

THE KINETICS OF CALCITE PRECIPITATION AND RELATED PROCESSES

W. A. HOUSE

Introduction

This review is concerned with the kinetics of calcium carbonate formation and related processes which are important in many hard waters. Although the emphasis is on inorganic precipitation, the mechanisms involved are fundamental to the understanding of calcification in biological systems.

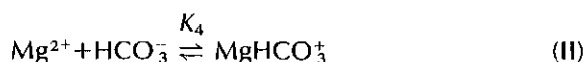
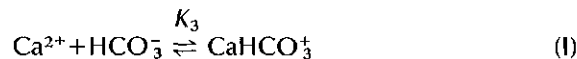
The equilibrium chemistry and speciation of the major ions in fresh water is reasonably well documented. Given our limited knowledge of the precise temperature-dependence of some of the ion-pair association constants, the equilibrium properties of a fresh water can be estimated from the concentration of the major ions and the temperature in the field. Such computations normally ignore heterogeneous reactions, i.e. those reactions between chemicals in different states of matter. Both precipitation from solution and gas transfer between the atmosphere and fresh waters fall into this broad category. This description of the water composition inevitably leads to a thermodynamic disequilibrium between some chemicals in the solution and the other phases. Whether there is a perceptible change in the solution composition towards thermodynamic equilibrium depends on the kinetics of the processes involved. In chemically dynamic and biologically productive systems such as rivers, this thermodynamic equilibrium is rarely achieved. Attempts to include heterogeneous reaction kinetics (in this context I include adsorption-desorption interactions) within the framework of an equilibrium model have been unsuccessful. This failure is caused by our lack of understanding of the detailed mechanisms of the reactions and how the reaction rates vary with changing environmental conditions. This article focuses on the inorganic carbon system in fresh water and aspects of the kinetics of the processes which have some relevance to the biology. Because of the predominance of bicarbonate and calcium ions in fresh water, the primary consequences of the thermodynamic disequilibrium are particularly noticeable through the formation of calcite and changes in pH associated with the variation in the concentration of carbon dioxide. The latter is complicated by the metabolic activity of bacteria, algae and higher plants.

Observations of the precipitation of calcium carbonate and concomitant composition changes of a groundwater from a chalk aquifer have been reported in detail by Ladle et al. (1977) and also related to the seasonal growth of chalk-stream algae by Marker & Casey (1983). Studies of calcium carbonate precipitation and the accompanying coprecipi-

tation of inorganic phosphate have been reported by a number of people, the most recent of which include Strong & Eadie (1978), Stewart & Wetzel (1981), Dandurand et al. (1982) and Murphy et al. (1983). In contrast the study of carbon dioxide transfer between fresh waters and the atmosphere is less well documented, although crude estimates of the kinetics are often used to calculate net photosynthetic rates. The most notable study is that of Emerson (1975) concerning the ingress of CO₂ into low ionic strength ($\approx 0.0001 \text{ mol dm}^{-3}$) softwater lakes.

Chemical speciation

The concept of chemical speciation has been discussed by Davison (1980). For hard waters dominated by Ca²⁺ and HCO₃⁻ ions, the equilibrium reactions which control the composition of the water are well known (see for example Manahan 1975). The temperature dependence of the various ion-pair association constants, in particular for the formation of CaHCO₃⁺ and MgHCO₃⁺, are uncertain. A joint research project between the FBA and Reading University has led to the determination of the associations K_3 and K_4 for the reactions (Cassford 1983):



The temperature dependence of the association constants is given by: $\ln K_i = c_1 + c_2/T + c_3 \ln T$ where $i = 3$ or 4 , c_1 , c_2 and c_3 are -132.57688 , 4950.7346 , 20.845357 for K_3 and -243.49258 , 9819.6436 , 37.513949 for K_4 . The temperature dependence of K_4 was previously unknown. These constants were derived from an analysis of the conductance data of a series of electrolyte mixtures (KHCO₃+MgCl₂ and KHCO₃+CaCl₂) in water and over a temperature range 0–55 °C. Reaction (I) has a direct impact on processes involving Ca²⁺ and HCO₃⁻ because ion-pairing effectively decreases the concentrations and thus activities of these two ions in the solution. The extent of ion-pairing in fresh waters varies according to the composition of the water and the temperature. This was demonstrated in a study by Howard et al. (in press), who examined a range of water compositions along the Leeds to Liverpool canal having alkalinities between 1.7 and 4.7 mmol dm⁻³ at about 14 °C. They found that the monovalent ions Na⁺ and K⁺ were not significantly involved in ion-pairing whilst Ca²⁺, Mg²⁺ and SO₄²⁻ ions were involved to various degrees. For instance the ratio of the 'free' to total ionic concentrations of calcium varied between 77% and 94% in these waters.

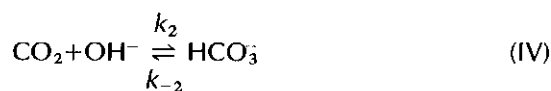
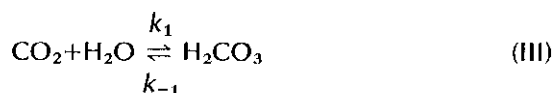
The concentrations and speciation of minor components such as inorganic phosphate and dissolved organic materials may also influence

the kinetics of the precipitation reaction. Inhibiting agents may stabilize the water and prevent calcium carbonate formation. Chemicals such as polyphenols, phosphonic acid derivatives, polyphosphates, fulvic acid compounds as well as magnesium and inorganic phosphate, influence the kinetics of calcite formation in conditions encountered in the natural environment. When present at sufficiently low concentrations, these inhibitors may be coprecipitated and removed from the solution. For inorganic phosphate, this pathway may be of importance in some hard water systems (Murphy et al. 1983). A knowledge of the chemical speciation of the minor components in these circumstances is a prerequisite to understanding the mechanism for the inhibition and coprecipitation as well as necessary for the evaluation of the solubility products of the relevant mineral phases (Davison 1980). For instance, the solubility product of calcium hydroxyapatite is defined by:

$$K_{sp}^{HAP} = a_{Ca^{2+}}^5 a_{PO_4^{3-}}^3 a_{OH^-} \quad (i)$$

where a_i is the activity of the i th ion. In a fresh water, such as the R. Frome (a large chalk stream whose inorganic chemistry has been reviewed by Casey (1976)), with an inorganic phosphate concentration of about $2 \mu\text{mol dm}^{-3}$ and calcium concentration around 2mmol dm^{-3} , the concentration of HPO_4^{2-} is around 66% of the total dissolved inorganic phosphate, with less than 0.01% occurring as PO_4^{3-} at pH = 8.0. At this pH the remaining phosphate is distributed mainly as CaHPO_4 (19.8%), CaPO_4 (11.4%) and MgHPO_4 (2.2%).

The hydration reactions of CO_2 may influence the precipitation rate and exchange with the atmosphere. The two hydration reactions are:



These reactions cannot be considered instantaneous. For calcite precipitation from bicarbonate solutions, the rate of formation of CO_2 through the reaction:



must be compared with the rates of the hydration reactions. If reaction (V) is fast compared with (III) and (IV), the solution composition becomes dependent on both the kinetics of the hydration reactions and the precipitation reaction. For CO_2 transport across the air-water interface at moderate alkalinities, i.e. 0.002mol dm^{-3} , and pH values greater than

8.3, the hydration reaction (IV) may influence the rate at which CO_2 can leave and enter a water body (House et al. 1984).

The equilibrium chemical speciation in a fresh water is expected to be complex. In practice, the composition is usually estimated using the large speciation computer programs such as WATEQ (Truesdell & Jones 1974) with revisions of the equilibrium constants and their temperature dependencies made whenever data become available. In simpler systems such as $\text{Ca-CO}_3\text{-PO}_4\text{-H}_2\text{O}$ at constant temperature, it is possible to compute the composition of the water in terms of three independent variables. It is convenient to choose these variables to be quantities which are routinely measured in the analytical laboratory such as the total dissolved calcium and phosphate together with pH. Within the constraint of electroneutrality, i.e. the water is not electrically charged, the composition may be calculated by an iterative procedure using the relationship between concentration and activity, i.e. $a_i = \gamma_i c_i$ where c_i and γ_i are the concentration and activity coefficients of the i th ion. γ_i is determined from the Davies equation (Davies 1938)

$$\gamma_i = -A_{DH} z_i^2 [I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) - 0.3I] \quad (2)$$

where A_{DH} is the Debye-Huckel constant, z_i the electrical charge of the i th ion and I is the ionic strength of the solution. From the composition, the thermodynamic stability of the water with respect to calcium carbonate and calcium phosphate mineral phases may be computed. The stability may be expressed as a growth affinity, β , or saturation index, s . These quantities are defined according to the equation:

$$\beta = \sum_i \Delta \mu_i / RT = 2.3026 \times s \quad (3)$$

where i denotes the lattice ions, $\Delta \mu_i$ the difference in chemical potential between the ions when in solution and in the solid phase. For calcite:

$$s = \log (a_{\text{CO}_3^{2-}} a_{\text{Ca}^{2+}} / K_{\text{sp}}^{\text{cal}}) \quad (4)$$

where $K_{\text{sp}}^{\text{cal}}$ is the solubility product for calcite. Similar expressions can be written for the calcium phosphate phases such as hydroxyapatite (equation (1)) and octacalcium phosphate.

Figure 1 illustrates a coexistence diagram derived by this method. The solubility lines (when $s = 0$) for calcite, calcium hydroxyapatite and octacalcium phosphate are shown, together with lines indicating the supersaturation of the solution with respect to calcite and a line of constant CO_2 concentration. The partial pressure of CO_2 in equilibrium with a dilute solution is

$$P_{\text{CO}_2} = K_H [\text{CO}_2] \quad (5)$$

where the square bracket indicates concentration and K_H is the Henry's law solubility coefficient.

A description of calcite precipitation

A fresh water of composition shown as point B in Fig. 1 e.g. a chalk aquifer water mentioned by Ladle et al. (1977), has a high CO_2 concentration (typically $P_{\text{CO}_2} = 0.008 \text{ atm}$) but is close to equilibrium with respect to calcite. The subsequent movement of the water and exposure to the atmosphere leads to a decrease in the CO_2 concentration and subsequent increase in pH and supersaturation of the water with respect to calcitic minerals, e.g. if the temperature remains constant and no precipitation occurs, the composition moves along the line B to A. The rate of change in pH accompanying the loss depends on the rate of CO_2 transfer from the water to the atmosphere ($P_{\text{CO}_2} = 0.00034 \text{ atm}$). This in turn is controlled by the temperature, pH, alkalinity, flow-rate

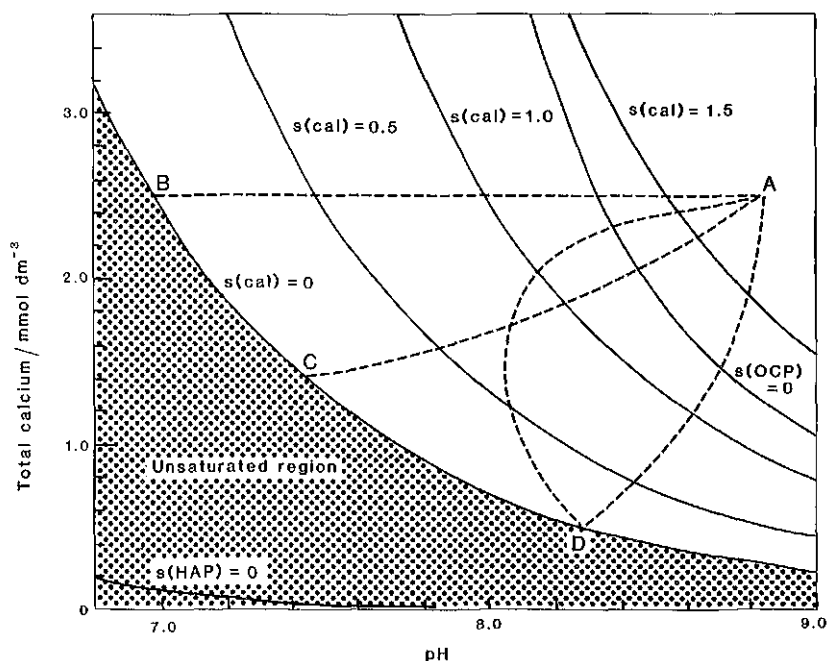


FIG. 1. Coexistence diagram showing solubility lines for calcite (cal), calcium hydroxyapatite (HAP) and octacalcium phosphate (OCP) and lines of constant supersaturation with respect to calcite all at 25 °C and $[\text{PO}_4] = 20 \mu\text{mol dm}^{-3}$. Dashed line A-C indicates the precipitation route in a closed system, A-D (lower) the route at constant P_{CO_2} ($= 0.34 \times 10^{-3} \text{ atm}$) and A-D (upper) possible route in free-drift conditions. Shaded region indicates compositions undersaturated with respect to calcite.

and turbulence of the water. In a hypothetical situation, where the water is completely free of particles and not exposed to any solid surface, then the degree of supersaturation could reach such a high level that homogeneous precipitation of calcium carbonate occurs, i.e. the spontaneous nucleation of solid nuclei which are stable enough to grow into larger particles. The nucleated particles are thought to be amorphous $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (House 1981a). In laboratory experiments they are only visible for a few minutes and gradually transform to a more stable phase. It is probable that homogeneous nucleation does not occur until $s \geq 2.3$, i.e. at $\text{pH} > 9$ as shown in Fig. 1 (House unpublished).

If particles or surfaces are present, then heterogeneous nucleation is possible, i.e. the calcium carbonate solid nucleates on particles or surfaces already present in the solution. The heteronucleation site may be on an algal surface or plant leaf where the local environment is conducive to calcite deposition. Chalk and limestone particles act as effective nucleators producing a loss of calcium from the solution and subsequent release of CO_2 . The composition of the solution changes according to the balance between the precipitation reaction and the CO_2 evasion rates. If no carbon is lost to the atmosphere, the composition moves along the line labelled A to C (Fig. 1) to reach equilibrium with respect to calcite at C. When CO_2 transfer to the atmosphere occurs, the composition follows a route such as A to D (upper line) and finally comes to equilibrium with both calcite and the atmosphere. In natural conditions the CO_2 concentration is likely to fluctuate on a daily cycle because of photosynthetic and respiration activity.

Heterogeneous nucleation

Very little has been published on heterogeneous nucleation in spite of the importance of epitaxial crystal growth in the formation of scale and in biological mineralization. It is necessary to control the solution conditions during nucleation so that both the nucleation ability of the particles and particle numbers are known. An attempt to elucidate the mechanism for heterogeneous nucleation of calcite with glass has been made by House & Tutton (1982). Any efficient nucleating substrate which is insoluble in water would have been suitable for study. They interpreted their results using the polynuclear layer mechanistic model. In this model the surface nucleation of calcite is so fast that each layer of the crystal is a result of the intergrowth of many individual nucleated surfaces. According to the model, the growth rate may be expressed in the form (House & Tutton 1982):

$$\alpha^{(1/3)} = \frac{0.6 k_m^{(1/3)} d^{(7/3)} D^{(2/3)}}{r_1} \int_0^t [\text{Ca}^{2+}] [\text{CO}_3^{2-}]^{(m+2)/3} dt \quad (6)$$

where m and k_m are constants, d the lattice spacing of calcite, D is the mean diffusion coefficient of the ions, r_1 the crystal dimension when the solution reaches equilibrium (assuming a monodispersion of heteronucleated calcite particles) and α is the extent of precipitation defined according to the equation:

$$\alpha = \frac{[Ca_T(t = 0)] - [Ca_T(t)]}{[Ca_T(t = 0)] - [Ca_T(t = \infty)]} \quad (7)$$

where the subscript T denotes the total concentration in solution. A plot of α^4 against the integral in equation (6) should be linear.

The initial period of precipitation was studied by House & Tutton (1982) with the purpose of assessing whether an induction period existed. The data were plotted according to equation (6) with $m = 1$. All the data showed deviations from linearity in the region of $\alpha = 0.12$. The extrapolated lines pass close to the origin suggesting the absence of an induction period. Repeating the analysis with $m > 1$ only tended to produce deviations from linearity at lower extents of precipitation. For $\alpha \geq 0.12$ the models for calcite growth, which are discussed below, described the data.

The number of particles nucleated depends on both the number of heteronuclei introduced to these solutions, the maximum supersaturation when nucleation commenced and the nature of the surface of the substrate. As an example, increasing the initial supersaturation in the above experiments from $s = 1.39$ to 1.65 produced a 70-fold increase in the number of nucleated particles. Treating the surface of the glass to decrease the number of high energy sites decreased the particle numbers by a factor of almost 800. At constant initial supersaturation, the number of particles nucleated was found to increase with increasing seed mass. It is important to note that in freshwater systems, none of the parameters found to be important in heteronucleation are known. Each potential nucleator has a critical supersaturation at which nucleation is likely to start. The adsorption of microcomponents such as phosphate onto the nucleation sites is also very probable and in the event should lead to an increase in the critical supersaturation needed to produce surface nucleation and so determines the subsequent precipitation rate.

Calcite crystal growth

In most natural systems where calcite is precipitated from the water, we are presented with a *fait accompli*. Our lack of knowledge of the nucleation ability of the various substrates and the localized extreme conditions reached in the vicinity where precipitation is possible, makes it difficult, if not impossible, to predict the initial nucleation and growth

rates. However once precipitation has started and supersaturation lowered, the rate of loss of calcium and carbonate may be measured and interpreted.

The growth of calcite has been studied by a number of people using the 'seeded' growth method. With this technique, a seed suspension of calcite is added to the water under study and the subsequent growth of the crystals monitored by measuring the solution composition. The method eliminates some of the problems discussed above because heteronucleation is no longer important. Unfortunately most of the work has been done using metastable solutions prepared by mixing CaCl_2 and NaHCO_3 or $\text{Na}_2\text{CO}_3/\text{NaOH}$ with low concentrations of CO_2 and high pH. These compositions do not occur in natural waters and it is more realistic to use $\text{Ca}(\text{HCO}_3)_2$ solutions prepared from calcite/ $\text{CO}_2+\text{H}_2\text{O}$ mixtures for comparisons with experiments in fresh water. The artificial $\text{Ca}(\text{HCO}_3)_2$ solutions may be supersaturated with respect to calcite by outgassing dissolved CO_2 with N_2 gas. By controlling the composition of the $\text{N}_2/\text{CO}_2/\text{H}_2\text{O}$ gas mixture, it is possible to control accurately the highest supersaturation attained subsequent to seed addition. Two different experimental methods are possible:

(i) Free-drift (House 1981a). After the seed material is added, the solution composition is monitored using measurements of pH and electrical conductivity. The combined conductivity and pH value enables the ionic composition to be computed using an iterative method involving adjusting the growth affinity in a systematic manner, at constant pH, until the ionic composition produces agreement between the observed and theoretical conductivities. The theoretical values may be calculated from the point charge model of Onsager & Fuoss (1932). House (1981a) found agreement within 1½% with the total calcium values obtained by EDTA titration. In these experiments it is necessary to have good control of the temperature (± 0.002 K, Williams & House 1981) and to correct for increases in conductivity that are caused by the leakage of KCl from the reference electrode. With this method, the $\text{Ca}(\text{HCO}_3)_2$ solution changes composition according to the balance between the precipitation rate and CO_2 transfer rate to the atmosphere and along a path similar to A to D illustrated in Fig. 1. (upper curve). The free-drift method may also be applied to fresh waters but here it is necessary to measure the calcium concentration by standard analytical methods because of the precipitation of ions other than Ca^{2+} and CO_3^{2-} into the calcite lattice.

(ii) Constant composition. In this method the ionic composition is maintained through the precipitation experiment by the addition of solutions containing the lattice ions. This is usually possible by using electrochemical sensors in the reaction solution to transmit signals to

a mechanized burette system. For $\text{Ca}(\text{HCO}_3)_2$ solutions, it is convenient to control the concentration of CO_2 in the solution and keep the Ca^{2+} activity or pH or electrical conductivity constant by the addition of a titrant $\text{Ca}(\text{HCO}_3)_2$ solution. The apparatus that is used to perform this type of experiment is illustrated in Fig. 2. Here the Wayne-Kerr B642 a.c. bridge measures the conductivity and the corresponding analog signal is input to the ion meter. This is used by the autoburette-titration system to decide whether addition of $\text{Ca}(\text{HCO}_3)_2$ solution is needed to maintain a constant conductivity and so compensate for the loss of Ca^{2+} and CO_3^{2-} caused by precipitation. The temperature, conductivity and volume of titrant addition are plotted and stored by the microcomputer. This method permits precipitation to be observed over periods of several days and so is particularly suitable for studies in fresh water.

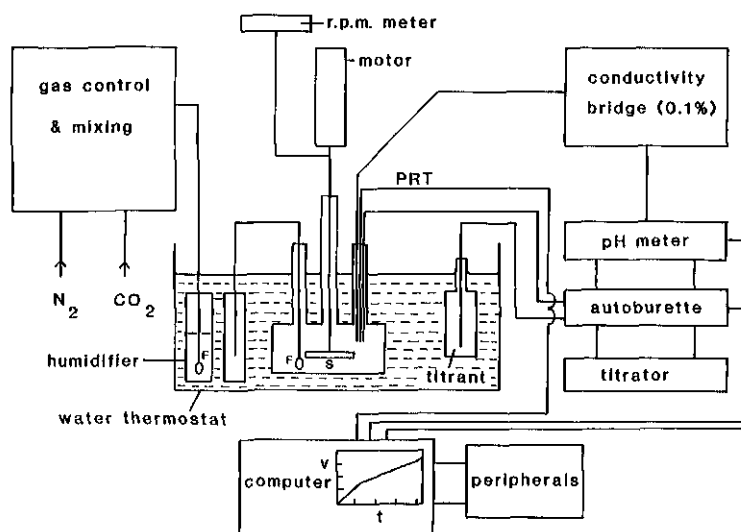
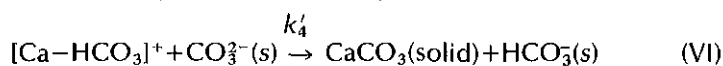


FIG. 2. Apparatus for constant composition experiments. Key: F, glass frit; S, glass stirrer; PRT, platinum resistance thermometer; r.p.m., revolutions per minute; V, volume of titrant; t, time.

House (1981a) has reviewed the mathematical models which have been applied to the crystal growth of calcite and tested them against precipitation results from seeded growth experiments in $\text{Ca}(\text{HCO}_3)_2$ solutions under free-drift conditions. The main conclusion from this comparison was that the growth rate was not a unique function of the growth affinity. The kinetics were best described by applying a chemical mechanistic approach (House 1981a and Cassford et al. 1983) along

similar arguments proposed by Plummer et al. (1978) to describe the dissolution kinetics. The individual chemical reactions that could occur on the calcite surface may be formulated as the interaction between partially dehydrated $[\text{Ca}-\text{HCO}_3]^+$ complex and various possible anionic reaction sites in the crystal's adsorbed layer:



where (s) denotes the surface adsorbed layer. If each of these reactions is considered separately with the corresponding dissolution reaction, the following rate equations are obtained (Cassford et al. 1983):

(i) Reaction with $\text{OH}^-(\text{s})$

$$R = k_3 a_{\text{H}_2\text{O}} [1 - (a_{\text{H}^+}/a_{\text{H}^+(\text{s})}) \exp \beta] \quad (8)$$

with $a_{\text{H}_2\text{O}} = a_{\text{H}_2\text{O}(\text{s})}$

(ii) Reaction with $\text{HCO}_3^-(\text{s})$

$$R = k_2 a_{\text{H}_2\text{CO}_3} [1 - (a_{\text{H}^+}/a_{\text{H}^+(\text{s})}) \exp \beta] \quad (9)$$

with $a_{\text{H}_2\text{CO}_3} = a_{\text{H}_2\text{CO}_3(\text{s})}$

(iii) Reaction with $\text{CO}_3^{2-}(\text{s})$

$$R = k'_1 a_{\text{HCO}_3} [1 - (a_{\text{H}^+}^2/a_{\text{H}^+(\text{s})}^2) \exp \beta] \quad (10)$$

with $a_{\text{H}_2\text{CO}_3(\text{s})} = a_{\text{H}_2\text{CO}_3}$

In these rate equations k'_1 , k_2 and k_3 are the rate constants and the unscripted activities refer to the bulk phase. The reaction rate is $R = A^{-1} dn_{\text{Ca}}/dt$ where A is the crystal surface area and n_{Ca} is the number of moles of calcium. The value of $a_{\text{H}^+(\text{s})}$ is calculated from the condition that $a_{\text{H}_2\text{CO}_3(\text{s})} = a_{\text{H}_2\text{CO}_3}$ and that $\beta = 0$ at the interface of the crystal. The rate equation (8) has been applied by House (1981a) with the rate constant k_3 determined by Plummer et al. (1978) to predict changes in $P_{\text{CO}_2(\text{s})}$ during the reaction. The approach has been extended by Cassford et al. (1983) by considering reactions (VI) to (VIII), the corresponding rate equations (8) to (10) and assuming $P_{\text{CO}_2(\text{s})} = P_{\text{CO}_2}$ i.e. there is no gradient in CO_2 between the crystal surface and bulk of solution. The rate constants were evaluated for two different specific surface area (area per unit mass) materials over a temperature range of 5 to 30 °C. The mechanisms were tested by minimizing the function:

$$\gamma = \sum^n (P_{\text{CO}_2(\text{s})}^i - P_{\text{CO}_2}^i)^2/n \quad (11)$$

where n is the number of data points. Using 20 equally spaced points

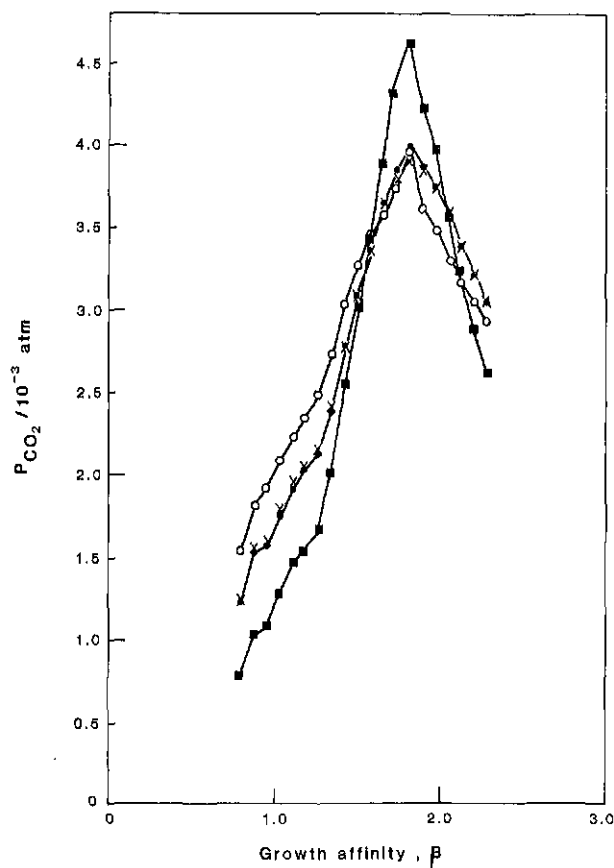


FIG. 3. Comparison of the P_{CO_2} curves obtained for the precipitation of calcite in free-drift conditions at 25 °C and analysed using the three surface reaction mechanisms. ●, P_{CO_2} in the bulk of solution (from solution composition); X, $P_{CO_2(s)}$ from the $CO_3^{2-}(s)$ mechanism; O, $P_{CO_2(s)}$ from the $OH^-(s)$ mechanism; ■, $P_{CO_2(s)}$ from the $HCO_3(s)$ mechanism.

over the range of β produced a series of optimized $P_{CO_2(s)}$ curves, an example of which is shown in Fig. 3. In all cases the values of γ indicated that the agreement between $P_{CO_2(s)}$ and P_{CO_2} is always best for the $CO_3^{2-}(s)$ mechanism (equation 10) over the range of temperatures that were studied. The assumption of $P_{CO_2(s)} = P_{CO_2}$ used in deriving equation (9) for $HCO_3(s)$ mechanism is not valid. The data show that if this mechan-

ism is rate controlling i.e. reaction (VII) applies, then if it is assumed that $P_{\text{CO}_2(s)} = P_{\text{CO}_2}$ at $t = 0$, the surface concentration of CO_2 is greater than the bulk value over the entire range of β .

The $\text{CO}_3^{2-}(s)$ mechanism led to the following temperature dependence of k'_1 (Cassford et al. 1983):

$$\log k'_1 = 1.396 - 2445.2/T \quad (12)$$

for temperatures between 5 and 30 °C and with k'_1 in units of $\text{m}^3 \text{g}^{-1} \text{s}^{-1}$. The activation energy for growth was derived from the Arrhenius plot as $46.8 \pm 4.2 \text{ kJ mol}^{-1}$. This high activation energy is strong evidence in support for a surface controlled mechanism of growth proposed by equations (8)–(10).

The constant composition method has been used to verify the application of equation (10) to synthetic solutions and freshwater systems. Fig. 4 compares the results obtained at different seed concentrations using the conductivity-stat method with P_{CO_2} controlled with a $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ gas stream. The theoretical prediction of the precipitation rates from equation (10) and (12) agrees with the experimental values obtained from the slopes of the lines in Fig. 4. The conditions and detailed results are given in the legend.

In applications to natural systems where nucleation has occurred, equation (10) may be written as:

$$\frac{dn_{\text{Ca}}}{dt} = K_{\text{eff}} a_{\text{HCO}_3} \left[1 - \frac{a_{\text{H}^+}^2}{a_{\text{H}^+(s)}^2} \exp \beta \right] \quad (13)$$

where the effective rate constant $K_{\text{eff}} = A k'_1$ and dn_{Ca}/dt is the rate of loss of calcium from the water. Knowing the precipitation rate and temperature, the value of K_{eff} may be estimated and if inhibiting micro-components do not vary greatly in concentration, then the variation of the precipitation rate under different environmental conditions of pH, alkalinity and temperature may be calculated using equation (13) in combination with the temperature dependence of k'_1 (equation (12)). With a knowledge of the interaction between inhibiting agents mentioned previously, e.g. inorganic phosphate and organic materials, and the calcite surface it should in the future be possible to evaluate the coprecipitation rates in the field. This approach should be valuable in assessing the contribution of inorganic processes to the fluxes of biologically important chemicals in freshwater systems that are susceptible to calcium carbonate precipitation.

Carbon dioxide transfer

The precipitation reaction produces CO_2 (reaction (V)) which reacts through the carbonate equilibrium to alter the solution composition

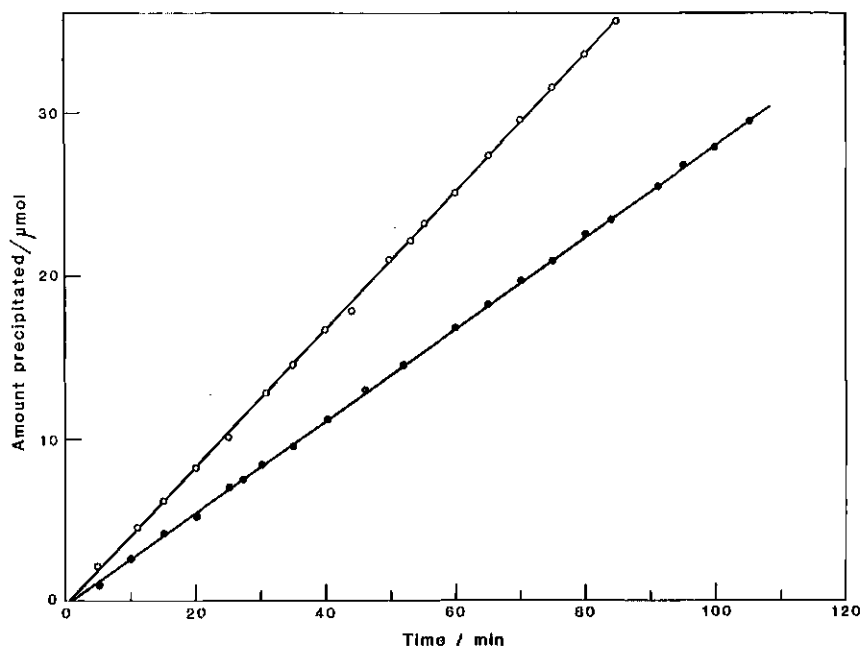


FIG. 4. Effect of seed concentration on calcite precipitation rate. An example of the results obtained using the constant composition method. ●; $s = 0.56$, $P_{\text{CO}_2} = 4.26 \times 10^{-3}$ atm and mass of seed = 14.71 mg. Experimental precipitation rate = $0.28 \mu\text{mol min}^{-1}$ and theoretical rate = $0.26 \mu\text{mol min}^{-1}$. ○, $s = 0.52$, $P_{\text{CO}_2} = 4.27 \times 10^{-3}$ atm and mass of seed = 28.56 mg. The experimental and theoretical precipitation rates agree ($0.42 \mu\text{mol min}^{-1}$).

and supersaturation level. In situations where the water is well buffered and mixed, the release of CO_2 will have little effect on the kinetics. However if the water mass is localized, the flux of CO_2 released during precipitation may be important. Another aspect of CO_2 transfer concerns the release of CO_2 from hard waters supersaturated with respect to the atmospheric partial pressure. The kinetics of the CO_2 evasion determines whether precipitation is probable.

During precipitation in an environment where the exchange of CO_2 with the atmosphere occurs, the paths to thermodynamic equilibrium with the atmosphere and calcite may be simply explained by considering the carbon mass balance in the solution (House 1981b). In solutions which are mixed and at moderate pH values i.e. $\text{pH} < 8.4$ (House et al. 1984), the hydration reactions (III) and (IV) may be neglected and the transfer rate expressed in the form:

$$V \frac{d \Sigma[\text{CO}_2]}{dt} = K_L A \{[\text{CO}_2(\text{s})] - [\text{CO}_2]\} \quad (14)$$

where A is the surface area, V the volume of the solution, $\Sigma[\text{CO}_2]$ is the total inorganic carbon concentration and $[\text{CO}_2(\text{s})]$ is the concentration of CO_2 at the air-water interface. In these conditions the transfer velocity K_L is independent of pH and the solution alkalinity, but does depend on the temperature and hydrodynamics at the interface. When the pH > 8.4 , the hydration reaction (IV) may be important and lead to a chemical augmented flux of HCO_3^- and CO_3^{2-} ions. The major effect of the hydration reaction is to produce and maintain a high CO_2 concentration gradient in the boundary layer between the surface and the bulk of the solution i.e. CO_2 is effectively reduced by chemical reaction with OH^- ions. The augmentation effect increases in importance with increasing solution pH, alkalinity and decreasing flow-rate. The effects have been investigated in detail by House et al. (1984).

In low pH conditions, equation (14) may be integrated and written in the form:

$$\Delta C = \int_{\alpha_1}^{\alpha_2} \frac{dt}{d\alpha} \frac{K_L A}{V} \{[\text{CO}_2(\text{s})] - [\text{CO}_2(\alpha)]\} d\alpha \quad (15)$$

where α is the extent of precipitation (equation (7)) and ΔC is the change in total inorganic carbon. Combining equation (15) with a precipitation rate expression for $dt/d\alpha$, e.g. an equation derived from (10), it is possible to predict the path to equilibrium, such as A to D (upper curve) on Fig. 1, by using a numerical procedure (House 1981b) for chosen values of K_L . This method produces good agreement with the composition changes observed in free-drift experiments with values of $K_L \approx 5 \times 10^{-5} \text{ m s}^{-1}$.

Conclusion

The biological implications concerning the inorganic carbon system in fresh water are three-fold. Firstly the stability of a particular water with respect to calcite deposition depends not only on the degree of supersaturation of the water but on the availability of nucleating surfaces and the concentration of inhibiting agents of which few have been characterized. Secondly, once precipitation has commenced in a well-mixed environment and the supersaturation reduced, the rate of calcium loss may be estimated using eqn (13) with K_{eff} determined experimentally from the precipitation rate, temperature and solution composition in the field at a particular moment. Thus with a knowledge of the partition of a particular nutrient such as inorganic phosphate between the solid

and solution, it should be possible to estimate the loss of nutrient through inorganic precipitation. Finally, the magnitude of the CO₂ flux through the air-water interface for particular field conditions may be estimated for a limited range of alkalinities, flow-conditions and temperatures.

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