REPRINT

INCORPORATION OF COPRECIPITATION REACTIONS IN PREDICTIVE GEOCHEMICAL MODELS

John Mahoney
Hydrologic Consultants, Inc.
Lakewood, Colorado

Incorporation of coprecipitation reactions in predictive geochemical models

John J. Mahoney
Hydrologic Consultants, Inc. of Colorado, Lakewood, Colo., USA

ABSTRACT: The geochemical model used to predict the composition of water in the pit lake formed after cessation of mining at Echo Bay Mineral's Cove pit (Lander County, Nevada) included reactions to describe the coprecipitation of cadmium into calcite. Models that include coprecipitation reactions provide more realistic estimates of water compositions than do models that only use mineral precipitation and adsorption reactions. At Cove, coprecipitation reactions reduce the predicted concentration of cadmium to below regulatory limits.

Programs that are typically used to perform predictive calculations (e.g., *PHREEQC* and *MINTEQA2*) do not explicitly contain routines to assess coprecipitation, but such reactions can be easily included in the conceptual geochemical model. For the coprecipitation of cadmium into calcite, values for the distribution coefficient (D) in the range of 70 to 1500 were obtained from the literature. The values for D are large and indicate that coprecipitation is an important process in controlling concentrations of cadmium in systems that also contain calcite. Initial calculations used the Doerner and Hoskins equation. However, the large values for D resulted in final concentrations of cadmium that were unrealistically low. An alternative equation developed by Riehl was employed in the final estimates. For large values of D, the assumptions in the Doerner and Hoskins equation are not valid and the estimated dissolved concentrations of cadmium become extremely small. The estimates using the Riehl equation are reasonable, and agree with observed conditions.

INTRODUCTION

Geochemical models have typically employed the processes of precipitation and adsorption to describe the fate of metals in surface waters and ground waters. For the majority of geochemical models, coprecipitation reactions, also known as solid solution reactions, are not included in the calculations. Reasons for the omission of coprecipitation reactions include lack of understanding of the importance of such reactions by the modeler, lack of a computational method to evaluate the role of coprecipitation reactions, and a perceived lack of data. Answers for the first two issues identified above will be provided in this paper. This paper will also demonstrate that in many cases sufficient data are available to reliably model coprecipitation reactions.

IMPORTANCE OF COPRECIPITATION REACTIONS

In addition to precipitation and adsorption reactions, coprecipitation reactions provide a third method to evaluate the fate of inorganic compounds in geochemical models. Concentrations

of dissolved components calculated using coprecipitation reactions will usually be lower than the concentrations obtained from the simpler precipitation reactions that are available in programs such as *MINTEQA2* (Allison et al. 1991) and PHREEQC(Parkhurst 1996). Reasons for the significant reductions in concentration caused by coprecipitation reactions are explained in the following example.

The concentration of Sr^{2+} in seawater is believed to be the result of solid solution reactions with calcite (Stumm 1992). In the following example, conditional constants (p^cK_{sp}'s) are employed to describe the solubility of calcite and strontianite in seawater. The solubility product constants used in this example are not the same as the constant used in the fresher water conditions described later. The p^cK_{sp} for calcite (CaCO$_3$) is 6.1 and the p^cK_{sp} for strontianite (SrCO$_3$) is 6.8, the concentration of CO_3^{2-} in seawater is $10^{-3.6}$ M or 2.5×10^{-4} M. If strontianite controls the concentration of Sr^{2+} then the following equation applies:

$$[Sr^{2+}] = \frac{^cK_{sp_{SrCO_3}}}{[CO_3^{2-}]} \tag{1}$$

Using Equation 1 produces a calculated concentration equal to 6.3×10^{-4} M (or $10^{-3.2}$ M), but the actual measured concentration in seawater is 1.0×10^{-4} M, which is approximately 15 percent of the estimated concentration. Solid solution reactions account for the difference.
The distribution of Sr^{2+} between the aqueous phase (seawater) and a solid carbonate phase can be described according to Equation 2.

$$\frac{[Ca^{2+}]X_{SrCO_3}}{[Sr^{2+}]X_{CaCO_3}} = 0.14 \tag{2}$$

Where X represents the activity of the component in the solid phase, and the brackets represent the concentration (activity) in solution. The value of 0.14 is the distribution coefficient and is obtained from laboratory measurements. In subsequent discussions, the distribution coefficient will be identified with the letter D. The activity of Ca^{2+} in seawater is 3.2×10^{-3} M, using Equation 2 and the measured concentration of Sr^{2+}, the ratio X_{SrCO_3}/X_{CaCO_3} is equal to 0.004, and therefore X_{CaCO_3} is approximately 0.996.

The difference between the concentration of Sr^{2+}, estimated using the simple solubility calculation and the concentration measured in seawater is the result of a high activity coefficient for Sr^{2+} in the solid phase (f_{SrCO3}). Incorporation of solid state activity coefficients (X now becomes the mole fraction) and allowing that $X_{CaCO3}f_{CaCO3}$ equals 1.0, produces a final equation to describe the concentration of Sr^{2+} in seawater.

$$[Sr^{2+}] = \frac{X_{SrCO_3}f_{SrCO_3}{}^cK_{sp_{SrCO_3}}}{[CO_3^{2-}]} \tag{3}$$

In Equation 3, the solid state activity coefficient equals 38 and the product X_{SrCO3} times f_{SrCO3} equals 0.15, which equals the difference between the estimate from the simple solubility calculation and the estimate from the solid solution calculation. Therefore, the solubility of a minor component in a solid solution is greatly reduced when compared to the solubility of its end member phase. The effect can be quite significant. For example, calculations presented in Langmuir (1997) and Appelo and Postma (1993) indicate that a regular solution model for (Ca,Cd)CO$_3$ solid solution may reduce the concentration of Cd by a factor of 500 when compared to the solubility of otavite (CdCO$_3$).

INCORPORATION OF COPRECIPITATION REACTIONS

As part of an assessment of the chemical composition of the pit lake that will form at Echo Bay Minerals Cove pit (Lander County, Nevada) a detailed geochemical model of the pit lake was developed. The majority of the calculations were performed using the program *PHREEQC* (Parkhurst 1996). The model consisted of four steps.

In the first step of the model, the various ground waters that will enter the pit are mixed, and the resultant solution is identified as the baseline water. The geochemical model used hydrologic data to estimate the proportions of various ground waters that will enter the pit; compositions of the water were obtained based upon current analyses of samples from dewatering wells. The second step adds solids in the form of a hypothetical mineral to the baseline water. The solids represent material that will leach into the lake from oxidized wall rock. The composition of the hypothetical mineral phase was calculated based on results from humidity cell tests. The water produced after completion of the second step of modeling is called the initial water. In Step 3 a water identified as the interim water is produced. The initial water produced from Step 2 is allowed to equilibrate with mineral and gas phases. Selected minerals are allowed to precipitate; adsorption reactions are also included in the calculations during this step. After equilibration with the mineral and gas phases the composition is defined as the interim water. In the last step of the model, evaporation and other long term processes are considered and a final water composition is predicted. Because evaporation of the lake water will further concentrate the solution, mineral precipitation reactions were also included in Step 4.

The Cove pit is hosted in carbonate rich rocks and mixing of ground waters will occur as the pit fills. Equilibration with atmospheric pressures of carbon dioxide (degassing) will cause a slight increase in pH and concomitant precipitation of carbonate minerals. Leach tests (humidity cell tests) of the sulfide bearing rock indicated that cadmium will be added to the solution. Initial modeling to assess the fate of cadmium relied upon the precipitation of otavite $(CdCO_3)$ and adsorption of cadmium onto hydrous ferric oxides. Concentrations of cadmium predicted from the model calculations were elevated relative to concentrations measured in the ground waters and in waters collected from the bottom of the pit. Therefore, a detailed review of cadmium coprecipitation reactions was performed, and the subsequent geochemical model included the results from the coprecipitation calculations.

The coprecipitation reactions used simple equations that will be described in detail below. Basically, data from the various model steps were obtained from the *PHREEQC* output files and used to estimate the extent of coprecipitation. As described below, the calculations require an estimate of the amount of calcite that precipitates and the concentration of cadmium in the interim solution. The difference in concentrations of calcium between Steps 2 and 3 provide an indication of the amount calcite that precipitates. One additional parameter is required, that parameter is the value of the distribution coefficient for cadmium in calcite.

DISTRIBUTION COEFFICIENTS FOR CADMIUM IN CALCITE

The partitioning of cadmium into calcite is a well documented procedure, that numerous researchers have quantified (Lorens 1981; Davis et al. 1987; Fuller and Davis 1987; Konigsberger et al. 1991; Tesoriero and Pankow 1996; Comans and Middelburg 1987; and Zachara et al. 1991). Experimental evidence indicates that partitioning of cadmium into calcite is a significant process that will control the fate of cadmium in solutions that are oversaturated and actively precipitating calcite.

In general, partitioning reactions can be described by the following equation

$$\left[\frac{Me}{Ca}\right]_{CaCO_3} = D \left[\frac{Me}{Ca}\right]_{Solution} \tag{4}$$

where Me = concentration of trace metal in calcite solid (*CaCO₃*) or in aqueous solution (Solution); *Ca* = concentration of calcium in calcite or in solution; and D = distribution coefficient for particular metal. Equation 4 is a more general example of Equation 2.

Distribution coefficients (D) for cadmium partitioning into calcite have been measured by numerous researchers (Table 1). Values typically are much greater than 1.0, indicating a preference for cadmium to enter the solid rather than remaining in solution. The reasons that cadmium has such a strong affinity to coprecipitate with calcite are. because the electronic configuration of cadmium and calcite are similar, and the ionic radii are nearly identical; calcium (Ca^{2+}) has a radius of 0.99 angstroms and cadmium (Cd^{2+}) has a radius of 0.97 angstroms. The similarity of their ionic radii is also reflected in the similarity of their crystal structures. Both the cadmium carbonate mineral, otavite, and calcite are rhombohedral.

There is also some evidence that otavite (log K_{sp} equal to -12.1) may form an ideal solid solution with calcite (log K_{sp} equal to -8.48) (Konigsberger et al. 1991). For an ideal solid solution, the distribution coefficient equals the ratio of the two solubility products. Assuming that the solid solution is ideal, and using the solubility products defined above, the calculated value for the distribution coefficient would be 4,170 (equivalent to $10^{-8.48-(-12.1)}$).

Table 1. Distribution coefficients for cadmium in calcite

Distribution coefficient (D)	Reference
71	Lorens (1981)
1240 (range of 1000 to 4500 suggested)	Tesoriero and Pankow (1996)
1510 ±300	Davis et al. (1987)
4170	Konigsberger et al. (1991)

Distribution coefficients that are measured in laboratory experiments are commonly a function of the rate of mineral precipitation. Slow rates of precipitation allow equilibrium processes to dominate and result in values of D close to the actual equilibrium values. Lorens (1981) reported a value of 71 for the distribution coefficient of cadmium in calcite. Tesoriero and Pankow measured a value of 1,240, but in consideration of the possibility that the system may be ideal, - stated by Konigsberger et al. - they indicated that the value could range between 1,000 and 4,500. Davis et al. (1987) estimated that the D value was approximately 1,510 ±300 (equivalent to ±20 percent). Their value is close to the value reported by Tesoriero and Pankow.

In reviewing the previously published values for D, Tesoriero and Pankow suggest that the precipitation rates used by Lorens to measure the distribution coefficient may have been too fast. Compared to the work by Tesoriero and Pankow the rates of precipitation were approximately 100 times faster in the work performed by Lorens. Tesoriero and Pankow also state that the method used to calculate the distribution coefficient may also be responsible for the low value reported by Lorens. Lorens used a method to calculate distribution coefficients based upon the Doerner and Hoskins (1925) approach. The Doerner and Hoskins equation allows for depletion of the cadmium in the solution (heterogenous system) and the method could lead to a large degree of analytical uncertainty. Tesoriero and Pankow used a method that replaced the cadmium that was consumed by the precipitating solid.

COMPARISON OF CALCULATIONAL METHODS

The final concentration of cadmium in the solution was estimated using two different approaches. The method that was initially used was the Doerner and Hoskins method, the alternative method assumed a more homogenous system.

The Doerner and Hoskins method was initially selected for three reasons;

1. Textbooks on aquatic chemistry (Stumm and Morgan 1981) identify the Doerner and Hoskins equation as a standard method to evaluate coprecipitation; Sturnm and Morgan used the Doerner and Hoskins method to describe manganese coprecipitation with calcite.

2. Lorens used the Doerner and Hoskins method to calculate D for his measurements of cadmium coprecipitation with calcite.

3. The method was included, along with an alternative method that was finally selected, in the review by McIntire (1963).

The availability of alternative methods in one reference reduces possible biases in the selection of a method to estimate the concentrations of cadmium in water. The alternative method was developed by Riehl et al. (1960). The alternative approach was more similar to the experimental methods employed by Tesoriero and Pankow. It is applicable to more homogenous systems where recrystallization of calcite is apt to occur. The homogenous system method was also described by McIntire (1963) in his review of trace metal behavior in geologic systems.

For the reasons outlined above, the calculations were originally performed using the Doerner and Hoskins equation,

$$\log \left[\frac{Me_i}{Me_f} \right] = \lambda \log \left[\frac{Ca_i}{Ca_f} \right] \tag{5}$$

where the i and f subscripts indicate initial and final quantities of metal (Me), cadmium in this case (Ca), calcium in solution, and λ represents D at the specified rate of precipitation. The initial concentration of cadmium, and the initial and final concentrations of calcium were obtained from PHREEQC simulations. The value of λ was replaced by the various values of D reported above. Using the Doerner and Hoskins equation produced extremely low values for the final cadmium concentration. The values were not considered to be realistic so an alternative equation was used. The extremely low concentrations were an artifact of the calculational method used in the Doerner and Hoskins equation. Under the conditions expected to exist in the pit lake, subsequent calculations demonstrated that the Doerner and Hoskins equation and the equation presented by Riehl et al. (1960) (described below) diverge when the values of D are greater than approximately 2.

The Doerner and Hoskins method assumes that the precipitation reactions produce a solid that is composed of a series of layers, like the layers of an onion. The composition of each layer represents a composition that was in equilibrium with the solution when that layer precipitated. However, compositions of the crystal and the solution are constantly changing as precipitation proceeds. Because of the large values of D, for the system cadmium and calcite, the first layer to precipitate (interior of the crystal) will have the greatest concentration of cadmium. As calcite continues to precipitate, the amount of cadmium relative to the amount of calcium in the solution will decrease. Therefore, each subsequent layer of the calcite crystal will contain less cadmium than the preceding layer. For the D values described above, the Doerner and Hoskins equation produces extremely low concentrations of cadmium (dissolved) when the solution has reached saturation with calcite. Even with a D of 10, which is smaller than any of the measured values, the estimated concentration of dissolved cadmium at the end of Step 3 of the geochemical model was 9.6 x 10^{-5} mg/L. Using the larger values of D, which are reported in the literature, produced concentrations many orders of magnitude lower.

The very low concentrations of dissolved cadmium estimated using the Doerner and Hoskins method were not considered to be reasonable. The concentrations of cadmium in the interior portions of the crystals are not in equilibrium with the composition of the solution that is present as precipitation reactions are completed. After a review of the calculations, the assumptions inherent in the Doerner and Hoskins approach were deemed not applicable to the Cove pit lake system and an alternative method, which would produce a more realistic concentration for cadmium in the pit lake, was selected.

The alternative calculation method assumes a more homogeneous system than the logarithmic method of Doerner and Hoskins. Calcite that precipitated early in the reaction sequence can dissolve and be reprecipitated in the later stages of the reaction. Therefore, the cadmium in the calcite, which is partitioned to the solid solution phase early in the precipitation process, will also be available during the later stages of precipitation reactions. McIntire (1963) provides an equation that describes the behavior of a trace metal in a homogeneous system. The equation, which was originally derived by Riehl et al. (1960), is

$$C_{Tr}^0 = \frac{C_{Tr}^i C_{Cr}^0}{\lambda(C_{Cr}^i - C_{Cr}^0) + C_{Cr}^i} \tag{6}$$

where C_{Tr}^o = concentration of trace component in boundary layer immediately adjacent to surface of crystal (cadmium); C_{Tr}^i = initial concentration of trace component in solution; C_{Cr}^i = initial concentrations of carrier (calcium) in solution, and C_{Cr}^o = concentration of carrier in boundary layer.

McIntire also defines the degree of supersaturation (S) as

$$S = \frac{C_{Cr}^i}{C_{Cr}^0} \tag{7}$$

where C_{Cr}^i is the concentration of the carrier in the bulk solution.

When the solution has completed precipitating calcite, S equals 1.0 and the concentrations in the bulk solution and at the boundary layer are equal. Therefore, Equation 6 can be used
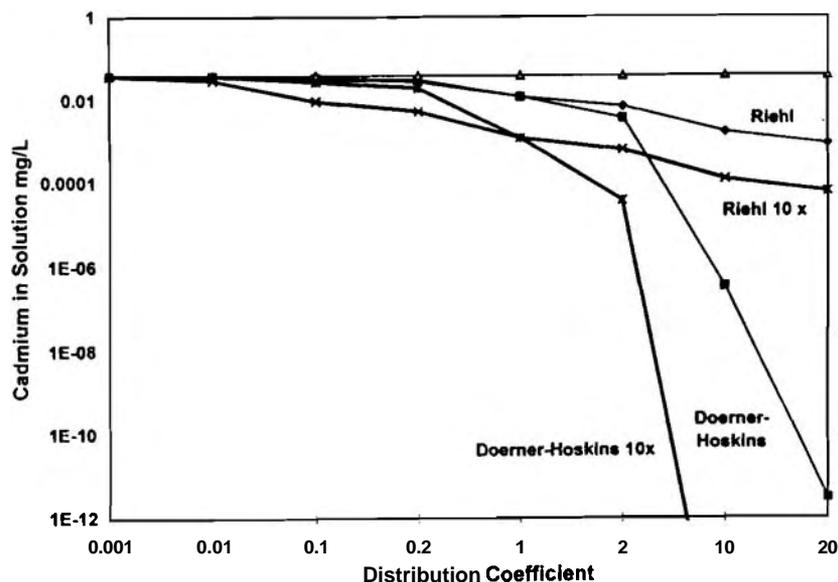

Figure 1. Comparison of the Doerner and Hoskins equation, and the equation developed by Riehl et al.

to estimate the concentrations of the tracer and carrier in the solution.

Figure 1 presents a comparison of the behavior of the two equations for a variety of distribution coefficients. The distribution coefficients used in the figure are all too low to represent the actual distribution coefficient for cadmium. As described earlier, the smallest distribution coefficient for cadmium coprecipitation with calcite is approximately 70. Using the Doerner and Hoskins equation for such a high value for D would result in a calculated concentration of dissolved cadmium that is less than $1x10^{-100}$ mg/L. The value would reduce the resolution on the y axis to a level that would not permit comparison of the two equations. One pair of lines on Figure 1 was produced using the Doerner and Hoskins equation and the other pair of lines was produced using the equation presented by Riehl et al. Also included on the figure is a horizontal line which is used for reference. In all cases the initial concentration of cadmium equals $3.49x10^{-7}$ m or 0.039 mg/L. The differences between the points on each pair of lines are based upon the amount of calcite that is assumed to precipitate. For each pair of lines, the upper line represents an initial concentration of calcium equal to $1.83x10^{-3}$ m and a final concentration of calcium equal to $5.73x10^{-4}$ m. The lower line for each pair (designated with the 10x symbol) uses an initial calcium concentration of $1.83x10^{2}$ m. The difference in calcium concentrations represents the amount of calcite that has precipitated.

Several features inherent to the equations can be seen on the figure. At extremely small values of D, the calculated concentration is equivalent for both equations. As the distribution coefficient increases the concentration of cadmium in solution decreases. The Riehl equation demonstrates a greater initial sensitivity to the amount of calcite that precipitates, and this sensitivity is further reflected in the essentially constant ratio between the two sets of conditions as the distribution coefficients increase. The difference in concentration is equal to a factor of ten. The calculations that assume that more calcite is available for precipitation result in a smaller mole fraction of cadmium in the solid; hence, a lower final concentration of cadmium in solution.

Concentrations calculated using the Doerner and Hoskins equation are similar to the concentrations calculated using the Riehl equation for small amounts of calcite and for small distribution coefficients. At a distribution coefficient equal to 1, the concentrations are identical for both equations assuming that the mass of calcite that precipitates is equal. Problems appear with the ability of the Doerner and Hoskins equation to calculate concentration when the distribution coefficient is slightly greater than 1.0.

Table 2 provides a comparison of cadmium concentrations for a variety of scenarios. The data were obtained from a preliminary model of the Cove pit lake. Scenarios include a simpler model without coprecipitation reactions, and models that include coprecipitation reactions. Most model comparisons were prepared during the fall of 1996, while the final calculations were performed in early 1997 and used the most current hydrologic data. Therefore, the values listed in Table 2 do not reflect the estimated concentrations for the Cove pit study. (The parameters used to generate Figure 1 are a better reflection of the conditions used in the Cove pit lake model.) Table 2 clearly shows that coprecipitation reactions lower trace metal concentrations to a greater extent than simple precipitation (otavite) reaction or a combination of precipitation reactions and subsequent adsorption reactions.

The calculations used the concentrations of calcium and cadmium estimated from PHREEQC. For this particular example the initial concentration of cadmium was 0.072 mg/L. The coprecipitation calculations assumed that the initial calcium concentration was $1.87x10^{-3}$ m and the final calcium concentration was $9.8x10^{-4}$ m. The first estimates used a value of 1.0 for D. The value of 1.0 was used to provide a check between the two calculational methods; at a D of 1.0 both the Doerner and Hoskins, and Riehl equations provide the same final concentration.

Table 2. Comparison of model calculations

Model	Distribution coefficient	Concentration of Cd (mg/L)	Concentration of Cd with adsorption (mg/L)
Initial concentration (no reaction)	NA	0.072	--
Otavite precipitation	NA	0.033	--
Otavite/adsorption	NA	0.032	--
Adsorption only	NA	0.059	--
Riehl et al.	1.0	0.038	0.030
Riehl et al.	10	0.007	0.006
Riehl et al.	70	0.001	0.0009
Riehl et al.	1240	0.00006	0.00005
Doerner and Hoskins	1.0	0.038	0.030
Doerner and Hoskins	10	0.0001	0.00009
Doerner and Hoskins	70	(2×10^{-21})	(1×10^{-22})

The second estimate used a value of 10 for D. The literature does not report a value of D this low, but because the value of D can decrease as a function of precipitation rate, the value of 10 was selected as a lower limit. Using the value of 10, the concentration after coprecipitation with calcite was estimated to be 0.007 mg/L. Using a D of 70 as reported in Lorens reduced the concentration to 0.001 mg/L.

The table also demonstrates the problems inherent with the Doerner and Hoskins equation for large values of D. Values decrease dramatically and reach unrealistically low concentrations when a D of 70 is used. The Riehl equation, even with a D of 1240, still provides concentrations that, although low, appear to be more reasonable than estimates produced with the Doerner and Hoskins equation.

The concentrations in column four of Table 2 use a lower initial concentration of cadmium. The results in column four reflect the concentration of cadmium in the solution after adsorption reactions with hydrous ferric oxide (HFO) have removed some of the cadmium. Therefore the initial concentration of 0.059 mg/L was used as the starting concentration for the subsequent coprecipitation calculation. The differences in concentrations between columns three and four are slight. Because the calcite precipitation reactions are inherently slower than the adsorption reactions on the HFO surface it is reasonable to assume that adsorption reactions will reduce the concentration of cadmium in solution before any significant amount of calcite *can* precipitate.

CONCLUSIONS

Coprecipitation reactions provide an important control on trace metals in many geochemical systems. Output from the commonly used programs PHREEQC and *MINTEQA2 can* be easily incorporated into coprecipitation calculations. At least two different equations can be employed to calculate the extent of coprecipitation. The equation presented by Riehl et al. appears to cover a broader range of conditions than the equation presented by Doerner and Hoskins.

Failure to consider coprecipitation reactions can result in unrealistically high predicted concentrations. If the concentrations predicted from a model that does not include

coprecipitation reactions are near or exceed a regulatory level, such concentrations may result in unnecessary regulatory scrutiny.

REFERENCES

Allison, J.D., D.S. Brown & K.J. Novo-Gradac 1991. *MINTEQA2/PRODEFA2,* a geochemical assessment model for environmental systems, Version 3.0 User's Manual. U.S. Environmental Protection Agency, EPA/600/3-91/021, 106 p.

Appelo, C.A.J., and D. Postma 1993. *Geochemistry, groundwater and pollution:* Rotterdam: A.A. Balkema.

Comans, R.N.J. & J.J. Middelburg 1987. Sorption of trace metals on calcite - applicability of the surface precipitation model. *Geochimica et Cosmochimica Acta.* 51:2587-2591.

Davis, J.A., C.C. Fuller & A.D. Cook 1987. A model for trace metal sorption processes at the calcite surface - adsorption of Cd^{2+} and subsequent solid solution formation. *Geochimica et Cosmochimica Acta.* 51:1477-1490.

Doerner, H.A. & W.M. Hoskins 1925. Co-precipitation of radium and barium sulfates. *Journal Amer. Chemical Society* 47:662-675.

Fuller, C.C. & J.A. Davis 1987, Processes and kinetics of Cd^{2+} sorption by a calcareous aquifer sand. *Geochimica et Cosmochimica Acta*. 51:1491-1502.

Konigsberger, E., R. Hausner, & H. Gamsjager 1991. Solid-solute phase equilibria in aqueous solution, V - the system $CdCO_3\text{-}CaCO_3\text{-}CO_2\text{-}H_2O$. *Geochimica et Cosmochimica Acta.* 55:3505-3514.

Langmuir, D. 1997. *Aqueous environmental geochemistry.* Upper Saddle River: Prentice Hall.

Lorens, R.B. 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochimica et Cosmochimica Acta.* 45:553-561.

McIntire, W.L. 1963. Trace element partition coefficients - a review of theory and applications to geology. *Geochimica et Cosmochimica Acta.* 27:1209-1264.

Parkhurst, D.L., 1995, *PHREEQC* - A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. *U.S. Geological Survey Water-Resources Investigations 95-4227.*

Riehl, N., R. Sigmann & P. Hidalgo 1960. Explanation of the distribution of very small amounts of foreign substances between a growing crystal and the solution (title translated from original German). *Z. Phys. Chem.* 25:1359.

Sturnm, W. 1992. *Chemistry of the solid-water interface.* New York:Wiley Interscience.

Sturnm, W. & J.J. Morgan 1981. *Aquatic chemistry (2nd edition).* New York:Wiley Interscience.

Tesoriero, A.J. & J.F. Pankow 1996. Solid solution partitioning of Sr^{2+}, $Ba2+$, and Cd^{2+} to calcite. *Geochimica et Cosmochimica Acta.* 60:1053-1063.