# Calcium Carbonate Formation and Dissolution

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## 1. Introduction

Calcium carbonate is an important and often dominant component of marine sediments. This is reflected by the observation that about 20% by volume of Phanerozoic (0−547 Ma; Ma = million years ago) sedimentary rock is made up of the carbonate minerals calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).[1] Over the history of the Earth, the primary source of marine carbonate minerals has shifted from abiotic precipitation to biogenic sources. The biogenic sources have in turn shifted from being primarily relatively shallow water benthic organisms to the current situation where small open ocean pelagic organisms, living mainly in the photic zone, dominate calcium carbonate formation. Much of the calcium

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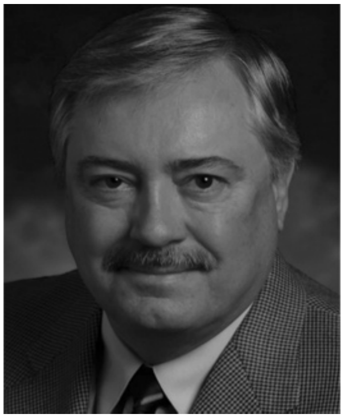
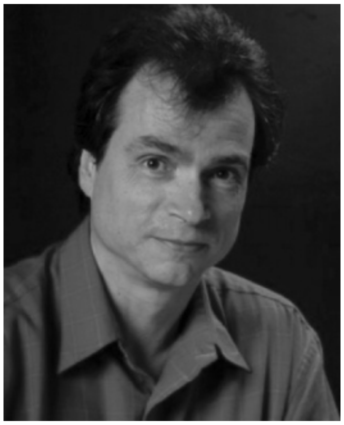


John Morse is originally from Minnesota where he received his B.S. from the University of Minnesota's Institute of Technology in Geology (1969). From there he went to graduate school at Yale University where, under the mentorship of Robert Berner, he received both his M.S. (1971) and Ph.D. (1973) degrees in Geology. In 1973, he joined the faculty at Florida State University where he held a joint appointment in the Oceanography and Chemistry departments. Subsequently, he served on the faculty of the University of Miami (Florida) from 1976–1981 and then went to Texas A&M University where he currently holds the Louis and Elizabeth Scherck Chair in Oceanography. His primary research interest has been in the physical chemistry of sedimentary minerals and their nonequilibrium interactions with natural waters.

Rolf Arvidson received a B.S. in Geology from the University of Washington (1980). After working as an exploration geologist in Denver, he received a M.S. in Geology from the University of Iowa under Philip H. Heckel and a Ph.D. in Oceanography with Fred T. Mackenzie in 1997. He collaborated with John Morse as a Postdoctoral Researcher at Texas A&M University (1997–1999), and at Rice University with Andreas Lüttge (1999–2001). He is currently Research Scientist at Rice. His research interests include experimental, theoretical, and modeling approaches to mineral precipitation and dissolution kinetics, as well as integration of this understanding to both short- and long-term biogeochemical cycling.

carbonate that is formed is dissolved in the water column and, more importantly, in sediments through processes collectively known as diagenesis.

The occurrence of carbonate minerals in modern marine sediments can readily be divided into those found in shoal-to-shallow (0 to less than ~200 m) and deep water (generally >1 km) environments associated with the world's major ocean basins. 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 (composed mainly of detrital minerals such as clays and quartz sands) sediments.



Andreas Lüttge started his scientific education in Braunschweig (Germany) in 1979. In 1982, he went to Tübingen (Germany) where he got his Ph.D. in 1990 and his "Habilitation" in 1995 (Eberhard-Karls Universität). Next, he followed an invitation from Yale University where he worked first as a Humboldt Fellow and later as an associate research scientist. In 1998, Lüttge accepted an offer from Rice University in Houston. Currently, he holds a double appointment in Earth Science and Chemistry at Rice. His research interest is focused on the processes that govern fluid/solid interactions from low-temperature conditions to the pressures and temperatures of the deep crust. He is particularly interested in the participation of microorganisms in these processes. His work includes experimental and modeling techniques that he applies to questions of mineral reactions in sedimentary basins, weathering, the fate of nano-particles in the environment, atmospheric and global change, and microbial fuel cells.

Almost all deep sea carbonate-rich sediments are composed of calcite low in magnesium (>99% $CaCO_3$). This material is primarily derived from pelagic skeletal organisms, with coccolithophores (plants) usually being the most important quantitatively, followed by foraminifera (animals). 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. Since the time of the HMS Challenger expeditions in the late 19th century, it has been recognized that that the saturation state of seawater overlying sediments in the deep ocean exerts a major influence on the distribution and abundance of calcium carbonate in these sediments

Shoal-to-shallow water, carbonate-rich sediments are largely confined today to the subtropic and tropic climatic zones but are found even at high latitudes. These carbonates are primarily produced by the disintegration of the skeletons of benthic organisms, such as corals, echinoids, mollusks, benthic foraminifera, and coralline algae. In some environments, inorganic precipitates such as cements and oöids are also abundant. The source of aragonite needle muds remains controversial. In siliciclastic sediments, the major source of carbonates is also primarily from benthic organisms. These include bivalves, sea urchins, and foraminifera.

Interest in calcium carbonate formation and dissolution in the ocean has increased because of the central role these reactions will play in the ocean's response to the increasing partial pressure of carbon dioxide ($pCO_2$) in the atmosphere. This is causing acidification of the ocean. Reactions resulting in the formation and dissolution of calcium carbonate are also of central importance to the sequestration of carbon dioxide in subsurface carbonate reservoirs and saline waters.

The objective of this paper is to review the major aspects of the chemistry of carbonate mineral formation and dis-

**Table 1. Stabilities of Common Carbonate Minerals under STP Conditions**[a]

| phase | formula | $K'_{sp(stoich)}$ ((mol$^2$ kg$^{-2}$) × 10$^{-7}$) | p$K$ |
|---|---|---|---|
| aragonite | $CaCO_3$ | 6.65[7] | 8.30[155] |
| calcite | $CaCO_3$ | 4.39[7] | 8.48[155] |
| magnesite | $MgCO_3$ | | 8.04[9] |
| siderite | $FeCO_3$ | | 10.52[9] |
| rhodochrosite | $MnCO_3$ | | 10.08[9] |
| dolomite | $CaMg(CO_3)_2$ | | 18.15[9] |
| kutnahorite | $CaMn(CO_3)_2$ | | 21.81 ± 0.07[10,39] |

[a] $K'_{sp(stoich)}$ is the stoichiometric solubility product in seawater. p$K$ values are thermodynamic $-\log K_{sp}$.

solution in the marine environment. Because the primary readership of this journal is among the chemical, rather than Earth science community, we will put our primary effort into dealing with the chemistry of important marine carbonate minerals and their interaction with seawater. In doing so, we will not attempt to cover all that is known about carbonate mineral−aqueous solution chemistry, but rather focus primarily on those aspects of direct relevance to their behavior in seawater.

Following this chemical review (sections 2 and 3), section 4 will deal with observations of processes controlling the sources of carbonate minerals in the ocean, and section 5 will address the processes leading to their dissolution; the fate of a major fraction of the carbonate minerals produced. Section 6 will focus on the likely responses of oceanic carbonate minerals, in different marine environments, to the acidification of the oceans because of the central importance of this response to impact of increased $pCO_2$ on the marine environment and climate change. It should be noted that a review paper on the carbonic acid system in seawater by Millero[2] also appears in this issue. We will therefore not cover this topic in any detail in this paper. However, the Millero paper should be referred to because the behavior of the carbonic acid system and the processes giving chemical "texture" to the oceanic carbonic acid system components exert a primary control, along with temperature, pressure and salinity, on the saturation state of seawater with respect to carbonate minerals.

## 2. Major Marine Carbonate Minerals

### 2.1. General Considerations

In this section, we provide a basic overview of past and current work on the physical chemistry of carbonate minerals relevant to their reactions in modern marine environments. An accurate understanding of the relationship between seawater saturation state and the distribution of reef, algal, and associated carbonates in modern environments is also critical in evaluating the implications of rising sea surface temperatures and increasing acidity associated with anthropogenic $CO_2$ fluxes. Over the past half century, extensive laboratory and experimental work on carbonate minerals has yielded important insights documented in a voluminous literature. This section can by no means be encyclopedic but does attempt a selective review of seminal papers that have defined major benchmarks in understanding.

It is critical to recognize that the vast majority of sedimentary carbonate minerals deposited in modern marine environments is *biogenic* in origin; that is, these minerals are actively precipitated from seawater by organisms to form skeletal hard parts. A much smaller fraction of the total sedimentary burden of carbonate minerals is formed abiogenically, typically either as heterogeneously precipitated primary marine cements or through postdepositional, diagenetic reactions. Regardless of the organism responsible for their formation, biogenic skeletal carbonates bear distinct differences from their abiogenic counterparts in terms of basic physical properties, composition, structure, and reactivity. In many ways, biogenic carbonates form an entirely different class of materials, sufficiently complex and heterogeneous that intrinsic relationships between physical and chemical properties depart fundamentally from those of inorganic phases.

### 2.2. Physical and Chemical Properties

#### 2.2.1. General Considerations

The crystal structure of naturally occurring carbonates, as a group, is relatively simple, particularly when compared with oxides, silicates, and other sedimentary minerals. Despite their structural simplicity, the behavior of these minerals in seawater is complex. This complexity primarily reflects the fundamental role of chemical kinetics in this system. As a diagnostic illustration, a simple reaction path calculation predicts the formation of ordered dolomite ($CaMg(CO_3)_2$) in normal surface seawater. However, despite extensive supersaturation, unambiguous observations of direct dolomite precipitation from normal seawater are essentially nonexistent; aragonite and magnesian calcite are the phases that actually form, at least via abiotic reactions. Thus great care must be taken in the use of simple thermodynamic relationships as predictor functions in seawater systems where carbonate mineral distributions are dominated by metastable phases and where reactions may be governed by poorly understood surface phases whose properties differ from the underlying bulk mineral. As discussed later on, our current understanding of the kinetic mechanisms that control precipitation and dissolution of these phases is in some cases quite limited and requires both direct observations and an adequate theoretical framework. We begin with a basic review of the unique physical and chemical properties of marine carbonate minerals.

The most important carbonate minerals in seawater reactions are the $CaCO_3$ polymorphs aragonite and calcite. Marine calcite may also contain variable amounts (10 to >30 mol %) of $MgCO_3$ in solid solution, generically termed magnesian calcite. The solubilities of some carbonate minerals are given in Table 1. Aragonite is both denser and more soluble than calcite. These two phases also differ in their tendency to accept divalent cations other than $Ca^{2+}$ in solid solution. The *general* pattern of coprecipitation is governed by the following rule. Cations such as $Sr^{2+}$ and $Ba^{2+}$ whose ionic radii exceed that of $Ca^{2+}$ (1.00 Å, assuming 6-fold coordination with oxygen[3]) are more frequently accom-

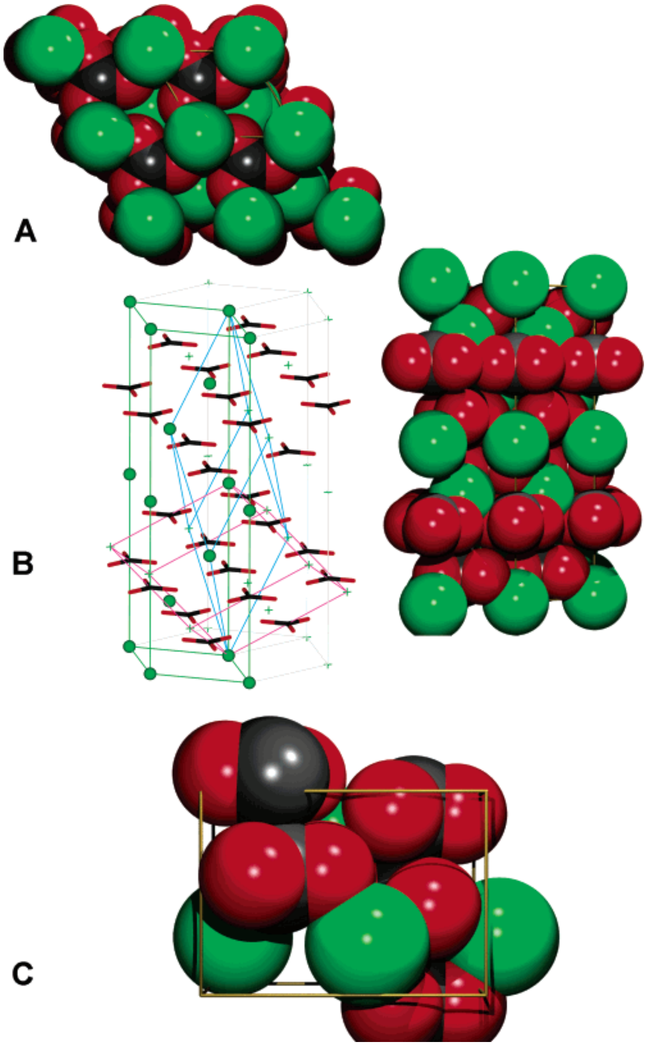


**Figure 1.** Carbonate mineral unit cells (Ca in green, C in black, O in red): (A) calcite hexagonal unit cell, viewed down the *c*-axis, showing coordination of metal atoms by oxygens belonging to different carbonate groups;[11,12] (B, left) relationship of hexagonal and rhombohedral unit cells (green and blue outlines, respectively, *c*-axis vertical) to cleavage rhombohedron (red outline, not a true unit cell[13,15]); (B, right) hexagonal unit cell, same orientation;[11,12] (C) orthorhombic unit cell of aragonite, *c*-axis vertical, showing staggered orientation of trigonal carbonate groups.[11,14] Crystallographic models were generated using PLATON software.[11]

modated in the orthorhombic aragonite structure, in which cations are in 9-fold coordination to carbonate oxygens. Conversely, smaller cations such as $Mg^{2+}$ are found more frequently in the hexagonal calcite structure, in which the cation is in octahedral (6-fold) coordination with oxygen, each of which belongs to a distinct carbonate (Figure 1). These coprecipitation trends are at best qualitative statements, and observed distributions have shown poor fidelity with attempts to define partitioning on purely thermodynamic grounds.[4] In general, it is difficult to make robust statements regarding the incorporation of “trace” elements into carbonates: careful studies of partition coefficients show that these terms are in many cases dependent on both precipitation rate and tracer concentration, thus obviating the expectation of a unique Doerner−Hoskins[5] proportionality between surface solid and solution tracer/carrier ratios. This issue is discussed in detail in Morse and Bender.[6] In complex multicomponent solutions such as seawater, the potential for interactions *between* tracers also introduces significant additional complexity in understanding or modeling partitioning behavior.

Phases other than aragonite and magnesian calcite are of far less abundance and importance. Vaterite ($\mu$-$CaCO_3$) is metastable with respect to calcite and aragonite and limited to minor biogenic occurrences; hydrated $CaCO_3$ phases (e.g., ikaite) are found only in very low temperature, high-pressure environments. Solid solutions and double carbonates are discussed below.

It should be noted that temperature and pressure vary enough in the ocean to have a significant influence on carbonate mineral solubility and equilibrium constants for the $CO_2$−carbonic acid system. Extensive discussion of the influences of *T* and *P* can be found in refs 1 and 2.

### 2.2.2. $R\bar{3}c$ Carbonates: Calcite, Magnesian Calcite, and Related Phases

Numerous books and monographs already contain extensive reviews of the chemical and physical properties of calcite,[1,16] and this discussion will thus serve only as a relatively brief summary of the issues relevant to marine systems. The structure of the $R\bar{3}c$ carbonates is best seen using the hexagonal unit cell, with calcite as the example. If the *c*-axis of the calcite unit cell is oriented vertically, calcium cations form horizontal layers separated by planar $CO_3$ groups (Figure 1). The distribution of carbonate solid solutions within this structure primarily reflect differences in cation size.[13] Complete miscibility exists between $MgCO_3$, $FeCO_3$, and $MnCO_3$ end members, whose differences in ionic radius are $\leq$0.11 Å in octahedral coordination. $CaCO_3$−$MgCO_3$ miscibility is discussed in detail below. Magnesite ($MgCO_3$) is virtually unknown in open marine environments, and its properties are primarily of interest in terms of their relationship to the other magnesium-bearing phases. Divalent iron (siderite, $FeCO_3$) is relatively rare in normal marine environments, because Fe(II) is typically first sequestered as sulfidic phases during microbial sulfate reduction. Siderite is thus more typically found in non-marine reducing environments. In contrast, mixed calcium−divalent manganese carbonates are potentially important in reducing environments, and interactions of $Mn^{2+}$ with carbonate surfaces are reviewed in more detail below.

The influence of magnesium on the properties and behavior of calcite in seawater is a long-standing and fundamental problem. Several key issues hinge on the precise nature of this interaction: (1) the accurate expression of calcite solubility as a function of magnesium concentration in the lattice, (2) how the properties and behavior of abiotic magnesian calcite differ from those of their biotic counterparts, and (3) how these terms control the rate of dissolution and precipitation reactions. We discuss the last issue separately in the sections on precipitation and dissolution; calcite solubility and factors that contribute to measured variations thereof are discussed in detail below.

Demonstration of equilibrium typically requires approach from conditions of both over- and undersaturation. In seawater, however, significant coprecipitation of $MgCO_3$ generally results in a (abiotic) magnesian calcite ($\sim$11 to 14 mol % $MgCO_3$); *abiotic* precipitation of a pure, Mg-free calcite is not observed. This is expected: simple Gibbs−Duhem relations demand that the chemical potential of $MgCO_3$ in the solid (magnesian calcite) and aqueous (seawater) phase be equivalent at equilibrium. Uncertainty in the solubility of magnesian calcites has been a source of historical controversy, in part animated by basic disagreements as to the nature of the equilibrium condition with respect to this phase. Early attempts to measure magnesian calcite solubility adopted a somewhat controversial approach. For example, in free drift, pure water-fixed $pCO_2$ dissolution experiments, Plummer and Mackenzie[17] attempted to circumvent lengthy equilibration times by extrapolating solution activities to infinite time ($t^{-1/2} \rightarrow 0$).

This "kinetic" approach to true saturation is sensitive to the onset of incongruent reaction legs and, in general, has been regarded as somewhat controversial.[18] There is also the potential for large variability in the reactivity of biogenic phases, discussed below.

Formation of magnesian calcite can be expressed as

$$\mathrm{Ca}_{(1-x)}\mathrm{Mg}_{(x)}\mathrm{CO}_3 = (1-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+} + \mathrm{CO_3}^{2-} \tag{2.1}$$

where $x$ is the mole fraction of $MgCO_3$ in solid solution. One means of expressing the solubility of magnesian calcite is by writing the thermodynamic equilibrium constant for this reaction ($K$),

$$K_{\mathrm{mc}}(x) = a_{\mathrm{Ca}^{2+}}{}^{1-x} a_{\mathrm{Mg}^{2+}}{}^{x} a_{\mathrm{CO_3}^{2-}} \tag{2.2}$$

where $x$ is taken from eq 2.1 and $a_i$ is the activity of species $i$. The problem with this expression, however, is that it predicts relationships between the composition of the solution and the solid phase ($x$) that may not, in fact, exist. This can be seen by reorganizing eq 2.2 in terms of the cation concentration ratio, where $\gamma_i$ is the total ion activity coefficient of species $i$,

$$\frac{[\mathrm{Mg}^{2+}]}{[\mathrm{Ca}^{2+}]} = \frac{\gamma_{\mathrm{Ca}^{2+}}}{\gamma_{\mathrm{Mg}^{2+}}} \left( \frac{K_{\mathrm{mc}}(x)}{a_{\mathrm{Ca}^{2+}} a_{\mathrm{CO_3}^{2-}}} \right)^{1/x} \tag{2.3}$$

Putting aside for the moment the issue of activity coefficients, for a given calcium and carbonate ion concentration, we are still free to vary the left-hand cation ratio by changing magnesium concentration. For the equality to be preserved, however, the right-hand side of eq 2.3 would have to vary simultaneously in some complex fashion: the action of aqueous magnesium concentration (or activity) has no explicit representation here. More to the point, solid-phase composition ($x$) could be varied at no apparent expense to the left-hand side, implying an arbitrary range of possible solid compositions for a given cation ratio. This freedom is inconsistent with what is actually observed in seawater experiments (see below), where precipitation of calcite at a given Mg/Ca seawater ratio yields a unique solid-phase composition. Moreover the observed relationship of this solid with the solution cation ratio is linear in $x$.

In a theoretical treatment, Thorstenson and Plummer[19] argued that if magnesian calcite reacted as a solid of *fixed composition*, then the Gibbs–Duhem equality of chemical potentials of individual components (i.e., $CaCO_3$, $MgCO_3$) in solid versus aqueous phases no longer has meaning. In the case of a congruently dissolving magnesian calcite, this entails a loss of a degree of freedom because of the kinetic restriction of mass transfers of components with respect to the solid. Thorstenson and Plummer invoked the term "stoichiometric saturation" to describe this condition. It should be emphasized that because of this path constraint, stoichiometric saturation states would form a superset of the true (stable or metastable) equilibrium condition. In $CaCO_3$–$MgCO_3$ solid solutions, the primary point of their argument is that mere equality of the ion activity products (IAP) and $K_{\mathrm{eq}}$ (eq 2.2) may demonstrate stoichiometric saturation ($\mu_{\mathrm{Ca}_{(1-x)}\mathrm{Mg}_{(x)}\mathrm{CO_3(aq)}} = \mu_{\mathrm{Ca}_{(1-x)}\mathrm{Mg}_{(x)}\mathrm{CO_3(s)}}$) but is an otherwise insufficient demonstration of equilibrium ($\mu_{\mathrm{MgCO_3(aq)}} = \mu_{\mathrm{MgCO_3(s)}}$, $\mu_{\mathrm{CaCO_3(aq)}} = \mu_{\mathrm{CaCO_3(s)}}$). Thorstenson and Plummer applied this thinking to the earlier dissolution data of Plummer and Mackenzie[17] and concluded that true equilibrium, or for that matter stoichiometric saturation, was probably not achieved for calcites with substantial mol % $MgCO_3$: either condition would necessitate a solution Mg/Ca ratio or an $\mathrm{IAP_{calcite}}$ atypical of natural systems. They thus concluded that thermodynamic equilibrium with respect to magnesian calcite exists only for solids with less than ~5 mol % $MgCO_3$. Arguments regarding stoichiometric saturation with respect to the magnesian calcites have been debated extensively.[20–23]

Morse and Mucci addressed the issue of magnesian calcite solubility directly in a series of key experiments, taking a distinctly different approach from that described above (description of this work will also overlap with that of precipitation kinetics). Morse et al.[7] measured the solubility of pure calcite in contact with seawater for extended periods (from 5 days to 1 month). Their measured apparent constant for calcite ($K'_{\mathrm{sp}} = 4.39 \times 10^{-7}$ $\mathrm{mol^2\ kg^{-2}}$, see Table 1) was relatively consistent with other contemporary values, although less (~20%) than that computed from the thermodynamic solubility product for calcite and total activity coefficients for calcium and carbonate ion, a discrepancy they attributed to the formation of a magnesian calcite surface phase. This latter hypothesis was investigated in extensive experimental work,[24–26] and because of their bearing on how saturation develops between calcite and Mg-bearing fluids, we enumerate the principal findings of these papers in more detail below.

1. The extent of Mg uptake is a function of the solution concentration *ratio* $[\mathrm{Mg/Ca}]_{\mathrm{soln}}$, not the absolute concentrations of each component. Using data from pH-stat precipitation runs, Mucci and Morse[24,25] argued that the behavior could be best understood in the context of an "*exchange equilibrium*" between the crystal surface and the solution and between surface and the underlying crystal emphasis added. At low solution ratios ($[\mathrm{Mg/Ca}]_{\mathrm{soln}} < \sim 7.5$), surface adsorption of Mg is favored over Ca, such that $[\mathrm{Mg/Ca}]_{\mathrm{surf}} > [\mathrm{Mg/Ca}]_{\mathrm{soln}}$. Under these conditions, sorbed Mg has the greatest influence on the net incorporation of Mg into the overgrowth itself, and the ratio of $[\mathrm{Mg/Ca}]_{\mathrm{solid}}/[\mathrm{Mg/Ca}]_{\mathrm{soln}}$ is negatively correlated to the $[\mathrm{Mg/Ca}]_{\mathrm{soln}}$. The amount of Mg incorporated within the lattice in this region is significant but small, limited by the Mg content of the solution.[24]

2. As solution ratios increase ($[\mathrm{Mg/Ca}]_{\mathrm{soln}} > \sim 7.5$), the ratio of $[\mathrm{Mg/Ca}]_{\mathrm{solid}}$ to $[\mathrm{Mg/Ca}]_{\mathrm{soln}}$ approaches the constant value of a classical homogeneous distribution coefficient ($D_{\mathrm{Mg}}$). However, Mucci and Morse[24] argued that this observation was inconsistent with a simple Langmuir adsorption isotherm, because progressive saturation of surface sites should give rise to a variable $D_{\mathrm{Mg}}$ with increasing $[\mathrm{Mg/Ca}]_{\mathrm{soln}}$. They thus concluded that a feedback control is established at the growing crystal's interface, in which the formation of magnesian calcites having preferential affinity for magnesium establishes a dynamic equilibrium be-

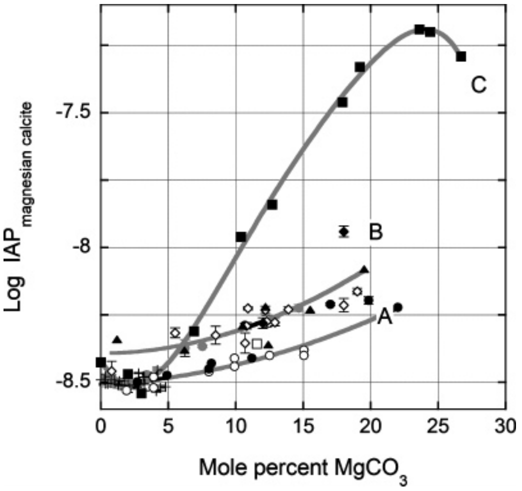


**Figure 2.** Solubility of magnesian calcite computed from eq 2.2. Data are from *synthetic* (gray solid circles, Busenberg and Plummer;[29] open circles, Bischoff et al.;[27] black solid circles, Mucci and Morse;[25] open squares, Lafon[30]), *natural inorganic* (crosses, Busenberg and Plummer[29]), and *biogenic* phases (open diamonds, Busenberg and Plummer;[29] closed triangles, Bischoff et al.;[27] closed diamonds, Walter and Morse;[18] solid squares, Plummer and Mackenzie[17] recalculated by Thorstenson and Plummer[19]). Trends A, B, and C are discussed in text. Adapted from ref 31 with permission. Figure was redrafted with data added. Copyright 1991 Mineralogical Society of America.

tween the solution, the surface, and the nascent overgrowth. Overgrowth composition may additionally reflect crystallographic control.[20]

3. The above data link a given $[\mathrm{Mg/Ca}]_{soln}$ with a corresponding $[\mathrm{Mg/Ca}]_{solid}$. In free drift experiments, Mucci and Morse[25] subsequently derived stoichiometric solubility constants from seawater solutions of variable $[\mathrm{Mg/Ca}]_{soln}$ equilibrated with pure calcite. On the basis of these results, they concluded that $MgCO_3$ coprecipitation does *not* change calcite solubility, as computed from the ion activity product for $CaCO_3$; if ion pairing is accurately represented, calcite saturation can be adequately described by the $CaCO_3$ ion molal product alone ($K'_c = [\mathrm{Ca}^{2+}]|_{eq}[\mathrm{CO_3}^{2-}]|_{eq}$); *cf.* eq 2.2). Furthermore, they introduced the notion that a "solubility-controlling" phase of invariant composition satisfied the exchange equilibrium identified above. Furthermore, Bischoff et al.,[27] in computing solid phase activity coefficients, concluded that magnesian calcites forming as overgrowths in Mucci and Morse[26] were indeed equilibrium phases. Most importantly, magnesian calcite solubilities, recalculated from these data according to eq 2.2, are substantially less than those measured compared with the biogenic phases measured previously (see below). These relationships are summarized in Figure 2.

In general, the solubility versus composition data show a solubility minimum at approximately 2 mol % $MgCO_3$, with increasing solubility thereafter. Although outstanding issues remain, the current consensus is that the solubility versus composition data (Figure 2) can be divided into three basic trends. The first trend (curve A) incorporates well-crystallized, inorganic solids from the work of Mucci and Morse[26] and Bischoff et al.[28] This curve defines the lowest solubilities for magnesian calcites, and the intercept at $x = 0$ of the fitted curve is very close to the accepted value for pure calcite (p$K$ = 8.48 at 25 °C). Although these data represent equilibrium approaches from both over- and undersaturated conditions and include material formed under both room temperature and hydrothermal conditions, the data set's overall variability is remarkably small. An important observation is that the increase in solubility with $x$ is sufficiently small that abiotically precipitated magnesian calcites with greater than or equal to ~20 mol % $MgCO_3$ are all less soluble than aragonite (see below).

The second trend (curve B) is a "best fit" through the biogenic, skeletal magnesian calcites.[18,27] These data show significantly higher solubilities (~0.15 differences in p$K$, or about ~1.1 kcal mol$^{-1}$), although the overall trend in $x$ is similar to that of the abiotic phases. The intercept at zero $MgCO_3$ also places this phase very close to aragonite and a 20 mol % $MgCO_3$ synthetic phase in solubility. The origin of this increase in free energy is unclear but may include substantial contributions from excess water and impurity defects (sulfate, hydroxyl, and bicarbonate); these contributions would be present independent of $MgCO_3$ content. In addition, it is well-documented that positional disorder of the carbonate anion (rotation out of the basal plane) is associated with both abiotic and biogenically formed magnesian calcites,[32] a trend that is also reflected in unit cell $c/a$ axial ratios. In general, the variation in solubility of biogenic calcites with $12 \leq x \leq 15$ mol % $MgCO_3$ is also greater than the corresponding variation in the synthetic phases. An important conclusion from these findings is that magnesium content is not an accurate predictor of solubility for biogenic phases. Reactivities of biogenic phases are thus most likely dominated by characteristics introduced directly or indirectly by the organism itself.

Most biogenic magnesian calcites from curve B in the 12−15 mol % $MgCO_3$ range are slightly more soluble than aragonite. However, these solubilities are substantially less than those recovered in the dissolution experiments of biogenic magnesian calcite by Plummer and Mackenzie,[17] subsequently revised by Thorstenson and Plummer,[23] in which 12−15 mol % $MgCO_3$ magnesian calcites exceed aragonite solubilities by a factor of ~5. These latter data (curve C of Figure 2) may likely reflect the influence of kinetic, rather than thermodynamic, factors, including the retention of reactive surface particles after minimal sample cleaning and lack of annealing but may also reflect reactivity in nature. These issues are also discussed in Bischoff et al.[33]

### 2.2.3. R$\bar{3}$ Carbonates: Dolomite and Other Double Carbonates

Dolomite $CaMg(CO_3)_2$ is the most important double carbonate. It is found primarily in marginal, restricted regimes that suffer extremes in terms of temperature, saturation state, or salinity or that otherwise differ from normal open marine environments. There are two oft-cited truisms involving this mineral. First, it is a significant component of ancient sedimentary carbonate rocks, in contrast to its meager present-day distribution. Second, there has been little success in synthesizing dolomite at low temperatures in the laboratory. These two observations are the basis of the oft-cited "dolomite problem". However, this perception may reflect inadequate recognition of (1) differences in laboratory versus geologic time scales and (2) strong environmental controls over carbonate mineral distributions. In general, we still require a better understanding of how ordered mineral phases form at low temperature and, in particular, how microbial communities may mediate these reactions.[34,35]

Determinations of the calcite−dolomite solvus at high temperatures show complete miscibility between pure calcite and carbonates of dolomite composition only above temperatures of 1075 °C.[36] Composition and cation ordering distinguish ideal dolomite from magnesian calcite. Phases that deviate from dolomite's cation stoichiometry (e.g., Ca/Mg > 1) and show enlarged unit cells and diffuse diffraction peaks are collectively termed "protodolomites". Graf and Goldsmith first used this label to refer to both synthetic and naturally occurring materials that would presumably react, given sufficient time, to form ideal, fully ordered dolomite.[37] Ordered dolomite is essentially a calcite structure in which every other cation layer is fully occupied by magnesium atoms. This results in a symmetry reduction ($R\bar{3}c \rightarrow R\bar{3}$) through loss of calcite's *c*-glide axis. In contrast, magnesium atoms in a magnesian calcite are not segregated to their own cation plane but substitute for calcium in a completely random manner. Sedimentary dolomites are often poorly ordered and calcium-rich, with increasing disorder detectable as a progressive weakening in the superstructure reflections (101), (015), and (021).[38] Other metal ions may also substitute for magnesium, notably iron and manganese; ferroan dolomite (ankerite) can accommodate a maximum of ~70% $CaFe(CO_3)_2$. The manganoan equivalent of dolomite, lying on the $CaCO_3$−$MnCO_3$ join, is termed kutnahorite ($CaMn(CO_3)_2$).[39]

We know of no solubility determinations for dolomite in seawater. Because of the large effects of ordering and composition, the uncertainties surrounding dolomite stability are quite large. Determinations of enthalpies of formation ($\Delta H_f^\circ$) of ideal, ordered dolomite vary by several kilojoules. Because the contribution of $T\Delta S$ at Earth surface temperatures is small (with good agreement on entropy determinations), these variations in measured enthalpy yield corresponding uncertainties in free energy. An early attempt to measure dolomite solubility by a similar approach to that described above for the magnesian calcites (extrapolation to infinite time) shows a very low value of (p$K_{25\,°C} = 19.7$[40]); current accepted p$K$ values range from 18.1 to 17.3. The effect of ordering and composition on dolomite stability has been investigated extensively by Navrotsky and co-workers.[41] Solution calorimetry[42] showed that enthalpies become strongly endothermic with increasing calcium enrichment; similar determinations for magnesian calcites[33] show negative enthalpies by comparison, so clearly calcite accommodates substantial lattice magnesium with far less loss of stability than dolomite accommodates calcium.

### 2.2.4. Orthorhombic Carbonates: Aragonite

Aragonite constitutes a major phase of marine sediments, occurring both as marine cement and as the principal skeletal component of many marine taxa. $Sr^{2+}$ and $Ba^{2+}$ are important coprecipitating cations for $Ca^{2+}$ in 9-fold coordination in aragonite. The solubility product for aragonite in pure (nonseawater) solutions is relatively well-known, with a p$K_a$ at 25 °C ranging from 8.34 ± 0.02[43] to 8.28 ± 0.02.[44] In seawater, determinations of the stoichiometric constant (p$K'_a$, note that $K'_a$ has units of mol$^2$ kg$^{-2}$) range from 6.09 ± 0.03[45] to 6.18 ± 0.02.[7] The substantially lower solubility found for aragonite by Morse et al.[7] reflects the exceedingly long equilibration time (2 months) used in their seawater determinations, as previously published determinations employed shorter (hours to days) periods. This measured value is 22% less than that predicted for aragonite solubility from thermodynamic solubility products (p$K_a$) and total ion activity coefficients in seawater; however, unlike the magnesian calcites, no recognizable difference exists between solubilities obtained from synthetic versus biogenic materials. It is critical to recognize the dependence of the apparent solubility product of aragonite on equilibration time (Figure 3). This result is observed consistently, is apparently reversible, and indicates unsolved complexities in the behavior of aragonite in seawater. The observed reduction in solubility may reflect the formation of a surface phase of (as yet) unknown composition and structure, although aragonite dissolution after extended exposure to seawater cannot obviously begin until seawater is undersaturated with respect to this putative solubility-controlling phase. A time-sensitive surface phase is also consistent with experimental results of Tribble and Mackenzie,[46] in which the composition of neoformed overgrowths are not constant but tend to alter with time as the nascent phase progressively excludes Mg from the lattice. Thus the solid-phase composition is both a function of time, and in the case of a calcite overgrowth, depth from the substrate. This problem also has direct bearing on the issue of "kinetic solubility" and the response of seawater saturation states to $pCO_2$ changes as discussed later in this paper.

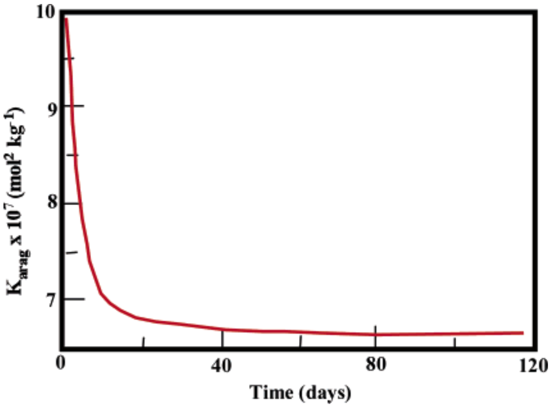


**Figure 3.** Trend of equilibration time and apparent solubility of aragonite. Modified from ref 7, Copyright 1980, with permission from Elsevier.

## 3. Carbonate Mineral Precipitation and Dissolution Kinetics Relevant to Seawater

### 3.1. General Overview

A successful approach to the general problem of calcite and aragonite reaction kinetics in seawater solutions must solve several difficult problems. These derive both from general issues related to the kinetics of mineral−solution interaction and from the specific properties of seawater and carbonate minerals as reactants. We give a brief overview of general concepts first and dwell on the latter in specific subsequent sections.

Although seawater chemistry is covered extensively elsewhere in this issue, before continuing we should make some brief remarks concerning the carbonic acid system in seawater and its relationship to carbonate mineral reaction kinetics. First, constraint of the carbon speciation in seawater requires a minimum of two measured parameters: pH, $pCO_2$, dissolved inorganic carbon (DIC), or total alkalinity (in addition to salinity or ionic strength, temperature, pressure, etc.). Dissolution or precipitation must at some point in the reaction sequence involve carbonate ion, and thus carbonate ion concentration and activity are clearly key quantities. The log activity of carbonate ion can be computed as the sum of $\log K_2 + \log \text{pCO}_2 + 2\text{pH}$.[1] However, this computed activity is relevant for the bulk solution; at the mineral surface itself, the distribution of surface and near-surface species reflects both equilibrium hydration and hydrolysis reactions, as well as the kinetics of the dissolving or precipitating mineral itself, and thus may differ significantly from the bulk solution.

## 3.2. Mineral Reactivity and the Mineral–Solution Interface: The Link Between Thermodynamic Driving Force and the Overall Rate

### 3.2.1. General Rate Equations

A governing principle in the chemical kinetics of precipitation or dissolution is that the overall process can be divided into a sequence of discrete reaction steps: (1) transport of material to the mineral surface from the bulk solution through some sort of boundary layer environment, (2) adsorption of reactive solutes to the surface itself, (3) surface diffusion, essentially a random walk down a concentration gradient to the reactive site, and (4) once the reactant arrives at this site, the reaction itself may proceed through a series of individual steps entailing bond formation or cleavage, ionic exchange with the solid, acquisition or loss of solvent water, and other steps. In the case of dissolution, the products of the reaction are original lattice components as solutes, which may then follow the reverse of diffusion and transport steps 3 through 1, resulting in their final departure from the surface to the bulk solution. Detailed treatment of these steps is available elsewhere.[47] Our key point here is that the slowest step in this series is limiting and thus determines the rate of the overall process. For the majority of carbonate mineral reactions involving seawater, the rate of integration or disintegration of ionic components at the reactive site itself is the slowest step in this chain. This limitation reflects the relative insolubility of most carbonate minerals, as well as the confined range of disequilibrium (extent of over- and undersaturation) in marine environments, at least within the water column. Thus in general, carbonate precipitation and dissolution rates in seawater are *surface-controlled*.

In order to understand variation in the rates of mineral surface processes, a basis must exist to evaluate reaction mechanisms and their relationship to primary environmental variables. The complexity of seawater poses a fundamental challenge in this requirement. A substantial number of observations now exist of the overall carbonate mineral reaction rate's dependence on saturation state, temperature, salinity, and other variables. However, these results have been understood primarily on an empirical basis, and conclusions regarding mechanism are often speculative. This limitation is slowly receding, however, with the integration of direct observations of the reacting mineral surface, discussed below. We preface this with a review of current rate equations.

Thermodynamic equilibrium establishes the limiting condition at which the overall reaction rate must be zero. As discussed at length in Lasaga[47] and other texts, the relationship of the equilibrium point and reaction rate is often illustrated through the application of detailed balancing. This approach implicitly recognizes the principle of microscopic reversibility, in which the maintenance of equilibrium provides that the forward reaction path followed by a molecular assembly be the reverse equivalent of the backward reaction. This condition allows the ratio of rate constants for these reactions to be related to the equilibrium constant. For example, if the reversible reaction of reactant R and product P are represented as the forward- and back-reactions,

$$\mathrm{R} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{P} \tag{3.1}$$

the forward and backward rates are proportional to the concentrations of R and P, respectively. At equilibrium, these rates will be equivalent: $k_+[\mathrm{R}]_{\mathrm{eq}} = k_-[\mathrm{P}]_{\mathrm{eq}}$. Under this equality the ratio of rate constants is proportional to the equilibrium constant,

$$\frac{k_+}{k_-} = \frac{[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{R}]_{\mathrm{eq}}} = \frac{\gamma_{\mathrm{R}}}{\gamma_{\mathrm{p}}} K_{\mathrm{eq}} \tag{3.2}$$

where $\gamma$ is the coefficient relating concentration and activity terms. This oft-described relationship provides a basic link between equilibrium thermodynamics and chemical kinetics. Lasaga[47] used detailed balancing to derive the general reaction for calcite dissolution,

$$-r = k_- \frac{A}{V} K_{\mathrm{sp}}{}^{n}(1 - \Omega^{n}) \tag{3.3}$$

Here $r$ is the rate, $A/V$ is the ratio of total mineral surface area to solution volume, and $K_{\mathrm{sp}}{}^{n}$ and $\Omega^{n}$ are the solubility product and saturation ratio ($\Omega \equiv a_{\mathrm{Ca}^{2+}} a_{\mathrm{CO}_3{}^{2-}}/K_{\mathrm{sp}}$) for calcite, respectively, both raised to the power of the parameter $n$. Equation 3.3 is identical to that derived by Sjöberg from experimental work with calcite in 0.7 M KCl solutions (pH 8−10), in which $n$ assumed a value of $^{1}/_{2}$.[48] However, this equation does not accommodate any dependency that the dissolution rate may have on the composition of the solution, other than that explicitly provided by the saturation state term. If it is assumed to hold over large changes in saturation state, it also makes an implicit assumption with respect to mechanistic control (see discussion below). In contrast, empirical expressions generally employed for the dissolution of carbonates represent the overall rate as[49]

$$-r = k \frac{A}{V} (1 - \Omega)^{n} \tag{3.4}$$

An equivalent expression for precipitation can be formed by a simple change of sign. As discussed in more detail in Morse and Arvidson,[50] eqs 3.3 and 3.4 clearly differ, particularly in terms of the function of the parameter $n$. In eq 3.4, $n$ is the order of the overall reaction; in eq 3.3, $n$ acts on the product of activities and thus operates identically on the activity of calcium and carbonate ion. The latter relationship reflects simple reaction stoichiometry in eq 3.3, where net steady-state dissolution must liberate equal amounts of oppositely charged lattice ions.

More generally, there is a critical distinction between "linear" rates, such as the following,

$$\pm r = \pm k_{\pm}(\Omega^{n} - 1) \tag{3.5}$$

where the − and + signs apply to dissolution and precipitation, respectively, and $n = {}^{1}/_{2}$, $n = 1$, etc.,[51,52] versus the commonly used expression in eq 3.4. Truncation of a Taylor series expansion for the free energy function in eq 3.5 (recall that $\Omega = e^{\Delta G_r/(RT)}$) shows that as $\Delta G_r$ approaches 0, $e^{\Delta G_r/(RT)} \approx \Delta G_r/(RT) + 1$, and the rate (written here as dissolution) thus becomes linear in free energy:

$$r = k(1 - \exp(\Delta G_r/(RT))) \rightarrow -n\frac{\Delta G_r}{RT} \qquad (3.6)$$

However, even close to equilibrium, our conventional expression, eq 3.4, for carbonate reactions remains nonlinear (assuming $n \neq 1$), and more generally

$$r = -k\left[\frac{|\Delta G_r|}{RT}\right]^n \qquad (3.7)$$

where $|\Delta G_r|$ denotes the absolute value of free energy, the negative sign applies to dissolution, and the positive applies to precipitation.[53] This is not a trivial point concerning the fitting of rate data, but a fundamental insight into the role of reaction mechanism. Lasaga elegantly emphasizes this point in terms of irreversible thermodynamics: expressions such as eqs 3.4 and 3.7 are inconsistent with the guarantee of microreversibility implied by eqs 3.1 and 3.2. Why? Because *dislocations are not equilibrium defects*;[47] if growth or dissolution of carbonate surfaces is limited at low super- or undersaturations, respectively, by nonequilibrium surface defect distributions, then these surfaces cannot be considered to be at equilibrium even for $\Delta G_r \approx 0$. Nielsen also suggested that rate equations having the general form of a concentration *difference* raised to some power (e.g., $r = k(c - s)^2$) likely reflect the nonlinear dependencies inherent in spiral dislocation-controlled crystal growth.[54] Thus, in the case of carbonates, both the general form of rate equations (eqs 3.4 and 3.7) and experimental evidence (see below) point to the fundamental role of defect control in both dissolution and growth kinetics. Limited attempts have also been made to express explicitly the rate's control by defect density.[55] Strained calcites have been used to show that the influence of dislocations could be accommodated by differentiating between perfect surface sites and dislocation sites, each characterized by distinct energy distributions and corresponding rate constants. Although reaction rate does not scale linearly with defect density, Schott et al.[56] found that dislocation densities greater than $10^7$−$10^8$ cm$^{-3}$ result in an increase in dissolution rates under near-equilibrium conditions.

Despite this evidence of nonlinear controls on reaction rate, many practitioners incorrectly use simple carbonate ion concentration difference terms to drive reaction rate expressions. There are additional reasons for application of first-order linear kinetics for carbonate precipitation and dissolution in seawater to be incorrect in practice: in addition to the potential variation of reaction mechanism with changing saturation state, dissolved impurities may play a fundamental role. For example, there is substantial evidence that dissolved magnesium and phosphate inhibit both precipitation and dissolution reactions in seawater (discussed below). Impurities may strongly influence the reaction rate itself via simple sorption but may also exert more complex, mechanistic controls, changing the nature of the rate's relationship to saturation state or controlling the mineralogy and composition of the phase that nucleates on pre-existing crystal surfaces. Surface interactions with impurities are not understood in detail, although recent experiments suggest possible reasons for this inhibition to couple strongly with saturation state. In addition, simple first-order expressions are virtually certain to fail in pore water environments where the constancy of major ion ratios is not maintained.

A more general rate equation can be used to represent the action of catalyst and inhibitor species, and Lasaga[57] has suggested the following form to accommodate these terms:

$$r = kAg(I)\prod_i^N a_i^{n_i} f(\Delta G_r) \qquad (3.8)$$

Here the Arrhenius temperature dependence can be shown explicitly as

$$k = k_0\, e^{E_a/(RT)} \qquad (3.9)$$

where $k_0$ is the intensive, temperature-independent prefactor, $E_a$ is activation energy, and $A$ is *reactive* surface area. This expression, applicable to both precipitation and dissolution, provides a means of calibrating the effect of ionic strength, $g(I)$, independent of that provided by the use of activity coefficients, as well as $a_i$, the action of $N$ inhibitors, catalysts, proton activity, etc. The term $f(\Delta G_r)$ is the free energy term describing the rate's functional relationship to disequilibrium. If we neglect the inhibition and ionic strength terms, replace $f(\Delta G_r)$ with a saturation state function, administer signs such that $\Delta G_r$ corresponds to the dissolution reaction, and allow the rate constant $k$ to collect the (reactive surface) area and volume terms, we effectively recover our conventional expression (eq 3.4),

$$r = -k(1 - \exp(\Delta G_r/(RT)))^n \qquad (3.10)$$

With increasing undersaturation, $\Delta G_r \rightarrow -\infty$, $f(\Delta G_r) \rightarrow 1$, and the dissolution rate approaches a constant value $k$, the dissolution plateau. With increasing oversaturation, that is, $\exp(\Delta G_r/(RT)) - 1$, the precipitation rate increases exponentially; however, the precipitation or crystal growth rate obviously cannot increase infinitely. As sufficient difference in chemical potential develops, new heterogeneous and ultimately homogeneous crystal nuclei will appear whose minimum size reflects the system's critical radius (discussed in terms of Gibbs−Thompson relations in nucleation below). Note that although the form of the equations described above permits application to both growth and dissolution, different values of $k$ and $n$ would obviously be used for each.

### 3.2.2. Relationship to Mineral Surface Processes

At the core of the existing theoretical framework for surface-controlled reaction rates is the concept of surface free energy distribution. Because precipitation or dissolution rates bear an exponential energy dependence (see previous rate equations), heterogeneity in this distribution potentially gives rise to large variations in rate over the mineral surface. This heterogeneity reflects the physical distribution of dislocations in the crystal (plane, line, and point defects, see Figure 4). Seminal work by Burton et al.[58] recognized the central role of screw dislocations in terms of providing a continuous source of atomic surface steps during crystal growth. More recently, direct surface observations of the cleavage surfaces of rhombohedral carbonates[59−61] have shown that step movement can be related to the overall rate measured in bulk solution (see also Figure 5). The symmetry relations of kink and step geometry in calcite also controls

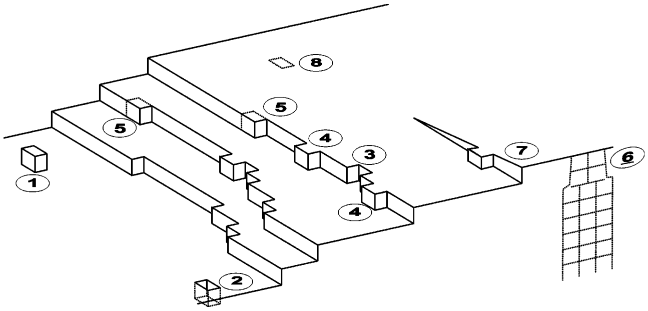


**Figure 4.** Schematic view of defects and specific sites on a crystal surface: (1) terrace adatom; (2) terrace vacancy; (3) step vacancy or "double" kink site; (4) step adatom; (5) single kink site; (6) outcropping edge dislocation; (7) outcropping screw dislocation; (8) imminent hole.

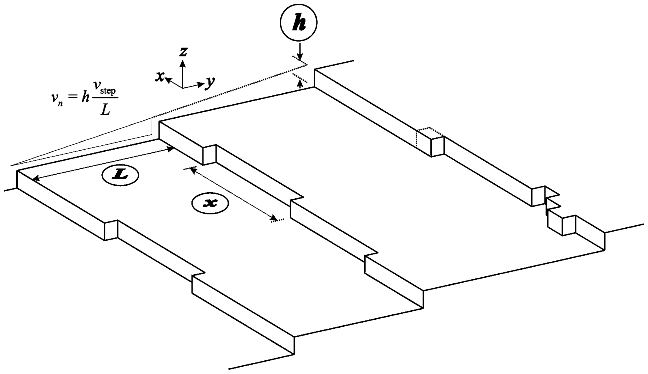


**Figure 5.** Schematic representation of parameters relating crystal growth and dissolution rate with bulk rate: surface step height, *h*; kink spacing, *x*; interstep spacing (terrace width), *L*.

site-specific uptake of impurities. The control of step velocity, the manner by which steps propagate, and the overall distribution of steps on the surface (step density or spacing) is thus the link between reaction mechanism and its phenomenological expression as a material flux between mineral and solution.

Recognition that the speciation of surface sites may be correlated with the reaction kinetics has led to the development of the *surface complexation model*, developed and initially applied to calcite dissolution by Van Cappellen et al.[62] This model is entirely analogous to the system of relating the distribution of aqueous complexes and ion pairs by equilibrium mass and charge balance expressions. Thus the ratio of surface complexes varies in concert with that of dissolved carbonic acid species, establishing a relationship between the surface concentrations and dissolved activities, and yielding potential insight into surface-controlled reaction kinetics. For example, Arakaki and Mucci[63] derived a general rate equation for calcite dissolution and precipitation in simple solutions through application of this model to diverse datasets. This general approach has also been campaigned as a general solution to the problem of variation in carbonate mineral reactivity, arguing that dissolution reaction kinetics can be described in the context of rate-controlling surface complex distributions.[64] Recent attempts have also been made to integrate this model with mineral surface observations.[65] However, under conditions where reactive transport control becomes important, uncertainties in evaluating the diffusion of carbonic acid species may make this approach problematic. In addition to providing no means for transport via surface diffusion, this approach also contains no intrinsic description of the variation in reactive site distribution (e.g., attachment/detachment at kink sites and steps versus terraces). This issue is discussed later in the text, as well as in Morse and Arvidson.[50]

Although the previous section has emphasized the importance of understanding reaction mechanism and its relationship to saturation state, there is currently no over-arching theoretical framework that would relate the form and parametrization of rate equations driven by seawater saturation state to surface reaction mechanisms. Most experimental measurements of mineral reaction rates, for example, in a laboratory flow-through or batch reactor, are done through evaluation of changes in the composition of the bulk solution. Changes in the mineral surface, and thus the link between rate and mechanism, are not observed directly. There is also a long-standing recognition of the problem of surface reactivity distribution, described briefly above and discussed in more detail below in section 3.2.4. These limitations have given rise to an increasing interest in understanding the relationship between the macroscopic or "bulk" rate and mineral surface processes through direct observation, sponsored initially by the advent of the atomic force microscope (AFM[66,67]). The AFM has been used extensively on calcite,[61,68−73] magnesite,[74] and dolomite[75] because of the relative ease of generating excellent cleavage surfaces. In concert with a suitable fluid cell, AFM permits direct, nanoscale observation of real-time precipitation and dissolution reactions. In fluid, AFM provides angstrom-level vertical resolution at nanometer-scale lateral resolution. Rates are typically measured by comparison of fixed area raster images as a function of time. This practice limits the measurement of very fast rate; conversely, measurement of very slow rates is a function of the lifetime of the cantilever tip. However, there are problems associated with the extrapolation of AFM step velocities to surface-area-specific rates measured by conventional powder methods: e.g., the relationship of step velocity to a surface-normal velocity is given by (Figure 5)

$$v_n = h\frac{v_{step}}{L} \tag{3.11}$$

where $v_n$ is the surface-normal velocity, *h* is step height (e.g., 0.3 nm for calcite), $v_{step}$ is the velocity of the step, and *L* is the average step spacing. Although measurement of the step height is a trivial matter for the AFM, step spacing is a dynamic property and thus requires care in acquisition. In addition, there is the more important problem of how localized measurements, conducted over small regions of the mineral surface for brief duration, can be applied to larger space and longer time scales. This problem is a fundamental one and is discussed in more detail in sections 3.2.4 and 3.2.5 below.

### 3.2.3. Treatment of Kinetic Inhibition

There has been recognition of the strong potential role of reaction inhibitors on carbonate mineral reaction kinetics since the early work of metal inhibition of calcite dissolution by Weyl[76] and Terjesen et al.[77] The problem with using past results to form an overall, integrated understanding of the role of inhibitors is the lack of a "standard model" for comparing work in disparate bulk solution compositions, saturation states, temperatures, solid preparation, etc. Thus much of the existing results can be compared only on a qualitative basis. Because of the nonlinear nature of both growth and dissolution kinetics in carbonates in terms of free energy control discussed previously, comparison of the extent of inhibition at similar inhibitor concentrations but different $\Delta G_r$ is neither practical nor desirable.

The theoretical treatment of inhibition on a surface derives from a number of competing model approaches, for which the distinction hinges on the reversibility of the adsorption step. The Langmuir−Volmer model[78] assumes that a reversible Langmuir adsorption isotherm prevails on the surface. Although this model is often employed as a means of interpreting inhibition, the reversibility requirement may often not have been demonstrated. In contrast, the "dead zone" model of Cabrera and Vermilyea[79] assumes irreversible adsorption of impurities on terraces or step edges. When this scenario is applied in the context of crystal growth, advancing steps are pinned and thus blocked from further advance as impurities are encountered. Step pinning creates a "curved" step whose radius exceeds a critical value (see discussion on nucleation below). The reduction in step velocity leads to a subsequent increase in saturation state of the solution because of the reduced demand for lattice ions; when oversaturation is sufficient, the pinned steps are able to break the impurity barrier and resume migration. As bulk impurity concentrations increase, the "dead zone" of step pinning may increase proportionally.

If impurities bind irreversibly at appropriate surface sites, they may be physically incorporated within the solid during crystal growth. In this scenario of impurity incorporation, this produces a defect, resulting in a change in the strain field of the crystal lattice and thus increasing the solubility of solid crystal itself at this site (e.g., Davis et al.[72]). This action results in a decrease in the driving force ($\Delta\mu$ between solid and solution), and step velocity $v$ is decreased by a factor of $1 - r^*/r$, where $r^*$ is the critical radius (see below), relative to the pure, impurity-free crystal growth system ($v_\infty$). In crystal dissolution, attachment of an impurity at a kink site, rather than increasing strain, may conversely have the effect of stabilizing the site against further detachment, thus interfering with kink detachment dynamics and preventing proper step flow. As a whole, impurity interaction with carbonate surfaces is a very complex topic, because it involves both the surface chemistry and the changes brought about by variations in solution composition; see Gutjahr et al.[80] for a more detailed discussion.

### 3.2.4. Mineral Reaction Rates and Surface Area

The following discussion is an abbreviated version of the one presented in Lüttge,[81] and we refer the interested reader to this book chapter for a more detailed discussion. Fluid−mineral interactions, for example, dissolution and growth processes of carbonates and other minerals, can be observed in two principally different modes, either directly at the solid−liquid interface or—what has been the standard procedure in the past—indirectly through changes in the solution chemistry. For a variety of reasons most laboratory studies that were designed to investigate reaction kinetics have successfully focused on the solution chemistry and its changes. By increasing the ratio of crystal surface area to reactor volume, even very slow rates become measurable. This is important because slow reaction rates on the order of $10^{-8}$−$10^{-16}$ mol m$^{-2}$ s$^{-1}$ are often characteristic for mineral dissolution and growth reactions at Earth surface temperatures. Analytically and experimentally, the indirect approach is often easier because the result of many microscopic processes can be quantified at a larger scale over longer periods of time. Thanks to the dedication of many experimentalists, we can build today on a large pool of rate data and observations (e.g., White and Brantley[82] and references therein; Morse and Arvidson[50] and references therein).

The left-hand sides of eqs 3.3−3.7 are equivalent to the "bulk" rate, expressed as a function of free energy ($\Delta G$) implicitly or explicitly proportional to surface area ($A$). The bulk rate constant $k$ may also assume, in addition to temperature, additional dependencies related to solution composition. Experimentally measured bulk rates have also been expressed in terms of the formation of surface molecular complexes by surface reaction with solution species, applied primarily to dissolution.[63,83−92] This approach highlights the chemical bonding properties of mineral surfaces, as well as the role of adsorption−desorption steps on the crystal dissolution rate. The equilibrium distribution of surface complexes has been used to predict the pH dependence of the rate. The molecular approach, therefore, has emphasized the role of *surface speciation* on mineral surfaces as a function of solution composition and temperature. The model then tries to identify particular surface complexes whose activities limit the overall dissolution rate.[87,92,93]

All experimental studies that use the indirect approach have one major problem in common: all rates are integrated over the entire mineral surface. Thus, these experiments cannot resolve the surface distribution of the integrated rate, the reaction mechanism cannot be observed directly, and surface area in contact with the solution has to be quantified and rates must be normalized by the *relevant* surface area. The quantification of the relevant surface area, however, has proven to be a nontrivial problem and one of concern.

A challenge is already the definition of the "correct" surface area with which to normalize the bulk rates or fluxes measured experimentally or in nature. Authors such as Hochella;[94] Brantley et al.;[95] Brantley and Mellott;[96] Jeschke and Dreybrodt,[97] and most recently Lüttge[98] have discussed this problem in detail. Unfortunately, this problem remains still largely unsolved and indicates that our understanding of the processes at the mineral−solid interface is not yet sufficiently advanced to provide a satisfying theoretical description.

Independent of this fact, as long as mineral−fluid reactions are surface-controlled, we need to normalize bulk reaction rates, $R$, by the surface area involved in the process to obtain a rate constant, $k$, in units of moles per square meter per second. This rate constant is important because it is a critical input parameter for any kinetic model, and, therefore, a prerequisite for our predictive capabilities. Consequently, the quantitative treatment of surface area has been given considerable attention in the geochemical literature.[94,97−99] Theoretically there are at least three different quantities: (1) geometric area, (2) total or Brunauer−Emmett−Teller (BET) surface area, and (3) the "reactive" surface area. In this context, we can only summarize the discussion. Currently, only so-called BET surface area[100] is a robust measurement. Geometric surface area is merely an abstraction or estimate, and *reactive* surface area is problematic and more of a conceptual tool than a directly measurable quantity. Geometric surface area is usually calculated from the crystal dimensions and ignores surface roughness (cf, Anbeek[101]).

This calculation may also involve assumptions of an ideal geometric body, such as a cube, rhombohedron, or sphere. If the geometric surface area is calculated for a mineral powder, it will depend on the way the average grain diameter of the grain population is computed. Because of the nature of grain size distributions, it is likely that an estimate of geometric surface area derived from a model underestimates the true value.

The term "total surface area" is often used synonymously with BET surface area, which is measured by gas-adsorption techniques developed in 1938 by Brunauer, Edward, and Teller.[100] The extent to which the BET surface area measurement reflects the total surface area is a function of both the gas used and the structure of the solid surface. Unless the crystal surface is atomically flat, that is, there is no surface roughness, the total/BET surface area is always larger than the geometric surface area. Consequently, the calculated reaction rate constants in moles per square meters per second are slower than they would be by normalization with geometric surface area. This is discussed in detail by Lüttge.[98] These model calculations show that the differences between different types of surface area measurements may change significantly during a dissolution reaction due to the development of etch pits and other dissolution features.

In general, the surface area (however described) will change over the course of a reaction. The extent to which the surface is self-modifying reflects the balance between two competing processes: (1) a particle's tendency to minimize its total surface energy and exposure to the solution by reducing its area to volume ratio and (2) the mechanistic restriction of possible paths by which the bulk free energy can be minimized, through material transfer to solution through propagation of kinks, steps, and etch pits, which tend to increase the surface area.

The situation may be significantly complicated if we take into account that the mineral surface is usually not homogeneously reactive, and thus certain areas of the crystal surface react faster than other areas. This has been observed by scanning electron microscopy (SEM), AFM, and vertical scanning interferometry (VSI) studies, which often show the formation of etch pits, hillocks, and other features at crystal surfaces during the reaction process. These features are often linked to some microdamage within the crystal lattice (e.g., microcracks) or lattice dislocations (e.g., line defects such as screw dislocations or edge or point dislocations) that form high-energy sites at the crystal surface. The observation that some parts of the surface are significantly more reactive while others remain more passive has led to the idea of reactive surface area.[48,94,102] Unfortunately, this term is merely of conceptual importance because it is currently impossible to measure reactive surface area. It is usually assumed that the reactive surface area value is a fraction of the total surface area. However, Lüttge[98] has raised the question whether reactive and total surface area can even be compared directly suggesting that the correct description of reactive surface area would require an energy term in addition to the geometric term expressed in area units. In current rate equations, this reactivity term is usually "buried" in the rate constant and may account for the wide range of values reported for the same mineral at similar conditions.[103] In this context, the development toward an often assumed quasi-steady-state surface may be questionable. These questions should motivate a reappraisal of our current approach that we take to quantify surface area.

#### *3.2.5. Dependence on Distance from Equilibrium and Scaling*

After we have correctly quantified and applied the surface area to the normalization of reaction rate, any quantitative treatment of processes involving fluid flow and mineral reactions needs to extract a crystal dissolution or growth rate law or both from these experimental data. This approach must include the possibility of approaching mineral−fluid equilibrium. While many computer models routinely input such rate laws,[104] the experimental studies of mineral dissolution reactions have not provided definitive results in many cases,[105] except for conditions that are quite far from equilibrium. Unfortunately, in natural systems, such far-from-equilibrium conditions are not very common. For mineral dissolution, this situation would be represented by the so-called "dissolution plateau", where the dissolution rates of minerals become usually independent of the difference in Gibbs free energy ($\Delta G$) (for further information see, Lasaga[47]). However, extrapolation of laboratory data to natural conditions necessitates a description of the kinetic changes expected as conditions approach near-equilibrium conditions. Recently, Beig and Lüttge,[106] Dove,[107] Hellmann,[108] and Lüttge[109] have presented new experimental results and theoretical discussion seeking to address this topic. However, the application of laboratory data to natural systems remains often difficult or even unsuccessful.[110−112]

With the $\Delta G$ dependence of the dissolution reaction rate, the surface area quantification, and our common struggle of how to link experimental observations at atomic or near-atomic scales to bulk dissolution rates, we have identified the major reasons for potential failure in transferring laboratory data to natural systems. The latter problem results from the fact that results of interface processes at the molecular scale can be observed at a variety of different time and length scales. And independently of the scale at which the rates are measured, they need to be extrapolated, compared, or applied to a largely different scale. Therefore, a major goal must be to generate an understanding of reaction kinetics that it is fundamental enough to provide the theoretical concept that allows us to link the processes and their rates over the entire range of scales, both in time and length. Ultimately, this will be the prerequisite for a general applicability of laboratory data to natural systems.

## 3.3. Precipitation of Carbonate Minerals from Seawater and Related Solutions

### *3.3.1. General Remarks*

There is a substantial theoretical and observational underpinning to the general understanding of precipitation reactions available from the crystal growth literature. This focus on precipitation and growth derives from the obvious practical value of controlling reaction yields in industrial crystallizers and chemical process reactors. However, application of this understanding to precipitation reactions involving carbonate minerals in seawater has been limited. The reasons for this should be at least partly evident from the discussions in the previous section on solubility: the behavior and reactivity of aragonite and magnesian calcite phases in seawater are strongly influenced by as yet incompletely understood surface reaction mechanisms and potential formation of "solubility-controlling" surface phases that differ in reactivity from the bulk mineral, making even simple seawater solubility determinations problematic. Because of the nature of the relationship between free energy and surface-controlled dissolution and precipitation rates introduced in the preceding subsection, progress has in general been greater in understanding carbonate mineral dissolution versus precipitation, in simple solutions versus complex brines, in part reflecting the significant laboratory challenges in precipitation work due to the difficulty in controlling reaction path.

Second, the bulk of carbonate precipitation in seawater is skeletal, and organisms may orchestrate processes of precipitation and crystal growth (biomineralization) through sophisticated regulation of an internal chemistry that may depart significantly from the “constant ionic medium” of seawater. Marine calcifiers may thus be able to accomplish skeletal growth in seawater solutions at rates that depart significantly from those predicted by the “baseline” process under strict abiotic control.

Third, both precipitation and dissolution reactions in seawater are also strongly influenced by inhibition. Although quantifying this inhibition in terms of net reaction rate may be straightforward, a fundamental understanding of this process in seawater ultimately requires knowledge of the actual inhibition mechanism. This knowledge in turn requires insight into the role of free energy (i.e., lattice ion activities) as a driving force versus that of specific dissolved or surface “impurity” species. Because growth surfaces inherit their own substrates, precipitation reactions reflect dynamic controls imposed by feedback interactions between mineral surface configuration and seawater solutes. It is only relatively recently that sufficiently sophisticated thermodynamic models have been available that simultaneously accommodate the strong seawater electrolytes, the potential inhibitors that may be present over a large concentration range, and the additional complexities imposed by the carbonic acid system itself. Below, we adopt a “divide and conquer” strategy in an effort to parse what is understood about the individual roles of the principal physical parameters and chemical components that exert fundamental control over the rate and fate of carbonate mineral precipitation.

### 3.3.2. Saturation State Controls and Their Relationship to Inhibition

As described in the previous section, seawater saturation state, $\Omega$ (expressed as IAP/$K$ or ICP/$K'$, where ICP = ion concentration product), occupies a central role in the rate equations for carbonate mineral precipitation. We should be careful to distinguish between controls on homogeneous and heterogeneous nucleation and precipitation. Homogeneous nucleation from solution occurs in the absence of pre-existing surfaces and thus must involve initial formation of precursor phases whose assembly and growth will progress toward the properties of the bulk crystal. The supersaturation required for sustaining this process is described by the Gibbs−Thompson (also Ostwald−Freundlich) equation (discussed below), representing a balance between the decrease in free energy incurred by dint of the phase transition itself versus the penalty of work (surface tension) expended in the construction of new surface area. With increasing supersaturation, the minimum (critical) radius of nuclei that can survive subsequent disassembly decreases. We will discuss the possible controls on nucleation rates below. In contrast, heterogeneous precipitation, such as an overgrowth, involves addition of material to a preexisting (large) surface.

The action of inhibitors greatly complicates the relationship between free energy and the observed rate; rate equations may attempt to isolate this effect by casting inhibitor concentrations outside the $\Delta G_r$ term (e.g., eq 3.8). However, we should note that there is a gap between what can be incontrovertibly demonstrated in terms of the mechanistic role of impurities and what model assumptions are. In the classic crystal growth model of Cabrera and Vermilyea[79] described previously, adsorption of impurity ions at step edges or terraces blocks proper step advance until sufficient supersaturation is available and step motion can resume: step pinning is what is actually observed. Adsorption of impurity ions may decrease the difference in chemical potential between the solid and the solution, thus depressing the driving force for reaction. Depending on saturation state, growth (and dissolution) processes may not be active everywhere on the surface, but limited to high-energy sites; competitive impurity attachment at these sites can effectively shut down the net reaction even at low relative coverage. If impurities are incorporated with the growing lattice, this reduction can be accomplished through the generation of defects (e.g., misfits or dislocations) that destabilize the surface through an increase in the local strain field. Alternatively, dissolved impurities may simply decrease the IAP through homogeneous formation of a ligand involving a growth ion (e.g., $MgCO_3^0$ formation).

These potential complexities between inhibition and saturation state are manifest in both precipitation and dissolution reactions. If introduction of the inhibitor does not alter the actual reaction mechanism (reflected in a reaction order with respect to ion activity product or a given component thereof that is independent of inhibitor concentration), the observed rate will still obviously suffer. In the canonical expression of the seawater precipitation rate, that is

$$r = k(\Omega - 1)^n \tag{3.12}$$

introduction of inhibitors (magnesium, sulfate) may change the rate constant ($k$) but not the reaction order ($n$). Alternatively, variation in inhibitor concentration may give rise to little change in $k$ but produce significant changes in reaction order (e.g., phosphate). Our point here is that the overall compositional sensitivity of reaction rate parameters is a function of the specific inhibitor. We discuss these effects separately in the sections below.

### 3.3.3. The Effect of Salinity and Ionic Strength

The effect of salinity and ionic strength on calcite precipitation rate has been extensively investigated in a variety of solutions.[113,114] Relatively recent results are available from Mucci and co-workers. In synthetic seawater, Zhong and Mucci[115] found that calcite precipitation rates were essentially invariant as a function of salinity ($S = 5-44$, $\Omega > 2.6$, $pCO_2 = 10^{-2.5}$), permitting a single fit to eq 3.12. As an aside, Mucci[8] also investigated the effect of salinity on the stoichiometric solubility products, finding that the solubility products of both aragonite and calcite tend to increase with increasing salinity in a similar fashion. Zhong and Mucci[115] also found that aragonite precipitation rates tended to decrease (2.5−5×) with increasing salinity, although this decrease was only observed for $S \geq 35$. Further evaluation of the ionic strength sensitivity of calcite precipitation rate was extended in subsequent work by Zuddas and Mucci.[116] In this work, they also attempt to formulate a rate law on the basis of carbonate ion and describe calcite’s net precipitation rate as a balance between forward (f) and backward (b) reactions,

$$r = k_f a_{Ca^{2+}}^{\ n_1} a_{CO_3^{2-}}^{\ n_2} - k_b \tag{3.13}$$

Zuddas and Mucci reorganized this expression to yield a function of carbonate ion concentration only:

$$\log(r + k_b) = \log K_f + n_2 \log [CO_3^{\ 2-}] \tag{3.14}$$

where $K_f$ contains both activity coefficients for calcium and carbonate ion and is thus a function of ionic strength. This separation of terms showed that as ionic strength is varied over a large range (0.1 mols/kg $\leq I_z \leq$ 0.93 mols/kg), the reaction order with respect to carbonate ion, $n_2$, and the forward reaction rate constant, $K_f$, both increase. These experiments also vary $I_z$ in $NaCl-CaCl_2$ solutions and thus show the effect of ionic strength independent of the inhibiting effect of magnesium and sulfate (see below). Zuddas and Mucci[116] argued that the positive effect of ionic strength on precipitation rate could *not* be understood as a simple consequence of a decrease in the energetic costs of dehydration associated with decreasing water activity; the decrease of $a_w$ is too small as ionic strength increases.

### 3.3.4. The Role of Temperature

Variation in temperature affects precipitation reactions in two fundamental ways. First, temperature is assumed to influence fundamentally the reaction rate constant through the classical Arrhenius equation,

$$k = A \exp(-\epsilon_A/(RT)) \tag{3.15}$$

Here $A$ is a prefactor term (assumed to be independent of temperature), and $\epsilon_A$ is the activation energy. At the risk of some repetition, we emphasize that precipitation rates as measured in seawater reflect overall, and not elementary, reactions. Although some observational constraints exist, the reaction mechanisms by which, for example, a magnesian calcite, aragonite, or protodolomite forms on a molecular basis are largely unknown. For magnesian calcite, variations in temperature could potentially give rise to variations in reaction mechanism, leading to respective differences in temperature dependency ($\epsilon_A$) as well.

Second, mineral solubility and the equilibrium distribution of dissolved species (ion activity product) are both temperature-dependent, and thus temperature variations even at fixed composition give rise to variations in the driving force for the reaction as well. The solubility of all pure carbonates decreases with increasing temperature. In the case of a precipitating magnesian calcite, temperature also affects the extent to which magnesium dissolves in solid solution (see preceding section on the relationship of magnesium content to calcite solubility). Early experiments all showed positive increases in magnesium content of calcite with respect to temperature.[117−120] As mentioned previously, the composition of magnesian calcite overgrowths formed in 25 °C seawater depended solely on Mg/Ca solution ratio and was independent of rate or seawater saturation state.[24,26] The explicit role of temperature in controlling overgrowth composition and rate of magnesian calcite precipitation was subsequently explored in Mucci.[121] When plotted versus temperature (Figure 6), these results confirm a positive temperature dependence on the extent of magnesium uptake, with a similar slope as that observed in previously cited work, although with significant variation in intercept. With the exception of the results of Fuchtbauer and Hardie,[120] these synthetic compositions also lie outside the domain of the common magnesian calcite cements in modern oceans, leading Mucci[121] to conclude that temperature variations are of insufficient strength to explain the natural distribution of abiotic marine calcite cement composition. However, temperature may have a more important effect in determining the mineralogy of the phase that initially nucleates in seawater; this aspect is discussed in section 3.3.8.

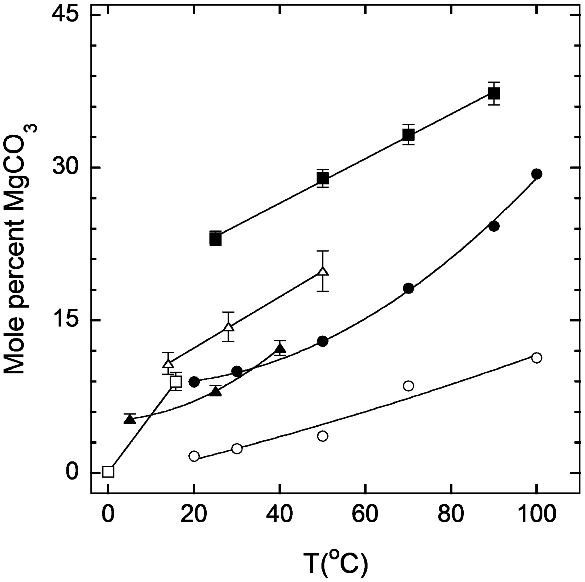


**Figure 6.** Variation of $MgCO_3$ content of magnesian calcite with temperature, precipitated in seawater or seawater-like solutions, adapted from Mucci[121] (see Mucci[121] for references to original data). Solid squares are $CaCl_2 + MgCl_2 + NaCl$; solid circles are seawater + $Na_2CO_3$ + $Ca(HCO_3)_2$; open circles are seawater + $Na_2CO_3$; open triangles are $CaCl_2 + MgCl_2 + Na_2CO_3$; open squares are seawater + $Na_2CO_3$ + aragonite seeds; solid triangles are seawater + calcite seeds. Reprinted from ref 121, Copyright 1987, with permission from Elsevier.

### 3.3.5. The Roles of Magnesium and Sulfate

As discussed in the previous sections, the effects of magnesium, although well-documented, are complex and poorly understood from a mechanistic standpoint. We summarize those effects here in terms of the relevance to precipitation reactions:

1. Lattice incorporation of magnesium in both naturally occurring abiotic and biogenic calcite results in a more soluble phase, provided that solubility is computed according to eq 2.2; however, this increase may be accompanied by little relative change in the activity product of calcium and carbonate ion. In seawater, magnesian calcite composition appears to be primarily controlled by the Mg/Ca ratio of seawater and is otherwise largely independent of saturation state and precipitation rate. If variations in $MgCO_3$ composition exist in a given overgrowth, these differences may drive selective, time-dependent *dissolution* of more soluble compositions during subsequent equilibration episodes.[45]

2. At a given mole percent of $MgCO_3$, abiotic (synthetic and marine cement) phases are less

> soluble than biogenic marine calcites. The work of Bischoff and co-workers[21,22,122] and Gaffey[123] demonstrates that regardless of magnesium content, biogenic calcite contains variable water and exhibits more carbonate ion and cation disorder compared with synthetic phases. In an extensive review, Morse and Mackenzie[1] concluded that the structural and compositional heterogeneity of biogenic magnesian calcites, together with additional complications such as $Mg(OH)_2$ inclusion,[124] in general warranted their exclusion from conventional determinations of thermochemical stability.

Although our understanding of the mechanism of magnesium incorporation is sufficiently limited as to preclude definitive statements, there is some evidence that magnesium may play a role in terms of introduction of water into the calcite structure. For example, Lippmann[125] suggested that water molecules may be incorporated in magnesian calcite due to the large amount of energy required to completely dehydrate the $Mg^{2+}$ ion during precipitation. The incorporation of water and its possible correlation with magnesium content is also consistent with spectroscopic data,[16,123] leading to the hypothesis of a “hydrated magnesian calcite”.[1] Excess water may also exist in biogenic phases poor in $MgCO_3$, suggesting that calcium ion may also be partially hydrated. This mechanism would also be temperature-sensitive, because complete dehydration and incorporation of anhydrous calcium and magnesium ions into the solid would become increasingly difficult with decreasing temperature.[121,126,127]

In contrast to its affinity for calcite, magnesium has a significantly lower affinity for the aragonite surface. Mucci and Morse[128] were able to use profiling Auger spectroscopy to demonstrate that in supersaturated seawater, magnesium shows more than an order of magnitude less adsorption on aragonite surfaces compared with that on calcite. In addition, although increasing saturation state ($\Omega$) leads to a slight increase in the adsorbed $Mg^{2+}/Ca^{2+}$ ratio of the calcite surface, increasing $\Omega$ has a strong negative effect on the aragonite surface ratio.

Sulfate is recognized as a significant coprecipitating anion in marine biogenic calcites ($\sim$1 mol % in magnesian calcites), and its effect on calcite precipitation has been investigated in solutions similar to seawater.[129,130] In Mg-free solutions, Busenberg and Plummer[129] found sulfate incorporation by calcite tended to increase with the rate of precipitation; increasing sulfate activity in turn inhibited the precipitation rate, with increasing inhibition as a function of saturation state. By comparison, relatively little sulfate is taken up in aragonite, and natural marine aragonites typically contain less than 6000 ppm $SO_4^{2-}$.[129]

Last, we do not discuss dolomite reactions in this paper because of their limited importance in modern sediments in contact with normal seawater. However, experimental work by Brady et al.[130] may have general relevance to reactions involving carbonate surfaces in the context of interactions between magnesium and sulfate. This work, involving cation sorption on dolomite, showed that the uptake of both magnesium and calcium to the mineral surface is potentially enhanced by the addition of dissolved sulfate. At the moderate pH values of seawater, this behavior was thought to reflect co-adsorption of metal sulfate complexes; in the case of magnesium, the uptake of sulfate could displace waters of hydration of adsorbed magnesium ion, providing a pathway for carbonation and subsequent lattice incorporation.

### *3.3.6. The Role of Other Impurities: Manganese, Strontium, Phosphate, and Organic Matter*

There has been considerable effort devoted to understanding the role of manganese in calcite precipitation reactions. In general, this work has shown that $Mn^{2+}$ is adsorbed strongly on the calcite surface, even at concentrations well below rhodochrosite ($MnCO_3$) solubility. $Mn^{2+}$ is partitioned into solid calcite ($D_{Mn} > 1$), although it has been demonstrated that this partitioning is sensitive to precipitation rate, with increasing rate producing a reduced partition coefficient.[131,132]

Early work in dilute solutions demonstrated that at sufficient surface concentrations, initial chemisorption of $Mn^{2+}$ is followed by nucleation of $MnCO_3$.[133] Reactions involving $Mn^{2+}$ and calcite were explored in seawater by Franklin and Morse,[134] with the finding that the interaction of $Mn^{2+}$ with calcite is strongly influenced by $Mg^{2+}$ availability. In magnesium-free seawater, the pattern is similar to that observed in dilute solutions, with an initially rapid period of $Mn^{2+}$ uptake, followed by $MnCO_3$ nucleation and subsequent growth that is first order with respect to dissolved $Mn^{2+}$ concentration. Franklin and Morse[134] observed that the introduction of magnesium at seawater concentrations apparently interfered significantly with $MnCO_3$ nucleation, possibly through site competition, thus slowing the growth rate of manganese carbonate. In addition, attempts to measure rhodochrosite solubility in seawater from supersaturated conditions resulted in formation of a mixed solid. Subsequent work by Mucci[135] confirmed the inverse dependence on precipitation rate observed in previous work, with manganese carbonate forming as a $(Ca,Mn)CO_3$ solid solution containing up to 40 mol % $MnCO_3$. However, this dependence of solid-phase manganese composition on precipitation rate precludes the condition of exchange equilibrium suggested above in explanation of the relationship between seawater and magnesian calcite composition. In fact, Mucci[135] argued that the overall precipitation rate of the solid could be successfully modeled as a cumulative function of the end member rates. In addition, although manganese content of the overgrowths decreased in response to increasing precipitation rate, the Mg/Ca ratio was constant (again consistent with earlier results for magnesian calcite). Mucci[135] suggested that composition of this mixed phase pseudokutnahorite[137] was consistent with the observed composition of manganoan carbonates derived from reducing pore waters.

The interaction of strontium with calcite and aragonite has been the focus of numerous experimental studies. Lorens[131] showed that at seawater salinities, the observed Sr partition coefficient in calcite is strongly dependent on precipitation rate, increasing by a factor of $\sim$3 as rate increases by a factor of $10^3$. Mucci and Morse[24] also observed that Sr uptake in magnesian calcite overgrowths was linearly related to the $MgCO_3$ content, possibly reflecting changes in lattice dimension. Morse and Bender[6] summarized these data in the context of earlier experimental results, and showed that $SrCO_3$ content is clearly correlated with variation in rate despite additional increases in the Sr content of magnesian calcites. Strontium accommodation in aragonite is much more extensive than in calcite, reflecting lattice differences described earlier. Plummer and Busenberg[136] have investigated the strontianite ($SrCO_3$)−aragonite solid solution in extensive experiments and thermodynamic modeling. They concluded that although marine aragonites (~1 mol % $SrCO_3$) have compositions close to the maximum stability observed, excess Sr in these phases suggests that they are in neither stoichiometric saturation (see discussion above for the magnesian calcites) nor equilibrium with respect to the seawater strontium concentration.

Orthophosphate adsorbs strongly to calcite and aragonite surfaces in seawater, exhibits complex interactions with the carbonate surface, and generally strongly inhibits carbonate precipitation. In dilute solutions, Stumm and Leckie[137,138] observed a period of rapid initial uptake and a resting period, followed by a period of renewed uptake, indicating chemisorption, recrystallization−nucleation, and growth of apatite. In seawater, the presence of magnesium has been shown to inhibit apatite formation.[139] In seawater experiments, de Kanel and Morse[140] observed that the rate of phosphate uptake to the calcite and aragonite surfaces actually declined with time. Although the initial uptake of phosphate was greater for aragonite than calcite, the subsequent decline in calcite uptake rate was slower than that for aragonite. These trends are inconsistent with a Langmuir adsorption isotherm but may be explained by either an exponential decrease in the availability of reactant sites or a linear increase in the energy of activation related to phosphate uptake. Mucci[126] modeled the strong inhibition of phosphate as a shift in reaction order, from $n = 2.8$ in phosphate-free seawater to a constant $n = 3.4$ in the presence of phosphate, and as a variation in the rate constant itself, thus amending the logarithmic form of the canonical rate equation as

$$\log r = a + b \log [\mathrm{PO_4}^{3-}] + n \log(\Omega - 1) \quad (3.16)$$

where $a + \log a + b \log [\mathrm{PO_4}^{3-}]$ represents a linear expansion of the rate constant in phosphate concentration.

Last, the interaction of organic matter with carbonate mineral surfaces is significant and diverse. For example, in early experimental work (discussed later in section 3.6.3), Suess[141] showed that calcite exhibits a strong but selective affinity for dissolved organic matter and suggested that adsorption to the point of formation of monomolecular surface layers could result in chemical isolation of carbonate particles. Berner et al.[142] have demonstrated that introduction of carboxylic, humic, and fulvic acids will inhibit nucleation of aragonite in supersaturated seawater. Zullig and Morse[143] examined the adsorption of fatty acid homologs (butyrate, octanoate, laurate, myristate, palmitate, and stearate) on calcite, dolomite, aragonite, and magnesite, finding that surface affinity increased with alkyl chain length, such that little adsorption was observed for chains shorter than $C_{14}$ and essentially quantitative and irreversible adsorption for $C_{18}$ acids. This pattern is essentially the inverse of fatty acid solubility. This behavior is consistent with the interaction of these hydrophobic acids with the carbonate surface via the carbon chain itself, as opposed to the interaction between the exposed surface calciums and carboxyl groups.

### *3.3.7. Nucleation of Calcium Carbonate*

This description is similar to that available in Nielsen;[54] treatments found in related texts will also be similar. In order to describe the dependence of nucleation on saturation state, we begin with the critical assembly of molecular units to a small cluster. If we assume that the change *per molecule* in chemical potential from the dispersed to assembled state is $\mu_2 - \mu_1$, then the total free energy change for $n$ molecules of material is

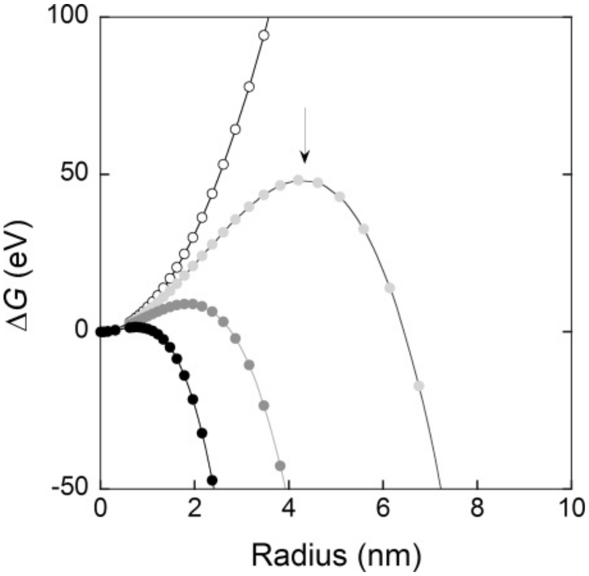


**Figure 7.** Variation of free energy ($\Delta G$) versus crystallite size (radius), computed as a function of increasing oversaturation ($\Delta\mu$) of the solution, using eqs 3.19 and 3.20. Open circles represent equilibrium condition, light gray circles represent $\Omega = 2$ (arrow indicates position of critical radius), dark gray circles represent $\Omega = 5$, and black filled circles represent $\Omega = 50$.

$$\Delta G = n(\mu_2 - \mu_1) \quad (3.17)$$

or per molecule

$$-\Delta G/n = \mu_1 - \mu_2 = -\Delta\mu \quad (3.18)$$

where the left-hand quantity ($-\Delta G/n$) must be $>0$ for a spontaneous assembly to occur. If we now approximate the volume of this cluster of $n$ units as a sphere having volume $V$, the surface area $A$ is proportional to $n^{2/3}$. Thus the free energy change for the homogeneous formation of a crystal assembly involving $n$ units from solution is

$$\Delta G = -n\Delta\mu + \sigma \mathrm{A} \quad (3.19)$$

or letting $\psi = \mathrm{A}\sigma/n^{2/3}$ express the proportionality between surface work ($\sigma$) and the number of molecules in the crystal, we now have as a function of crystal size (or number of assembled molecules)

$$\Delta G = -n\Delta\mu + n^{2/3}\psi \quad (3.20)$$

Equation 3.20 is plotted for a range of $\Delta\mu$ values in Figure 7 and represents the free energy change as a balance between the benefit of assembly (the phase change itself) and the cost of increasing surface area, scaled by surface tension, as the number of assembled units, $n$, increases. $\Delta G$ is positive for $\Delta\mu < 0$ (undersaturation) and becomes infinitely so with increasing $n$. However, under supersaturated conditions ($\Delta\mu > 0$), although $\Delta G$ will be positive in the region of small $n$, because $n$ grows faster than $n^{2/3}$ as $n$ increases, $\Delta G$ will eventually reach a maximum value and become increasingly negative thereafter. This maximum is an equilibrium point, although an unstable one, and may be computed from the derivative

$$n^* = (2\psi/(3\Delta\mu))^3 \quad (3.21)$$

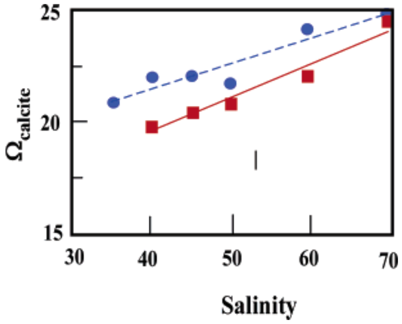


**Figure 8.** The supersaturation with respect to calcite ($\Omega_{calcite}$) necessary for pseudo-homogeneous nucleation of calcium carbonate from seawater at different salinities. Red line and symbols are at 25 °C, and blue line symbols are at 40 °C. Modified from ref 149, Copyright 1993, with permission from Elsevier.

This number $n^*$ thus defines the critical radius: crystals with radii smaller than this size (fewer molecular units) will tend to disintegrate, and ones that become larger than $n^*$ will tend to grow (Ostwald ripening). As can be seen in Figure 7, the critical size is also a function of supersaturation: the higher $\Delta\mu$, the smaller a given crystal assembly need be to survive and grow.

Early experimental studies of the conditions under which calcium carbonate can undergo pseudohomogeneous nucleation from seawater have been conducted that indicated calcium carbonate can nucleate during seawater evaporation (for summaries see Braitsch[144] and Sonenfeld[145]) and that increasing salinity should promote calcite nucleation. Studies of calcium carbonate nucleation from seawater with salinities typical ($S \approx 35$) of most oceanic waters demonstrated that nucleation was promoted by increasing salinity and decreasing temperature.[146] Results obtained by Pytkowicz,[147] as recalculated by He and Morse,[148] showed that a supersaturation of about 20−30 times with respect to calcite was necessary for nucleation of calcium carbonate within a few hours to a day. Subsequently, Morse and He[149] conducted experiments to investigate the influences of $pCO_2$, temperature, and salinity on calcium carbonate nucleation from seawater. They found only modest influences of temperature and salinity on the degree of supersaturation (about 20−25 times with respect to calcite) necessary for calcium carbonate nucleation to occur from seawater as shown in Figure 8. This is about 3−4 times the typical supersaturation of surface seawater.

The nucleation of calcium carbonate from seawater has also been of considerable interest from the standpoint of which mineral is precipitated. At 25 °C and close to normal salinity (35), aragonite is nucleated and precipitated from seawater even though it is unstable relative to calcite or dolomite. However, observations of ancient sediments indicate that at times in the past, when the composition of seawater may have differed from that of modern seawater, particularly with respect to lower Mg/Ca ratios, calcite was probably favored over aragonite.[150−152] Also, natural observations indicate that in cold waters calcite is more likely to form than aragonite. The literature on this topic has been reviewed by Morse et al.[153] who also conducted experimental studies of factors controlling which calcium carbonate phase nucleates and grows from seawater under differing composition and temperature conditions. Their major results are summarized in Figure 9. Calcite forms over a wide temperature range (0−35 °C) in Mg-free seawater, but only below about 8 °C in seawater of normal (∼5:1) Mg/Ca ratio. From these results, it is evident that both the Mg/Ca ratio and temperature control the calcium carbonate mineral that forms from seawater, effectively dividing the resulting "phase space" between calcite and aragonite.

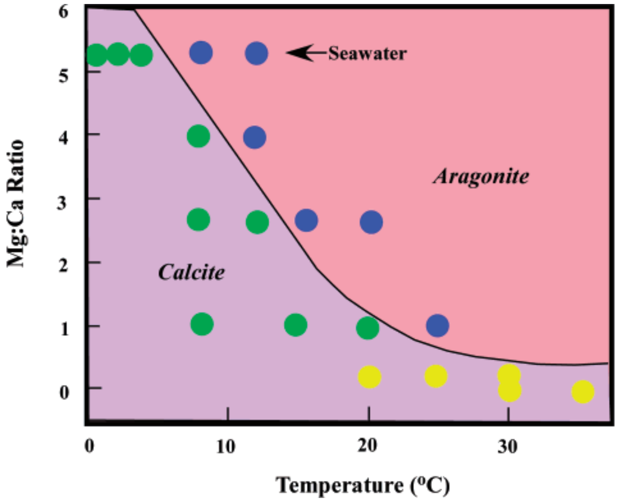


**Figure 9.** Influences of seawater Mg/Ca ratio and temperature on the nucleation of calcium carbonate from seawater. Blue circles are aragonite; yellow circles are calcite; green circles are initially calcite with aragonite overgrowths. Modified from ref 153 with permission. Copyright 1997 Geologic Society of America.

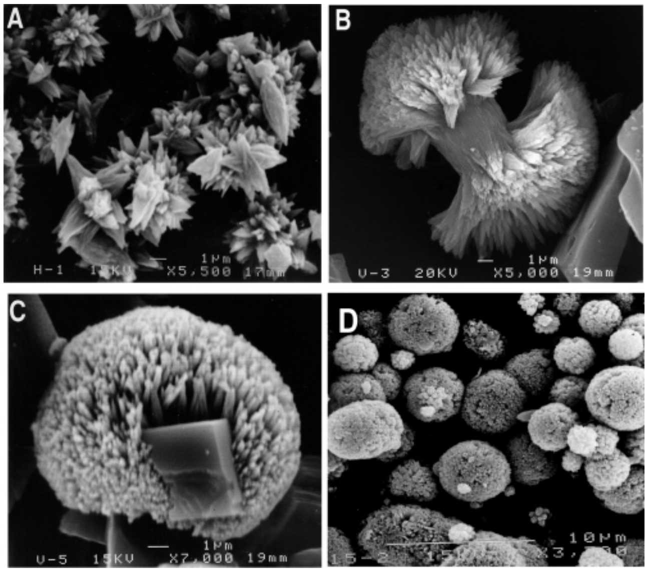


**Figure 10.** Scanning electron photomicrographs of calcium carbonate precipitated from seawater of various Mg/Ca ratios and temperatures: (A) aragonite with needle morphology from warm normal sweater; (B) aragonite with "broccoli" morphology from cold normal seawater; (C) aragonite needles growing on initially nucleated rhombohedral calcite for low Mg/Ca cold seawater; (D) radially fibrous aragonite sphere from 15 °C normal seawater. Panels A, B, and C reproduced from ref 153 with permission. Copyright 1997 Geologic Society of America. Panel D photo taken by J. Morse.

Another interesting aspect of this work is that Mg/Ca ratio and temperature control not only which calcium carbonate polymorph precipitates but also the morphology of the precipitate itself (Figure 10). In some experiments calcite was observed to nucleate initially, but as precipitation proceeded the solution Mg/Ca ratio increased until aragonite epitaxially nucleated on the calcite, followed by growth of aragonite needles (Figure 10C).

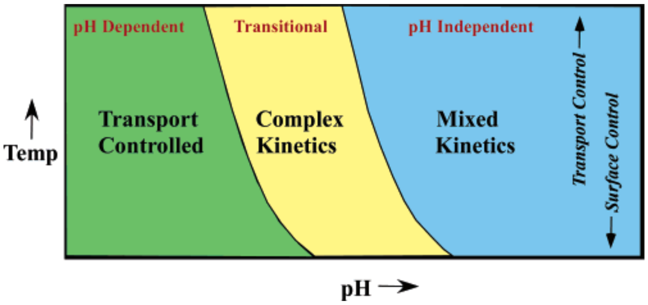


**Figure 11.** Summary diagram of relationship of transport versus surface-controlled dissolution based on the work of Sjöberg and Rickard.[162] Modified from ref 50, Copyright 2002 with permission from Elsevier.

## 3.4. Dissolution Reactions

### 3.4.1. Calcite Dissolution Kinetics

There are significant differences between dissolution and precipitation reactions, and although approaches that cast the two regimes in the same theoretical light may yield insight,[154,155] in general we would argue that dissolution cannot be understood simply as crystal growth operating with a negative sign. This limitation is important in the context of seawater reactions, where our lack of quantitative understanding of reaction paths and the role of “precursor” surface phases is particularly acute.

Although there is a large experimental literature on carbonate mineral dissolution, much of this work has been done at extreme undersaturations and low pH regimes that are in the province of diffusion-controlled kinetics and have limited relevance to reactions in seawater. Under these conditions, dissolution rate may reflect primary control by the hydrodynamic conditions that maintain the thickness of the stagnant boundary layer. For example, under acidic conditions ($\mathrm{pH} < 4$), reaction rates can be described simply by (compare also eq 3.8),

$$r = k a_{\mathrm{H}^+}{}^{n} \tag{3.22}$$

where $n$ is ∼1 and the rate constant (25 °C) varies between $50 \times 10^{-3}$ cm s$^{-1}$ [147] and $3 \times 10^{-3}$ cm s$^{-1}$.[156] The range of these values reflects the uncertainty and sensitivity to estimates of the thickness of the boundary layer. The progress to equilibrium from a purely transport-controlled regime is characterized by a transitional region. This transitional region, in which reaction rates may be intermediate between strong dependence on hydrodynamic conditions (rotating disk velocity) and complete surface control, was the focus of much work by Sjöberg and Rickard[156−158] and gave rise to the notion of “mixed kinetics”. This transitional behavior was described by expressing the observed rate constant as a nonlinear function of a transport-controlled ($k_{\mathrm{T}}$) and chemically controlled ($k_{\mathrm{C}}$) rate constant. Thus if $k_{\mathrm{T}} \gg k_{\mathrm{C}}$, the rate is chemically controlled; conversely for $k_{\mathrm{C}} \gg k_{\mathrm{T}}$, the rate is transport controlled:

$$k = k_{\mathrm{C}} k_{\mathrm{T}}/(k_{\mathrm{C}} + k_{\mathrm{T}}) \tag{3.23}$$

Once surface-controlled dissolution kinetics are established, reaction mechanisms vary through this near-equilibrium region until equilibrium is attained. These relationships are summarized in Figure 11. We also refer the reader to a recent and relatively exhaustive review of the carbonate mineral dissolution literature.[50]

Although there is a general consensus regarding the critical importance of understanding surface-controlled reactions in the limited range over which saturation states vary in normal seawater, much fundamental knowledge is lacking. The majority of studies of dissolution in seawater consist of application of painstaking analysis of solution chemistry as a means of deriving insight into activities on the surface itself. The results of this work have provided a large dataset that describes the overall relationship between bulk solution composition and reaction rates. However, mechanistic interpretation of surface reactions is limited by a lack of direct surface observations and measurements. In addition, there is the more fundamental problem of how to integrate the enormous detail derived from current AFM studies of mineral surfaces over significant length and time scales to provide net reaction rates relevant to mesoscale processes. Thus a major outstanding challenge is the integration of these various approaches and observations to yield models of practical utility.

The overall relationship of temperature to calcite dissolution rate reflects the differences between transport versus surface-reaction control described above. Early work, summarized by Plummer et al.,[159] shows substantial variation in activation energies, although reliable values in dilute solutions are similar (e.g., 10.5 kcal mol$^{-1}$ [160]). Experiments by Sjöberg and Rickard[158] far from equilibrium show that the role of temperature on calcite dissolution kinetics is complex and are summarized in Figure 11. Closer to equilibrium, Gutjahr et al.[161] confirmed surface control of calcite dissolution with an activation energy of 8.3 kcal mol$^{-1}$. The temperature dependency of dissolution inhibitors is poorly known close to equilibrium.

The role of inhibitors in dissolution reactions has generally been best described for conditions far from equilibrium in dilute solutions. These results are reviewed in more detail in Morse and Arvidson[50] and only summarized briefly here.

1. Although substantial experimental observations exist for inhibition of dissolution reactions, the variation in terms of saturation state and major ion composition makes it difficult to draw overall conclusions regarding the role of specific inhibitors. This is important because the degree of inhibition is often quite sensitive to the distance from equilibrium.

2. As described previously in the section on precipitation, inhibition is often described according to competing models: (a) a reversible adsorption (Langmuir−Volmer) model, which assumes that a Langmuir adsorption isotherm controls uptake at specific surface sites, or (b) an irreversible adsorption (Cabrera and Vermilyea) model in which the distribution of impurities on terraces controls the advance of steps. Control by either of these two mechanisms is often simply assumed and not clearly demonstrated.

3. In addition to impurities, lattice components (calcium and carbonate ion) may also influence reaction rate beyond their simple appearance in saturation state terms.[160] In addition, the role of inhibitors in seawater is also influenced by calcium and magnesium concentrations. Other than sulfate and phosphate, Sjöberg[160] observed that other major and minor ions of seawater have little influence on calcite dissolution rate.

4. Trace metals (e.g., Ni, Cu, Mn, or Co) exert strong control on calcite dissolution even at micromolar concentrations, possibly by selective blocking of active sites.[80] The effectiveness of these metals may also be dependent on saturation state, but they have not been extensively studied in seawater where they may be less influential due to site competition.

Early work involving *in situ* Pacific Ocean experiments[163,164] related dissolution rates to seawater saturation state. This critical work showed that the seawater dissolution rate of calcite is not simply proportional to undersaturation, obviating the use of first-order kinetics (see above). Similar results were also obtained for the Atlantic Ocean.[165] Morse and Berner[49,166,167] performed extensive experiments over a broad range of saturation states, using ΔpH (the difference between the equilibrium and experimental pH) to describe saturation state. The primary difficulty in the study of seawater dissolution kinetics of calcite is the small variation in seawater saturation state ($\Omega$ typically $>0.7$ with respect to calcite). This thus limits the range of relevant undersaturation ($\Delta\text{pH} \leq \sim 0.2$). Using the canonical rate law written for dissolution, the observed reaction order ($n$) for phosphate-free seawater is ∼3 for inorganic calcite powders[166] and 4.5 for biogenic calcite tests.[49,168] This work was critical in terms of establishing the increase in dissolution rate associated with an undersaturation close to that observed for the foraminiferal lysocline in deep sea sediments.[166] In addition, Morse[49] identified phosphate as the most important inhibitor in terms of calcite dissolution in seawater. Although the presence of seawater phosphate exerts a minor influence on the rate constant $k$, reaction order $n$ is increased to ∼16 at 10 $\mu$M phosphate. Berner and Morse[167] argued that selective binding of phosphate at high-energy sites progressively raised the "critical undersaturation" necessary to maintain step retreat.

As with precipitation reactions, understanding of dissolution is critically hampered by fundamental gaps in the understanding of how microbial processes, both in the water column and in sediments, exert controls over dissolution reactions. In addition, application of rate laws such as those defined previously to actual dissolution in marine environments is handicapped by an inadequate understanding of how to extrapolate these terms in time and space. This problem is covered in more detail in section 7.

### 3.4.2. Aragonite Dissolution

Compared with calcite, the attention directed at aragonite dissolution in seawater has been relatively modest. Morse et al.[169] showed that synthetic aragonite and pteropod tests dissolved under conditions of near-equilibrium to $\Omega = 0.44$ with an overall reaction order $n = 2.93$, similar to that observed for calcite. With increasing undersaturation, $n$ increased to 7.27. The behavior of phosphate is complex and differs substantially from that observed for calcite, in that introduction of phosphate gives rise to an initial increase in dissolution rate. However, this effect is dependent on both saturation state and phosphate concentration[169] and is also time-dependent.

In subsequent work, Busenberg and Plummer[170] showed overall similarities between reaction kinetics and rate constants determined for aragonite and calcite; these rates were treated according to a substantially different set of rates than presented above and attempt to assign mechanistic roles to carbonate surface species. Gutjahr et al.[161] derived a reaction order for aragonite of ∼3, in good agreement with the earlier work of Morse et al.[169] in seawater.

### 3.4.3. Magnesian Calcite Dissolution Kinetics

We have previously discussed the problems related to the determination of the solubility of magnesian calcite. In early work, Land[171] observed that biogenic magnesian calcite dissolved in pure water incongruently, which he argued reflected a faster $MgCO_3$ versus $CaCO_3$ dissolution rate. Subsequent work by Plummer and Mackenzie[17] essentially used the dissolution of magnesian calcites to derive equilibrium constants from reciprocal time. Plummer and Mackenzie[17] concluded that although the initial dissolution was congruent, the dissolving phase differed in composition from the bulk solid. They argued that this behavior was controlled by dissolution of a range of magnesian calcite mineralogies, with variations in solubility producing variations in rate. Wollast and Reinhard-Derie[172] confirmed these results in similar free drift experiments, including reprecipitation of a calcite poorer in Mg than the initial reactant. Walter and Morse[18] have also shown that the reaction order $n$ for magnesian calcite dissolution computed from rate versus $1 - \Omega_{MgCO_3}$ (i.e., stoichiometric saturation) are similar to pure calcite. Bertram et al.[31] showed that the solubility of synthetic magnesian calcites decreases with temperature in a manner similar to pure calcite.

Walter and Morse[173] measured dissolution rates of carefully prepared biogenic magnesian calcites, computing rate constants and reaction orders from stoichiometric activity products and stoichiometric constants.[18] The important observation made in these experiments was that microstructural differences exert the principal control on their dissolution reactions, rendering determination of the role of solubility problematic or irrelevant. Rates were reported on a per unit mass (versus per unit area) basis because of large differences in reactive versus BET surface area. Walter and Morse[18,173] observed that the critical differences in rates were controlled not by solid-phase composition but by relationships between total surface area, grain size, and microarchitecture. Rates increased with BET surface area but not in any simple linear way. They found that complex microstructures of biogenic Mg calcites may have apparent "reactive" surface areas of $\leq 1\%$ of total area. In these cases, BET area measurements are an unreliable measure of reactive area.

In common with their behavior in supersaturated solutions, magnesian calcites exhibit unique properties that complicate determination of their reaction kinetics. As stated previously, an adequate representation of their kinetics hinges on accurate representation of the distance from equilibrium. The use of stoichiometric saturation in this regard may permit comparison of phases of different composition, but it trades this utility for ambiguous theoretical constraints. In the case of biogenic magnesian calcites, solution to this "solubility problem" may require approaches entirely divorced from those employed in the description of synthetic or cement phases, in which magnesium content is only a minor factor. Despite a wealth of observations, conclusions regarding the actual dissolution mechanism of magnesian calcites and the action of specific inhibitors remain largely speculative regardless of origin. Last, these properties ($MgCO_3$ content, heterogeneity, grain size, microstructure, defect density, etc.) need to be understood in terms of their implications for reaction path during stabilization in natural environments.[33]

## 3.5. Biominerals and Nanophase Carbonates

### 3.5.1. General Considerations

Life imprints its signature upon Earth's solid surface and the oceans by causing and modifying important fluid–solid processes. The rapidly growing literature records the increasing number of attempts to understand the nature and role of this effect at scales ranging from global to microscopic.[174–177] At the microscopic level, the interactions between microorganisms and minerals have repercussions that have a variety of implications for the biogeochemical cycling of chemical elements, the formation of minerals and the contrary, that is, the dissolution and weathering of minerals and rocks and therefore the formation of soils. Below, we will discuss briefly *biomineralization*, *biogeochemistry and geobiology of carbonates*, and *nanophase carbonates* only with their relevance to seawater and oceanography.

### 3.5.2. Biomineralization

The term biomineralization, in contrast to *abiotic* mineral formation, describes the production of mainly crystalline matter by organisms, that is, crystal nucleation and growth generated by organisms or even inside an organism. The product of this process is a biomineral. While in the past Earth scientists were mainly focused on abiotic inorganic material, that is, minerals per definition, this focus has changed in the more recent past. Comprehensive reviews of this new and rapidly growing field of biomineralization have been provided by Lowenstam and Weiner[178] and Dove et al.[179] The interested reader will find a wealth of references to key research articles as well as to more specialized and detailed reviews in these volumes. Dove et al. have assembled an interesting review volume that contains a dozen articles. Together, this assembly provides a glimpse on the cutting edge of this field and an overview and great start to explore this exciting subject in more detail.

In our present article, however, the focus is almost exclusively on abiotic carbonate minerals and their behavior in oceanographically relevant settings. Therefore, we restrict ourselves here to a few short remarks on biominerals and biomineralization. Today, this field has developed so successfully and covers such a broad range of interdisciplinary research that a satisfying coverage would require a full review article on this subject. Our decision is also supported by the fact that biominerals are formed by organism-induced processes that are very different from abiotic processes governed by abiotic nucleation, growth, and dissolution kinetics. Due to the distinctly different way of formation that often involves organic molecules and matter, biominerals commonly behave very different compared with their abiotically formed counterparts. Thus certain aspects of our discussion of abiotic carbonates may not apply to biominerals.

### 3.5.3. Biogeochemistry, Geomicrobiology

While we decided not to focus in detail on biomineralization (see above), it makes more sense to discuss the influence of microorganisms, such as *Shewanella* spp. and *Geobacter* spp., on the abiotic reaction kinetics in terms of biogeochemistry and geomicrobiology. Here, we define biogeochemistry as geochemistry altered or influenced by biological factors and accordingly geobiology as biology influenced or altered by geology or geochemistry.

Bacteria can help formation of precipitation of carbonate minerals,[180–182] but they can also do the opposite, trigger or enhance dissolution or corrosion. We will show below that an intermediate action is also possible, that is, the inhibition of dissolution or corrosion kinetics. For example, it has been observed in a relatively large number of studies[183,184] that bacteria will attach to metal, metal oxide, mineral, and other solid surfaces. In many cases, this process will develop into the formation of a biofilm (e.g., Escher and Characklis[185]), that is, a mixture of microorganisms (bacteria) and extrapolysaccharides (EPS) and other organic material that "grows" on the solid surface. It is easy to imagine that such a complex biofilm will eventually alter abiotic reaction kinetics of dissolution or growth processes at the water–solid interface because it creates its own microenvironment with respect to the solution chemistry, pH, etc., or at least it alters the pre-existing conditions significantly. Banfield and Nealson[183] have devoted an entire review volume titled: "*Geomicrobiology: Interactions between Microbes and Minerals*" to this interesting phenomenon. This work is an excellent source for our understanding of microbe–mineral interactions and contains a wealth of references.

While the complex interplays between bacteria, biofilm, and water–solid interface are still difficult to quantify and understand in detail, we have begun to make substantial progress. Today, the forces and interactions between single microbes and mineral surfaces can be measured,[184,186] and we have also started to elucidate the mechanisms that bacteria use to interact with the mineral surface. In this context, electron shuttles and nanowires are just a couple of recent observations that are defining our progress. An improved insight and understanding of these mechanisms is important for several reasons. One example is the observation reported recently by Lüttge and Conrad[187] who demonstrated experimentally that *Shewanella oneidensis* MR-1 not only attach to calcite cleavage surfaces but also are capable of attaching to specific high-energy sites, that is, the outcrops of screw dislocations at the mineral surface (Figure 12). It is well-known from crystal growth and dissolution theory[188,189] that these high-energy sites are also key features in both crystal dissolution and crystal growth processes. They are both the sites where etch pit formation begins during dissolution and also centers for the development of so-called growth spirals that form hillocks and later new crystal faces during the growth process. Lasaga and Lüttge[190,191] have shown that etch pits are the main source for the formation of steps that will progress[192] and cause the surface-normal retreat of the entire crystal surface, leading to overall crystal dissolution.

It has been suspected and demonstrated for some time now that microorganisms could cause or at least increase corrosion of metal and mineral surfaces.[193,194] The new observation that microorganisms attach preferentially to high-energy sites is interesting because this observation changes the assumption of corrosion or dissolution enhancement in an important way.

Lüttge and Conrad[179] have observed that MR-1 organisms are capable of shutting down the abiotic dissolution processes of calcite even at significantly undersaturated conditions. The reason is simply that the high-energy sites that become almost completely occupied by MR-1 do not open up into etch pits. Consequently, no steps are generated at the outskirts of the pits that would move across the crystal surface and would dissolve the crystal layer by layer. However, individual organisms would then begin to entrench themselves in the calcite surface (Figure 13), but atomic force microscopy

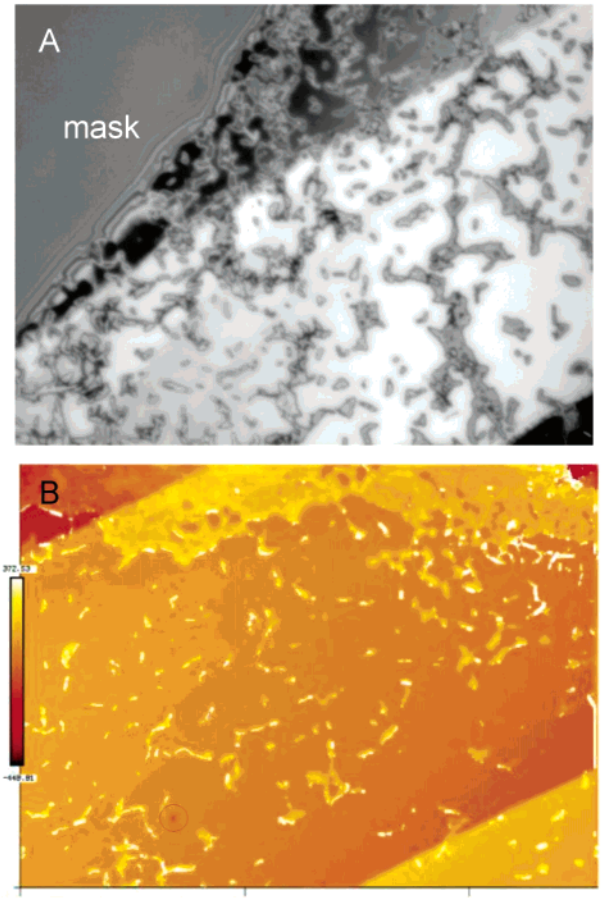


**Figure 12.** (A) Reflected light image showing colonies and single individuals of *Shewanella oneidensis* MR-1 with superimposed interference fringes and (B) two-dimensional false-color height map calculated from the interferogram, taken from Lüttge and Conrad.[187] Three different terraces can be identified. At the upper part of the figure MR-1 has started successfully to establish a biofilm. Reproduced with permission from ref 187 Copyright 2004 American Society for Microbiology.

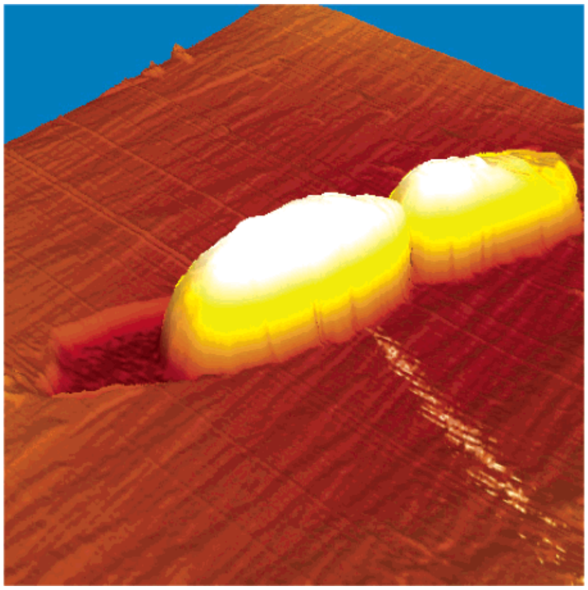


**Figure 13.** Atomic force microscopy image of two MR-1 cells entrenched in a 104 calcite cleavage face. The cells are entrenched in a biotically formed pit. The pit is about 130 nm deep, and its walls are well preserved (Davis and Lüttge, unpublished).

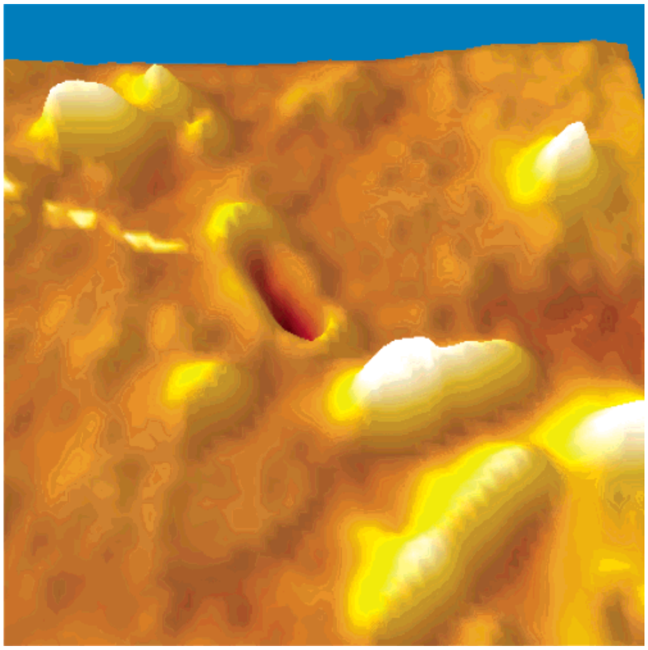


**Figure 14.** Vertical scanning interferometry image of a trench formed by a single MR-1 organism in a calcite cleavage face. The microbial cell has been removed. The pit is about 2 $\mu$m long and about 130 nm deep; note the elevated rim surrounding the pit (Davis and Lüttge, unpublished).

(AFM) and vertical scanning interferometry (VSI) images show that the resulting pit is no longer crystallographically controlled as in the case of etch pits. Instead, after MR-1 has been removed from the surface, the pits show the oval, negative-body shape of the *Shewanella* organisms (Figure 14). The outer rim seems to be quite well controlled by MR-1; that is, it does not start to spread steps. The depth of the pits formed by MR-1 was usually no deeper than about a third of the organisms diameter, that is, about 140−200 nm. This result indicates that MR-1 can indeed control the dissolution process independent of the abiotic solution chemistry in contact with the carbonate surface. These observations are in close agreement with model results published by Lüttge et al.[195] Davis and Lüttge[196,197] have reported that this behavior is not limited to calcite but was observed also for dolomite and magnesite, as well as rhodochrosite.[198]

Future work will need to be undertaken to substantiate these still somewhat preliminary results. In particular, it will be important to demonstrate that other microorganisms such as *Geobacter* or at least other microbial strains of *Shewanella* can operate in a similar manner. If more evidence will be collected, we may have identified an important phenomenon that could explain unexpected or unexplained dissolution and growth rates in natural systems that are not in agreement with expectations based solely on abiotically measured or estimated reaction rates.[50,99]

### 3.5.4. Nanophase Carbonates

An extensive literature search reveals that our recognition and knowledge of abiotic nanoparticles in the carbonate system at least with relevance to seawater and oceanography are mostly lacking. Most available articles are focused on biologically formed nanoparticles that are not the subject of this review (see above). Banfield and Navrotsky[199] have published an interesting and comprehensive review volume on nanoparticles and the environment. This volume provides important general information on nanoparticles in the environment; however, with respect to oceanographic settings, not much information can be extracted from this work.

Despite this fact, we should note that all carbonate minerals that form through either homogeneous or heterogeneous nucleation (as opposed to simple crystal growth by step flow) must experience a nanophase stage during which specific nanophase behavior is likely.[200] Specific nanophase behavior is any behavior or property that sets nanoparticles apart from their bulk equivalent, for example, solubility, tensile strength, or hardness. This distinct change in behavior or property is then used to define a "nanoparticle".[200] Therefore, future research should eventually include this interesting and potentially very important subject. Nanoparticles are distinct from their bulk-phase counterparts for several reasons. One important fact is that nanoparticles have a large surface to bulk ratio. That means most of a nanoparticle's molecules are included in the solid−water interface or at least very close to it. Navrotzky[201] conducted a very interesting thought experiment based on thermodynamic properties of nanoparticles. Navrotzky argues that the observed differences in surface (free) energies of polymorphs that are in the nanophase state may stabilize those polymorphs not stable in the bulk solution. Because a relatively large number of important minerals "show polymorphism with relatively small free energy differences between polymorphs, such crossovers in stability at the nanoscale may be a rather general phenomenon".[201] If we accept that a nanoparticle state is a precursor phase for all precipitating minerals, this effect may be indeed a significant one particularly in low-temperature environments. It could even explain the formation and existence of metastable phases, particularly if in the bulk or macroregime, the driving force for converting the metastable polymorph into a stable one is not too large.

## 3.6. Calcium Carbonate–Organic Matter Interactions

### 3.6.1. Overview

Nonthermodynamic behavior of calcium carbonates that cannot be explained by the influence of inorganic seawater constituents is frequently ascribed to the effects of associated organic matter. However, organic matter−carbonate associations in natural systems are complex. Only a small component of dissolved organic material in seawater has been characterized at the compound level and the remaining macromolecular aggregates have generally been classified by convention into several molecular weight fractions. The problem of an uncharacterized organic matter fraction is compounded by the manner of its association with carbonate grains. Organic matter can be found occurring on carbonate mineral surfaces via adsorption, precipitation, and coprecipitation. This may include dead cellular material and surface-attached living organisms, such as bacteria. In addition, organic matter associated with carbonates differs from clastic or metal oxide minerals by its association within carbonate grains as either occluded biogenic material, living tissue, or organic membranes interspersed between mineral layers.

Investigations of organic matter associated with calcium carbonate can be divided into two categories. The first and largest category of study is the behavior of carbonates in the presence of dissolved organic matter. These investigations demonstrate effects that imply indirectly that organic matter is associated with carbonate surfaces in natural systems. The second and much smaller group of investigations has examined the adsorption of organic compounds to carbonate surfaces under laboratory conditions. Differences in methodology in adsorption investigations have led to discrepancies in the reported affinities of organic compounds for carbonate surfaces. Processes other than adsorption, such as the influence of bacteria at surfaces, precipitation or dissolution of the carbonate surface during adsorption, coprecipitation of organic material with calcium carbonate, reaction vessel wall adsorption, solubility of organic compounds in seawater, and methods of data analysis, combine to conceal genuine adsorption. Use of nonsterile conditions in most experiments is a further potential complicating factor.

### 3.6.2. Indirect Evidence of the Influences of Organic Matter on Calcium Carbonate

The importance of the interactions of organic matter with calcium carbonate mineral surfaces in marine systems was recognized in the early 1960s. These interactions were studied primarily because of their effect on carbonate reaction kinetics and, to a lesser extent, the apparent control organics have on determining crystal morphology.

Surface seawater is supersaturated with respect to calcite and aragonite and thermodynamic calculations indicate that this supersaturation should be alleviated by massive inorganic precipitation. The sediment record shows instead that most precipitation of carbonates is biogenic in origin. The absence of inorganic precipitation has been partially attributed to the presence of surface-associated organic matter by two possible mechanisms: (1) organic sheaths, which prevent nucleation or dissolution by physical isolation, and (2) adsorption of dissolved organic material poisons on sites where active nucleation or dissolution would have occurred.

Kitano and Hood[202] carried out a detailed investigation on the influence of organic material on calcium carbonate precipitation. Using a "homogeneous" precipitation procedure, they found that one type of organic compounds favored the formation of calcite, while other compounds resulted in aragonite precipitation. Inhibition of precipitation roughly correlated with complex formation of the organic compound $Ca^{2+}$ salt and also increased with increasing organic concentration. Calcite precipitation was favored by a slower reaction rate indicating that organic material that inhibited precipitation the most also promoted calcite formation. Kitano and Kanamori[203] demonstrated that Mg-calcite formation was favored in the presence of the sodium salts of citrate and malate. Investigations by the Kitano group also suggested that a site-specific association of the organic material with surficial $Ca^{2+}$ could be responsible for inhibition of precipitation. Other investigations[142,204−207] revealed that carbonate particles in the water column were coated with organic material forming organic "sheaths" that isolated the normally reactive surface from seawater and prevented equilibration. Site specific chemisorption or physical coatings were implicated as mechanisms for isolation.

Wollast[208] and Berner[209] confirmed that at the supersaturation state of surface seawater, homogeneous precipitation of calcite or aragonite did not occur and that there was no indication of heterogeneous nucleation on abundant suspended particulates in shallow-water marine environments. These findings increased the likelihood that surface-associated organic material was responsible for the observed behavior of carbonates in natural systems. Pytkowicz[210]

**Table 2. Effect of Organic Substances on the Seeded Precipitation of Aragonite from Synthetic Seawater at a Supersaturation of 2.8**

| organic compound | max mg of C $L^{-1}$ | $R$ |
|---|---|---|
| A. Little or No Inhibition ($R \geq 0.9$) | | |
| amino acids/proteins | | |
| aspartic acid | 4.2 | 1.0 |
| glutamic acid | 3.0 | 1.0 |
| glycine | 2.4 | 0.9 |
| arginine | 4.8 | 1.0 |
| aliphatic polycarboxylic acids | | |
| sodium oxalate | 0.6 | 1.0 |
| succinic acid | 1.7 | 0.9 |
| disodium EDTA | 2.4 | 1.0 |
| aromatic acids | | |
| trimesic acid | 2.2 | 0.9 |
| pyromellitic acid | 1.8 | 1.1 |
| B. Weak Inhibition ($0.9 > R \geq 0.3$) | | |
| amino acids/proteins | | |
| egg albumin | 18.0 | 0.3 |
| fatty acids | | |
| sodium stearate | 108.0 | 0.7 |
| aliphatic polycarboxylic acids | | |
| dipotassium tartrate | 1.3 | 0.6 |
| potassium H-tartrate | 0.5 | 0.8 |
| sodium citrate | 2.0 | 0.3 |
| tricarballylic acid | 0.7 | 0.8 |
| aromatic acids | | |
| potassium H-phthalate | 2.7 | 0.8 |
| gallic acid | 0.3 | 0.6 |
| C. Strong Inhibition ($R < 0.2$) | | |
| aromatic acids | | |
| gallic acid | 0.8 | $<0.2$ |
| mellitic acid | 1.7 | $<0.1$ |
| tannic acid | 9.1 | $<0.2$ |
| humic and fulvic substances | | |
| humic acid from marine mud | 6.3 | 0.02 |
| fulvic acid from pore water | 2.7 | 0.18 |

[a] $R$ is the ratio of precipitation relative to organic free solution. Adapted from ref 142 with the permission of the *American Journal of Science*.

concluded that inorganic precipitation of carbonates did not occur to a large degree due to organic carbon coatings. He observed inhibition of calcium carbonate precipitation in the presence of citrate; however, aragonite formation was unaffected by stearate. Sodium glycerophosphate was used as an analog for organic phosphorus in natural waters and inhibition of calcium carbonate precipitation, which was ascribed to adsorption at active growth sites.

Berner[211] examined the effect magnesium had on calcite precipitation and observed that at seawater concentrations $Mg^{2+}$ retarded calcite precipitation but did not affect aragonite precipitation. He concluded that $Mg^{2+}$ was not adsorbed to the surface of aragonite nor was it found in significant concentrations within the aragonite lattice. In contrast, dissolved $Mg^{2+}$ was adsorbed to calcite surfaces and incorporated into its lattice. Supersaturation with respect to calcite could be partially credited to the effect of $Mg^{2+}$ in seawater; however, $Mg^{2+}$ adsorption cannot resolve aragonite supersaturation.

Berner et al.[143] conducted an extensive investigation to determine inhibition of aragonite precipitation in the presence of a suite of organic compounds. Short-term laboratory experiments using the pH-stat technique to observe precipitation rate under steady-state conditions were carried out using a suite of pure organic compounds and natural fulvate and humate (Table 2). Aspartate and stearate had little effect on precipitation rate, but orthophosphate, humate, fulvate, and several polyfunctional aromatic acids produced large decreases in precipitation rates. The inhibitory effect of precipitation increased with organic and phosphate concentration. In addition, rate of precipitation in pore waters was also markedly retarded. Berner concluded with short-term laboratory experiments that aragonite precipitation was significantly retarded at low concentrations of dissolved phosphate and humic matter. However, he stressed that the role of organic matter in inhibiting precipitation is speculation without "hard data on the surface chemistry of natural suspended particles and the effects of changes in this chemistry upon the ability of the particles to act as seeds for both aragonite and calcite crystallization".

Experimental studies have been carried out that emphasized the role of organic matter in the formation of oöids (see section 4.3.3. for definition and discussion of these sand-sized abiotic carbonates). The primary reason for this emphasis is the observation of abundant protein matrices in oöids.[212−215] Mitterer[214] noted the abnormally high contents of aspartic and glutamic amino acids in these proteins and stressed the similarity of this protein composition to that of fluids in carbonate-secreting organisms and suggested that this proteinaceous matter may play an important role in the precipitation of aragonite on oöid surfaces. The role of organic matter in the formation of oöids is further discussed in section 4.3.3.

Less work has been done on the effects of organic matter on carbonate dissolution kinetics. Morse[49] examined the effect of dissolved organic matter on calcite dissolution rate using a number of organic compounds. Two dissolution trials were conducted using 0.200 and 1.000 mg $L^{-1}$ of each organic component and dissolution rate was reduced by 5% and 25%, respectively. In addition, calcite was soaked for 2 weeks in natural seawater to which 10 mg $L^{-1}$ of each organic component was added. A dissolution rate of approximately 90% that of calcite not soaked prior to dissolution, and 80% that of calcite which had been soaked for the same period of time in organic-free seawater was observed. Reproducibility was approximately ±10%, which indicated that the observed changes were marginally significant. Morse[49] and Sjöberg[216] both concluded that dissolution rate was unaffected in the deep sea by organic matter but may be affected in pore waters. In addition, they asserted that natural inhibition of carbonate dissolution was a function of organic physical isolation, rather than organic coatings derived from chemical adsorption.

From the preceding synopsis of organic inhibitory effects on reaction kinetics, it is clear that organics do have an influence on carbonate reactivity. However, there is some evidence that surface-associated organic matter may perform additional functions other than that of inhibition of precipitation. Hare[217,218] and Simkiss[219] investigated the protein−mineral matrix found in mollusk shells and suggested that organic material acted as a template for calcium carbonate nucleation in addition to possibly determining the crystal morphology of the mineral overgrowth.

The chief proponent of this hypothesis has been Mitterer and co-workers.[212−214,220−223] Mitterer and Cunningham[223] demonstrated that surface-active organic material that adsorbed to calcium carbonate mineral surfaces also complexes some dissolved $Ca^{2+}$. This would form an environment at the adsorbed organic−seawater interface having a $Ca^{2+}$ concentration higher than the bulk solution and permit nucleation of calcium carbonate.

These investigations are useful because they demonstrate observed effects on carbonate behavior in seawater and indirectly imply that surface-adsorbed organic matter is responsible. However, the question that must be raised is *how* do they influence carbonate behavior? Little information is available about the chemistry of the interfaces that produce these effects. Clearly, there is a need for determining the extent and manner that organics adsorb to carbonate mineral surfaces.

### 3.6.3. Direct Evidence for Organic Matter Adsorption on Calcium Carbonate

There are few adsorption investigations quantifying the partitioning of dissolved organic material in seawater with carbonate surfaces. Studies have focused primarily on fatty acid and amino acid adsorption over a range of solution compositions from distilled water to seawater.

Biogenic carbonates and inorganic carbonates such as öolites are characterized by an organic matrix, which is largely proteinaceous and has a preponderance of acidic amino acids.[212,218−219] Jackson and Bischoff[224] studied the effect of amino acids on the calcite to aragonite transformation and the adsorption of free aspartic acid on calcite and aragonite surfaces. Rates of recrystallization were measured at 66 °C in 0.01 M NaCl solutions in the presence and absence of individual acidic, neutral, and basic amino acid monomers. Trials were conducted in the presence of an amino acid and employed 0.01 M solution concentrations of the respective amino acids. The rate of recrystallization of aragonite to calcite was accelerated in the presence of neutral and basic amino acids and retarded in the presence of acidic amino acids. Inhibition of reaction rate was attributed to the formation of a protective layer of adsorbed aspartate or glutamate. The extra carboxyl group of aspartate and glutamate, in their dissociated, negatively charged state, theoretically substituted for $CO_3^{2-}$ ions at the carbonate surface resulting in chemisorption. Surficial $Ca^{2+}$ ions were assumed to be partially chelated by the amino acid molecules and partially coordinated with $CO_3^{2-}$ ions in the crystal. Basic and neutral amino acids contained only one carboxyl group and this was believed to be unavailable for adsorption due to interaction with an amine group on the amino acid.

The concentration of amino acid used by Jackson and Bischoff[224] is many orders of magnitude higher than what is found in surface seawater or pore waters. Extrapolation of the results of experiments conducted at high temperature and high adsorbate concentration to conditions found in shallow-water marine environments is not necessarily justified. The variability of solution pH at which the trials were conducted raises questions about the carbonate saturation state of the system and increases the likelihood that processes other than adsorption prevail. These processes include precipitation or dissolution of the carbonate surface and coprecipitation of the amino acid in surface overgrowths. The experimental trials were conducted under nonequilibrium conditions with respect to the carbonate mineral surface and this raises the possibility that coprecipitation in an overgrowth was responsible for uptake of amino acid monomers rather than adsorption.

Muller and Suess[225] found acidic amino acid selectivity over other amino acids in the adsorption of natural organic material to carbonate grains. Despite lack of bacterial controls and an undefined saturation state of the solution relative to the carbonate mineral phase, the investigations of the Mitterer group and Muller and Suess appear to reflect the selective acidic amino acid enrichment that is undeniably observed in natural carbonate systems.

The adsorption of fatty acids onto calcium carbonate surfaces has been less extensively studied. Suess[142,206] investigated the adsorption of stearic acid on calcite and dolomite surfaces in distilled water and hexane. Stearate was adsorbed strongly onto both surfaces in the two solution media examined. Investigations with distilled water indicated a surface saturation monolayer coverage of approximately 280 nmol $m^{-2}$ for calcite and roughly half as much surface coverage with dolomite. Adsorption was alleged to occur by chemisorption of the stearate carboxyl in its dissociated, negatively charged form with surficial $Ca^{2+}$. This mechanism is identical to the site-specific mechanism proposed for acidic amino acid adsorption. It is unclear whether the distilled water solutions employed in the adsorption trials were in equilibrium with calcite. If they were not, the potential for dissolution of the calcite surface during adsorption is possible. Dissolution of $CaCO_3$ in distilled water will introduce $Ca^{2+}$ and $CO_3^{2-}$ ions, which may reduce the solubility of stearate and restrict the range over which adsorption measurements could be conducted. In addition, the potential problems of stearate sorption onto reaction vessel walls and bacterial degradation of stearate were not addressed.

Lahann and Campbell[226] investigated the adsorption of palmitic acid on calcite surfaces. In distilled water, adsorption partitioning between equilibrium surface concentration and initial solution concentration yielded an isotherm that was "S" shaped. Adsorption increased up to 25 NaCl-salinity and decreased thereafter with increasing NaCl-salinity. Decreasing solubility with increasing salinity was believed to be responsible for the increased adsorption up to a salinity of 25, and the onset of micelle formation resulted in the decrease in adsorption between salinities of 25 and 35. Magnesium at concentrations found in seawater at a salinity of 35 completely blocked palmitate uptake. Lahann and Campbell hypothesized that palmitate bonded to the calcite surface by site-specific association with surficial calcium ions (chemisorption) and that hydrophobic stabilization was obtained by a parallel arrangement of hydrocarbon chains perpendicular to the mineral surface. Magnesium was believed to inhibit uptake by (1) surface exchange of $Mg^{2+}$ for surficial $Ca^{2+}$, resulting in a surface with a higher energy of hydration, thereby preventing or severely retarding bond formation, and (2) the formation of a Mg-palmitate complex in solution, reducing the activity of free palmitate available for surface adsorption. Phosphate cosorption results were interpreted as indicating that orthophosphate competed for surface sites on a one-to-one basis with phosphate desorption accompanying palmitate uptake. Readsorption of phosphate was presumably blocked by adsorbed palmitate molecules. Bacterial metabolism of adsorbate, reaction vessel wall adsorption, the saturation state of the solution with respect to calcite, and palmitate solubility were not considered in this study. In addition, isotherms were reported using initial solution concentration.

The adsorption behavior of several normal saturated fatty acid homologs, twelve free amino acids, and three polyglutamate molecules of different monomer unit size on the carbonate mineral surface in seawater and related solutions have been described and quantified.[144,227] Synthetic polyglutamic acids were employed to model acidic amino acid-rich proteins. Laboratory investigations required extensive procedural modifications from those of previous investigators to ensure that observed partitioning was a function of sorption processes. Sorption behavior of fatty acids adhered to Traube's rule and was complex as indicated by S-shaped isotherms. Free amino acids did not sorb, but polyglutamic acids did.

The classes of organic compounds investigated contain the carboxyl function. The carboxyl group has been widely mentioned as the function responsible for the adsorption of fatty acids, amino acids, fulvates, and humates onto $CaCO_3$. Although no direct proof of a mechanism for sorption of this nature has been observed, sorption was hypothesized to occur by ligand exchange with surficial $Ca^{2+}$. Results of the Zullig and Morse[144] investigation indicate that sorption is far more complex and the presence of a carboxyl function and surficial $Ca^{2+}$ does not necessarily ensure adsorption onto $CaCO_3$ surfaces. For example, at low solution concentrations consistent with levels reported in seawater, shorter chain fatty acids ($C_1$ to $C_{12}$) and all of the free amino acids, including the acidic amino acids, did not adsorb onto $CaCO_3$ surfaces. Yet, they all contain the carboxyl function. Sorption of $C_{14}$ to $C_{18}$ fatty acid homologs onto dolomite and magnesite surfaces at low solution concentrations is similar to sorption onto calcite and aragonite surfaces. This behavior is difficult to explain as a function of a single site-specific mechanism, even if surface sorption site heterogeneities are considered. Free glutamate did not adsorb, but the peptide-bonded polymer of glutamate sorbed onto calcite surfaces.

In summary, the interactions of different organic compounds and their influences on calcite and aragonite reaction kinetics varies widely. Observations of carbonate mineral diagenesis in marine sediments indicates that biologically derived organic matter may have little influence on calcium carbonate dissolution but may play a major role in inhibiting precipitation on sedimentary carbonates.

## *4. Oceanic Sources of Marine Carbonates*

### 4.1. Overview

Although near-surface seawater is strongly supersaturated with respect to calcite (∼6×), aragonite (∼4×), and ideal dolomite (∼50×), these minerals fail to precipitate directly from it under near-normal oceanic conditions (see sections 2 and 3). In the modern ocean, the strongly dominant source of carbonate minerals comes from a wide variety of organisms that yield "skeletal" carbonates. In the pelagic realm of the open ocean, the primary carbonate mineral formed is low-Mg calcite ($<4$ mol % $MgCO_3$), with smaller amounts of aragonite also being derived from organisms. Deep ocean sediments contain high-Mg calcite ($>4$ mol % $MgCO_3$) from benthic organisms and occasional abiotic marine cements usually as a very minor component of total sedimentary carbonate minerals.

In the shoal-to-shallow water depth of temperate-to-tropical regions of the ocean, biogenic aragonite is the most abundant carbonate mineral, followed by high-Mg calcite and then low-Mg calcite. In cold water environments, typical of high latitudes, low-Mg calcite is dominant. Dolomite is relatively rare and largely confined to "special" environments. Although in a great many instances, it is clear that the sedimentary carbonates are the skeletal remains of organisms, considerable controversy exists as to the role of organisms in forming fine-grained aragonite muds, marine cements, and more recently dolomite. In siliciclastic sediments Fe(II)- and Mn(II)-containing carbonate minerals and massive or nodular calcite and aragonite are the result of processes taking place in sediments that involve organisms but are abiotic products of these biologically driven reactions.

It is important to keep in mind that the sources, deposition and, diagenesis of marine carbonate minerals to a large extent reflect the biology of the ocean at least as much as its chemistry. This can lead to circumstances where dissolution of carbonate minerals in apparently supersaturated waters and their deposition from apparently undersaturated waters can occur because of local biologically driven environments of altered saturation state. Furthermore, most oceanic carbonate minerals may be repeatedly passed through the guts of organisms feeding on suspended matter or near-surface sediments. In recent years, the role of organisms has been argued to be important even for carbonates that have traditionally been considered abiotic (e.g., dolomite) through the role of highly controversial "nanobacteria" that are much beloved in sections of the Earth science community and denounced as impossible by many microbiologists.

Considerable effort has gone into modeling the cycling of carbonates in the ocean. Although biogenic formation of calcium carbonate is domoninantly in the open ocean basins, the accumulation of calcium carbonate in sediments is greater in the coastal oceans.[228] Most commonly oceanic carbonates are considered as part of the broader general oceanic or global carbon cycles. These can be quite complex such as the recent shallow-water ocean carbonate model (SCOM).[3,229] In this paper, we will not go into a discussion of these types of models. For those interested in pursuing this area further, a good start would be the recent review by Sabine et al.[230] "Current status and past trends of the global carbon cycle".

### 4.2. Primary Carbonate Sources for Deep Sea Sediments

The primary sources of calcium carbonate for deep sea sediments are pelagic calcitic coccolithophores and foraminifera that grow dominantly in the phototic zone (typically upper ∼100 m) and to a lesser extent aragonitic pteropods. 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, those 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 (siliceous skeletons) dominate. Coccolithophores are numerically much more abundant (usually ∼10 000-fold) than pelagic foraminifera. Benthic foraminifera can be formed of either aragonitic or high-Mg calcite. Because of their general scarcity in deep sea sediments, aragonitic pelagic organisms have received relatively little attention. Pteropods and heteropods are the most abundant pelagic aragonitic organisms. It is estimated[231] that the percentage of the $CaCO_3$ flux is about 12% of the calcium carbonate flux from near-surface waters, although this percentage may vary considerably in different areas of the ocean and seasonally.

The mechanisms and rates of transfer of biogenic carbonate material from near-surface waters to deep sea sediments have been intensely investigated. Major questions have been concerned with the transition from living organism to carbonate test, rates of sinking, extent of dissolution in the water column and on the sea bottom (dissolution is discussed in section 5), and the relation between life and death assemblages.

Because of their small size, individual coccoliths sink slowly[232,233] and, consequently, may spend long periods of time (on the order of 100 years) in the water column. This long residence time should lead to substantial to complete dissolution of the 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 by considerations based on settling rates of individual particles.[234,235] Data obtained from sediment traps has shown that most coccoliths reaching the seafloor do so by aggregation caused by zooplankton grazing and encapsulation in fecal matter.

Submarine lithification and precipitation of cements in deep sea carbonate sediments are relatively rare processes in typical major ocean basin sediments.[235−238] The cements are of both aragonitic and magnesian calcite mineralogies, and are largely restricted to shallow seas such as the Mediterranean and Red seas, and sediments in the shallower parts of major ocean basins in which biogenic aragonite is also present. Many shallow water and deep sea carbonate cements fall in the range of 10−15 mol % $MgCO_3$ with a strong maximum in abundance at about 13 mol % Mg.[21,239]

Another often local source of aragonite and high-Mg calcite to the open ocean water column and deep sea sediments is shallow-water carbonate-rich sediments. During events such as major storms sediments in the shallow-water environments can be resuspended and transported to nearby deep-water environments. Dissolution can occur in the upper water column, as demonstrated near Hawaii for high-Mg calcite[240] or be deposited in deep sea sediments (e.g., near the Bahama Islands[241,242]).

## 4.3. Shallow Water Biogenic Carbonate Sources

### 4.3.1. General Considerations

As previously described, the grains of carbonate sediments can be subdivided into skeletal and nonskeletal components. Carbonate muds, composed dominantly of silt- and clay-sized ($<63\ \mu$m) particles, are common deposits in low-energy environments, such as tidal flats and subtidal areas. Larger carbonate grains, which may dominate to form carbonate sands, include pellets that are formed by the ingestion of sediment by marine organisms and excretion of fecal material; oöids, which are spherical to ovoid 0.2−1 mm grains with an internal concentric or radial structure; lithoclasts, which are fragments of previously deposited and usually somewhat lithified carbonate sediment; and relict grains 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 like corals, mollusks, and rocks. The wide diversity in the types of shoal−shallow water organisms and their complex compositional and morphologic characteristics, in combination with the varied processes causing their disaggregation, lead to a very complex mixture of biogenic carbonate grains in shoal−shallow water sediments.

### 4.3.2. Sources of Fine-Grained Carbonate Sediments

The origin of carbonate mud is a long-standing topic of considerable debate and controversy. The three major potential sources generally considered are (1) physiochemical or biochemical precipitation, (2) postmortem disintegration of calcareous algae, and (3) physical or biological abrasion of skeletal material.[243] Research has generally focused on either aragonite or high-Mg calcite mud components. Generally within the silt and clay sizes ($<63\ \mu$m), there is little mineralogic, elemental, or stable isotopic variation among subdivisions of this grain-size fraction.[244]

Fine-grained carbonate-rich sediments that are dominated by small (a few micrometers) needle-shaped aragonite grains are referred to as aragonite needle muds. The two major sources for the aragonite needles generally considered are calcareous algae and abiotic precipitation.[245,246] The fine size of this material has resulted in most of the interpretation of its origin being largely based on chemical data, although needle morphology has also been used.

Attempts at making budgets of carbonate production and accumulation have also been used to attempt to answer the question of 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.[247] A basic difficulty in determining the origin of aragonite needles is that precipitation of aragonite from seawater produces needles with a very similar size and morphology to those resulting from breakdown of common codiacean green algae. It is necessary, therefore, to examine the chemistries of the needles to determine their origin. However, even the chemical characteristics have generally not proven unambiguously diagnostic.[244,245,248,249]

The waters and sediments of the Great Bahama Bank have been intensely studied by carbonate geochemists. Following is a brief summary of some of the more recent findings that provide an excellent opportunity to tie laboratory results to field observations.[250] The study was aimed at understanding “whitings”, which are suspended “clouds” of fine-grained $CaCO_3$ that can even be observed from space (Figure 15). They occur on the northern part of the Great Bahama Bank (GBB) and on the Little Bahama Bank (LBB). Their abiotic versus biotic origins have been widely disputed. On the GBB, the waters have a long residence time (∼240 days), and about a third of the specific alkalinity is lost due to $CaCO_3$ precipitation.

The “kinetic solubility” of suspended whiting material has been determined to be about 1.9 times that of aragonite and inner Bank waters are close to equilibrium with the phase that gives this kinetic solubility.[250] Similar values of the ion concentration products were observed for many pore waters from carbonate-rich sediments in this region.[251] The kinetic solubility value obtained for the dominantly aragonitic suspended sediment from the Bahamas was very similar to that obtained for thin overgrowths on calcite.[250]

The rate of calcium carbonate precipitation in waters on the GBB was calculated from changes in specific alkalinity, estimated water mass ages and the amount of suspended carbonate solid in the waters. The rates were in good agreement with experimentally determined rates using sea-

**Figure 15.** NASA space shuttle photograph of whitings (filamentous white linear features near center) taken of the central Little Bahama Bank (Roll 719; Frame 29). Image courtesy of the Image Science & Analysis Laboratory, NASA Johnson Space Center (http://eol.jsc.nasa.gov).

water at similar saturation states and a fine fraction of sediments obtained from the area where the whitings occurred. These results are encouraging in demonstrating that solubilities and precipitation kinetics obtained from both the field observations and laboratory experiments were in good agreement.

Although not nearly as much attention has been paid to the production of lime mud from calcitic sources as aragonite, it can be the dominant component in perireefal[251] and lagoonal[237] environments where Mg-calcite may constitute from 70% to 90% of the mud. The mud can form from micritization and recrystallization of skeletal grains.[237] Breakdown of foraminiferal tests can often be a primary source of Mg-calcite in muds.[252]

### 4.3.3. Sources of Carbonate Sands

Carbonate-rich sediments that are dominated by sand-sized ($>63\ \mu$m) grains are common in shoal-water sediments. They are usually associated with moderate- to high-energy environments such as beaches, edges of carbonate banks, and behind fringing reefs. Carbonate sands are often composed of carbonates of mixed mineralogy from a variety of biogenic sources (Table 3). These components are produced by physical abrasion, boring, and other biological processes.

Subspherical carbonate grains, generally referred to as oöids because of their resemblance to fish eggs, comprise sandy sediments called oölites that are common members of modern shoal-water tropic and subtropic carbonate-rich sediments. Oöids are variable in both mineralogy and structure. Aragonite, high magnesian calcite, and calcite have been observed to occur in oöids.[253] Radial, concentric-tangential (laminated), and micritic structures are commonly observed around a central nucleus of nonoöid material. Oöids are believed to be of nonbiogenic origin and represent one of the most important modes of nonbiogenic removal of $CaCO_3$ from the ocean. In addition, it has frequently been pointed out that their mineralogy and structure reflect those of marine carbonate cements.[253,254] In fact, they grade into each other in the case of Bahamian grapestone. Because of their importance as presumably abiotic marine carbonates, oöids have been extensively studied and brief summary of the primary findings follows.

There are three primary classes of hypotheses for the processes responsible for the existence of oöids. They are based on bacterial−mechanical, algal, or chemical mechanisms for oöid formation. Some investigators have made hybrid models involving more than one of these mechanisms. We will only present these hypotheses in a general manner

**Table 3. Skeletal Composition of a Calcareous Sand from a Grass Bed, Ferry Reach, Bermuda**[a]

| taxa identified | number of grains | percent |
|---|---|---|
| gastropods | 162 | 6.4 |
| bivalves | 81 | 3.2 |
| foraminifera | 722 | 28.7 |
| grass fragments | 205 | 8.2 |
| *Halimeda* spp. | 1117 | 44.5 |
| *Cymopolia* spp. | 26 | 1.0 |
| ostracods | 36 | 1.4 |
| encrusting red algae | 9 | 0.4 |
| serpulid (?) worm tubes | 9 | 0.4 |
| agglutinate worm tubes | 11 | 0.4 |
| caecum gastropods | 10 | 0.4 |
| unidentified grains | 90 | 3.6 |
| total grains counted[b] | 2515 | 98.6 |

| type of organism | number of species |
|---|---|
| gastropods | 9 |
| bivalves | 5 |
| foraminifera | 21 |
| grasses | 3 |
| *Halimeda* spp. | 3 |
| *Cymopolia* spp. | 1 |
| other green algae | 1 |
| encrusting red algae | 1 |
| chitons | 1 |
| ostracods | 3 |
| echinoids | 1 |
| agglutinated worm tubes | 1 |
| crabs | 1 |
| serpulid worms | 1 |
| scaphopods | 1 |
| caecum gastropods | 1 |
| sponges | 1 |
| total species counted | 55 |

[a] Adapted from ref 1. [b] The remainder included non-calcareous green algal fragments, chitons, echinoid spines, scaphopods, sponge spicules, and crab carapace fragments.

and not attempt to reference the large number of papers relevant to the topic.

One of the earliest nonbiological hypotheses[255] for the mechanism of oöid formation was that oöids with a concentric structure form by a process similar to that which forms a snowball. In this model, an organic coating is biologically deposited (the infamous “mucilagenous slime”) on the surface of the oöid and then, as the oöid is rolled back and forth by wave action, small aragonite needles, which are common in most modern depositional environments where oöids are found, become imbedded in the organic matter. During subsequent quiescent times a new organic coating is added. This process is repeated many times (up to 200 lamellae have been observed in oöids) causing growth of the oöid. This model has the attractive characteristics of not requiring biotic or chemical formation of $CaCO_3$ directly on oöid surfaces and offering an explanation for the observation that oöids appear to require “rest” between depositional cycles. It also provides a reasonable explanation for the concentric organic-rich layers generally observed in laminated aragonitic oöids.

There are, however, some problems with the model.[1] It clearly does not apply to radial oöids. When examined carefully, it fails to explain the general excellent sorting in grain size and mineralogy, tangential arrangement of the aragonite rods, or the formation of relatively thick lamellae on typical aragonitic oöids. It is also questionable how well such coatings could hold up on grain surfaces in the abrasive, high-energy hydrodynamic environments characteristic of laminated aragonitic oöid formation. It may be best to consider this bacterial−mechanical hypothesis for the formation of laminated aragonitic oöids as a precursor to more recent models, where adsorption of organic matter on oöid surfaces influences the precipitation of $CaCO_3$.

The hypothesis that oöids form by direct chemical processes has gained increasing popularity, and there is a growing body of experimental and observational evidence to support it. Stable isotope[240−245] and Sr concentration data are generally compatible with nonbiogenic formation. In recent years, particular emphasis has been placed on the possible role of organic compounds.[256,257] This hypothesis is also not without its problems. It fails to explain why it has been difficult to produce nonradial oöids by direct precipitation, it fails to give an explanation for organic lamellae or the general distribution of oöids, and it cannot explain why high magnesian calcites are formed in calcitic oöids.

Bathurst[258] has presented a model that solves some of the problems associated with laminated aragonitic oöid formation. His suggestion involves a means for growing inorganic precipitates of tangentially oriented rods. His arguments also offer plausible explanations for limitations on oöid size and other characteristics. One of the difficulties in understanding typical aragonitic oöid formation is the fact that the aragonite needles, or battens, are arranged with their *c* crystallographic axes parallel to the solid surface. Bathurst[258] observed that the radial-fibrous fabric found in calcitic oöids can be explained as the result of competition between crystals that grow most rapidly in a direction parallel to one crystallographic axis. The perpendicular orientation of the aragonite *c*-axis is commonly observed for aragonite crystals on the walls of Foraminiferida and in the utricles of *Halimeda*. It is also the preferred orientation of aragonite in beach rock. However, it is not the typical orientation of aragonite on free calcrete grains where the aragonite grains are arranged with their *c* axes parallel to the surface. Bathurst[259] observed the growth of aragonite needles with their *c* axes parallel to the surface in 3 $\mu$m thick films on a variety of calcarenite grains outside of the oölitic shoal environment in the coralgal, stable sand, grapestone, and mud habitats at a number of locations. He suggested that the tangential orientation may result from the adsorption of colloidal sized aragonite nuclei on the solid surface, with their longest axis parallel the surface providing the most stable arrangement.

Contrary to the contention of many investigators of oöid formation, Bathurst suggests that there is not a strong correlation between the degree of water agitation and the orientation of aragonite needles. He cites his observation of the similarity between grains with oölitically structured films in the Bimini Lagoon and the oöids of Brown’s Cay, Bahamas, which exhibit no petrographic differences, including the existence of lamellae, in spite of the radically different hydrographic environments. His ideas have been reinforced by the observations of Land et al.[253] in Baffin Bay, Texas, where calcitic radial-fibrous and aragonitic tangential oöids coexist in the same sands and show no significant correlation with the probable wave energy differences at the different sampling sites.

Bathurst[259] also examined the question of size and sorting of oöids and the thickness of individual oölitic coats. He feels that the thickness of the coats may reflect growth rates, which are in turn a reflection of the degree of agitation. Higher energy waters will expose the oöids to more supersaturated water for a longer period of time. A problem with the sorting and size of oöids on banks is that the oöids are usually of similar size. Small ones should be winnowed from the oölite banks by the intense hydrodynamic conditions generally present. The source of the oöids, therefore, must be in deeper waters where hydrodynamic conditions are less intense. Bathurst suggested that the upper size limit on oöids may be governed by a balance between abrasion and growth rates.

Weyl[260] observed carbonate precipitation in seawater flowing over a column of oöids. After an initial period of precipitation, the reaction between the oöids and supersaturated seawater appeared to stop. If the oöids were allowed to sit for a period of time with no water flowing, they would again become reactive. This experimental observation led to the idea that oöids need to "rest" between reactive periods. It was hypothesized that a high magnesian calcite coating initially formed, which later dissolved in pore waters of an oölite bank before more aragonite would precipitate. This hypothesis has been quite popular ever since Weyl's work, although it is far from proven.

By far the most extensive experimental study of the chemistry of oöid formation was done by Davies, Bubela, and Ferguson.[261,262] Their primary emphasis was on the influence of different types of organic compounds and agitation conditions on the mineralogy and morphology of the precipitated carbonates. After studying the influences of a variety of organic compounds on the mineralogy and morphology of the precipitates, it was found that humic acids were most effective in producing magnesian calcite (composition was not reported), with a fabric similar to that of radial oöids. It was also observed that, while low molecular weight humic acids were preferentially adsorbed relative to high molecular weight humic acids, the high molecular weight humic acids were most effective in producing oöid-like products. A lengthy discussion of the possible reasons for this observation was presented, which noted that the high molecular weight humic acids had a higher Mg to Ca ratio and that humic acids through hydrophilic−hydrophobic interactions could possibly make membrane-type structures. Tangentially oriented batten-like aragonite crystals were synthesized on the surfaces of quartz grains and Bahamian oöids without the intervention of organic compounds. A high degree of agitation was found necessary, and like Weyl, Davies, Bubela and Ferguson observed the necessity of a "resting" period during which surfaces were reactivated, possibly by the release of $Mg^{2+}$ or $H^+$. Their studies are remarkable in indicating that organic matter may be important for the formation of magnesian calcite radial oöids but not aragonitic tangential oöids. This observation is contrary to general consensus on the formation of these two types of oöids. It may also offer a major clue to the formation of aragonitic and calcitic carbonate cements.

### 4.3.4. Carbonate Cements

The formation of carbonate overgrowths and cements is certainly one of the most important and highly studied aspects of the behavior of carbonates in sediments and sedimentary rocks[1,263−265] Carbonate cements in calcareous sediments fall into three major groups. The most common are those that occur in voids found in biogenic carbonates. This group is especially important in reefs. 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.[254] 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, there are abundant carbonate surfaces for overgrowths to form on, and both overlying seawater and many pore waters are supersaturated with respect to carbonate minerals. Morse and Mucci[266] demonstrated that precipitation of cements from pore waters of carbonate sediments is severely inhibited by burying Iceland spar calcite crystals in a variety of carbonate sediments in the Bahamas for several months. After recovery and analysis using depth-profiling Auger electron spectroscopy, they were able to detect overgrowths 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 probably severely inhibited by organics such as humic acids.[267] Thus, inhibition of precipitation, coupled with slow transfer of fresh supersaturated seawater into sediment pores, seems to account for lack of extensive early cementation.

Factors controlling the mineralogy and chemical composition of carbonate cements in the marine environment have also been extensively investigated. Bathurst[268] summarized many of the observations[269] indicating that in some cases the host carbonate mineral is a factor in determining composition. Usually aragonite grains have aragonite overgrowths, whereas high-Mg calcite grains have high-Mg calcite overgrowths of similar Mg 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 from their host grains.[1]

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 strong evidence for cement formation from normal seawater comes from stable isotopes. The $\delta^{13}C$ values of cements are usually close to those predicted for carbonates precipitating from seawater.[270] Another possible source of the ions necessary for cement formation is from the dissolution of carbonate phases more soluble than the cements. High-Mg calcites could provide such a source, as has been demonstrated in periplatform oozes in the Bahamas[271] and for coastal carbonate sediments of the Bay of Calvi in Corsica.[272] This process, leading to cement precipitation, 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-Mg calcite[273] is generally inferred from a decrease in dissolved pore water calcium.[274,275] 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.[209] Carbonate precipitation can also occur via methane oxidation instead of organic matter oxidation, resulting in distinctly "light" $\delta^{13}$C values for authigenic carbonates.[276]

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 to 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.[277] In addition, Fabricius[254] has presented a lengthy discussion in favor of the formation of grapestone cements and oöids by algae.

### 4.3.5. 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.[125,278] A plausible explanation for the slow precipitation kinetics of dolomite is that the requirement of cation ordering puts a major limit on the rate at which the phase can form.[279] It is likely that the dehydration kinetics of $Mg^{2+}$ also play a role.[245] Because the precipitation kinetics of dolomite are too slow to be studied in the laboratory at near Earth-surface temperatures,[280] experiments on dolomite reaction kinetics have generally been conducted at elevated temperatures (typically between 100 and 300 °C). While considerable interesting information has been gathered from these experiments, the applicability of the results to lower temperature and slower reaction kinetics remains highly questionable.

Observations of dolomite formation in natural systems also have been used as the basis for discerning additional factors that may influence the rate of dolomite formation. These include catalysis by certain clay minerals[281] and production of organic byproducts by bacteria.[282] $Mg^{2+}$ transport to sites of dolomite precipitation can inhibit the reaction in hemipelagic sediments.[283] However, the true influence of reaction rates is largely speculative because the kinetic factors are generally deduced primarily from the presence or absence of dolomite in different environments.

Most modern dolomite is forming from high ionic strength solutions that are typically 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, 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 Spring Lake in California. A general feature of many of these areas is that high $Mg^{2+}$ to $Ca^{2+}$ solution ratios appear to promote dolomitization. Friedman[284] discussed the general 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 an evaporite mineral − an opinion that is not universally accepted.

The importance of inhibition of dolomite formation by sulfate has been widely debated.[285] While dolomite formation is usually associated with sediments where sulfate reduction is active, the observation that dissolved sulfate concentrations can remain high and dolomite still can form argues against dominant control by dissolved sulfate. This observation suggests that reaction products of sulfate reduction, such as increased alkalinity, may play a more important role in increasing the formation rate of dolomite than sulfate does in inhibiting it. This conclusion has been expanded upon by Compton,[286] who emphasized the general observation that highly elevated solution supersaturations with respect to dolomite are usually associated with sediments containing above average concentrations of organic matter. He termed dolomite that forms under these conditions "organogenic dolomite." More recently, Mazzullo[287] has further explored and summarized the data supporting the early formation of dolomite in organic-rich sediments where extensive sulfate reduction and methanogenesis occur.

Arvidson and Mackenzie[288,289] conducted experiments on dolomite growth at elevated temperatures from which they were able to derive a rate equation where temperature and saturation state were used to predict growth rates. This equation was used to extrapolate to conditions where dolomite formation is currently occurring in sediments, and reasonable (within an order of magnitude) agreement between calculated and observed growth rates was found.

Another factor that may promote dolomite formation during early diagenesis is direct participation by bacteria. The literature relating to this possible avenue of low temperature dolomite formation was reviewed by Vasconcelos and McKenzie[290] in their study of microbial mediation of dolomite formation in Lagoa Vermelha in Brazil.

### 4.3.6. Carbonate Minerals Formed in Siliciclastic Sediments

Carbonate minerals that are formed in siliciclastic sediments are dominantly the result of diagenetic reactions taking place in the sediments. The quantitatively most important reactions generally occur very close to or within less than a meter of the sediment−water interface. These reactions are often associated directly or indirectly with a variety or terminal electron acceptors, such as solid iron and manganese oxides and dissolved sulfate, used by bacteria metabolizing sedimentary organic matter or hydrocarbon gases. Not only do bacteria play an important role in the formation of carbonate minerals in sediments, but they are also, as will be discussed in section 5, the primary driving force for dissolution of sedimentary carbonate minerals. This is a large and complex field of study that we will only briefly touch on in this paper. However, reviews dealing specifically with the topic are available.[1,291,292]

A very important reaction for both the formation and destruction of calcium carbonate in marine sediments is bacterial sulfate reduction, which can be represented as an approximation for marine organic matter as given in eq 4.1.

$$\frac{1}{53}(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + SO_4^{2-} \rightarrow CO_2 + HCO_3^- + HS^- + \frac{16}{53}NH_3 + \frac{1}{53}H_3PO_4 + H_2O \quad (4.1)$$

Because the components of the organic matter are at constant ratios, fixed pH can be established after a moderate degree of sulfate reduction in a closed system.[293] During these early stages of reaction in seawater, the pH drops to about 6.9, in the absence of other reactions, and remains constant. This can result in pore waters becoming undersaturated and carbonate dissolution occurring. Further sulfate reduction causes the alkalinity to rise while the pH remains constant. At about 35% sulfate reduction, the pore waters regain supersaturation with respect to calcium carbonate and further sulfate reduction can result in calcium carbonate precipitation.

Massive carbonate crusts and nodules can be formed in sediments rich in organic matter. Sediment through which hydrocarbon gases, usually dominantly methane, are seeping are especially noteworthy in this regard and are commonly associated with deeper sedimentary methane hydrates.[294−296]

"Reactive" forms of Fe(III) and Mn(IV) are found in siliciclastic sediments that can be reduced either by bacteria or through reactions with dissolved reduced pore water components such as $H_2S$. The resulting dissolved Fe(II) and Mn(II) can react with $CO_3^{2-}$ ions to either coprecipitate with calcium carbonate minerals or form distinct iron and manganese carbonate minerals. For Fe(II) the common mineral formed is siderite ($FeCO_3$), which is most common in estuarine and freshwater sediments where little sulfide is formed that competes for the Fe(II) to form minerals such as pyrite ($FeS_2$). Although Mn(II) can form simple $MnCO_3$ (rhodochrosite), careful studies[10] indicate that it is more likely to form a poorly ordered Mn analogue to dolomite, (pseudo)-kutnahorite ($CaMn(CO_3)_2$).

# 5. Dissolution of Calcium Carbonate

## 5.1. Dissolution of Carbonate Minerals in the Pelagic Environment

### 5.1.1. General Considerations

One of the most controversial areas of carbonate geochemistry has been the relation between calcium carbonate accumulation in deep sea sediments[297] and the saturation state of the overlying water (see Millero[2] in this issue). The accumulation of calcium carbonate in deep sea sediments has been mapped for over 100 years based on the "carbonate compensation depth" (CCD). Although this has been defined using various concentrations of $CaCO_3$ in sediments, it basically divides deep sea sediments into those with little (less than ~10 wt %) to no $CaCO_3$ from those containing substantial $CaCO_3$ concentrations that commonly exceed 80 wt %. Analogous to the CCD is the aragonite compensation depth (ACD), which is defined in reference to the mineral aragonite rather than simply total $CaCO_3$ content as is the CCD. Two other commonly used sediment markers of carbonate dissolution based on foraminifera tests are the foraminiferal lysocline (FL) and the $R_0$ depths. The CCD, FL, $R_0$, and ACD have been carefully mapped in many areas. However, with the exception of complete $CaCO_3$ dissolution at the CCD and complete aragonite dissolution at the ACD, the extent of dissolution that has been observed in most deep sea sediments is difficult to quantitfy. 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 and constants used to calculate the saturation states of seawater have been a source of contention. A reason that there has been so much controversy associated with 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 co-incident with calcite and aragonite saturation levels,[298] to a strongly kinetically controlled system[299] where major differences in the CCD, FL, and saturation depth exist. However, it now appears that the long cherished idea of a "tight" relation between seawater chemistry and carbonate depositional facies must be reconsidered.[300] This is a fertile field for further research.

### 5.1.2. Dissolution in the Water Column

Millero[2] (this issue), discussed that, based on changes in water chemistry, it is estimated that probably 40−80% of the $CaCO_3$ formed in the pelagic environment dissolves in the upper water column. Maximum dissolution rates occur near the aragonite saturation depth.[228] An extensive investigation of planktonic foraminifera in sediment trap samples from the tropical Pacific and central Atlantic oceans has been conducted, and at both study sites, the total foraminiferal flux and the carbonate flux tend to decrease with depth.[301] In addition, the flux of individual species of planktonic foraminifera varies significantly with depth, with the number of small, solution-susceptible species decreasing with increasing depth. These results indicate that there is significant dissolution of small ($<150$ $\mu$m) foraminifera as they settle through the water column. Material 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.[301,302]

A study of the sedimentation of pteropods and foraminifera in the North Pacific using sediment traps confirmed that considerable dissolution of pteropods was taking place in the water column.[303] It was calculated that approximately 90% of the aragonite flux was remineralized in the upper 2.2 km of the water column. It should be noted that the depth for total dissolution in the water column is considerably deeper than the aragonite compensation depth. This is probably due to the short residence time of pteropods in the water column because of their rapid rates of sinking.

### 5.1.3. Dissolution on the Deep Sea Floor

Early models for the process of calcium carbonate dissolution in deep sea sediments were based on simple diagenetic models in which calcium carbonate dissolved into the pore waters of the sediments.[304] 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, causing 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 of the relatively rapid dissolution rate of calcium carbonate, the depth in the sediment calculated for equilibrium has generally been only a few millimeters.

A major benthic process that had only casually been considered for its potential influence on carbonate accumulation in deep sea sediments is the oxidation of organic matter. Although this reaction was widely recognized as being important in coastal and continental slope sediments, which are relatively rich in organic matter, it was generally ignored in deep sea sediments, which usually have less than 0.2 wt % organic C. With the advent of sediment traps, however, it became apparent that significant amounts of organic matter were reaching the sediment–water interface. Consequently, near-interfacial oxidation of organic matter is potentially a major diagenetic process even in deep sea sediments. A detailed review of this process has recently been made[293] for the reader interested in pursing the topic further.

Understanding of the factors that control the diagenesis of deep sea carbonates that leads to their partial to complete dissolution can be considered largely one of scale. For differences among major ocean basins, it is clear that the primary variable is the saturation state of the water at a given depth, which is largely controlled by its $pCO_2$. A secondary influence is the deposition rate of siliciclastic sediments. Within ocean basins, variations in 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 subsequent 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 exerts even a greater influence on carbonate diagenesis.

The approach that has generally been used is to estimate carbonate dissolution rates via diagenetic models that incorporate organic matter oxidation by oxygen (assuming a C/O ratio) that produces undersaturated conditions.[305] A relationship is then established between the calcite dissolution rate and pore water saturation state. The general kinetic equation for calcite dissolution in seawater (eq 3.12[166]) has been most commonly used.

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 the composition of the pore waters but also the solubility of the calcium carbonate must be known under *in situ* conditions. Therefore, many studies of carbonate chemistry in deep sea sediment pore waters have focused on the apparent solubility behavior of carbonates in these sediments. Early results[306,307] indicated that, despite 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 calculated equilibrium with calcite. Higher ion concentration products in pore waters where $Mn^{2+}$ was detectable were observed[306] indicating possible control by a carbonate phase other than calcite and a much higher ion concentration product in one sediment containing aragonite was also found.[307] Hales and Emerson[308] have observed different apparent solubilities for sediments from the Ceara Rise and Ontong-Java Plateau, but the reasons for this remain uncertain.

Perhaps no aspect of the diagenesis of deep sea carbonates has been more controversial than the values of rate constant and reaction order. Most investigators have modeled rates that demand rate constants orders of magnitude less than those measured for deep sea sediments in the laboratory. Also, the values for the reaction order have ranged from 1[309] to 4.5.[310] Even within a given study, as with apparent solubility products, different values for the rate constant have been required.[308,310] A puzzling observation was made by Jahnke and Jahnke[311] who found that in sediments above the saturation depth containing 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 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. Although considerable speculation has been put forth to attempt to explain these large variations in deep sea carbonate dissolution kinetics, at this time it appears our ability to make predictions is still quite limited and that a number of parameters may contribute to these variations.

## 5.2. Dissolution of Carbonate Minerals in Carbonate-Rich Shallow Water Sediments

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 (∼2% to 35%) this reaction may not cause precipitation, but rather results in undersaturation with respect to carbonate minerals because the impact of lowered pH is greater than that of increased alkalinity. 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 Fe-poor shallow water carbonate sediments from the Bahamas[251] and has been confirmed in other studies of Florida Bay,[312−314] Checker Reef, Oahu,[315] and Bermuda sediments.[316] There are three primary processes that have been identified that can cause undersaturation, in addition to the undersaturation that may result during the early stages of sulfate reduction. These are early postdeath microenvironments within organisms, oxidation of organic matter by processes preceding sulfate reduction, and oxidation of sulfides. These processes commonly will be most important near the sediment–water interface.

Prior to the onset of sulfate reduction, extensive organic matter degradation can occur by bacterially mediated oxygen reduction as described for deep sea sediments. The influence of benthic bacterial activity under aerobic conditions on carbonate mineral dissolution has been nicely demonstrated for pore waters from sediments of the Gulf of Calvi in Corsica.[272] Other reactions of probable less importance than those above leading to undersaturated conditions with respect to calcium carbonate near the sediment–water interface include nitrate reduction and fermentation.[317]

Lynn Walter and her associates[312−314] demonstrated the major quantitative importance of dissolution of calcium carbonate from shallow carbonate sediments. Up to about 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 then basically can only be buried in dissolved form in pore waters, be oxidized, or diffuse out of the sediments. For most carbonate-rich sediments, the oxidative process strongly dominates the fate of the sulfide. Figure 16 shows the strong relationship that generally occurs, in carbonate muds from Florida Bay, among total carbon dioxide, excess dissolved calcium (calcium at a concentration above that predicted from salinity), and the amount of sulfate

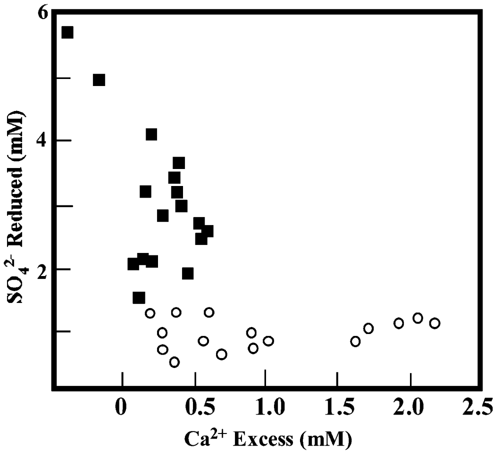


**Figure 16.** Dissolved sulfate versus excess $Ca^{2+}$ in the pore waters of carbonate-rich Florida Bay sediment: closed squares, unburrowed mud bank; open circles, burrowed mud bank. Modified from ref 313, Figure 2 with permission of the authorand the Royal Society, Copyright 1993.

that has been reduced. It is noteworthy that the burrowed banks show much more extensive increases in calcium than the other mud banks. This is in good agreement with the observations in Long Island Sound siliciclastic sediments, where increased bioturbation leads to increased sulfide oxidation and carbonate dissolution.[318]

## 6. Response of Carbonate-Rich Sediments to the Acidification of the Ocean Due to Rising Atmospheric $pCO_2$

### 6.1. General Principles and Considerations

There is now overwhelming scientific evidence that human activities, such as burning of fossil fuels and land use practices, have caused a major disruption of the natural global carbon cycle resulting in a major increase in atmospheric $pCO_2$.[319] This has changed the global ocean from a net source to a sink for $CO_2$ and a consequence of this has been an uptake by the ocean of roughly half of the excess $CO_2$ released.[2,228,320] Although there remains considerable scientific debate regarding the extent and distribution of climate change caused by rising atmospheric $CO_2$, there is no question that the uptake of $CO_2$ by the ocean is causing pH to decrease[321] and along with it the saturation state of seawater with respect to carbonate minerals.[322] It is hypothesized that this decrease in saturation state is in turn leading to a decrease in calcification by organisms and an increase in carbonate mineral dissolution.[323−325] These effects are likely to lead to major changes in the biology and chemistry of the ocean over a rather short period of time.

In considering the reactions involved between carbonate minerals and the carbonic acid−$pCO_2$ system, there are few important fundamental relationships that will be represented here in a simple form to illustrate the basic concepts generally following the conventions of ref 320. Intuitively, it might be expected that the precipitation of calcium carbonate would decrease solution $pCO_2$ and dissolution of calcium carbonate would increase $pCO_2$ because total dissolved inorganic carbon (DIC) concentrations and total alkalinity (TA) change in this manner. However, the opposite is true as shown in eq 6.1. Consequently, the addition of $CO_2$ to the ocean will be buffered by calcium carbonate dissolution and an associated increase in DIC and TA.

$$Ca^{2+} + 2HCO_3^- \underset{dissol}{\overset{ppt}{\rightleftharpoons}} CaCO_3 + H_2O + CO_2 \qquad (6.1)$$

Previously the relationship of organic matter oxidation to carbonate diagenesis was discussed. Organic matter production is also important and results in $CO_2$ uptake from seawater. Production and respiration can be written simply as opposing reactions as in eq 6.2. Organic matter production can occur along with calcification for formation of biogenic carbonate minerals from important organisms such as coccolithophorids and various coralline algae. These processes can be combined resulting in eq 6.3.

$$CO_2 + H_2O \underset{respiration}{\overset{production}{\rightleftharpoons}} CH_2O + O_2 \qquad (6.2)$$

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CH_2O + O_2 \qquad (6.3)$$

Although increasing the $pCO_2$ of the surface ocean may lead to a decrease in $CaCO_3$ production[326] and the release of $CO_2$ associated with this process, this will be counterbalanced by the formation of organic matter, which will be stimulated by higher $pCO_2$ values and possibly increased nutrient input to the ocean as well.[320] In fact, fertilization of the ocean is being considered as a possible way of removing $CO_2$. The subsequent oxidation of a major portion of the produced organic matter in the water column and at the seafloor in sediments will locally release $CO_2$, lowering saturation state and causing increased carbonate mineral dissolution. Thus, in the future the ocean will likely have a decrease in biogenic formation of carbonate minerals and an increase in the fraction of carbonate minerals produced that undergo dissolution.[297]

### 6.2. The Major Ocean Basins

It is estimated that probably 40−80% of the $CaCO_3$ formed in the pelagic environment dissolves in the upper water column (see section 5.1.2). The calcium carbonate that does survive and becomes buried on the seafloor is mostly calcite. We can therefore divide the impact of lowering the saturation state of seawater due to increasing $pCO_2$ into basically upper ocean processes, lowering the saturation state in the deep water column, and impacts on processes occurring near the sediment−water interface of deep sea sediments above the current CCD.

The upper water column, via air−sea exchange and relatively rapid mixing, will be first impacted by rising $pCO_2$ resulting in a probable lowering of $CaCO_3$ production and as previously described an increase in organic matter production, but nutrient availability may limit changes in primary productivity. This will result in changing the rain-rate ratio of $CaCO_3$ C to organic C into deep waters and sediments. Oxidation of the increased organic matter will result a rise of $pCO_2$ in the deep ocean prior to the penetration of $CO_2$-rich upper waters into the deep sea. This will lower saturation states with respect to carbonate minerals and lead to increased dissolution both in the water column and sediments. Subsequently, in a complex pattern reflecting deep water formation, mixing, and circulation, anthropogenic $CO_2$ will be transported from surface waters into the main volume of seawater that resides in the deep ocean basins. This mixing and equilibration will take thousands of years.[327] In conjunction with the associated major decrease in deep sea sediment calcium carbonate accumulation, this will be the primary

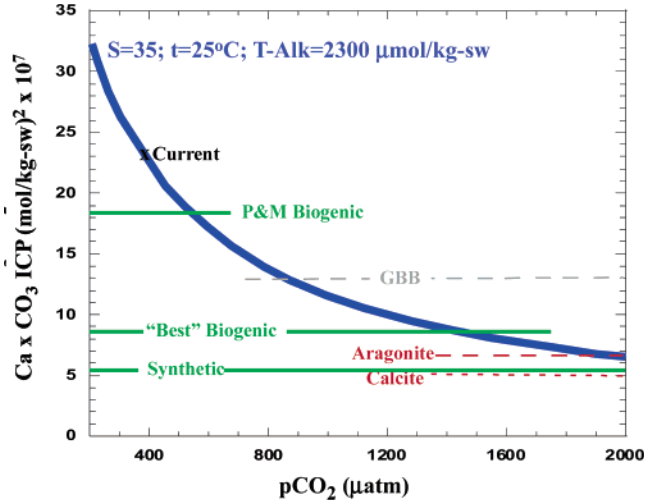


**Figure 17.** Change in the calcium carbonate ion concentration product in surface seawater at constant alkalinity as a function of $pCO_2$. Horizontal lines are for various solubility products. Green is for 15 mol % Mg calcite based on various solubility estimates. The gray line is based on observations from the Great Bahama Bank. Adapted from ref 329, Figure 11, Copyright 2006 with permission from Elsevier.

process that ultimately reduces atmospheric $pCO_2$ following the current pulse of anthropogenic input.[228]

## 6.3. Shallow Water Carbonate-Rich Sediments

As previously discussed, the shallow ocean will be most immediately impacted by rising atmospheric $pCO_2$ resulting in a lowering of pH and decreasing saturation state with respect to carbonate minerals. An impact that is already occurring is a decrease in calcification rates of organisms such as aragonitic corals. Attempts have been made to estimate the change that is expected in net shallow water (coastal margin) ecosystem calcifications rates that indicate a rather slow drop with time up until about the year 2000 to 2050 followed by a rapid decrease in the net calcification rate.[328]

In order to make predictions about the dissolution of shallow water marine carbonates in the future ocean in response to rising atmospheric $pCO_2$, the anticipated calcium carbonate ion concentration product can be computed as a function of time for surface ocean water and compared with the stoichiometric solubility product of different calcium carbonate minerals. An example of such calculations is given in Figure 17.[329] As discussed previously, a major difficulty occurs with the high magnesian calcites where the influences of magnesium and other factors lead to large certainties in their solubility. This is of particular concern in making predictions about the response of shallow marine high magnesian calcites to declining seawater pH because these minerals are the most soluble common carbonate minerals and therefore would be the "first responders" to a declining saturation state.

A simple schematic model utilizing this concept is presented in Figure 18. In this model,[329] reservoirs of various sizes for the different magnesian calcite, aragonite, and calcite compositions are allowed to react until they are exhausted in sequence of their solubility. This results in the changes with time in solution chemistry and reservoir sizes presented in Figure 19. Two scenarios were used based on the Plummer and Mackenzie[17] and "best fit" biogenic magnesian calcite stoichiometric solubilities (see Figure 2). The results of the two scenarios are quite different reflecting the large uncertainties in the solubilities of high magnesian calcites, but both do point to the large changes in dissolution expected for shallow water carbonates in the relatively near future due to changing atmospheric $pCO_2$.

## 7. Summary and Thoughts on Possible Future Research Directions

### 7.1. Summary

Our objective in writing this paper was to review the major aspects of the chemistry of carbonate mineral formation and dissolution in the marine environment. In doing so, we did not attempt to cover all that is known about carbonate mineral aqueous solution chemistry but rather focused primarily on those aspects of direct relevance to their behavior in seawater. Sections 2 and 3 of the paper dealt with basic properties and results of laboratory experiments, whereas sections 4 and 5 cover observations concerned with carbonate mineral formation and dissolution in the ocean. Section 6 briefly covers the response of the ocean and, in particular, carbonate minerals to rising atmospheric carbon dioxide concentrations.

While we have attempted to be reasonably comprehensive on the topics we addressed, there are many related subjects that were only touched on or not addressed to which different authors might have given greater attention. These include, for example, the oceanic carbon cycle, biomineralization, incorporation of trace components and isotopes used largely as proxies for paleooceanographic conditions, studies of early diagenesis, and how the ocean's chemistry and carbonate minerals have varied over geologic time. There is an extensive body of literature on all these topics and the reader who has gained interest in the chemistry of marine carbonates from this paper is encouraged to pursue these related areas. Also, it should be noted that a review paper on the carbonic acid system in seawater by Millero[2] appears in this issue, and therefore, we did not cover this topic in any detail.

Laboratory research related to carbonate mineral behavior has primarily been aimed at determining the solubility and reaction kinetics of calcite (including high-Mg calcites) and to a lesser extent aragonite in seawater under varying conditions. Research on dolomite formation under oceanic conditions has been much more limited due to its very slow reaction kinetics under close to STP conditions. Until relatively recently, most of the research focused largely on the composition of the solution in contact with these minerals. A major challenge has been the use of equilibrium thermodynamic concepts as the basis for interpreting results, even though in most cases the system is at best metastable. In many instances, it is not even possible for the carbonate mineral being studied to be in metastable equilibrium with the seawater solution because the reaction is not reversible.

Another difficulty is that most of the carbonate minerals formed in the ocean are derived from biogenic sources where the composition of solution from which they are precipitated is controlled by biologic processes often referred to in general as "vital" effects. This can lead to biogenic carbonates that are heterogeneous, partially hydrated, and disordered. A prime example given for these differences between the properties of abiotic and biotic carbonates was that of Mg calcites. Additionally, the morphology of the biogenic carbonates is often complex and microporous in nature leading to a disconnect between true (e.g., BET) surface areas and "reactive" surface areas. In some instances, these

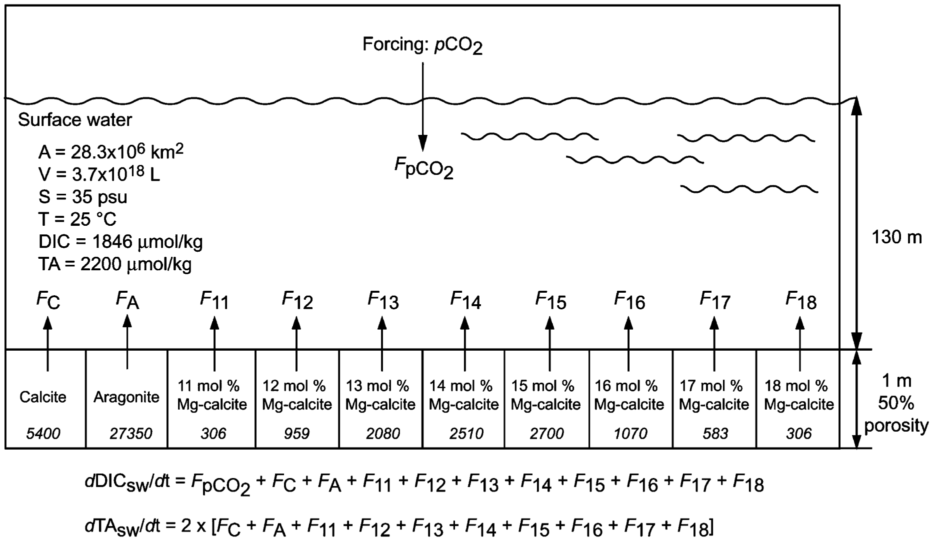


**Figure 18.** Model schematic of simple dissolution model representing the global coastal ocean. In the current simulations, the system was assumed to be closed and did not exchange water with the open ocean, the atmosphere, or input via rivers and runoffs. Arrows denote fluxes. The masses of carbonate phases are shown at the bottom of each carbonate mineral reservoir in $10^{12}$ mol. The major forcing of the model was $pCO_2$, which increased by 2 $\mu$atm year$^{-1}$. Reprinted from ref 329, Figure 4, Copyright 2006 with permission from Elsevier. Also see ref 330.

morphological properties can appear to override chemical properties such as solubility.

Considerable effort (and speculation) has gone into trying to establish the mechanisms responsible for observed kinetic behavior between carbonate minerals and a bulk seawater solution. It is now reasonably well-established that under conditions likely to be encountered in the ocean these reactions are surface-controlled rather than transport-controlled. Consequently, there has been an emphasis on trying to establish the chemical speciation of carbonate mineral surfaces under varying conditions and on identifying surficial mechanisms that are ultimately rate-controlling. The advent and increasing resolution and versatility of a variety of analytical techniques capable of determining composition, morphology, and structure at scales of a few nanometers has opened major opportunities for moving much of the research in this area from speculation to direct observation.

One of the more perplexing aspects of understanding the behavior of marine carbonates is the role of organic matter. Organic matter is ubiquitous in the marine environment. Most surfaces are covered with a film of adsorbed organic matter and many biogenic carbonate minerals have occluded organic matter. The use of the term organic matter is certainly not precise and reflects that much of this material is the result of the breakdown to various degrees of complex once-living tissue, of which only a small portion can be identified in terms of specific organic compounds. Consequently, the interaction and influences of "model" compounds have often been used to try to assess the potential impact of organic matter on marine carbonates. The interactions of different organic compounds and their influences on calcite and aragonite reaction kinetics vary widely. Observations of carbonate mineral diagenesis in marine sediments indicates that biologically derived organic matter may have little influence on calcium carbonate dissolution but may play a major role in inhibiting precipitation on sedimentary carbonates.

Near-surface seawater is supersaturated with respect to calcite (including abiotic high-Mg calcite), aragonite, and ideal dolomite. However, these minerals fail to precipitate directly from seawater under near-normal oceanic conditions. In the modern ocean, the dominant source of carbonate minerals comes from a wide variety of organisms that yield "skeletal" carbonates. In the pelagic realm of the open ocean, the primary carbonate mineral formed is low-Mg calcite (<4 mol % $MgCO_3$) coming from foraminifera and coccolithophores, with smaller amounts of aragonite also being derived from organisms such as pteropods and heteropods. Deep ocean sediments contain high-Mg calcite (>4 mol % $MgCO_3$) from benthic organisms and occasional abiotic marine cements usually as a very minor component of total sedimentary carbonate minerals. The sources and mineralogy of shallow water carbonates are much more highly varied and complex than deep water carbonates, with aragonite being the must abundant mineral followed by high and low magnesian calcites. In some regions, such as the Great Bahama Bank, the primary source of calcium carbonate is likely the abiotic precipitation of fine-grained aragonite needle "muds". Dolomite is rarely found and then usually only in "special" environments that typically show elevated salinity, temperature, or saturation state.

The production of calcium carbonate is greater in the pelagic environment than the shallow water environment, but the extent of dissolution is substantially less in the shallow water environment. In both environments, diagenesis in sediments, where carbon dioxide is added from remineralization of organic matter, can play an important role in calcium carbonate dissolution. However, deep ocean waters become undersaturated and the general distribution of calcium carbonate in deep sea sediments can be related to the variability in different ocean basins of the degree of undersaturation at equivalent depths. The processes controlling the finer scale distribution of deep sea carbonates include dissolution kinetics, organic matter content, and accumulation rate. Major hurdles remain to be overcome in determining the source of variations of apparent solubilities in pore water, and in resolving the differences in the dissolution kinetics determined in laboratory experiments with those obtained from modeling deep sea sediment pore water profiles.

The ongoing increase in anthropogenic $CO_2$ is having an impact on the degree of saturation of the surface ocean,

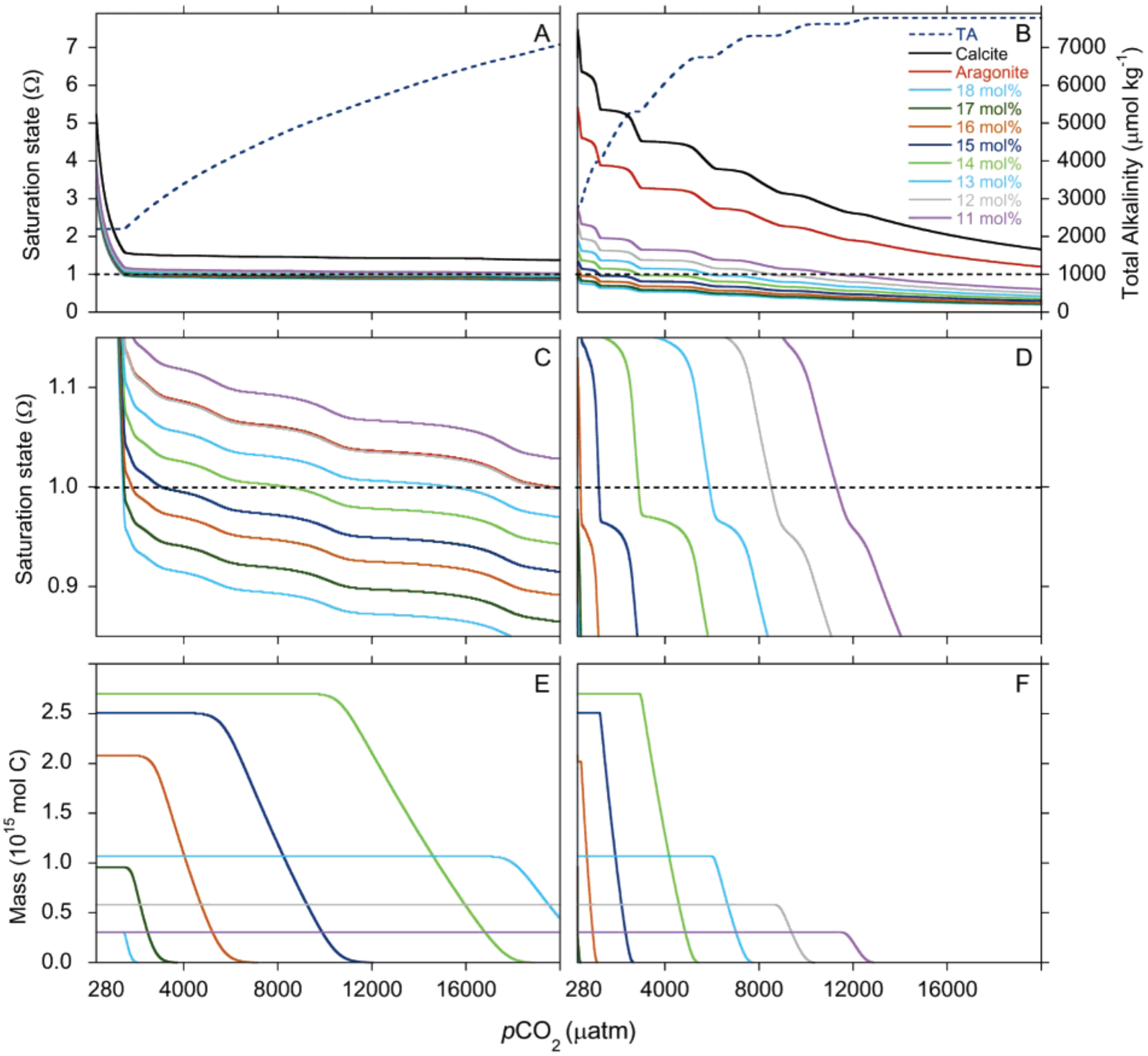


**Figure 19.** Model calculated responses of carbonate minerals to increasing pCO$_2$ (see text for details). The figure illustrates changes in saturation state with respect to calcite, aragonite, and 11−18 mol % Mg calcite and the total masses of Mg calcite minerals present in the sediments throughout the simulation in scenario 1 (A−C) and scenario 2 (D−E). The same saturation state data are shown in panels A and B and panels D and E but on different scales in order to highlight the sequential dissolution of the most soluble carbonate phase present in the sediments as well as the establishment of a metastable equilibrium between the seawater and this phase. Reprinted from ref 329, Figure 5, Copyright 2006 with permission from Elsevier. Also see ref 330.

generally referred to as the “acidification” of the ocean. The most immediate impact is on the shallow water environment, which is in close contact with the atmosphere. Here rates of calcification may be negatively impacted, and eventually it is likely that these waters will become undersaturated with respect to biogenic high-Mg calcites and in some regions even aragonite. The reduction in calcification rate and the increased dissolution of some shallow water sedimentary carbonates will lead to an increase in the oceanic uptake of CO$_2$. Over longer time spans this “excess” CO$_2$ will more extensively impact the deep sea leading to more extensive dissolution there, and features such as the calcium carbonate compensation depth will become less deep.

## 7.2. Thoughts on Possible Future Research Directions

Although research on the formation and dissolution of carbonate minerals in the ocean has been going on since at least the late nineteenth century, there remain many basic unanswered fundamental questions. Certainly three of the most important of these have to do with building bridges between different areas of research that have substantially evolved separately and where attempts to relate findings have often met with limited success at best.

The first area where better conceptual bridging is needed is between classic bulk solution−mineral work, in which the interaction between the solid and dissolved phases is often aproached using concepts derived from equilibrium thermodynamics, and more recent nanoscale mechanistic observations. Many of these concepts were the major focus of this paper. Future work will certainly have to focus on further development of experimental and analytical techniques. In particular, the improvement of time and spatial resolution will be of importance. The development of “super-resolution” methods is one possible pathway, and also the likely ability to combine techniques in one instrument, for example, the combination of confocal or fluorescence microscopy with interferometry or even AFM with VSI techniques, will further enhance our ability observe surface processes. However, being able to integrate these observations may also require a revised theoretical framework that provides a means of resolving relationships between surface composition and the distribution of surface energy. Development of this theoretical underpinning will also require an understanding of how overall reactivity varies as a function of length and time scales. More powerful Monte Carlo based computer simulations that treat crystal dissolution and growth as many-body problems also show promise. Computer simulations of this size and quality are the prerequisite for a direct comparison of high-resolution laboratory observations at the mineral surface.

Such a combined approach will allow the investigation of crystal dissolution and growth kinetics from the quantum mechanical to the macroscopic scale. Of course, modeling holds the most promise for those processes that are beyond the reach of laboratory experiments. Where possible, model predictions based on molecular simulations should be tested experimentally to provide a robust link between results from the nano-, micro-, and macroscales.

The second area where better conceptual bridging is needed is between results obtained from abiotic experiments and the characteristics of calcium carbonate “biominerals”. Clearly a major first step is a better understanding of how the biogenic carbonates that dominate the marine environment differ from experimentally studied abiotic phases. This does not mean that we have to know the details of how different organisms make their carbonate minerals, but we must develop an understanding of how the particular properties of biogenic carbonates influence solubility and kinetic behavior. This understanding must accommodate the fact that many biogenic carbonate minerals are likely to be heterogeneous on many different scales. As we have mentioned previously, this is a complex field in which even basic questions, such as how sample preparation may influence results, are still outstanding.

The third area where better conceptual bridging is needed is between what goes on under relatively simple and well controlled experimental conditions and what goes on in the “real” ocean. As discussed in this paper, there are often large differences between what is predicted and what is observed, often only indirectly. The problems in building bridges in this area have commonly been associated with two quite different communities of investigators, who have not only different experimental and observational methods but also often quite different philosophies about the potential of basic chemical approaches to ever resolve the behavior of very complex biogeochemical systems. However, until such approaches can be better brought to bear on these problems, our potential for a better understanding of the processes governing what we observe will be necessarily limited.

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