 1957; Milliman, 1974; Bathurst, 1975; Loreau, 1982).

Not nearly as much attention has been paid to the production of lime mud from calcitic sources, but these muds can be the dominant component in peri-reefal (Debenay, 1985) and lagoonal (Reid *et al.*, 1992) environments where 70–90% of the mud may consist of magnesium calcite. This can form from the micritization and recrystallization of skeletal grains (Reid *et al.*, 1992), and the breakdown of foraminiferal tests (Debenay *et al.*, 1999).

7.03.3.1.3 Formation of carbonate sands

Carbonate-rich sediments that are dominated by sand-sized grains are common in shoal-water sediments. In most cases they are associated with moderate- to high-energy environments such as beaches and behind fringing reefs. They are often composed of carbonates of mixed mineralogy from a variety of biogenic sources produced by physical abrasion, boring, and other biological processes.

Subspherical carbonate grains, generally referred to as ooids because of their resemblance to fish eggs, comprise sandy sediments called oolites. They are common members of modern shoal-water tropic and subtropic carbonate-rich sediments. Ooids are variable in both mineralogy and structure. Aragonite, high-magnesian calcite, and calcite have been observed to occur in ooids (e.g., Land *et al.*, 1979). Radial, concentric-tangential (laminated), and micritic structures are commonly observed around a central nucleus of non-ooid material. The majority of modern, and probably most ancient, ooids are (or originated as) either aragonite with a laminated structure or high-magnesian calcite with a radial structure. The laminated aragonitic ooids are by far the most abundant type of ooids in “recent” sediments and have received the majority of attention.

Ooids are believed to be of nonbiogenic origin and represent one of the most important modes of nonbiogenic removal of CaCO₃ from the ocean. In addition, it has frequently been pointed out that their mineralogy and structure reflect those of marine carbonate cements (e.g., Fabricius, 1977; Land *et al.*, 1979). In fact, they grade into each other in the case of Bahamian grapestone. Land *et al.* (1979) stressed the tie between carbonate cements and ooids, pointing out that ooids can be viewed as cements centrifugally deposited on grains, whereas submarine cements can be viewed as centripetally coated pores.

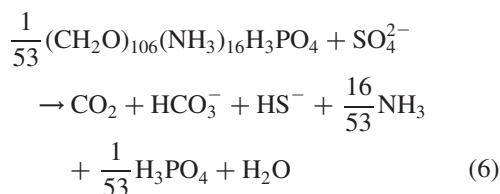
Hypotheses for the processes responsible for the existence of ooids are based on bacterial-mechanical, algal, and chemical mechanisms for ooid formation. Some investigators have suggested models that involve more than one of these mechanisms. An extensive review and discussion of the hypotheses for ooid formation can be found in Morse and Mackenzie (1990).

7.03.3.2 Early Marine Diagenesis of Shoal-water Carbonate-rich Sediments

7.03.3.2.1 Pore-water chemistry

The chemistry of sediment pore waters provides important information regarding chemical reactions in sediments. In many cases, the reactions between pore waters and solids are not obvious from observations of the solids alone, but because the solid-to-solution ratio in sediments is so large, major changes can occur in pore waters during diagenesis. If equilibration alone were to take place in carbonate-rich sediments between the pore waters and metastable solids, precipitation of a stable phase would occur until equilibrium was reached. However, the oxidation of organic matter can also be an important process in these sediments. The carbon dioxide generated by this process can be sufficient to cause undersaturation, resulting in dissolution—not precipitation—as the dominant early reaction.

A major complicating factor in the diagenesis of shoal-water carbonate-rich sediments is that much of the organic matter oxidation can take place via bacterially mediated sulfate reduction. If marine plankton-like organic matter is oxidized via sulfate reduction, the nutrients phosphate and ammonia are also produced (Equation (6)):



Because the products are generated nearly constant ratios, fixed pH can be established after a moderate degree of sulfate reduction in a closed system (Ben-Yaakov, 1973). During the early stages of reaction in seawater the pH drops to ~6.9 and then remains constant. This can result in undersaturated pore waters and carbonate dissolution. Further sulfate reduction causes the alkalinity to rise while the pH remains constant. At ~35% sulfate reduction, the pore waters regain supersaturation with respect to calcium carbonate. Further sulfate reduction can result in calcium carbonate precipitation (Figure 4). Furukawa *et al.* (2000) have emphasized that, due to the high

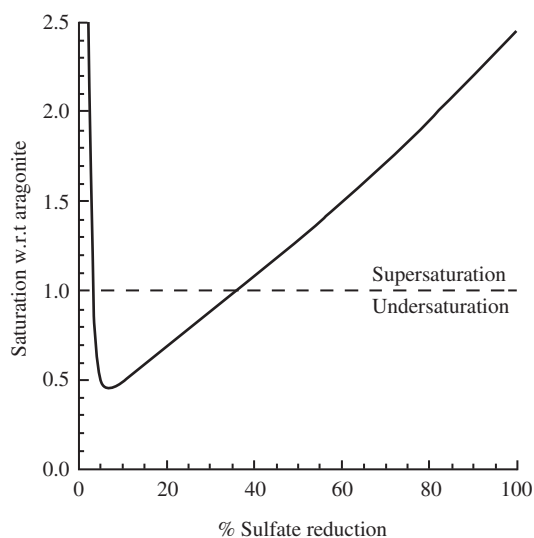


Figure 4 The saturation state with respect to aragonite versus the extent of sulfate reduction for a closed system containing seawater (after Morse and Mackenzie, 1990).

bioirrigation rates in many carbonate sediments, depth profiles of dissolved sulfate may be poor indicators of the importance of sulfate reduction in the oxidation of sedimentary organic matter in shoal-water carbonate sediments.

Several investigations of shallow-water carbonate-rich sediments have been made to determine which processes control the calcium carbonate IAP. Two major studies that investigated this topic were conducted by Berner (1966) in south Florida and Bermuda and by Morse *et al.* (1985) in the Bahamas. Berner's pioneering study was important in demonstrating through pore-water chemistry that, in sediments exposed to normal seawater, there is little diagenetic alteration of sedimentary carbonates. Evidence for the dissolution of magnesian calcites was found in pore waters from sediments in the northern part of Florida Bay where pore waters are fresher. Based on carbonate equilibrium constants available at the time, Berner concluded that most pore waters are close to equilibrium with low-magnesian calcite. Calculations using new constants indicate that this is not generally the case.

A number of pore waters in both coarse- and fine-grained sediments from the northern Great Bahama Bank and Little Bahama Bank were studied by Morse *et al.* (1985). Figure 5 summarizes their findings for the pH and TA in pore waters from sediments in different environments. Lines are also given in this figure for pore water in equilibrium with calcite, aragonite, and an 18 mol.% magnesian calcite, using the solubility constants of Walter and Morse (1984). Clearly, there is great variability

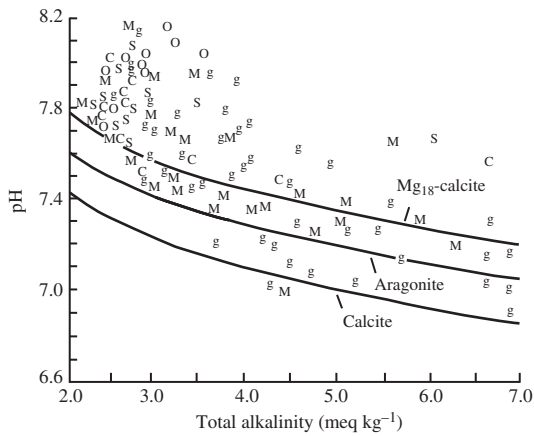


Figure 5 pH versus total alkalinity for pore waters in Bahamian carbonate-rich sediments. M = mud; S = sand; O = oölite; C = coarse-grained grassbed; g = fine-grained grassbed (after Morse *et al.*, 1985).

in pore-water composition, and many sediment pore-waters are substantially supersaturated with respect to all these phases. p_{CO_2} values are high in these sediments, typically at least 10 times the atmospheric value. Even within a given core it was found that calcium carbonate IAPs were highly variable (Morse *et al.*, 1985). Because aragonite is generally the most abundant carbonate phase in these sediments, control of the IAP by the most abundant phase does not explain these observations.

A number of solubility experiments, on sediments from the Bahama sites at which pore waters were collected, were performed by Bernstein and Morse (1985) in an attempt to understand the processes controlling the calcium carbonate IAP in these sediments. Equilibrium was approached from both supersaturation and undersaturation for different time periods up to 50 d. Generally good agreement was found between the field and laboratory observations for fine-grained sediments, indicating at least a dynamic steady state within the sediments between the pore water and some solid phase. Less agreement was found for coarse-grained sediments, where flow of water through sediments (e.g., oölite banks) may result in a residence time too short for dynamic equilibrium to be reached. An interesting observation was that oöids, although composed almost entirely of aragonite, were significantly more soluble than aragonite, in agreement with the Weyl (1965) hypothesis of a magnesian calcite coating.

Field and laboratory observations are consistent with the idea that dissolution in carbonate sediments can proceed faster than precipitation, and that the pore waters reach steady-state IAPs close to those of the most unstable phase (dissolution processes will be discussed later in

this chapter). Carbonate ion may be “pumped” down to values at saturation with less soluble phases, as dissolution of the more soluble material eventually causes its removal. However, the persistence of high-magnesian calcites in sediments for long periods of time indicates that this process does not involve a large amount of mass transfer under normal marine conditions.

The influence of seagrass beds on fine-grained sediments near San Salvador Island was investigated by Short *et al.* (1985), and Morse *et al.* (1987) studied their influence on pore-water chemistry in coarser-grained sediments near the Berry Islands. Their influence was less in these sediments, elevated p_{CO_2} and alkalinity values in sediments beneath the seagrass beds were apparent. This is probably the result of elevated organic matter concentrations associated with roots and debris from the plants. Jensen *et al.* (1998) observed that the carbonate matrix is dissolved in the seagrass rhizosphere resulting in a release of phosphorus, which is believed to limit seagrass production in carbonate sediments.

7.03.3.2.2 Precipitation of early carbonate cements

The formation of carbonate overgrowths and cements is certainly one of the most important and highly studied aspects of carbonates in sediments and sedimentary rocks. This section discusses the geochemical aspects of the formation of early diagenetic cements and overgrowths. An extensive literature exists on the occurrence of early carbonate precipitates in marine sediments, where they are generally termed cements. Included in this literature are books devoted solely to carbonate cements (e.g., Bricker, 1971; Schneidermann and Harris, 1985) and numerous reviews (e.g., Milliman, 1974; Bathurst, 1974, 1975; Harris *et al.*, 1985; Morse and Mackenzie, 1990). Many investigations have been largely descriptive and have focused primarily on the distribution, mineralogy, and morphology of the cements.

Carbonate cements in calcareous sediments belong to three major groups. The most common are those that occur in voids found in biogenic carbonates. This group is especially important in reefs, which are discussed in a separate section of this chapter. Cements also occur on the exterior of carbonate particles, where their intergrowth can cause formation of hardened pellets, grapestones, crusts, hardgrounds, and beachrock. This type of cementation may also be important in oöids (e.g., Fabricius, 1977). Micritic cements associated with boring algae comprise the third common type of cement.

One of the most interesting questions about carbonate cements in the marine environment is why they are not more abundant. In carbonate-rich sediments carbonate surfaces for overgrowths are abundant, and both overlying seawater and many pore waters are supersaturated with respect to carbonate minerals. Morse and Mucci (1984) demonstrated that precipitation of cements from pore waters of carbonate sediments is severely inhibited by studying Iceland spar calcite crystals that had been buried for several months in a variety of carbonate sediments in the Bahamas. After recovery and analysis using very sensitive depth-profiling Auger electron spectroscopy, overgrowths were detected on only a few crystals. The calculated growth rates of the precipitates were much less than those observed in laboratory experiments using seawater at the same supersaturation state.

At least part of the reason for these observations must be that precipitation is severely inhibited by organics such as humic acids (Berner *et al.*, 1978). Mitterer and co-authors (e.g., Mitterer and Cunningham, 1985) have explored the possible role of organic matter in cement formation. These authors suggested that, whereas some types of organic matter inhibit precipitation, other types, particularly those rich in aspartic acid, favor precipitation by complexing calcium. Inhibition of precipitation, coupled with slow transfer of fresh supersaturated seawater into sediment pores, seems to account for the lack of extensive early cementation.

The factors controlling the mineralogy and chemical composition of carbonate cements in the marine environment have also been investigated extensively. Bathurst (1975, 1987) summarized many of the observations (e.g., Glover and Pray, 1971). In some cases the host carbonate mineral is a factor in determining mineral composition. Usually aragonite grains have aragonite overgrowths, whereas high-magnesian calcite grains have high-magnesian calcite overgrowths of similar magnesium content. In some instances, syntaxial formation of cement is observed. Although this explanation of host control is a "comfortable" one, it does not explain the common occurrence of cements of mixed mineralogy or those that differ in mineralogy from their host grains.

Environmental factors have also been found to correlate loosely with cement formation, mineralogy, and morphology. The energy (waves, currents, etc.) of the environment and the rate of sedimentation are most often cited as important in shallow-water environments. The energy of the environment is important in supplying seawater, from which the carbonate cements can be derived. Formation of hardgrounds was originally thought to necessitate a

low-energy environment and low sedimentation rates (e.g., Taft *et al.*, 1968; Shinn, 1969). However, Dravis (1979) found that hardgrounds could form quickly even under high-energy and rapid sedimentation rate conditions. He found that in such environments endolithic algal filaments play an important role in binding the sediment and providing sites of cement formation. Aragonite and high-magnesian calcite cements can form under most environmental conditions, but aragonite is generally favored under higher-energy conditions. Given and Wilkinson (1985) suggested that this is because precipitation rates are faster under higher-energy conditions and that a faster precipitation rate favors aragonitic cements.

A major concern in studies of the chemistry of carbonate cement formation is the source of the calcium and carbonate ions necessary to form the cements. The obvious source is seawater, but large volumes of seawater are necessary if significant amounts of cement are to be produced. Cement formation is consequently favored near the sediment-water interface and in high-energy environments where water can be flushed through porous structures such as reefs. The observation that cements usually form only in thin crusts near the sediment-water interface also demonstrates the importance of normal seawater for cement precipitation. Further evidence for cement formation in normal seawater comes from stable isotopes. The $\delta^{13}\text{C}$ values of cements are usually close to those predicted for carbonates precipitating from seawater (e.g., see Given and Wilkinson, 1985). Another possible source of the ions necessary for cement formation is the dissolution of carbonate phases more soluble than the cements. High-magnesian calcites could provide such a source, as has been demonstrated in periplatform oozes in the Bahamas (Mullins *et al.*, 1985) and for coastal carbonate sediments of the Bay of Calvi in Corsica (Moulin *et al.*, 1985). This process is consistent with the previously discussed chemistry of many pore waters.

The precipitation of calcium carbonate (usually, but not exclusively, from petrographic evidence in the form of high-magnesian calcite, e.g., Alexandersson and Milliman, 1981) is generally inferred from a decrease in dissolved pore-water calcium (e.g., Thorstenson and Mackenzie, 1974; Gaillard *et al.*, 1986). Most studies of the impact of chemical diagenesis on the carbonate chemistry of anoxic sediments have focused primarily on the fact that sulfate reduction results in the production of alkalinity, which can cause precipitation of carbonate minerals (e.g., Berner, 1971). Carbonate precipitation can also occur via methane oxidation instead of organic matter oxidation, resulting in distinctly

“light” $\delta^{13}\text{C}$ values for authigenic carbonates (e.g., Ritger *et al.*, 1987).

Finally, it should be noted that while most investigators have rejected the idea that carbonate cements are directly or even closely linked to biological mechanisms of formation, some investigators hold the position that organisms may be very important for cement formation processes. Marine peloids (aggregates of cemented carbonate grains) have received considerable attention in this regard because of their close association with bacterial clumps (e.g., Chafetz, 1986). Fabricius (1977) has presented a lengthy brief in favor of the formation of grapestone cements and ooids by algae.

7.03.3.2.3 Dissolution of carbonates

Many studies of the impact of chemical diagenesis on the carbonate chemistry of anoxic sediments have focused primarily on the fact that sulfate reduction results in the production of alkalinity, which can cause precipitation of carbonate minerals (see previous discussion). However, during the early stages of sulfate reduction ($\sim 2\text{--}35\%$), this reaction may not cause precipitation, but dissolution of carbonate minerals, because the impact of a lower pH is greater than that of increased alkalinity (Figure 4). Carbonate ion activity decreases rapidly as it is “titrated” by CO_2 from organic matter decomposition leading to a decrease in pore-water saturation state. This process is evident in data for the Fe-poor, shallow-water carbonate sediments of Morse *et al.* (1985) from the Bahamas and has been confirmed in studies by Walter and Burton (1990), Walter *et al.* (1993), and Ku *et al.* (1999) for Florida Bay, Tribble (1990) in Checker Reef, Oahu, and Wollast and Mackenzie (unpublished data) for Bermuda sediments.

Three primary processes can lead to undersaturation, in addition to the one that may result during the early stages of sulfate reduction. These are early post-death microenvironments within organisms, oxidation of organic matter by processes preceding sulfate reduction, and oxidation of sulfides. Commonly, these processes are most important near the sediment–water interface.

Early studies by Hecht (1933) showed that dissolution of carbonate in mollusk shells can begin immediately after death. In laboratory studies he found shell weight losses of as much as 25% in two weeks. Other examples of this type of behavior come from a study by Berner (1969), who found calcium carbonate dissolution during bacterial decomposition of two types of clams, possibly as a result of the production of organic acids in addition to CO_2 during early degradation of organic matter. Birnbaum and Wiremen (1984) have also pointed out that a proton gradient can be

established across the cell wall of *Desulfovibrio desulfuricans*, resulting in calcium carbonate dissolution in the nearby microenvironment.

Prior to the onset of sulfate reduction, extensive organic matter degradation can occur by bacterially mediated oxygen use as described for deep-sea sediments. The influence of benthic bacterial activity on carbonate mineral dissolution under aerobic conditions has been demonstrated nicely by Moulin *et al.* (1985) for pore waters from sediments of the Gulf of Calvi in Corsica. Other processes, but probably less important, include nitrate reduction and fermentation (e.g., Aller, 1980).

Walter and co-workers (Walter and Burton, 1990; Walter *et al.*, 1993; Ku *et al.*, 1999) have made extensive efforts to demonstrate the importance of dissolution of calcium carbonate in shallow-water carbonate sediments. Up to $\sim 50\%$ carbonate dissolution can be driven by the sulfate reduction–sulfide oxidation process. In calcium carbonate-rich sediments there is often a lack of reactive iron to produce iron sulfide minerals. The sulfide that is produced by sulfate reduction can only be buried in dissolved form in pore waters, oxidized, or can diffuse out of the sediments. In most carbonate-rich sediments the oxidative process strongly dominates the fate of sulfide. Figure 6 (Walter *et al.*, 1993) shows the strong relationship that generally occurs in the carbonate muds of Florida Bay between total carbon dioxide, excess dissolved calcium (calcium at a concentration above that predicted from salinity), and the amount of sulfate that has been reduced. It is noteworthy that the burrowed banks show much more extensive increase in calcium than the other mud banks. This is in good agreement with the observations of Aller and Rude (1988) that in Long Island Sound siliciclastic sediments an increased bioturbation leads to increased sulfide oxidation and carbonate dissolution.

7.03.3.2.4 Carbonate diagenesis associated with reefs

Because of the difficulties inherent in obtaining pore waters from the interior of reefs, the chemical environment in reef structures went largely unstudied until the 1980s. Most of the studies of early reef diagenesis are those of Hawaiian and Australian reefs by Sansone and co-workers (Sansone, 1985; Sansone *et al.*, 1988a,b; Tribble, 1990, 1993; Tribble *et al.*, 1990, 1992). Fichez *et al.* (1997) and Andrié *et al.* (1998) have conducted studies of chemical changes in pore waters in a deep borehole within a Tahitian fringing reef. These changes occur during time periods substantially longer than those

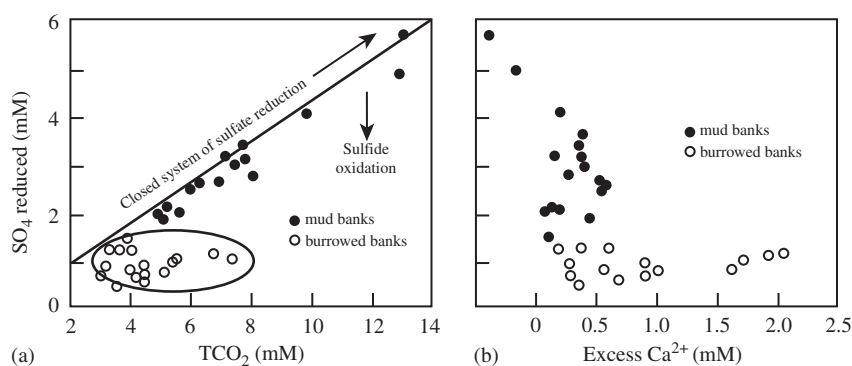


Figure 6 Dissolved sulfate versus: (a) TCO_2 and (b) excess Ca^{2+} in the pore waters of carbonate-rich Florida Bay sediments (after Walter *et al.*, 1993).

encompassed by the “early” diagenesis considered in this chapter.

The studies of Checker Reef, Oahu, Hawaii (a lagoonal patch reef) and Davies Reef, Great Barrier Reef, Australia (a platform reef), show that microbially mediated processes of oxic respiration, sulfate reduction, and, to a lesser extent, nitrate reduction and methanogenesis are important in these reef structures. The interstitial waters of these reefs are highly depleted in oxygen, and exhibit lower pH values and elevated concentrations of dissolved methane, sulfide, ammonium, phosphate, and silica relative to the seawater surrounding the reef. In Checker Reef the degree of alteration of interstitial waters increases from the margin to the center of the reef; in Davies Reef the most altered pore waters are at the margin of the reef.

The differences between these reefs probably reflect differences in their structural framework and variations in wave characteristics and tidal range in the two environments. Anaerobic reactions in reef interstitial waters may not progress far if reef structures are open and well flushed. If, however, the systems are nearly closed, little fresh reactant will enter via seawater exchange and mass transfer will be limited by the reactants trapped in the reef interstitial waters. An important conclusion of Sansone’s studies was that thermodynamic disequilibrium among dissolved species such as CH_4 and SO_4^{2-} implies microzonation of chemical reactions. Microzonation resulting in slight differences in reef interstitial water compositions may account for the coexistence of different cement mineralogies in reef structures.

A pattern of initial carbonate dissolution followed by carbonate precipitation as a function of the extent of sulfate reduction occurs within reefs in a manner similar to that previously described for sediments (Tribble, 1993). Throughout this process the interstitial waters maintain close to equilibrium compositions with aragonite. This buffers the pH of the waters. It was found that

FeS formation can play an important role in regulating pore-water chemistry. Systems with more intense FeS formation have a tendency to become more supersaturated with respect to aragonite. N-poor organic matter appeared to result in more corrosive conditions.

7.03.3.2.5 Early dolomite formation

The formation of dolomite under conditions encountered in modern marine sediments and sediment burial to moderate depths is strongly controlled by reaction kinetics that are slow even at high supersaturations (e.g., Lippmann, 1973; Morrow, 1982). A plausible explanation for the slow precipitation kinetics of dolomite is the requirement that cation ordering puts a major limit on the rate at which it can form (e.g., the “simplicity” principle, Goldsmith, 1953). It is likely that the dehydration kinetics of Mg^{2+} also play a role (e.g., Lippmann, 1973). Because the precipitation kinetics of dolomite are too slow to be studied in the laboratory at near Earth-surface temperatures (Land, 1998), experiments on dolomite reaction kinetics (e.g., Arvidson and Mackenzie, 1999) have generally been conducted at elevated temperatures (typically between 100°C and 300°C). Considerable interesting information has been gathered from these experiments. However, the applicability of the results to processes at lower temperatures and slower reaction kinetics remains highly questionable.

Observations of dolomite formation in natural systems have been used for defining additional factors that may influence the rate of dolomite formation. These include catalysis by certain clay minerals (e.g., Wanless, 1979) and production of organic by-products by bacteria (e.g., Gunatilaka *et al.*, 1985). Mg^{2+} transport to sites of dolomite precipitation can inhibit the reaction in hemipelagic sediments (e.g., Baker and Burns, 1985). However, the true influence of reaction rates is largely speculative, because the kinetic factors are

generally deduced from the presence or absence of dolomite in different environments.

Most modern dolomite is forming from high ionic strength solutions that are usually derived from the evaporation of seawater or lakes in arid regions. These environments have been studied extensively, because they provide an opportunity to observe directly systems in which substantial amounts of dolomite are currently forming. The associated hydrology and solution chemistry of the dolomitizing fluids can also be determined. Sites of particular note are the Persian Gulf sabkhas, the Coorong district in South Australia, Bonaire Island in the Caribbean Sea, Sugarloaf Key in Florida, supratidal sediments on Andros Island in the Bahamas, and Deep Springs Lake in California. A general feature of many of these areas is that high Mg^{2+}/Ca^{2+} ratios in solution promote dolomitization. Friedman (1980) discussed the importance of modern high salinity environments for dolomite formation and evidence in the rock record, indicating a strong relation between evaporites and dolomite. He claimed that most sedimentary dolomite should be considered as evaporite mineral, but this opinion is not universally accepted.

The inhibition of dolomite formation by sulfate has been widely debated (e.g., see discussion in Hardie, 1987). While dolomite formation is usually associated with sediments where sulfate reduction is active, the observation that dolomite can form even when dissolved sulfate concentrations are high argues against a dominant control by dissolved sulfate. Products of sulfate reduction such as increased alkalinity may increase the formation rate of dolomite more than it is inhibited by sulfate. This conclusion has been expanded by Compton (1988), who emphasized that highly elevated solution supersaturations with respect to dolomite are usually associated with sediments rich in organic matter. He termed dolomite that forms under these conditions "organogenic dolomite." Mazzullo (2000) has summarized the data supporting the early formation of dolomite in organic-rich sediments where extensive sulfate reduction and methanogenesis occur.

Direct participation by bacteria may also promote dolomite formation during early diagenesis. The literature relating to this manner of low-temperature dolomite formation was reviewed by Vasconcelos and McKenzie (1997) in their study of microbial mediation of dolomite formation in Lagoa Vermelha in Brazil.

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