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The $CaCO_3$–CO_2–H_2O system in soils[1]

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ABSTRACT

Equations used to develop the CO_2-Ca-pH relationships in calcareous soils are reviewed. The equation

$$P_{CO_2}(Ca) = (H)^2 K_c,$$

is used to draw a three-dimensional surface and to derive three partial differential equations to illustrate the relationships between CO_2 partial pressure, Ca activity and pH. K_c is a combination of Henry's Law constant, the first and second dissociation constants for carbonic acid and the calcite solubility product. The three dimensional CO_2-Ca-pH surface illustrates how the three parameters relate to each other under ideal conditions. The partial differential equations are presented to illustrate how changes in one parameter affect the other two. The CO_2-Ca-pH surface provides a graphical method for introducing the idea of three component equilibria, while the partial differential equations provide a mathematical representation of these interactions for those with chemical thermodynamics or strong mathematic or modeling backgrounds. Deviations from this ideal model in natural systems are discussed for those who wish to extend the discussion to natural systems.

Additional index words: **Calcite, Aragonite, Vaterite, Carbonate minerals, Calcareous soils, Lime.**

SOIL solutions and natural waters in contact with calcium carbonate minerals are buffered with respect to carbon dioxide (CO_2), pH, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), calcium (Ca^{2+}), and several complex ion pair activities. Equilibrium in natural calcium carbonate systems is also affected by other ions in solution that produce common ion effects, or activity coefficient changes due to total ion concentrations. Precipitation and dissolution rates and equilibria can also be affected by contamination of mineral surface sites by inorganic ions or organic solutes. Calcium carbonate systems have been described by a number of different approaches, but most models imposed arftificial constraints or simplifications on the system. The constraints make the system easier to describe, but limit the models' ability in describing natural systems. These simplifications are discussed in detail by Nakayama (1970).

Computer models (Robbins et al., 1980; and Tanji and Doneen, 1966) and graphical calculation methods (Suarez, 1982) have been developed for estimating calcium carbonate equilibrium. It is not always easy to look at these calcium carbonate models and gain an intuitive feel for what is actually happening when solution components are varied. The objective here is to describe a calcareous soil system in a way that is easier to visualize CO_2, water, and calcium carbonate equilibrium without oversimplification. The system is open with respect to Ca^{2+}, H^+, HCO_3^-, CO_3^{2-}, CO_2, and any other ions, ion pairs, or dissolved gases that may be found in a natural system. This approach allows for CO_2 addition from biological activity or removal by escape into the atmosphere or as a leachate solute. Cations and anions are allowed to enter or leave the system as solutes, dissolution and precipitation products or reactants, or cation exchange products or reactants. In the initial development, chemical equilibrium is assumed and then later, departure from equilibrium will be discussed.

As CO_2 gas dissolves in water, less than 0.3% of the $CO_{2(aq)}$ is hydrated to H_2CO_3 at 25°C (Ponnamperuma, 1967). Since it is difficult to distinguish between $CO_{2(aq)}$ and H_2CO_3, the composite acid $H_2CO_3^*$ is defined as the analytical sum of $CO_{2(aq)}$ and H_2CO_3. The pure acid, H_2CO_3 is much stronger ($pK_{H_2CO_3} = 3.8$) than the composite, $H_2CO_3^*$ ($pK_{H_2CO_3^*} = 6.3$) (Stumm and Morgan, 1970). The difficulty in identifying the species involved in the above reaction makes it more practical to use the "apparent" solubility expression

$$H_2O + CO_{2(g)} \rightleftharpoons H_2CO_3^*$$

with the equilibrium for the combined reactions expressed as

$$\frac{(H_2CO_3^*)}{P_{CO_2}} = K_H \qquad [1]$$

where P_{CO_2} is the CO_2 partial pressure and K_H is Henry's Law constant. The carbonic acid thus formed quickly dissociates to form HCO_3^- and H^+ ions, and at high pH the second dissociation produces CO_3^{2-} and a second H^+ ion.

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The first and second dissociation reactions are represented as

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$

and

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

with the equilibrium dissociation constants K_{d1} and K_{d2} calculated as

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3^*)} = K_{d1} \qquad [2]$$

and

$$\frac{(H^+)(CO^{2-})}{(HCO_3^-)} = K_{d2} \qquad [3]$$

where the species in parentheses represent activities.

By rewriting Eq. [3] in terms of (HCO_3^-) and substituting into Eq. [2], the equation

$$\frac{(H^+)^2(CO_3^{2-})}{(H_2CO_3^*)} = K_{d1}.K_{d2} \qquad [4]$$

is obtained. Now if eq. [4] is written in terms of $(H_2CO_3^*)$ and substituted into eq. [1] and the results rewritten in terms of P_{CO_2} the following expression is obtained.

$$P_{CO_2} = \frac{(H^+)^2(CO_3^{2-})}{K_H\, K_{d1}\, K_{d2}} \qquad [5]$$

This gives an expression for P_{CO_2}, (H^+), and (CO_3^{2-}) equilibrium in an aqueous system. This system can then be brought into equilibrium with calcium carbonate by first considering the dissolution reaction

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

with the solubility product, K_{sp}, calculated as

$$(Ca^{2+})(CO_3^{2-}) = K_{sp} \qquad [6]$$

By rewriting eq. [6] in terms of (CO_3^{2-}), and substituting it into eq. [5] the equation

$$P_{CO_2} = \frac{(H^+)^2\, K_{sp}}{K_H\, K_{d1}\, K_{d2}\, (Ca^{2+})} \qquad [7]$$

is obtained. If the equilibrium constants are combined such that

$$K_c = \frac{K_{sp}}{K_H\, K_{d1}\, K_{d2}} \qquad [8]$$

eq. [7] can be written as

$$P_{CO_2} = \frac{(H^+)^2\, K_c}{(Ca^{2+})} \qquad [9]$$

or

$$P_{CO_2}\,(Ca^{2+}) = (H^+)^2\, K_c \qquad [10]$$

Using the values of 4.45×10^{-9}, 3.38×10^{-2}, 4.45×10^{-7} and 4.67×10^{-11} for K_{sp}, K_H, K_{d1} and K_{d2} respectively (Adams, 1971), K_c has the value 6.34×10^9.

Equation [10] can be written in several other forms after taking the log of each term, such as

$$\log P_{CO_2} + \log(Ca^{2+}) = 2\log(H^+) + 9.80 \qquad [11]$$

or by rearranging

$$2pH = 9.80 - \log P_{CO_2} - \log(Ca^{2+}) \qquad [12]$$

or

$$pH = 4.90 + 1/2pP_{CO_2} + 1/2p(Ca^{2+}) \qquad [13]$$

When eq. [13] is plotted as a three-dimensional surface (Fig. 1) the variables pH, pP_{CO_2}, or $p(Ca^{2+})$ can be shown as a function of the other two.

An example for using Fig. 1 could be; if P_{CO_2} is 2% ($-\log 0.02 = 1.7$) and the pH is 7.5, the p(Ca) would be found by going up the constant pP_{CO_2} line 1.7 (a) until the pH 7.5 line is intercepted (b) and then by following the constant $p(Ca^{2+})$ line to the left margin, then p(Ca) is read as 3.5 which is equal to the (Ca^{2+}) of 2.5×10^{-5} moles/L. If the P_{CO_2} is increased to 5% ($-\log 0.05 = 1.3$) (c), the pH must drop to 7.30 if the (Ca^{2+}) is to remain constant or the (Ca^{2+}) will increae to 1.26×10^{-4} moles/L (p(Ca) = 3.9) if the pH remains constant. The third alternative is a combination of the pH decreasing while the (Ca^{2+}) increases as the P_{CO_2} increases. Equation [13] and Fig. 1 provide a graphical method for introducing the relationships between the three interactive components of the CO_2-Ca-pH system to students who have not been exposed to these kinds of systems.

In the (H^+), (Ca^{2+}), P_{CO_2} relationship that exists when $CaCO_3$ minerals are in aqueous or moist natural systems, each of the three variables can be taken, one at a time and considered as dependent on the other two and treated as a dependent variable in a differential function. If (H^+) is considered the dependent variable, the differential change in H ion activity can be expressed as

$$d(H^+) = \left(\frac{\delta(H^+)^2}{\delta(Ca^{2+})}\right)_{P_{CO_2}} d(Ca^{2+}) + \left(\frac{\delta(H^+)^2}{\delta P_{CO_2}}\right)_{(Ca^{2+})} dP_{CO_2} \qquad [14]$$

When (Ca) is considered the dependent variable the differential change in Ca ion activity can be expressed as

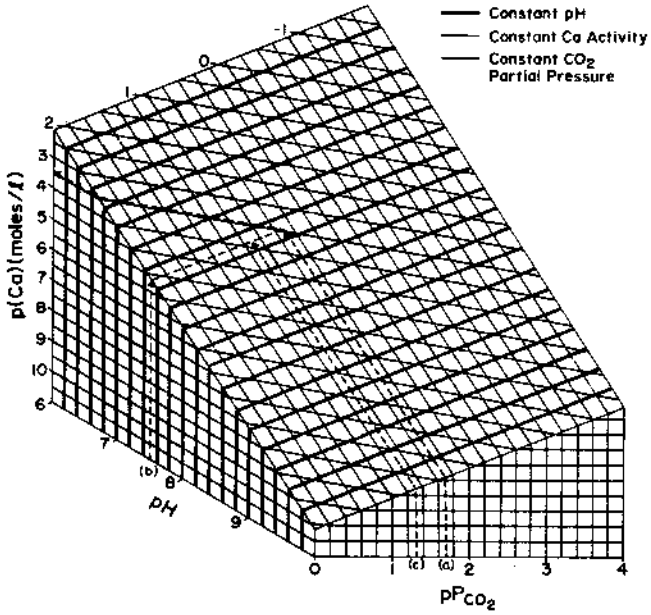

Fig. 1. The pP_{CO_2}-pH-pCa activity surface for gas-liquid-solid phase system in equilibrium with calcite.

$$d(Ca^{2+}) = \left(\frac{\delta(Ca^{2+})}{\delta P_{CO_2}}\right)_{(H^+)} dP_{CO_2} + \left(\frac{\delta(Ca^{2+})}{\delta(H^+)^2}\right)_{P_{CO_2}} d(H^+)^2 \quad [15]$$

and likewise the differential P_{CO_2} change when CO_2 partial pressure is the dependent variable can be expressed as

$$dP_{CO_2} = \left(\frac{\delta P_{CO_2}}{\delta(H^+)^2}\right)_{(Ca^{2+})} d(H^+)^2 + \left(\frac{\delta P_{CO_2}}{\delta(Ca^{2+})}\right)_{(H^+)} d(Ca^{2+}) \quad [16]$$

These differential functions can be expressed this way because the total differential of the dependent variable is the sum of the differential changes caused by changing the independent variables separately. Consequently, a change caused by one independent variable does not influence the change caused by another independent variable (Granville et al., 1957).

Equations [14], [15], and [16] can be used in teaching students with strong chemical thermodynamics or differential calculus backgrounds and students modeling calcareous systems. These equations illustrate i) that any two components can be varied independently of each other as long as the third component is allowed to vary, or ii) that one component can be varied with the effect being distributed over the other two. Adding calcium chloride to a soil would raise the pH and increase the (Ca^{2+}), thus causing the P_{CO_2} to increase, this being an example of the first case. Respiring plant roots producing CO_2 in the soil increases P_{CO_2} and thus increasing the pH which in turn increases $CaCO_3$ solubility. This is an example of the second case. If either of the above reactions take place in a sodic, calcareous soil, calcium will exchange with sodium, thus decreasing (Ca^{2+}) and again changing the balance between the three components.

This (Ca^{2+}), (H^+), P_{CO_2} equilibrium model requires that Ca^{2+} and H^+ are expressed as activities and that the system contains a solid phase $CaCO_3$ mineral in the aqueous phase, and CO_2 in the gas phase. Other minerals may be present in the solid phase, other ions or ion pairs may be present in the liquid phase, and there may be other gases in the gaseous phase. This model does not preclude cation exchange.

The K_{sp} value for the $CaCO_3$ mineral calcite is 4.45×10^{-9}. The product of Ca^{2+} activity times the CO_3^{2-} activity is the calcium carbonate ion activity product (IAP). When the IAP is greater than the K_{sp} for calcite that point will be above the surface in Fig. 1, and the solution will be supersaturated with respect to calcite. If the IAP is less than the K_{sp}, the point will be below the surface in Fig. 1, and the solution will be undersaturated with respect to calcite. When K_{sp} = IAP, the solution is in equilibrium with solid phase calcite, and the point will be on the surface shown. However, none of the three conditions just mentioned are by themselves proof of the presence or absence of calcite or any other $CaCO_3$ mineral.

Subsurface drainage waters and soil extracts from arid and semiarid region calcareous soils are seldom in equilibrium with calcite as indicated by their $CaCO_3$ IAP. The mean IAP from 28 wells below irrigated Arizona fields was 11.3×10^{-9}, and the mean IAP from 35 well water samples from The Grand Valley of Colorado was 10.7×10^{-9} (Suarez, 1977). When three calcareous soils were mixed at 1:5 soil:water ratios, and equilibrated for 29 and 41 days at 25°C, two solutions had IAP values greater and one less than that of calcite (Marion and Babcock, 1977). Many other examples of non-equilibrium with calcite in carbonate systems can be found in the literature.

These discrepancies between the calcite K_{sp} and the calculated IAP can be due to any of a combination of factors such as (i) carbonate minerals other than calcite controlling the IAP, (ii) calcite solubility differences due to ion substitution in the crystal lattice, (iii) variations in calcite specific surface area, (iv) crystal surface contamination, or (v) lack of precipitation-dissolution equilibrium.

MINERALS OTHER THAN CALCITE

Doner and Pratt (1969) found that when $CaCO_3$ was precipitated in the presence of $MgCl_2$, calcite and aragonite were formed, but when $CaCO_3$ was precipitated in the presence of SO_4^{2-} salts, vaterite, anhydrous $CaCO_3$, and calcite were formed. Argonite, vaterite, and anhydrous $CaCO_3$, which are all polymorphic forms, are more soluble than calcite (Marion and Babcock, 1977). If during soil solution concentration (due to evapotranspiration), $CaCO_3$ precipitates in the

presence of other ions, it is very likely that minerals other than calcite could form. When these more soluble species precipitate, the IAP would be greater than the calcite K_{sp}.

ION SUBSTITUTION IN THE CRYSTAL LATTICE

Hassett and Jurinak (1971) found that in low $Ca\text{-}HCO_3$ water, Millville soil which contains 45% calcareous material that was predominantly dolomite, released more moles/L of calcareous $[(Ca_xMg_{2-x})(CO_3)_2]$ materials into solution than did the Portneuf soil which contains about equal amounts of calcite and dolomite. Marion and Babcock (1977) present data that suggest that calcite solubility increases with a 2 to 10% Mg substitution in the crystal lattice. Levy et al. (1982) showed that as the ratio of solution Mg to Ca increases from 0.4 to 26.1 the log IAP increased from −8.52 to −7.15 and the Mg to Ca ratio in the solid phase increased from 0.01 to 1.75 when precipitated with CO_3^{2-} in the presence of bentonite.

SURFACE AREA DIFFERENCES

A calcite sample with a 13.5 m^3/g surface area was found to be more soluble than compared to one with a 0.8 m^2/g surface area sample, when equilibrated with an under-saturated solution. When equilibrated at a higher Ca^{2+} and HCO_3^- concentration the differences in the two materials were not significantly different (Hassett and Jurinak, 1971).

CRYSTAL SURFACE CONTAMINATION

Olsen and Watanabe (1959) found that clay, resin, or noncalcareous soil added to calcite suspensions did not affect calcite solubility, but when $CaCO_3$ was precipitated in suspensions of these same materials, the resulting precipitates were more soluble than calcite. Organic compounds present in natural systems during precipitation can also increase $CaCO_3$ solution IAP by coating or blocking crystal surfaces (Suess, 1970).

LACK OF EQUILIBRIUM

In addition to the above conditions which can cause $CaCO_3$ precipitates to be more soluble than calcite, other calcium containing minerals may be in contact with the soil solution. Reaction rate differences between calcite and metastable forms such as aragonite, vaterite or monohydrate $CaCO_3 \cdot$ will affect the soil system equilibrium. In soil solutions where the solution concentration is continually changing due to wetting and drying cycles, steady state equilibrium with calcite will seldom exist.

Weathering of non-calcareous minerals that contain Ca such as gypsum ($CaSO_4 \cdot 2H_2O$) or anorthite ($CaAl_2Si_2O_8$) in the presence of CO_2 producing soil organisms will produce a continual Ca^{2+} and HCO_3^- ion supply. If these ions are not removed by leaching, there may be an accumulation of these ions in solution whenever any process slows precipitation relative to the rate of weathering.

Under conditions where more soluble $CaCO_3$ minerals dissolve first and only calcite is left, the system may go from a supersaturated calcite condition to one that is in equilibrium with calcite as the soil solution is diluted (Levy, 1981a, 1981b). As the soil solution becomes more concentrated by evapotranspiration, more soluble $CaCO_3$ species may again form as a result of any of the mentioned conditions.

Realizing that the equilibrium model assumes that activities are used for Ca and that natural systems are seldom at equilibrium, Fig. 1 allows for a quick way of choosing a set of conditions in a calcareous soil. Then by changing one or two of the three variables, the changes in the remaining variable can be predicted. One must recognize that in soils the cation exchange capacity will buffer a change in Ca^{2+} activity to some degree by exchange with other cations (Cruz-Romero and Coleman, 1974). The principles discussed here can also be extended to lake and stream interactions with bottom and suspended sediments.

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