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CALCIUM CARBONATE EQUILIBRIA IN SOILS AND IRRIGATION WATERS

Technical Completion Report
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CALCIUM CARBONATE EQUILIBRIA IN SOILS
AND IRRIGATION WATERS

by

George A. O'Connor

Department of Agronomy
New Mexico Water Resources Research Institute
New Mexico State University
Las Cruces, New Mexico

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Abstract

Irrigation water degradation is of the utmost interest to water and soil scientists throughout the world yet meaningful and accurate equations to describe the equilibria of one of the most important solid phases controlling water quality, calcium carbonate, are lacking.

The objectives of this research were to: 1) develop a model capable of describing carbonate equilibria in aqueous systems open to the air, and 2) to test the model against data for aqueous and soil-water systems.

A chemical model was developed that adequately described calcite equilibria over a range of ionic environments that have practical significance to water and soil scientists. The model includes equations to account for activity coefficient and ion-pair effects, and was verified utilizing data from the literature for aqueous systems open to the air.

Acknowledgements

Appreciation is expressed to Fernando Cadena C., a former graduate assistant in the Department of Civil Engineering at New Mexico State University, for his efforts in the development of the chemical model of calcite systems. Mr. Cadena is currently pursuing the same area of research for his Ph.D. degree at California Institute of Technology in Pasadena, California.

"Calcium Carbonate Equilibria in Soils and Irrigation Waters"

G. A. O'Connor

Calcium carbonate (calcite) is an abundant and widely distributed mineral and hence is of major importance to geologists, water scientists, and soil scientists. The behavior and properties of calcite must be known, for example, to understand the conditions of geologic formation of calcite, to predict the composition of a calcareous soil solution irrigated with water of a given quality, or to predict irrigation water quality degradation. Considering the importance of calcium carbonate, it is not surprising that the literature dealing with calcite solubility is voluminous. And yet, attempts to characterize the calcite systems in terms of basic chemical principles have met with only limited success.

Akin and Lagerwerff (1965a,b) predicted CaCO_3 solubilities in aqueous solutions open to the air, but were forced to invoke the concept of an enhanced solubility due to modification of the calcite lattice in Mg^{++} and $\text{SO}_4^{=}$ solutions. Langmuir (1968) showed that the solubility product of calcite was constant (as dictated by chemical theory) in solutions of varying ionic strength, but failed to consider the effects of ion pairs in his model. Nakayama (1968, 1971) has shown ion pairs to represent a significant percentage of total Ca in saturated CaCO_3 systems and hence an effect that cannot be ignored. Langmuir's (1974) most recent model of CaCO_3 equilibria included ion-pair considerations, but predicted solubility products that varied markedly with ionic strength. Numerous other studies have met with similarly limited success.

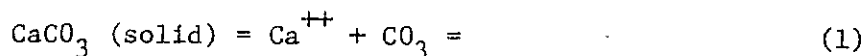
The objectives of this project were to 1) develop a model capable of describing carbonate equilibria in water that included as many of the factors

reported to affect the equilibria as possible; and 2) to test the model against data for calcareous soils irrigated with water of various compositions.

Efforts were restricted to developing a chemical model capable of describing calcite equilibria in aqueous systems open to the atmosphere. The approach was to show that the solubility product of calcite calculated via the model for literature data was constant when the appropriate equations were included to account for activity coefficients, partial pressure of CO_2 , and various ion-pairs. The model was shown to be adequate for aqueous systems but has not been verified for soil systems. The project was originally designed for two to three years, but was terminated after only one year due to lack of funds. Hence only the first objective of the proposal was accomplished. Application of the model to soil systems will be made when funding becomes available.

Theory

The dissociation of CaCO_3 in water is usually shown as



and the thermodynamic ionic activity solubility product, K_{isp} , is

$$K_{\text{isp}} = \frac{(\text{Ca}^{++}) (\text{CO}_3=)}{(\text{CaCO}_3 \text{ solid})}$$

where parentheses denote activities. The activity of a solid phase is usually taken as unity. Since K_{isp} is written in terms of activities, the value should be constant for all ionic environments at a given temperature. With few exceptions, the activity of the ionic constituents making up K_{isp} cannot be determined directly (Nakayama, 1971). Instead, concentrations are used and subsequently converted to activity units by multiplying concentrations by the individual ionic activity coefficients. The equation most often used to calculate activity coefficients is the extended form of

the Debye-Huckel relationship.

$$-\log \gamma_i = \frac{0.509 Z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} \quad (2)$$

where Z_i is the valence of the ion, a_i is an experimental parameter for each ion related to the hydrated diameter of the ion in solution and, B is a constant (3.28×10^7 at 25°C). The ionic strength of the solution μ is calculated by equation (3).

$$\mu = 1/2 \sum_{i=1}^n C_i Z_i^2 \quad (3)$$

where C_i is the concentration of the ion in solution. However, there is rarely a one-to-one relation between the analytical concentration measurement (C_i) and the ionic species due to an interaction among various ionic forms known as ion-pairs (Nakayama, 1971).

For example, in saturated CaCO_3 solutions, the dissolved Ca species include Ca^{++} , CaHCO_3^+ , CaCO_3^0 , and CaOH^+ (Nakayama, 1968). The equation describing the formation of the CaCO_3^0 ion pair is



$$K_{\text{CaCO}_3^0} = \frac{(\text{CaCO}_3^0)}{(\text{Ca}^{++}) (\text{CO}_3^{=})}$$

There has been considerable discussion (Halla and Van Tassel, 1958; Garrels and Christ, 1965; Nakayama, 1968; and Jacobson and Langmuir, 1974) as to the relative importance of ion-pairing in CaCO_3 systems, but the excellent work of Nakayama (1968, 1971) appears to verify ion-pair existence and significance. Many other ion-pairs are possible in mixed ion- CaCO_3 systems, e.g., MgCO_3^0 , CaSO_4^0 , CaHCO_3^+ , NaSO_4^- , etc. Ion-pairs considered in our model and the corresponding equilibrium dissociation constants are given in

Table 1. There is a wide variety of constants available in the literature, but those reported by Adams (1971) and Nakayama (1968, 1971) were used in most cases because of the techniques utilized in determining and verifying the values. A model (Cadena, Midkiff, and O'Connor, 1974) utilizing the constants in Table 1 successfully predicted the limiting hardness in water treatment, which also lends credence to the values.

The formation of ion-pairs in CaCO_3 systems causes an enhanced solubility of CaCO_3 due to the consumption of free ions released in dissociation of the solid phase (equation [1]) into ion pairs (equation [3]). More total Ca (Ca_T) is brought into solution and analytically measured as Ca^{++} . Free Ca^{++} ion activity, (Ca^{++}), however, should not change as dictated by the Kisp for equation [1]. The enhanced solubility of CaCO_3 noted in various ionic environments was likely a result of ion-pair formation or activity coefficient considerations. A model that correctly accounts for the effects of ion pair formation and activity coefficients should therefore result in a constant value of Kisp for CaCO_3 . The model described below was designed to test this hypothesis.

Model

The model applies to aqueous CaCO_3 systems open to the atmosphere. It does not apply to systems initially supersaturated with respect to CaCO_3 since the calculation of how much CaCO_3 should precipitate would require a value of Kisp for CaCO_3 which is being calculated.

Initial inputs include partial pressure of CO_2 , total Ca^{++} , and the total concentrations of all other species (Na, Mg, K, SO_4 , Cl) present in the solution. Carbonate species concentrations are calculated from pH, P_{CO_2} , and the dissociation constants of carbonic acid. Hydrogen ion concentration is calculated from the concentration of cations needed to effect

electrical neutrality following an initialization of $H = 10^{-7}$ M. Individual ionic concentrations are initialized as equal to the total concentrations of all species of a particular ion, e.g., $[Na^+] = Na_T$. All ion pairs are initialized as being equal to zero.

The program is divided into a number of subroutines which calculate 1) activity coefficients (equations [2 and 3]), 2) the various ion pair concentrations, 3) the concentration of individual free ions (as a difference between the total ion concentration and the sum of the various ion pair concentrations, and 4) the error in each cycle (error limited to 0.1% of the previous ion concentration). When the activities of each ion have been calculated, the product of (Ca^{++}) and $(CO_3^{=})$ is calculated as K_{sp} (equation [1]) and printed as output along with the pH and activities of all other species.

Data

Data from the literature were selected on the basis of the variety and range of conditions (P_{CO_2} , ionic environments) imposed. Some of the data were quite old: Frear and Johnson, (1929) - 36 points, Backstrom (1925) - 1 point, but more recent data were also examined: Shtermina & Frolova, (1952) - 5 points, Miller (1952) - 4 points, Yanteyeva (1954) in Langmuir, (1968) - 2 points, Cole (1957) - 13 points, Akin & Lagerwerff, (1965b) - 6 points, and some unpublished data furnished by J. D. Oster (USSL) only recently (1973) developed, 7 points. Data available from some sources (Akin and Lagerwerff, 1965a and b, Cole, 1957) were not included if the particular solutions were supersaturated with respect to $CaCO_3$. A total of 73 solutions (data points) were analyzed. The range of solution characteristics encountered is given in Table 2.

Results and Discussion

The variation of K_{sp} with ionic strength and, Ca, SO_4 , or Cl activities of the solutions examined are given in Figs. 1, 2, 3, and 4, respectively. Data in Figs. 3 and 4 represent only those solutions containing SO_4 or Cl ions; not all of the solutions analyzed contained these ions. Only four solutions contained Mg and the value of K_{sp} in these solutions varied from $3.11 - 3.30 \times 10^{-9}$. The two dashed lines on each figure represent the range of K_{sp} values within which most of the data fall and within which the coefficient of variation was 10%. The range of values, from 2.6 to 4.0×10^{-9} is reasonable considering the variety of 1) data sources, 2) ionic environments, and 3) equilibrium constants for ion-pairs, dissociations constants, etc. available in the literature.

Those data not enveloped by the two horizontal lines for the most part fall into two categories: 1) very high ionic strength solutions (Frear & Johnson, 1929), and 2) solutions in equilibrium with precipitated $CaCO_3$ from Baker Chemical (Cole, 1957).

The first group of data represent solutions of very high NaCl concentrations (Fig. 4), and have ionic strengths of 0.33 or greater (Fig. 1). There are at least two explanations for the lower K_{sp} values calculated from these solutions. The extended Debye-Huckel equation (equation [2]) is generally regarded as being restricted to solutions of ionic strength ≤ 0.1 . Activity coefficients calculated from equation [2] at ionic strengths >0.1 are likely in error; hence values of K_{sp} for these solutions should not be expected to represent true thermodynamic ionic activity solubility products.

The ionic strengths of some saline soil solutions or geologic deposits may reach values of ≥ 0.3 . Correction for activity coefficients in these solutions would be very difficult and prediction of equilibrium concentrations may be subject to considerable error.

A second explanation for the low values of K_{isp} calculated from these solutions is the possibility of non-equilibrium conditions in the solutions. Frear and Johnson (1929) reported that these solutions were probably not in equilibrium with solid phase CaCO_3 present but that equilibrium was so slowly approached so as to necessitate the assumption of equilibrium. The model, of course, assumes equilibrium conditions and may therefore be expected to result in calculated K_{isp} values unlike those for equilibrium solutions.

The presence of the CaCl^+ ion-pair has been suggested in solutions with high Cl^- concentrations (Corsaro, 1962). The CaCl^+ ion pair was not included in our model due to the uncertainty of its existence and formation constant. In any case, inclusion of the CaCl^+ ion pair would have increased the disparity between K_{isp} values for the high Cl^- solutions and the rest of the data since less free Ca^{++} would be available for reaction with $\text{CO}_3^{=}$ ions and lower K_{isp} values would therefore result for these solutions.

The data from the high Cl^- solutions are therefore felt to be exceptional and not regarded as failures of the model.

The second group of data not enveloped by the range of K_{isp} values suggested as reasonable for aqueous systems, are solutions described by Cole (1957). All of the solutions yielding calculated K_{isp} values greater than 4.0×10^{-9} were solutions equilibrated with precipitated CaCO_3 from Baker Chemical Company. Almost all of the other data points reported here represent solutions equilibrated with Iceland Spar CaCO_3 . The two solutions reported by Cole that were equilibrated with Baker's Iceland Spar yielded K_{isp} values within the 2.6 to 4.0×10^{-9} range indicated. Two of the solutions equilibrated with precipitated CaCO_3 also resulted in K_{isp} values within the 2.7 to 4.0×10^{-9} range, but seven did not (Cole, 1957).

It is in a sense, discouraging to identify an apparent dependence of K_{isp} for CaCO_3 on the form of CaCO_3 used since natural deposits of CaCO_3 or

soil precipitated CaCO_3 have been reported to vary considerably in character (Doner & Pratt, 1969). Variations of K_{isp} with the form of calcite would greatly restrict the general application of equilibrium models. However, many other solutions reported here that were equilibrated with calcite (some of which did not identify the source as Iceland Spar) yielded K_{isp} values in the range selected. One solution, in fact, equilibrated with Solenhofen limestone (Miller, 1952) yielded a K_{isp} value only slightly greater than the upper limit indicated here (4.05×10^{-9}).

More study is apparently needed before the limits of K_{isp} suggested here can be applied generally to calcite systems. However, the uniqueness of Cole's data (Cole, 1957) for precipitated CaCO_3 solutions does not appear to be critical to success of the model described herein.

Neglecting the two groups of data discussed above, the data presented in Figs. 1-4 exhibit a reasonable constancy expected on the basis of chemical thermodynamics. The data in Fig. 3 and the four solutions containing Mg^{2+} , lend credence to the argument that the enhanced solubility of CaCO_3 in solutions containing Mg and SO_4 ions is probably a result of ion pair formation rather than lattice modification (Akin & Lagerwerff, 1965b). The only solutions showing an effect on ionic concentration are the Cl^- solutions (Fig. 4) discussed previously.

The average value of K_{isp} for calcite in all 73 solutions is 3.27×10^{-9} with an individual standard error of 0.74 and a range of 0.95 to 5.2×10^{-9} . If the two groups of data discussed previously are neglected the average K_{isp} value for 60 solutions is 3.29×10^{-9} with an individual standard error of .33 and a range of 2.6 to 4.0×10^{-9} . Langmuir (1968) reported an average value of 4.0×10^{-9} for data from some of the same sources used herein, but did not consider ion pairs in his calculations of calcite solubility in pure

water. Langmuir (1974) later reported an average value of 3.38×10^{-9} (at 25°C) for data analyzed utilizing a model which accounted for ion-pairs with a range of $3.02 - 5.24 \times 10^{-9}$. He also reported, however, a marked decrease in Kisp values with increasing ionic strength that was not observed in this study. The average value of 3.3×10^{-9} determined herein is slightly lower than the values ($4.5 - 4.9 \times 10^{-9}$) usually given for calcite (Adams, 1971) although some researchers have reported using values of 4.0×10^{-9} . The large number, and variety of solution characteristics used to calculate Kisp values reported herein would appear to justify usage of the lower Kisp value. It is also important to note that although the dissociation constant for CaCO_3^0 used in our model is considerably different than the value reported by Langmuir (1974) (3.29×10^{-5} vs. 6.3×10^{-4}), the average value of Kisp for CaCO_3 in both studies was essentially the same (3.3×10^{-9} vs. 3.38×10^{-9}).

Summary and Conclusions

Calcite solubility is of major importance to numerous scientists and yet attempts to characterize the system in terms of basic chemical thermodynamics have met with limited success. Some approaches have been successful, but have necessitated oversimplification of the system, inclusion of crystal lattice modification considerations, or have resulted in dependences of Kisp values on ionic strength. The model reported herein adequately describes calcite equilibria in aqueous solutions without any of these undesirable characteristics. Equations accounting for activity coefficients and various ion-pair formations were sufficient to describe calcite equilibrium in solutions of widely varying ionic characteristics. Sixty out of the 73 solutions analyzed yielded calculated Kisp values for calcite ranging from 2.6 to 4.0×10^{-9} with an average of 3.3×10^{-9} . The average is slightly lower than the

values normally reported by soil scientists, but would appear to more realistically characterize solutions commonly encountered in nature.

The model has not been applied to soil systems, but a similar (unpublished) model has been developed independently by workers at the U. S. Salinity Laboratory in Riverside, California. Their model is fairly successful in describing CaCO_3 relationships in soils, but suffers presently from an assumed solubility of CaCO_3 much higher than that reported here and which has no clearly defined chemical basis. More study is apparently needed before the model described here can be applied to the important soil-water systems.

Table 1. Equilibrium constants used in the model at 25°C and zero ion strength for the reactions indicated

Reaction	K	Reference
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$	3.38×10^{-2}	Adams (1971)
$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	4.47×10^{-7}	Adams (1971)
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{=}$	4.68×10^{-11}	Adams (1971)
$\text{CaCO}_3^{\circ} = \text{Ca}^{++} + \text{CO}_3^{=}$	3.29×10^{-5}	Nakayama (1968)
$\text{CaHCO}_3^+ = \text{Ca}^{++} + \text{HCO}_3^-$	5.64×10^{-2}	Nakayama (1968)
$\text{CaOH}^+ = \text{Ca}^{++} + \text{OH}^-$	3.22×10^{-2}	Martynova (1971)
$\text{CaSO}_4^{\circ} = \text{Ca}^{++} + \text{SO}_4^{=}$	4.9×10^{-3}	Tangi (1969)
$\text{MgCO}_3^{\circ} = \text{Mg}^{++} + \text{CO}_3^{=}$	4.00×10^{-4}	Adams (1971)
$\text{MgHCO}_3^+ = \text{Mg}^{++} + \text{HCO}_3^-$	6.9×10^{-2}	Oster & McNeal (1971)
$\text{MgCl}^+ = \text{Mg}^{++} + \text{Cl}^-$	1.23×10^{-1}	Corsaro (1962)
$\text{MgSO}_4^{\circ} = \text{Mg}^{++} + \text{SO}_4^{=}$	5.88×10^{-3}	Adams (1971)
$\text{NaCO}_3^- = \text{Na}^+ + \text{CO}_3^{=}$	2.8×10^{-1}	Nakayama (1970)
$\text{NaHCO}_3^{\circ} = \text{Na}^+ + \text{HCO}_3^-$	6.8×10^{-1}	Nakayama (1970)
$\text{NaSO}_4^- = \text{Na}^+ + \text{SO}_4^{=}$	2.4×10^{-1}	Adams (1971)
$\text{K SO}_4^- = \text{K}^+ + \text{SO}_4^{=}$	1.1×10^{-1}	Adams (1971)

Table 2. Range of values encountered in solutions analyzed

Parameter	Range of Values
Ionic strength	$1.33 \times 10^{-3} - 1.19 \times 10^0$
P_{CO_2}	$3.1 \times 10^{-4} - 1.0 \times 10^0$ atmospheres
Mg^{++} activity	$0 - 6.8 \times 10^{-3}$ M
Ca^{++} activity	$2 - 70 \times 10^{-4}$ M
$CO_3 =$ activity	$3.4 - 95 \times 10^{-5}$ M
$SO_4 =$ activity	$0 - 4.75 \times 10^{-3}$ M
Cl^- activity	$0 - 0.62$ M

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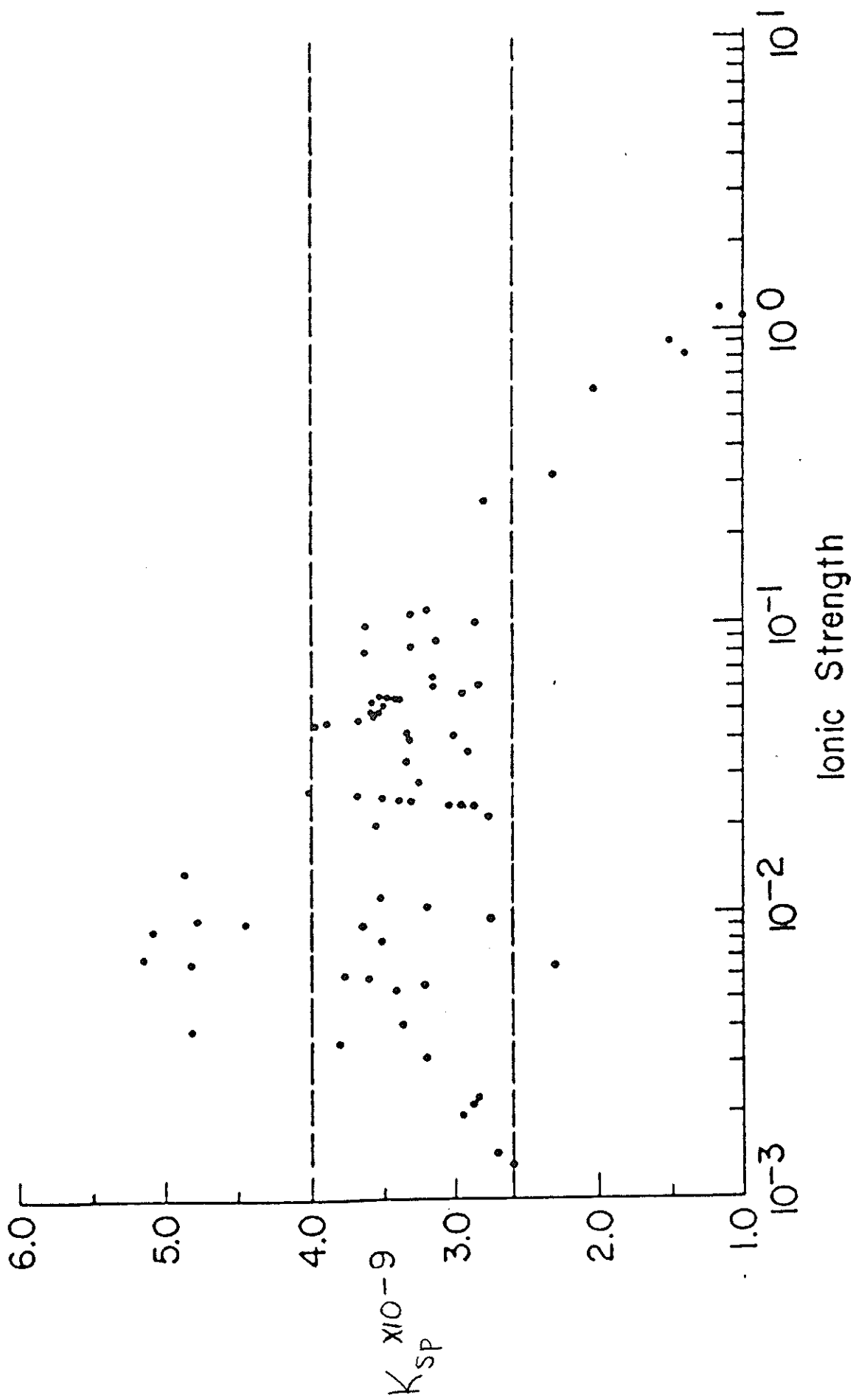


Figure 1. Solubility product of CaCO_3 as a function of ionic strength.

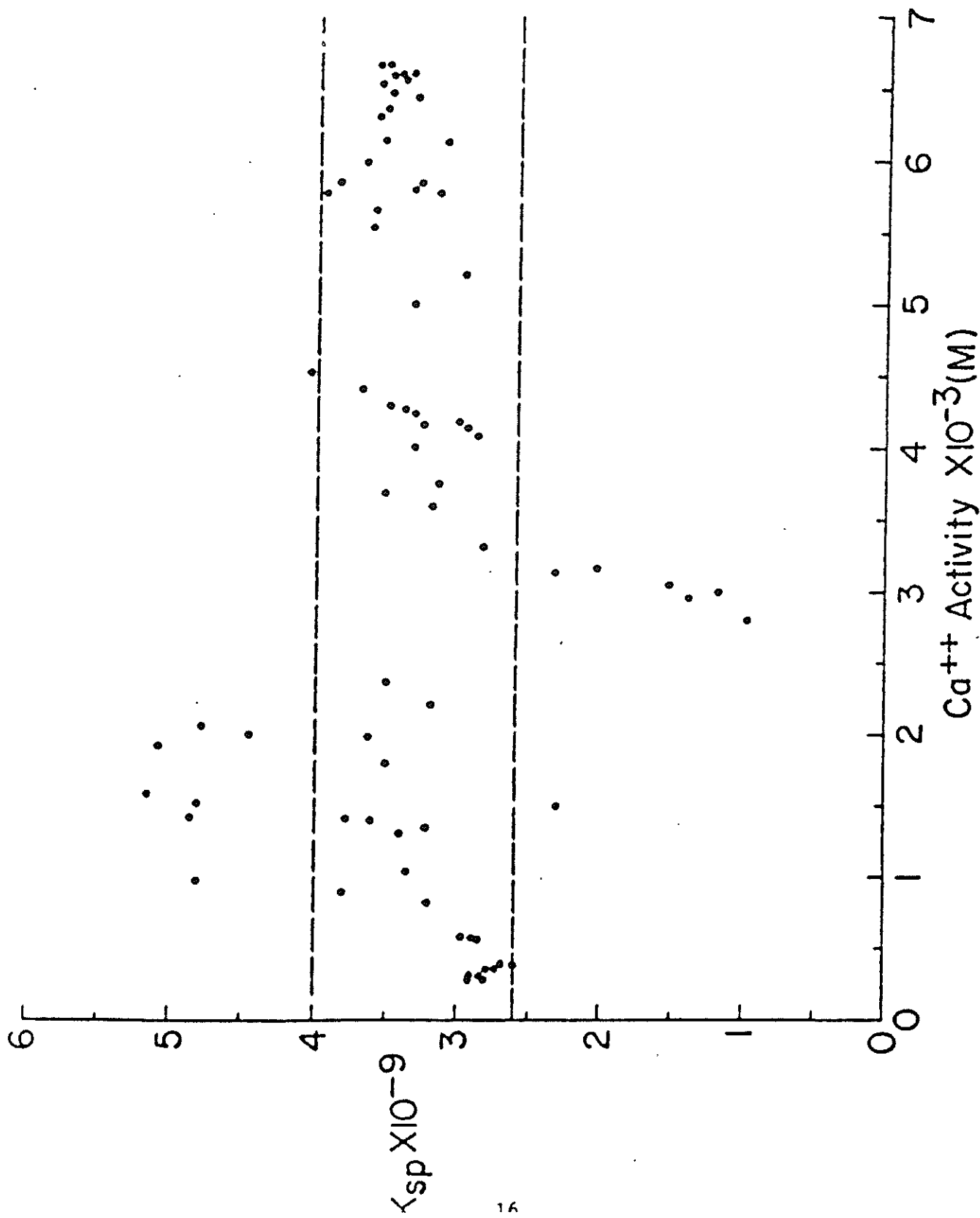


Figure 2. Solubility product of $CaCO_3$ as a function of Ca^{++} activity.

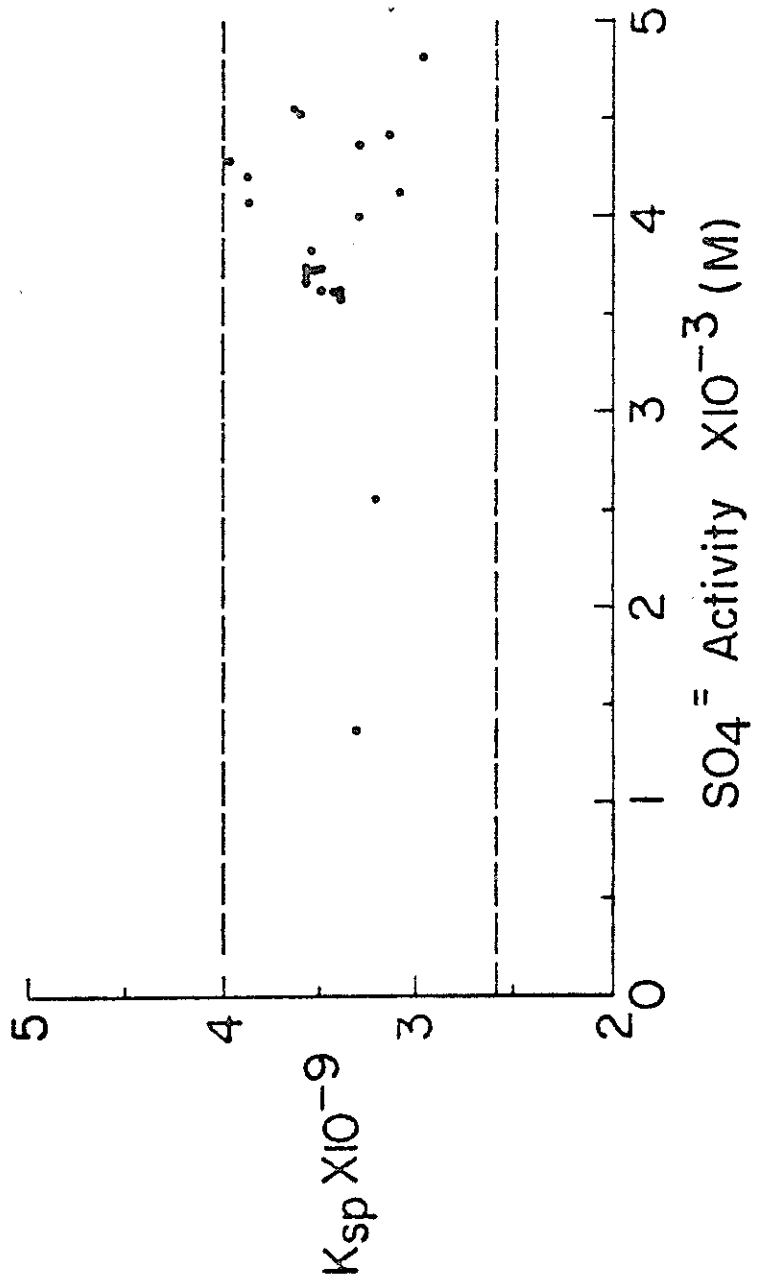


Figure 3. Solubility product of CaCO₃ as a function of SO₄²⁻ activity.

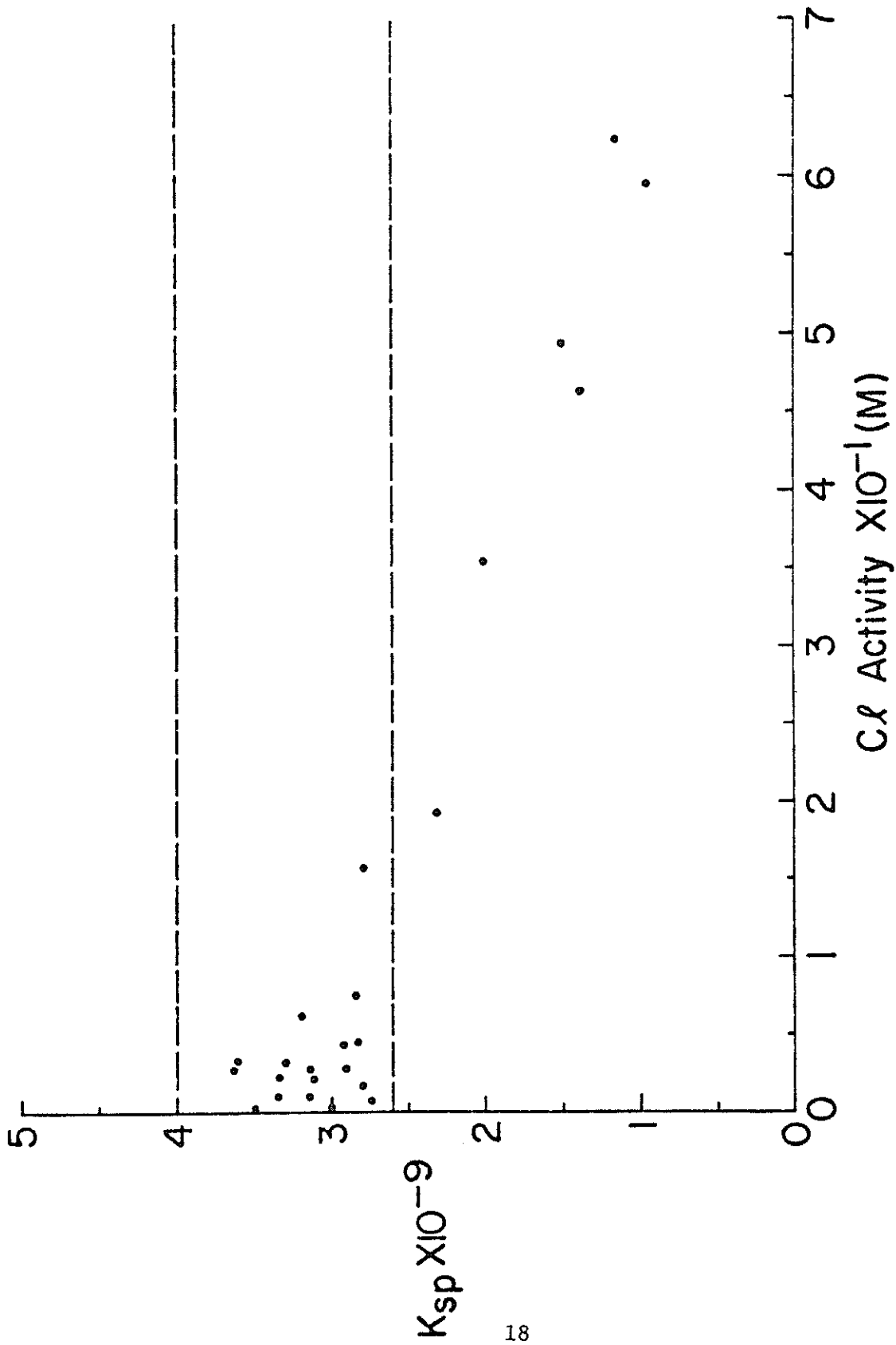


Figure 4. Solubility product of CaCO_3 as a function of Cl^- activity.