# SOLUTION—MINERAL EQUILIBRIA
PART 1: CARBONATES

Carbonic acid and the carbonate minerals provide another good illustration of the use of equilibrium reasoning in geochemistry. Interactions among these compounds determine the conditions under which limestones and dolomites are formed or dissolved, and likewise the conditions of formation of carbonate minerals as cements in soils and sandstones and as vein fillings. We start with some qualitative remarks about the most common of these substances, the carbonate of calcium, then go on to a more quantitative treatment and to the reactions of other common carbonate minerals.

3-1 SOLUBILITY OF CALCITE

Calcium carbonate occurs in nature as the two common minerals calcite and aragonite (Sec. 3-3). A third crystal form (vaterite) can be prepared artificially, and is known as a very rare mineral in nature. Under usual conditions near the Earth's surface calcite is the most stable and most abundant of the three forms, and for the discussion in this section and the next it will be the center of attention. Aragonite and vaterite may be assumed to show similar chemical behavior, but in general to react more rapidly and to have greater solubility.

A strong acid dissolves calcite by the familiar reaction

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2. \tag{3-1}$$

calcite
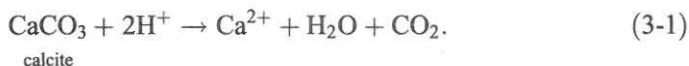
At low acid concentrations a more accurate equation would be

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{3-2}$$

calcite

showing that H^+ takes CO_3^{2-} away from Ca^{2+} to form the very weak (little dissociated) acid HCO_3^-. (Still greater accuracy would require consideration of the complex ion $CaHCO_3^+$, but under usual conditions its concentration is small and for the present can be neglected.) These reactions would take place in nature, for example, where acid solutions from the weathering of pyrite encounter limestone. The reactions can be reversed by any process that uses up H^+. For example, if a base is added,

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O. \tag{3-3}$$

calcite
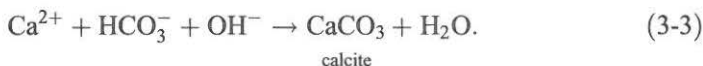
Quite evidently, the solubility of $CaCO_3$ is determined in large part by the pH of its environment. By using equilibrium constants for the above reactions we could express this dependence quantitatively, but we look first at some qualitative relationships.

Under natural conditions the dissolving of calcium carbonate is somewhat more complicated, because the acids involved are usually weak rather than strong. When limestone dissolves in carbonic acid, for example, the overall process may be summarized by the reaction

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-. \tag{3-4}$$

calcite
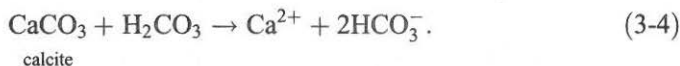
Note that the two HCO_3^- ions come from different sources: one is simply left over from the dissociation of H_2CO_3, and the other is formed by the reaction of H^+ from the acid with $CaCO_3$ [as shown by Eq. (3-2)]. Eq. (3-4) is the essential reaction for an understanding of carbonate behavior in nature. The forward reaction shows what happens when limestone weathers, when limestone is dissolved to form caves, or when marble is dissolved by ore-bearing solutions in the walls of a fissure. The reverse of Eq. (3-4) represents the precipitation of calcium carbonate in the sea, as a cementing material in sedimentary rocks, or where droplets evaporate at the tip of a stalactite.

The effect of pH on solubility is shown as well by Eq. (3-4) as by the simpler equations preceding it. At low pH, where most dissolved carbonate exists as H_2CO_3 [Fig. 2-3(a)], the forward reaction is favored; at high pH, the reverse reaction leads to precipitation. Eq. (3-4) shows also that the solubility depends on the partial pressure of CO_2 above the solution, since this pressure helps to determine the concentration of dissolved H_2CO_3 by the reaction,
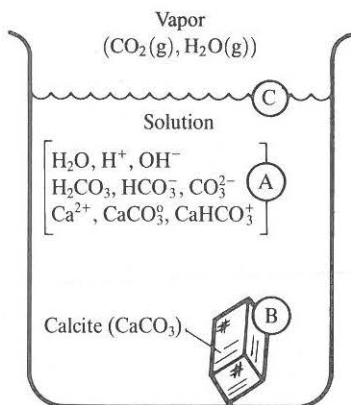
$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq). \tag{3-5}$$
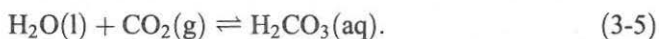
Any process that increases the amount of CO_2 available to the solution makes more $CaCO_3$ dissolve; anything that decreases the amount of CO_2 causes $CaCO_3$ to precipitate.

Reactions (3-1)–(3-4) have been written as one-way processes ($\rightarrow$) resulting in the dissolving or precipitation of $CaCO_3$. They could, of course, equally well represent heterogeneous equilibria ($\rightleftharpoons$), where calcite is in contact with a solution and with air, and where forward and reverse reactions are going at the same rate. The principal ions present in such a solution are shown in Fig. 3-1, and some of the ways in which equilibria among them respond to changes in conditions are described in the following paragraphs.
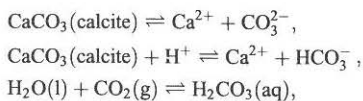
Temperature. The solubility of calcite and other crystal forms of $CaCO_3$ in pure water decreases somewhat as the temperature rises (Fig. 3-2). This is opposite to the behavior of most rock-forming minerals. An increase in temperature generally results in higher solubilities, but a number of carbonates and sulfates are exceptions. In addition to this effect, the solubility of $CaCO_3$ in natural waters decreases at higher temperatures because CO_2, like any other gas, is less soluble in hot water than in cold water. Generally the solubility of carbonates is influenced much more by this change in solubility of CO_2 than by the temperature dependence of the solubility itself. As an illustration of the effect of temperature, calcite dissolves at great depths in the ocean, where the water is perennially cold, but precipitates near the surface, especially in the tropics, where the water is warm.

Pressure. The effect of pressure by itself, independent of its effect on CO_2, is to increase the solubility of calcite slightly. Where pressure is very large, its effect can be substantial; in the deep parts of the ocean, for example, pressure alone increases the solubility to about twice its surface value. The main reason for an influence of pressure in near-surface environments, however, is the amount of dissolved CO_2 when the pressure of the gas changes in the surrounding atmosphere. Theoretically even day-to-day barometric changes should have a detectable effect on solubility,

Vapor
($CO_2(g)$, $H_2O(g)$)

Solution

$$\begin{bmatrix} H_2O, H^+, OH^- \\ H_2CO_3, HCO_3^-, CO_3^{2-} \\ Ca^{2+}, CaCO_3^0, CaHCO_3^+ \end{bmatrix}$$
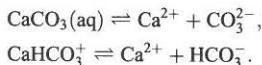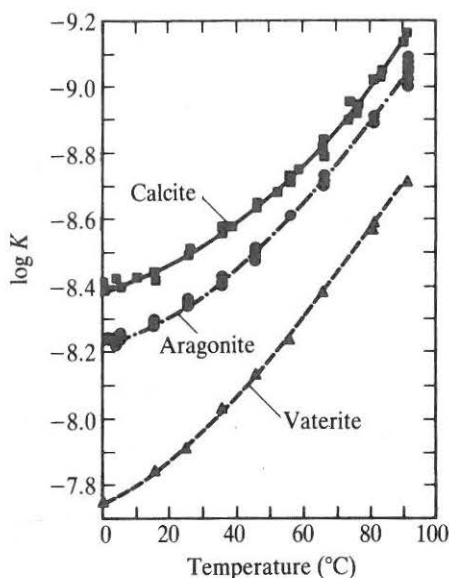
Calcite ($CaCO_3$)

FIGURE 3-1
Conditions for heterogeneous equilibrium between calcite and a solution of carbonic acid, and between solution and carbon dioxide in the gas. The principal ions present in the solution are indicated. Examples of heterogeneous equilibria would be:

$$CaCO_3(\text{calcite}) \rightleftharpoons Ca^{2+} + CO_3^{2-},$$
$$CaCO_3(\text{calcite}) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-,$$
$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq),$$

and examples of homogeneous equilibria would be:

$$CaCO_3(aq) \rightleftharpoons Ca^{2+} + CO_3^{2-},$$
$$CaHCO_3^+ \rightleftharpoons Ca^{2+} + HCO_3^-.$$

FIGURE 3-2
Change with temperature of the solubility products of three polymorphs of $CaCO_3$. The symbols represent experimental data. (Reprinted by permission from Plummer and Busenberg, 1982.)

and the local production of CO_2 in abnormal amounts, say by a forest fire, an industrial plant, or a volcanic eruption, could cause a marked increase temporarily. But circulation of the atmosphere is so effective in keeping the partial pressure of CO_2 uniform that this factor is probably less important than others.

Organic Activity. Many organisms use calcium carbonate in the construction of their shells. Just how they accomplish this is not certain, but they flourish in greatest numbers in water approximately saturated with calcite, where only a minor change in pH is needed to cause precipitation. Green plants may cause precipitation of calcium carbonate indirectly, by removing CO_2 from water in the process of photosynthesis. Abundant green algae in the warm waters of the Bahama Banks, for example, aid in the precipitation of the limy mud and sand with which the banks are covered.

Decay. Decay of organic matter in the presence of air or aerated water produces CO_2 in large amounts and hence makes calcium carbonate in the vicinity more soluble. If access of air is restricted or cut off entirely, the processes of decay are more complicated and the effect on solubility of carbonate minerals is not predictable. Any CO_2 or H_2S produced would make the water acid and lead to increased solubility, but ammonia is a common product of anoxic decay which would have the opposite effect. Measurements of pH in stagnant waters suggest that anaerobic decay most often causes increased acidity.

Carbonic acid, as these many examples show, is important in controlling the solubility of carbonate minerals in most natural environments, but carbonates are

somewhat soluble even in water containing no CO_2:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-. \tag{3-6}$$

calcite

This is a hydrolysis reaction, possible because HCO_3^- is a weak acid (meaning that the H-CO_3 bond is strong). Even the small amount of CO_3^{2-} produced by the dissolving calcite can take a little H^+ away from the OH^- of water. The reaction, of course, cannot go far in the forward direction, not nearly so far as the corresponding reaction for the CO_3^{2-} ion from a soluble carbonate [Eq. (2-24)], because here the reverse reaction is aided by the insolubility of calcite. But the reaction does go far enough to make water in contact with carbonates appreciably basic. In nature most water solutions are exposed to CO_2 from the atmosphere, and this complicates the hydrolysis. Experimentally it is found that water containing suspended calcite and left exposed to the air acquires a pH of approximately 8.

In summary, the solubility of calcite (and other carbonates) in nature is controlled by fairly simple equilibria involving H_2CO_3, HCO_3^-, CO_3^{2-}, and water. The principal equilibrium [Eq. (3-4)] is very sensitive to changes in the amount of dissolved CO_2, and this is dependent on a variety of influences. Much surface water and groundwater is approximately saturated with calcite, and such water can either dissolve or precipitate the carbonate, depending on slight alterations in external conditions. Hydrolysis of even fairly insoluble carbonates is sufficient to make solutions in contact with them slightly basic.

3-2   CALCIUM CARBONATE: SOLUBILITY CALCULATIONS

We set out now to apply the quantitative reasoning of the last chapter to these reactions involving calcite. We will try, for example, to answer such questions as: How much calcium carbonate can be dissolved in a solution of known composition and pH? What is the equilibrium pH of water standing in contact with limestone? If a base is added slowly to a solution containing calcium ion and carbonic acid, at what pH will calcium carbonate begin to precipitate?

For the solubility of calcite ($CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$) at 25°C we find from Appendix VII that the equilibrium constant is

$$K = \frac{a_{Ca^{2+}}a_{CO_3^{2-}}}{a_{CaCO_3}^{calcite}} = 10^{-8.35} = 4.5 \times 10^{-9}. \tag{3-7}$$

If the calcite is pure and the solution dilute the equilibrium constant is approximately equal to the product of $m_{Ca^{2+}}$ times $m_{CO_3^{2-}}$. (Here and elsewhere we will state equations in terms of the formally correct activities, but for applications to dilute solutions we will often substitute as approximations the more familiar molal concentrations. Whenever greater exactness is needed, or when more concentrated solutions are being considered, activities will of course be required.) The solubility in pure water, according to the methods of Chapter 1, should then be the square root

of this number, or about $6.8 \times 10^{-5} m$. Because of the hydrolysis of CO_3^{2-}, however, the process of dissolution is somewhat more complicated.

First we consider the calcite hydrolysis reaction, Eq. (3-6). The equilibrium constant can be evaluated by combining other constants as follows:

$$K_{(3-6)} = a_{Ca^{2+}} a_{OH^-} a_{HCO_3^-}.$$ (3-8)

Multiply the right-hand side by the ratio $(a_{H^+} a_{CO_3^{2-}})/(a_{H^+} a_{CO_3^{2-}})$ and rearrange to obtain

$$K_{(3-6)} = a_{Ca^{2+}} a_{CO_3^{2-}} \times a_{OH^-} a_{H^+} \times \frac{a_{HCO_3^-}}{a_{H^+} a_{CO_3^{2-}}},$$

which expresses $K_{(3-6)}$ as the product of equilibrium constants we have seen in Eqs. (2-7), (2-9), and (3-7),

$$K_{(3-6)} = K_{(3-7)} \times K_{(2-7)} \times \frac{1}{K_{(2-9)}}.$$

Substituting numerical values for these constants gives

$$K_{(3-6)} = 10^{-8.3} \times 10^{-14} \times \frac{1}{10^{-10.3}} = 10^{-12}.$$

In pure water, where the activity coefficients are approximately unity, the three ions Ca^{2+}, OH^-, and HCO_3^- should be formed in equal amounts [Eq. (3-6)], so that

$$m_{Ca^{2+}} = m_{OH^-} = m_{HCO_3^-}$$ (3-9)

and from Eq. (3-8) we solve for the value of $m_{Ca^{2+}}$,

$$m_{Ca^{2+}} = \sqrt[3]{10^{-12}} = 10^{-4} \text{ mol/kg H}_2\text{O}.$$

Hence calcite should dissolve in CO_2-free water to a concentration of $0.0001 m$ or about 0.01 g/kg H_2O, and the solution should acquire a pH of 10 (because $m_{OH^-} = 10^{-4}$).

This is not quite the end of the story, because at such a high pH the acid HCO_3^- is appreciably dissociated. From Fig. 2-3(a), in fact, we can read that the ratio $m_{CO_3^{2-}}/m_{HCO_3^-}$ should be about 0.5. This means that our assumption about the equality of the three ions is not valid and that more $CaCO_3$ must dissolve to maintain the ion product at 10^{-12}. Using the rough figure 0.5 for the carbonate–bicarbonate ratio, we guess that the concentrations of HCO_3^- and OH^- would be about two-thirds of the concentration of Ca^{2+}, instead of equal to it, so that the last equation should be

$$m_{Ca^{2+}} = \tfrac{3}{2} m_{OH^-} = \tfrac{3}{2} m_{HCO_3^-},$$ (3-10)

and from Eq. (3-8)

$$m_{Ca^{2+}} = \sqrt[3]{\frac{9}{4} \times 10^{-12}} = 1.3 \times 10^{-4} m.$$

Thus the solubility is raised to a figure about twice as large as the $6.8 \times 10^{-5}m$ obtained by simply taking the square root of the solubility product [Eq. (3-7)]. At the same time the OH^- concentration is lowered slightly, so that the pH is approximately 9.9 instead of 10.0.

This problem of calculating concentrations when calcite is in equilibrium with pure water may be set up more formally as follows. We note that the reactions contributing to the equilibrium involve a total of six concentrations: m_{H^+}, m_{OH^-}, $m_{Ca^{2+}}$, $m_{CO_3^{2-}}$, $m_{HCO_3^-}$, and $m_{H_2CO_3}$. To solve a problem with six unknowns requires that we have six equations. Three of these equations are supplied by the equilibrium constants for the dissociation of H_2O, H_2CO_3, and HCO_3^- [Eqs. (2-7), (2-10), and (2-11)], as required by homogeneous equilibrium in the solution, and a fourth equation comes from the reaction describing heterogeneous equilibrium of this solution with calcite [Eq. (3-4)]. Another equation expresses the fact that all carbonate in solution is supplied by dissolution of calcite, so that the sum of all carbonate species must equal the concentration of calcium:

$$m_{Ca^{2+}} = m_{CO_3^{2-}} + m_{HCO_3^-} + m_{H_2CO_3}, \tag{3-11}$$

The sixth equation comes from the requirement that the solution remains electrically neutral: the total concentration of positively charged ions must equal the total for negatively charged ions, with doubly charged ions counted twice:

$$2m_{Ca^{2+}} + m_{H^+} = 2m_{CO_3^{2-}} + m_{HCO_3^-} + m_{OH^-}. \tag{3-12}$$

The array of six equations can then be solved in various ways, most easily by using a computer program. An advantage of the formal approach is that results of greater accuracy can be obtained, but a simpler calculation like that in the last paragraph often provides all the accuracy that is justified by the quality of the original data.

The corresponding calculation for water containing CO_2 is based on Eq. (3-4), for which the equilibrium constant is [again following the procedure for Eq. (3-8) and assuming activity coefficients of unity],

$$K_{(3-4)} = \frac{m_{Ca^{2+}} m_{HCO_3^-}^2}{m_{H_2CO_3}}, \tag{3-13}$$

$$K_{(3-4)} = m_{Ca^{2+}} m_{CO_3^{2-}} \times \frac{m_{HCO_3^-} m_{H^+}}{m_{H_2CO_3}} \times \frac{m_{HCO_3^-}}{m_{CO_3^{2-}} m_{H^+}},$$

$$K_{(3-4)} = K_{(3-7)} K_{(2-8)} \times \frac{1}{K_{(2-7)}},$$

and

$$K_{(3-4)} = 10^{-8.3} \times 10^{-6.4} \times 10^{-10.3} = 10^{-4.4}.$$

In the reaction of Eq. (3-4), 2 mols of HCO_3^- are produced for every mol of Ca^{2+}. Hence, if there is no other source of these ions,

$$m_{HCO_3^-} = 2m_{Ca^{2+}}. \tag{3-14}$$

For equilibrium with CO_2 in the atmosphere, the concentration of dissolved CO_2 or H_2CO_3 is approximately $10^{-5}m$ (Sec. 1-4). We can then substitute in the expression for the equilibrium constant:

$$\frac{m_{Ca^{2+}} m_{HCO_3^-}^2}{m_{H_2CO_3}} = \frac{4m_{Ca^{2+}}^3}{10^{-5}} = 10^{-4.4}, \qquad (3\text{-}15)$$

whence

$$m_{Ca^{2+}} = 10^{-3.3} = 5.0 \times 10^{-4}, \qquad (3\text{-}16)$$

which is almost four times the concentration in pure water. To find the pH of the solution, we substitute values for $m_{HCO_3^-}$ [Eqs. (3-14) and (3-16)] and $m_{H_2CO_3}$ in the expression for the dissociation constant of carbonic acid [Eq. (2-10)]:

$$\frac{m_{H^+} m_{HCO_3^-}}{m_{H_2CO_3}} = \frac{m_{H^+} \times 10^{-3.0}}{10^{-5}} = 10^{-6.4}, \qquad (3\text{-}17)$$

whence $m_{H^+} = 10^{-8.4}$, and pH = 8.4.

This calculation, it should be noted, is only approximate because $m_{CO_3^{2-}}$ is assumed to be negligibly small. If the concentration of this ion were appreciable (in other words, if the simple dissolving of calcite to form Ca^{2+} and CO_3^{2-} is significant in comparison with the reaction of H_2CO_3), then it would no longer be true that $m_{Ca^{2+}} = \frac{1}{2}m_{HCO_3^-}$, and a more complicated procedure would be necessary. The magnitude of $m_{CO_3^{2-}}$ can be estimated from the relation [derived from Eq. (2-11)]

$$m_{CO_3^{2-}} = 10^{-10.3}\frac{m_{HCO_3^-}}{m_{H^+}} = 10^{-10.3}\frac{10^{-3.0}}{10^{-8.4}} = 10^{-4.9}m. \qquad (3\text{-}18)$$

This is only about 1/100 of the concentration of HCO_3^-, so for all ordinary purposes the assumption is justified. Alternatively, relations among the variables pH, $m_{Ca^{2+}}$, and P_{CO_2} can be usefully derived from the equilibrium for Eq. (3-1), for which the expression for the equilibrium constant can be written in logarithmic form as

$$\log \frac{a_{Ca^{2+}}}{a_{H^+}^2} = -\log P_{CO_2} + \log K_{(3\text{-}1)} \qquad (3\text{-}19)$$

(on the assumption that a_{H_2O} is 1). This is an equation for the straight line shown in Fig. 3-3(a) at 25°C and 1 bar total pressure where the value of $K_{(3\text{-}1)}$ is $10^{9.6}$. Then if we fix the partial pressure of CO_2, for example $P_{CO_2} = 0.1$ bar, the ratio of activities in Eq. (3-19) will be a constant equal to

$$\log \frac{a_{Ca^{2+}}}{a_{H^+}^2} = -(-1.0) + 9.6 = 10.6. \qquad (3\text{-}20)$$

Rearranging gives

$$\log \frac{a_{Ca^{2+}}}{a_{H^+}^2} = \log a_{Ca^{2+}} + 2pH = 10.6$$

or

$$\log a_{Ca^{2+}} = -2pH + 10.6, \qquad (3\text{-}21)$$

which defines an inverse linear relationship between the activity of Ca^{2+} and pH in a solution at equilibrium with calcite at a fixed partial pressure of CO_2 [Fig. 3-3(b)]. Results of similar calculations for pH and concentration of Ca^{2+} as functions of the partial pressure of CO_2 in Figs. 3-3(c) and (d) show that the solubility of calcite increases and pH decreases with increasing P_{CO_2}.

In dilute surface waters at temperatures near 25°C, then, the solubility of calcite ranges from about $1.3 \times 10^{-4} m$ [Eqs. (3-8) and (3-10)] to $5.0 \times 10^{-4} m$ [Eq. (3-16)], or 0.01 to 0.05 g/kg, depending on the degree of saturation with CO_2. The higher figure may be exceeded in colder water because CO_2 becomes more soluble; it will be exceeded also in places where CO_2 is unusually abundant or where some other source of acid keeps the pH low. In soils, for example, the decomposition of organic matter gives local concentrations of CO_2 often on the order of 0.1 bar, and sometimes as high as 1 bar. The pH's of solutions that have
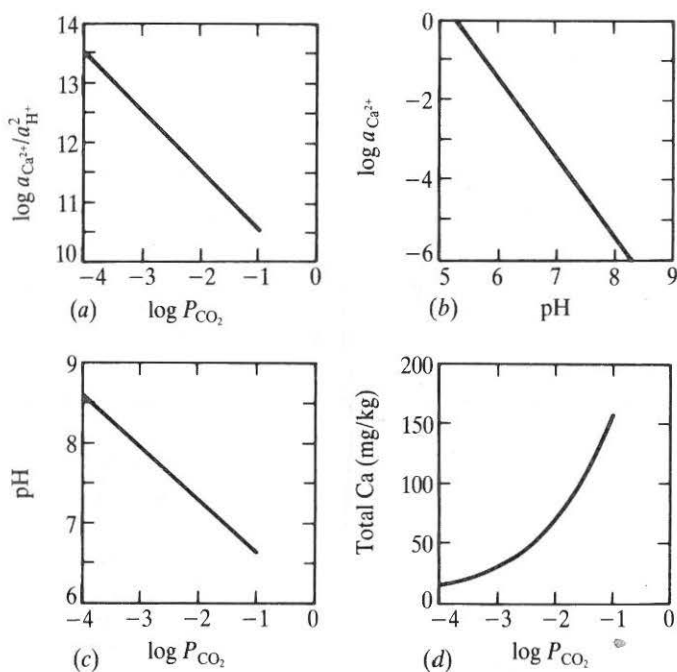
FIGURE 3-3

Relations among the variables pH, $a_{Ca^{2+}}$, and P_{CO_2} for heterogeneous equilibrium, at 25°C and 1 bar total pressure, of calcite in contact with solution [diagram (a), Eq. (3-19)], and in a particular solution containing carbon dioxide at a partial pressure of 0.1 bar [diagram (b), Eq. (3-21)]. The lines in the figures show conditions for calcite saturation. Further constraints may be placed on solution compositions by considering the total concentrations of solute components, the ionic strength, individual ion activity coefficients, and charge balance. Diagrams (c) and (d) show the computed increase in calcite solubility and the decrease in pH with increasing P_{CO_2}, using these variables with the equations and data in the computer program EQ3NR (see Sec. 2-8 and the reference to Nordstrom and Munoz on p. 56).
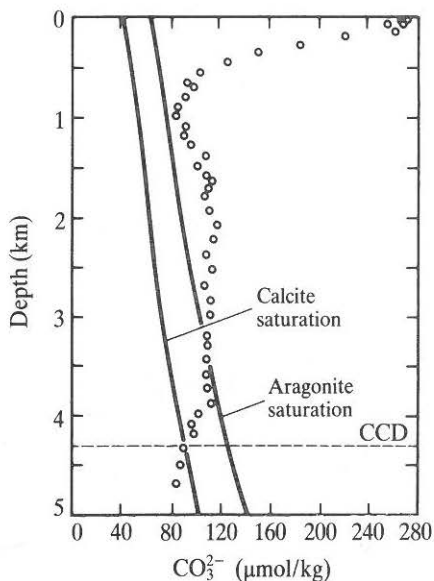
FIGURE 3-4
Measured carbonate-ion concentrations plotted against water depth for a station in the western South Atlantic Ocean. The lines show concentrations of carbonate ions in seawater at saturation with calcite and aragonite. The increase in concentration with depth is largely due to the change of solubility with pressure. The dashed line marked CCD is the calcite compensation depth; below this depth seawater is undersaturated with respect to calcite and above this depth seawater is usually supersaturated with respect to calcite. (Reprinted by permission from Broecker and Peng, 1982.)

come to equilibrium with calcite should be in the range 8 to 10—close to the lower figure at the Earth's surface, and close to the upper figure at a depth not influenced by the atmosphere.

These numbers give us a quantitative expression of the variation in solubility of $CaCO_3$ that we predicted from qualitative arguments at the beginning of this chapter. Our next move obviously should be to compare the theoretically derived numbers with actual measured concentrations of $CaCO_3$ in natural solutions. The comparison is easily made, but it turns out to be most disillusioning. Concentrations of $CaCO_3$ in natural waters are extremely variable and only rarely come close to the numbers predicted in the last few paragraphs. Low concentrations can be plausibly explained as the result of failure of solutions to reach equilibrium with solid carbonate. In many natural waters, such as seawater (Fig. 3-4), however, the discrepancy is in the opposite direction: concentrations are embarrassingly high, much higher than can be accounted for even with generous assumptions about temperature, CO_2 pressure, and acidity.

Possible reactions for these higher concentrations are discussed in the following six sections. They are worth examining in some detail, because they illustrate beautifully the difficulties in trying to make theoretical predictions adaptable to complex natural environments.

3-3   CALCITE AND ARAGONITE

One complication affecting solubility is the fact mentioned above that $CaCO_3$ is polymorphous. Measured solubilities of the three crystal forms are different, as is

shown by the solubility products in Fig. 3-2. A similar difference in solubility was noted earlier (Sec. 1-5) for the two common forms of calcium sulfate, gypsum and anhydrite.

The existence of different solubilities for the same chemical compound suggests an awkward question. Suppose that equilibrium has been established between solid aragonite and its saturated solution. The product of the concentrations of the two ions is larger than the equilibrium product for calcite. Why, then, does calcite not precipitate? Theoretically, it would seem that the excess Ca^{2+} and CO_3^{2-} should combine to form calcite; then more aragonite should dissolve to reestablish its own equilibrium, more calcite should precipitate, and so on—the net result being the slow replacement of aragonite by calcite.

Practically, this does not happen, or at least it does not happen rapidly enough to be observed. A plausible explanation is that nuclei are not present for calcite to precipitate around. The solution is supersaturated with respect to calcite, and like any supersaturated solution it is essentially unstable; but when supersaturation is very slight, as in this case, crystallization is extremely slow unless seed crystals are present. If finely ground calcite is added to the equilibrium solution, and if the mixture is warmed to speed up reactions, the change becomes appreciable.

Aragonite is therefore unstable with respect to calcite under ordinary conditions. It becomes the stable form of calcium carbonate at high pressures, as might be anticipated from its greater density (2.9 g/cm^3, in contrast to 2.7 for calcite). The necessary pressure is so high, however, that it cannot be a factor in environments of sedimentation near the Earth's surface. This leads to another set of awkward questions: Why does aragonite ever appear in sedimentary rocks? When conditions are right for calcium carbonate to precipitate, why doesn't the more stable calcite form in all cases?

There is no entirely satisfactory answer to this question. It is an empirical fact that many polymorphous substances show this same tendency to precipitate first in metastable forms, which change only slowly to the stable varieties. We can guess that the manner of crystallization depends at least in part on reaction rates, the metastable forms being able to crystallize more quickly. In the case of calcium carbonate, experiments show that calcite and aragonite often precipitate together, the proportion of aragonite being greater if the reaction is carried out at high temperatures. The presence of certain other ions in solution, notably Mg^{2+} and Sr^{2+}, also aids the formation of aragonite. Living creatures that use calcium carbonate in their shells may precipitate either polymorph, some species favoring one and some the other; many pelecypods precipitate both in alternate layers. In whatever way aragonite may form, during the course of geologic time it gradually alters to calcite, so that in old rocks and shells aragonite is a rare mineral.

3-4 SUPERSATURATION

The fact that calcite does not precipitate immediately from solutions at equilibrium with aragonite is proof that calcium carbonate can exist for extended periods in

supersaturated solution. Why do we not use this simple fact to explain all the anomalously high concentrations of calcium carbonate in natural solutions?

The question is a tricky one to handle, because the phenomenon of super-saturation is imperfectly understood. Some compounds, it is well-known, can remain in solution almost indefinitely at concentrations far above saturation equilibrium; others precipitate whenever the saturation value is exceeded by a very small amount; and there is little theoretical basis for predicting which way a given compound will behave. Furthermore, the onset of precipitation is influenced by a variety of factors that are difficult to control or predict: mechanical disturbances, dust particles in the solution, the material of the container, uneven-ness of surfaces in contact with the solution. Probably in any precipitation process at least momentary supersaturation exists before precipitation begins, but the persis-tence of supersaturation depends unpredictably on these factors as well as on the nature of the solute and on its concentration. In any given case predictions are possible only on the basis of empirical evidence.

For $CaCO_3$, laboratory experiments show that this compound ordinarily precipitates rapidly, without any lag ascribable to supersaturation. If the experiment is done carefully, so as to minimize external disturbance and to build up the concentrations of Ca^{2+} and CO_3^{2-} slowly, supersaturation up to about twice the normal solubility can be demonstrated and can be maintained for times that are long by laboratory standards. In natural waters, especially where CO_2 is being slowly removed by aquatic plants, apparent temporary supersaturation up to five times the solubility has been recorded. But such cases are rare, and in general the high concentrations of $CaCO_3$ sometimes found in nature can be more plausibly explained in other ways.

The suggestion that supersaturation might account for abnormal carbonate concentrations in nature is an example of a kind of explanation that often looks superficially attractive. It depends on a nonequilibrium phenomenon—on the hypothesis that carbonate solubilities in natural environments are determined by processes to which the laboratory-derived rules of chemical equilibrium do not apply. In effect, it appeals to a supposed slow rate of change from a metastable to a stable mixture. Now there is nothing basically wrong with this kind of assumption; certainly slow rates and nonequilibrium mixtures are commonplace in the labora-tory as well as in nature. Here, however, the hypothesis of large and widespread deviation from equilibrium in carbonate solutions is not supported by empirical data, so that it becomes a pure assumption. The assumption cannot really be proved wrong, because quantitative information on reaction rates is still meager, but it gives no insight into the geochemistry of carbonates, since no specific prediction can be made from it. This is the kind of hypothesis that at first glance seems promising, but on closer examination turns out to be so vague and general that it explains nothing. If equilibrium does not exist, or is not closely approached, then the field is wide open for almost any kind of speculation. In some cases this supposition is necessary, but ordinarily it is good policy to turn to nonequilibrium hypotheses only as a last resort, after explanations based on equilibrium have been tried and found wanting.

3-5 EFFECT OF GRAIN SIZE ON SOLUBILITY

Another factor that modifies the solubility relations of $CaCO_3$ is the size of crystals exposed to a saturated solution. Experimentally, very tiny grains show a greater solubility (and, of course, a greater solubility product) than do large crystals. The mechanism of dissolving furnishes a ready explanation: ions escape from a crystal most easily on exposed corners and edges, which are more numerous on small particles than on large ones. The effect is noticeable only when particle dimensions are extremely small, say of the order of a few millimicrons. Because of the greater solubility of small particles, ions in equilibrium with them constitute a super-saturated solution with respect to large particles. This means that the small ones should eventually dissolve, and the large ones should grow at their expense. A precipitate on first forming necessarily consists of very tiny grains; on standing the grains grow in size, at first rapidly and then more slowly, so that with most substances the crystals will have reached stable dimensions within a few seconds or minutes. Thus the measured solubility is the equilibrium solubility of larger crystals, and ordinarily the higher solubility of tiny particles is only a temporary phenomenon.

The growth of large grains at the expense of small ones in contact with a saturated solution is a familiar process both in geologic environments and in chemical laboratories. The chemist, faced with the problem of filtering a very fine-grained precipitate like $BaSO_4$ or $Fe(OH)_3$, often "digests" the precipitate by holding it near the boiling point for a few minutes. At the high temperatures the growth of particles is accelerated, and the crystals soon become large enough for a filter paper to hold them. A geologist sees in this same phenomenon an explanation for the recrystallization and increase in grain size of many rocks formed originally as fine chemical precipitates. The coarse grains of some limestones and the development of chalcedony or quartz from opal are common examples.

3-6 EFFECT OF ION ASSOCIATION ON SOLUBILITY

Another factor that might conceivably enhance the solubility of $CaCO_3$ is the possible association of its ions to form complexes. Thus far we have assumed that Ca^{2+} and CO_3^{2-} have no tendency to associate in solution, except to form a solid precipitate when the product of their concentrations exceeds the solubility product. This is nearly correct, but not quite. The two ions join to a slight extent into uncharged dissolved $CaCO_3(aq)$ molecules:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(aq), \tag{3-22}$$
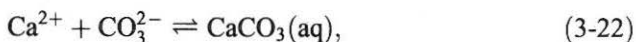
where

$$K = \frac{a_{CaCO_3(aq)}}{a_{Ca^{2+}}a_{CO_3^{2-}}} = 10^{3.2}. \tag{3-23}$$

As long as $a_{CO_3^{2-}}$ remains less than $10^{-3.2}$ (approximately $0.0006m$), most of the dissolved calcium remains as the free ion Ca^{2+}. Solutions with $a_{CO_3^{2-}}$ greater than this can exist in nature only in unusual, highly alkaline environments, so that ordinarily $CaCO_3(aq)$ plays a minor role. In most situations of geologic interest, the solubility of solid $CaCO_3$ would be increased no more than a percent or so by this factor.

More important than $CaCO_3(aq)$ in enhancing the solubility of $CaCO_3$ are other complexes that Ca^{2+} can form with ions that may be abundant in natural solutions, for example $CaHCO_3^+$, $CaCl^+$, $CaOH^+$, and $CaSO_4(aq)$. Of these the most stable is the neutral sulfate complex $CaSO_4(aq)$, which in seawater can increase the solubility of $CaCO_3$ minerals by about 10%. The others, except in solutions with unusually high concentrations of the complexing ion, have much smaller effects.

Neutral complexes like $CaCO_3(aq)$ and $CaSO_4(aq)$ are common in the chemistry of didivalent salts. The K's for the association reactions, so far as they are known, lie in the range 10^2 to 10^4. This means that the complexes have a significant effect on solubility only if the anion concentration is high, and in the dilute solutions found in most geologic situations the possibility of association can be safely neglected. Some of the charged complexes, however, particularly those formed by heavy metals like Cu, Pb, U, or Au, can influence solubility profoundly, as we have noted in Sec. 2-5 and will see again later when we consider the transport of these metals in ore-forming solutions (Chap. 19).

3-7 EFFECT OF ORGANISMS ON SOLUBILITY

Organic activity, as noted briefly in Sec. 3-1, affects solubility in various ways. Some inorganic compounds are used for the construction of shells and skeletons; the compound that is now the center of attention, calcium carbonate, is an excellent example. Some organisms in nearly every phylum of invertebrates have found calcium carbonate a useful structural material, and its use goes back in geologic time at least to the beginning of the Cambrian period. The mechanism of its precipitation in shells is not known, but apparently it can form only in water that is saturated or nearly so with respect to calcium carbonate. In part, at least, the precipitated shell substance is covered with a thin film of organic material that protects it from dissolving if the water becomes temporarily unsaturated, either by cooling or by dilution. Whether calcium carbonate can be made to precipitate by organisms in a solution not saturated with its ions, so that its apparent solubility is reduced below the equilibrium value, is an unanswered question. Certainly there is no evidence that any organism can cause its precipitation from solutions very far below the saturation concentration. Thus organisms can prevent supersaturation, and perhaps can lower the equilibrium solubility slightly, but at least in their shell-building activities they do not influence the solubility very greatly. Their role is chiefly to make use of a process which, in their absence, would take place inorganically.

Another way in which organisms can affect precipitation is by using the precipitation reaction to provide energy for their life processes. This applies chiefly to slow reactions that are far from equilibrium. Compounds of Fe(II) in solution, for example, react slowly with atmospheric oxygen to precipitate Fe(III) oxide, and some kinds of bacteria take advantage of this reaction to obtain energy. The ultimate solubility of Fe(III) oxide is not affected by the bacteria; they simply promote a reaction which would take place slowly in their absence, in this case a reaction that gives out considerable energy. They serve, so to speak, as an organic catalyst. The precipitation of calcium carbonate would probably not be used in this manner for obtaining energy, because the reaction is rapid and in natural solutions is seldom far from equilibrium, so that the amount of energy available is small.

A third sort of influence exerted by organisms is the causing of precipitation simply as an incidental consequence of their life processes. Water plants, as we have noted earlier, use up dissolved CO_2 during photosynthesis, thereby reducing the amount of H_2CO_3 in solution and leading to precipitation of $CaCO_3$ [the reverse of Eq. (3-4)]. Precipitation of $CaCO_3$ may also be favored by the decay of organisms, if the products of decay are alkaline, or impeded if the products are acid, but unfortunately the acidity or alkalinity to be expected from decay in particular circumstances is not predictable from present data.

Thus the effect of organisms on the formation of insoluble compounds is generally indirect, primarily by creating conditions favorable for their precipitation or dissolution.

3-8 PRECIPITATION OF CaCO₃ IN SEAWATER

As a way of summarizing this long discussion of the factors that influence solubility, we survey briefly the behavior of calcium carbonate in the ocean.

Seawater is an exceedingly complex solution (Table 2-1 and Appendix III), containing electrolytes in great variety plus an abundance of living and dead organic material. The ordinary laws of dilute solution cannot be applied, or at best need great modification. The chemistry of seawater can be described fairly satisfactorily in general terms, but details about the behavior of even so simple a substance as calcium carbonate remain obscure.

To evaluate the effects of individual ion activity coefficients and the formation of complexes on the solubility of calcite in seawater, we employ the computer program (EQ3NR), discussed in Sec. 2-8, to calculate the equilibrium distribution of aqueous species in seawater (see Table 2-1). In Table 3-1 we list the most abundant species, their molal concentrations, activity coefficients, and activities. The table shows that approximately 85% of the total calcium in seawater occurs as the Ca^{2+} ion, the rest as complexes with sulfate and chloride ions. Of the total carbonate in solution, most is in complexes, only about 2% as CO_3^{2-}. These complexes, together with the individual ion activity coefficients of 0.227 for Ca^{2+} and 0.223 for CO_3^{2-}, have the effect of increasing the apparent solubility of calcite in

TABLE 3-1

Concentration, activity coefficients (γ), and activities of aqueous species in seawater[1]

Aqueous Species	Molality ($\times 10^3$)	log γ	log Activity
Cl^-	523.600	−0.187	−0.468
Na^+	451.800	−0.190	−0.535
Mg^{2+}	47.390	−0.535	−1.860
SO_4^{2-}	26.700	−0.744	−2.318
NaCl(aq)	16.570	0.000	−1.781
K^+	9.879	−0.220	−2.225
Ca^{2+}	8.734	−0.644	−2.703
$MgCl^+$	5.398	−0.190	−2.458
HCO_3^-	1.540	−0.158	−2.970
$CaSO_4$(aq)	1.220	0.000	−2.914
KSO_4^-	0.312	−0.158	−3.664
$MgHCO_3^+$	0.250	−0.190	−3.793
$CaCl^+$	0.210	−0.190	−3.869
$MgCO_3$(aq)	0.110	0.000	−3.960
$CaCl_2$(aq)	0.052	0.000	−4.284
CO_3^{2-}	0.038	−0.652	−5.079
$CaHCO_3^+$	0.037	−0.190	−4.623
$CaCO_3$(aq)	0.035	0.000	−4.456
KCl(aq)	0.017	0.000	−4.774
CO_2(aq)	0.013	0.054	−4.835
$MgOH^+$	0.006	−0.190	−5.435
OH^-	0.003	−0.187	−5.785

[1] Calculated using computer program EQ3NR (see Sec. 2-8) and major element concentrations reported in Table 2-1 at 25°C and 1 bar pressure. Solution pH is 8.22, the calculated ionic strength is 0.66, and the activity of water is 0.98.

seawater relative to that in pure water. Thus the activity product for calcium carbonate in seawater is (from Table 3-1)

$$a_{Ca^{2+}}a_{CO_3^{2-}} = 10^{-2.7} \times 10^{-5.1} = 10^{-7.6} = 1.6 \times 10^{-8}, \qquad (3\text{-}24)$$

approximately 5 times greater than the equilibrium constant for calcite solubility and approximately 3 times greater than the constant for aragonite solubility. From a comparison of this number with the solubility curves and seawater compositions reported as a function of depth in Fig. 3-4, we can conclude that much of seawater is approximately saturated (or slightly supersaturated) with calcium carbonate. This seems reasonable, inasmuch as calcium carbonate is observed to be dissolving in some parts of the ocean and precipitating in other parts.

The slight shifts in the marine environment that exercise major control over precipitation and dissolution of calcite are so obvious that they hardly need pointing out. Precipitation is favored where the water is warm and where CO_2 is being lost through evaporation or photosynthesis, as on the shallow banks off Florida and the

Bahamas. Cold water and abundance of CO_2 promote dissolution; the scarcity of calcareous shells in parts of the deep ocean below about 4000 meters, for example, can be plausibly explained by the presence at these depths of cold masses of CO_2-saturated water moving slowly equatorward from the polar regions (cf. Sec. 12-3). Tide pools in temperate regions show evidence of precipitation of calcium carbonate when the trapped seawater warms up during the day, and of dissolution at night when the water becomes cold.

The calcium carbonate that precipitates from seawater may be either calcite or aragonite, the circumstances that favor one or the other being still not entirely clear. With time, either during or after diagenesis of the carbonate sediments, precipitated aragonite changes to the more stable calcite. Precipitation may occur either inorganically or through the agency of organisms; organisms may accomplish the precipitation either in the building of their shells, or incidentally as they remove CO_2 from the water, or during decay if they supply alkaline materials to the water. The old argument as to the relative amounts of limestone formed by inorganic precipitation on the one hand and by organic processes on the other has never been settled, but it is probably not a matter of great importance. In modern seas the places where abundant inorganic precipitation might be expected are precisely those places where organisms flourish most luxuriantly. Investigators disagree as to whether the fine-grained carbonate precipitated indirectly by organisms can be distinguished from an inorganic precipitate. If the distinction is difficult in modern sediments, it is doubtless impossible in older rocks where later recrystallization would have obscured whatever minute textural differences may have been present originally.

Once deposited as bottom sediment, calcium carbonate gradually hardens into limestone, through a series of processes that collectively come under the heading of *diagenesis*: growth of large crystals at the expense of small ones, conversion of aragonite into calcite, replacement of other materials by calcite, and deposition of calcite between the grains by circulating solutions. The ease with which $CaCO_3$ recrystallizes even at low temperatures is attested by the coarse, intergrowing grains of many older limestones. An unexplained detail in carbonate geochemistry is the fact that some limestones from far back in the Paleozoic remain very fine-grained, contrasting sharply with the recrystallized textures that are common even in much more recent limestones.

Thus the chemistry of calcium carbonate in geologic processes is fairly well understood. Much of it is embodied in simple displacements of the equilibrium with carbonic acid and bicarbonate. Additional concepts are needed to account for the relations of the two polymorphs, the behavior of very tiny grains, the effect of dissolved electrolytes, and the influence of organisms. Quantitative treatment is feasible only for relatively simple freshwater solutions, but numbers that show fair agreement with observation can be obtained even for solutions as concentrated as seawater. We shall find that the rules of solubility developed in this discussion apply to many other chemical precipitates of geologic interest. Other carbonates in particular are governed by equilibria similar to the ones we have used for calcium carbonate, as we note in the next section.

3-9 OTHER SIMPLE CARBONATES

All the carbonates that precipitate as sediments or form during metamorphism and hydrothermal processes are somewhat soluble in carbonic acid, and all of them crystallize out of solution when the concentration of carbonic acid diminishes. This means that other carbonates enter into equilibria like the major calcium carbonate equilibrium [Eq. (3-4)], according to reactions that can be symbolized by

$$MCO_3 + H_2CO_3 \rightleftharpoons M^{2+} + 2HCO_3^-, \tag{3-25}$$

where the M^{2+} represents Fe^{2+}, Sr^{2+}, Mn^{2+}, and so on. Representative solubility products of carbonate minerals are given in Table 3-2. Like $CaCO_3$, the other carbonates are more soluble when the concentration of dissolved CO_2 is high, whether because of low temperature or high pressure or decay of organic matter, and less soluble when CO_2 is removed from solution by heating, by decrease in pressure, by addition of alkali, or by the photosynthetic activity of plants. The chemistry of carbonates is essentially simple, and their solubilities can be described in terms of a few well-understood equilibria.

Replacement of one carbonate by another is often observed in metamorphic and sedimentary rocks and in hydrothermal veins. The conditions under which replacement can occur may be partly reconstructed from the data of Table 3-2. For example, conditions for the replacement of calcite by siderite can be evaluated using the reaction

$$\underset{\text{calcite}}{CaCO_3} + Fe^{2+} \rightleftharpoons Ca^{2+} + \underset{\text{siderite}}{FeCO_3}, \tag{3-26}$$

for which the equilibrium constant is (assuming unit activities of pure $CaCO_3$ and $FeCO_3$ and unit activity coefficients for aqueous species)

$$K = \frac{m_{Ca^{2+}}}{m_{Fe^{2+}}} = \frac{m_{Ca^{2+}} m_{CO_3^{2-}}}{m_{Fe^{2+}} m_{CO_3^{2-}}} = \frac{4.5 \times 10^{-9}}{2.0 \times 10^{-11}} = 225. \tag{3-27}$$

This means that at ordinary temperatures calcite should be replaced by siderite if it is in contact with a solution containing Fe^{2+} at a concentration more than $\frac{1}{225}$ that of

TABLE 3-2
Solubility products of carbonates

$MgCO_3$	3.2×10^{-8}
$CaCO_3$(calcite)	4.5×10^{-9}
$SrCO_3$	1.0×10^{-9}
$BaCO_3$	5.0×10^{-9}
$MnCO_3$	5.0×10^{-10}
$FeCO_3$	2.0×10^{-11}
$NiCO_3$	1.3×10^{-7}
$ZnCO_3$	1.0×10^{-10}
$PbCO_3$	8.0×10^{-14}

From Appendix VII-1.

Ca^{2+}, and likewise that siderite can be replaced by calcite only if the solution has more than 225 times as much Ca^{2+} as Fe^{2+}.

Because the concentration of Fe^{2+} in natural solutions is seldom greater than $\frac{1}{225}$ that of Ca^{2+}, replacement of calcium carbonate minerals by siderite is not often observed. Similarly the cations of other simple carbonates (Mn^{2+}, Sr^{2+}, Zn^{2+}, etc.) generally have such low concentrations in groundwaters and surface waters that replacement is not often to be expected. An apparent exception is Mg^{2+}, which forms the well-known mineral magnesite and exists in natural solutions at concentrations similar to those of Ca^{2+}. Rather than replacing calcite or aragonite with magnesite, however, Mg^{2+} in its reaction with $CaCO_3$ commonly undergoes a more complicated reaction—which is the subject of the next section.

3-10 THE DOLOMITE PROBLEM

The most stubborn question in carbonate geochemistry is the origin of the double carbonate dolomite [$CaMg(CO_3)_2$)]. The "dolomite problem" may be stated very simply: Dolomite rock is one of the commonest sedimentary materials, appearing as thick and extensive beds in strata of all ages from the Precambrian to the Cenozoic; there is no geologic evidence to indicate that its formation took place under unusual conditions of temperature or pressure; yet efforts to prepare dolomite in the laboratory under simulated sedimentary conditions have failed, and very little dolomite is observed to be forming in nature in ordinary sedimentary environments. It is true that laboratory precipitation of dolomite at low temperatures is possible, from solutions at pH's greater than 9.5 and containing high concentrations of SO_4^{2-} and NO_3^-; it is also true that formation of dolomite as a primary precipitate in nature has been reported in a number of unusual environments: hot springs, in sediments of salt lakes, and in muds from salt lagoons undergoing strong solar evaporation. But the extreme conditions represented by both the laboratory experiments and the field occurrences, compared with usual sedimentary environments, make the abundance of dolomite in the sedimentary record seem all the more mysterious. Why should this one common sediment be such a conspicuous anomaly?
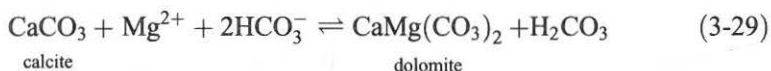
For an answer we look first to crystallography. The mineral dolomite is a double carbonate of magnesium and calcium, $CaMg(CO_3)_2$, with a structure that may be visualized as a distorted NaCl framework (Sec. 5-1) in which the anions are CO_3^{2-} groups and the cations are regularly alternating Ca^{2+} and Mg^{2+}. The regular alternation is important. This is a special, highly ordered crystal structure, which perhaps takes a long time to grow. When attempts are made to precipitate dolomite in the laboratory, the usual result is a mixture of calcite and hydromagnesite, simple compounds which can form rapidly in solution. The magnesium-rich calcium carbonates in the shells of some marine organisms are not dolomite but structures with a random distribution of Ca and Mg—again the sort of structure that might be expected to form fairly rapidly. Dolomite is readily prepared artificially at temperatures somewhat over 100°C, the function of temperature probably being to speed up the movement of ions so that Ca and Mg can find their places in the ordered structure within a reasonable time. Attempts to prepare the compound at

successively lower temperatures give precipitates whose x-ray diffraction patterns show the characteristic lines of dolomite becoming progressively less numerous and more fuzzy. A reasonable inference from these facts is that dolomite forms at ordinary temperatures so very slowly that we have no chance to observe the process in nature or to duplicate it in the laboratory. This slowness of formation, due to the necessity of attaining a highly ordered structure, seems a convincing answer to at least part of the dolomite riddle.
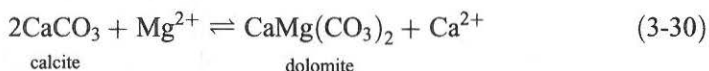
One might expect to gain information about the origin of dolomite from solubility data, as one can for other carbonates. The difficulty lies in the uncertainty about attainment of solution–mineral equilibrium. The amount of dolomite that goes into solution can be measured readily enough, but we cannot be sure that the solution has reached saturation because the ions will not recombine to form solid dolomite. An approximation to the solubility can be obtained by stirring dolomite in water and following the changes in concentration of one of its ions, or of the pH, until the concentrations no longer change; if reproducible results are obtained in such experiments, it seems likely that a condition approaching equilibrium has been reached. Experiments of this sort give an apparent solubility product,

$$K = a_{Ca^{2+}} a_{Mg^{2+}} a^2_{CO_3^{2-}}, \tag{3-28}$$

that is slightly less than the same product of ions obtained from a mixture of calcite and magnesite ($MgCO_3$) treated in the same manner. In other words, reactions like

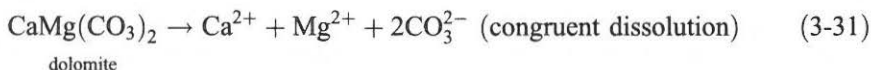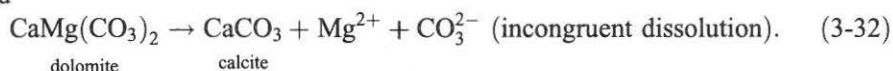$$\underset{\text{calcite}}{CaCO_3} + Mg^{2+} + 2HCO_3^- \rightleftharpoons \underset{\text{dolomite}}{CaMg(CO_3)_2} + H_2CO_3 \tag{3-29}$$

and

$$\underset{\text{calcite}}{2CaCO_3} + Mg^{2+} \rightleftharpoons \underset{\text{dolomite}}{CaMg(CO_3)_2} + Ca^{2+} \tag{3-30}$$

are displaced in the direction of dolomite at usual concentrations of Ca^{2+} and Mg^{2+}, but the difference in solubilities is so slight that there is little drive to make the two ions assume the ordered structure of dolomite.

Regarding the numerical value of K in Eq. (3-28) there is still wide disagreement. Published values range from 10^{-17} to 10^{-19}, most of them near the higher figure. Measurements of $a_{Ca^{2+}}$, $a_{Mg^{2+}}$, and $a_{CO_3^{2-}}$ in cave waters by Holland et al. (1964) give an activity product higher than 10^{-15}, with no precipitation of dolomite; whatever the true solubility product may be, this indicates that supersaturation with respect to dolomite can persist for long periods.

Another difficulty in measuring the solubility of dolomite, or of any similar double salt, stems from a question as to just how the dissolving takes place. Does the salt dissolve as a whole (*congruent* dissolution), to give equimolal quantities of Mg^{2+} and Ca^{2+}, or does the more soluble part of the salt, the $MgCO_3$, dissolve in greater amount (*incongruent* dissolution)? The two possibilities may be symbolized

$$\underset{\text{dolomite}}{CaMg(CO_3)_2} \rightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \quad \text{(congruent dissolution)} \tag{3-31}$$

and

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + Mg^{2+} + CO_3^{2-} \quad \text{(incongruent dissolution).} \quad (3-32)$$
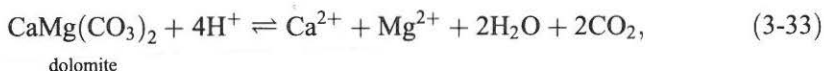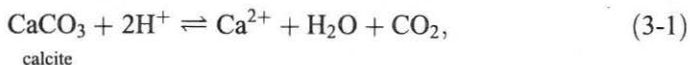
dolomite   calcite

Experiments show that dolomite dissolves congruently at ordinary temperatures, but at higher temperatures the dissolution is at least partly incongruent.
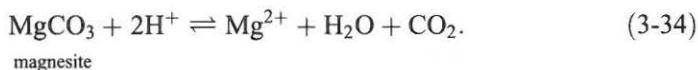
Geologically there is not much evidence that dolomites in older strata formed as primary precipitates, except possibly the dolomites associated with evaporite deposits. Many dolomites contain structures, particularly fossils, which originally must have been calcium carbonate, so that these dolomites certainly were formed by a reaction between Mg^{2+} and a $CaCO_3$ sediment. The characteristic poor preservation of fossils in dolomite, the coarseness of grain, and the commonly observed cavities and pore spaces are all indications that dolomite forms by reactions like Eqs. (3-29) and (3-30). The Mg^{2+} may come from seawater in contact with the limy sediment or buried with it, from ions taken up in the original $CaCO_3$ structure (particularly in shells), or from later solutions moving through the sediment; the reaction may represent an addition of bicarbonate [Eq. (3-29)], a replacement of original Ca^{2+} [Eq. (3-30)], or even in part a precipitation of small amounts of original dolomite. In general, for any particular dolomite, it is impossible to sort out the effects of these various reactions. The conversion of calcium carbonate to dolomite commonly takes place shortly after deposition of the original sediment (during diagenesis), as is shown by the replacement of entire beds by dolomite and by the lack of influence on dolomitization of later structures in the rock. On the other hand, partial dolomitization of some limestones along networks of veinlets must represent the work of later solutions acting on solid rock.

Thus details of the formation of dolomite remain obscure, but recent experimental studies plus geologic observations have furnished fairly convincing evidence that most dolomite is not a primary precipitate but forms rather as a product of slow reactions altering originally deposited calcium carbonate. Solutions that accomplish the alterations are most effective if they have a fairly high salinity and pH, a low Ca^{2+}/Mg^{2+} ratio, and a somewhat elevated temperature.

The effects of Ca/Mg ratios and temperature on the replacement of calcite by dolomite can be illustrated with the phase diagrams in Fig. 3-5, which show calculated phase relations among the carbonate minerals calcite, dolomite, and magnesite in contact with solutions. The three lines in Fig. 3-5(a) represent conditions for saturation of a fluid with respect to calcite, dolomite, or magnesite at 1 bar total pressure, 0.1 bar partial pressure of CO_2, and 25°C. The reactions for these equilibria are:

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + H_2O + CO_2, \quad (3-1)$$

calcite

$$CaMg(CO_3)_2 + 4H^+ \rightleftharpoons Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2, \quad (3-33)$$

dolomite

and

$$MgCO_3 + 2H^+ \rightleftharpoons Mg^{2+} + H_2O + CO_2. \quad (3-34)$$
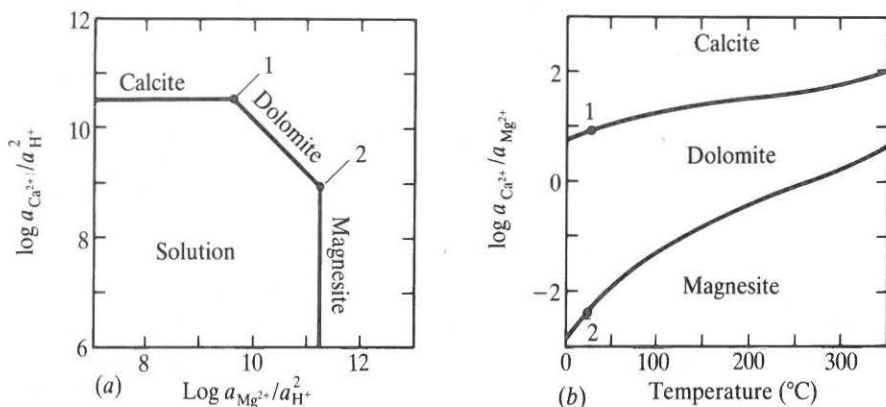
magnesite

FIGURE 3-5

Calculated phase relations among aqueous solutions and the carbonate minerals calcite, dolomite, and magnesite. The lines in diagram (a) show conditions for saturation with respect to the three minerals at 1 bar total pressure, 0.1 bar partial pressure of CO_2, and 25°C. Diagram (b) shows changes with temperature of the equilibrium ratios $a_{Ca^{2+}}/a_{Mg^{2+}}$ in solutions at equilibrium with the pairs calcite–dolomite and dolomite–magnesite. Pressure corresponds to liquid–vapor equilibrium for H_2O. The points 1 and 2 are the same in the two diagrams. (Diagrams computed using equilibrium constants listed in Bowers, T. S., K. J. Jackson, and H. C. Helgeson: *Equilibrium Activity Diagrams*, Springer Verlag, 396 pp., 1984.)

The saturation lines in Fig. 3-5(a) are calculated using equations written by rearranging the logarithms of the equilibrium constants for Eqs. (3-1), (3-33), and (3-34). Assuming that the activity of water is approximately unity, we write for these equations,

$$\log \frac{a_{Ca^{2+}}}{a_{H^+}^2} = -\log P_{CO_2} + \log K_{(3\text{-}1)}, \tag{3-35}$$

$$\log \frac{a_{Ca^{2+}}}{a_{H^+}^2} = -\log \frac{a_{Mg^{2+}}}{a_{H^+}^2} - 2 \log P_{CO_2} + \log K_{(3\text{-}33)}, \tag{3-36}$$

and

$$\log \frac{a_{Mg^{2+}}}{a_{H^+}^2} = \log P_{CO_2} + \log K_{(3\text{-}34)}. \tag{3-37}$$

Under the conditions of fixed temperature, total pressure, and partial pressure of CO_2 these equations form straight lines on a plot of $\log (a_{Ca^{2+}}/a_{H^+}^2)$ against $\log (a_{Mg^{2+}}/a_{H^+}^2)$, as illustrated in Fig. 3-5(a) (cf. Fig. 3-3).

The intersections of the saturation lines in Figure 3-5(a) denote the conditions for equilibrium among calcite, dolomite, and a solution at point 1, and among dolomite, magnesite, and a solution at point 2. Point 1 can be represented by a chemical reaction balanced by combining reactions (3-1) and (3-33) to give

$$2CaCO_3 + Mg^{2+} \rightleftharpoons CaMg(CO_3)_2 + Ca^{2+}, \tag{3-38}$$
$$\text{calcite} \qquad\qquad\qquad \text{dolomite}$$

where

$$\log \frac{a_{Ca^{2+}}}{a_{Mg^{2+}}} = \log K_{(3-38)}. \tag{3-39}$$

Note that the activity ratio of Ca^{2+} to Mg^{2+} in a solution in equilibrium with calcite and dolomite is a function only of the equilibrium constant and not a function of P_{CO_2}. This ratio is ~8 at 1 bar total pressure and 25°C, and it increases with rising temperature as shown in Fig. 3-5(b). We conclude from the phase relations plotted in Fig. 3-5 that dolomite is favored over calcite by low activity ratios of Ca^{2+} to Mg^{2+} and by an increase in temperature.

SUMMARY

The theoretical ideas about chemical equilibrium developed in the first two chapters have given us here a basis for understanding the geochemistry of carbonates in sedimentary environments. The influence of acids and bases, of changes in temperature and pressure, and of other ions in solution can be related to simple equilibrium processes. Given a deposit of calcium carbonate, we can set limits on the geologic conditions under which it could have been deposited. Given a solution of known composition, we can predict the conditions under which calcium carbonate would precipitate from it. If data are available on the geology of an area, we can suggest where calcium carbonate should be in process of solution and where in process of precipitation, and how much calcium the groundwater would contain at various points. From the properties of other carbonates, we can describe the conditions under which they might replace, or be replaced by, the carbonate of calcium. In these various senses, chemistry provides an "understanding" of carbonates.

For geochemical questions relating to the carbonates we can find particularly specific and clean-cut answers. The compounds have relatively simple structures, and processes of solution and precipitation (except for dolomite) involve rapid reactions in which ions in dilute solution play an important role. This is the kind of situation where the quantitative rules of chemical equilibrium are particularly effective as a basis for predictions. As we turn our attention to more complex, slower-reacting compounds, we shall find that our explanations necessarily become more general and less quantitative.

PROBLEMS

1. Explain why underground water in contact with limestone is alkaline. Why is the pH higher if the water is out of contact with air?

2. Would you expect calcite to be appreciably soluble in a solution whose pH is maintained at 4? A solution at pH 11? A solution containing $0.1m H_2S$? Where might you find such solutions in nature?

3. If calcite is in equilibrium with a solution containing $0.001m$ total dissolved carbonate (see Fig. 2-3), what is the concentration of dissolved Ca^{2+} in the solution as a function of pH? Make a graph of your results.