## Solid Solution/Aqueous Solution Partitioning of Divalent Cations to Calcite: Implications for the Mobility of Metals in Natural Waters

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#### ABSTRACT

Solid Solution/Aqueous Solution Partitioning of Divalent Cations to Calcite: Implications for the Mobility of Metals in Natural Waters

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Solid solution precipitates can significantly decrease the aqueous concentrations of metal contaminants in ground and surface waters. However, solid solution precipitates are often neglected when predicting metal transport because little is known about the behavior of solid solution/aqueous solution systems. Experiments were conducted over a range of precipitation rates to determine the equilibrium and nonequilibrium solid solution partitioning behavior for the substitution of  $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ , and  $Zn^{2+}$  for  $Ca^{2+}$  in calcite.

Metal partitioning between the aqueous and solid solution phases is often described by the distribution coefficient,  $D_{Me}$ , which is defined for metal ion Me<sup>2+</sup> partitioning into calcite as

$$D_{Me} = \frac{X_{MeCO_{3}(e)} / [Me^{2+}]}{X_{CaCO_{3}(e)} / [Ca^{2+}]}$$

At high precipitation rates, the partitioning of Ba<sup>2+</sup>, Cd<sup>2+</sup>, and Sr<sup>2+</sup> into calcite was found to be strongly dependent on precipitation rate. At low precipitation rates,  $D_{Sr}$ and to lesser degrees  $D_{Ba}$  and  $D_{Cd}$  did not vary appreciably as a function of precipitation rate. From these low precipitation rate experiments, the equilibrium values for  $D_{Sr}$ ,  $D_{Ba}$ , and  $D_{Cd}$  for dilute solid solutions have been estimated to be 0.021 ±0.003, 0.012 ±0.005, and 1240 ±240, respectively.

Aqueous solution effects on the partitioning of  $Sr^{2+}$  to  $Ca_{1-x}Sr_xCO_3$  solid solutions were evaluated by comparing the  $D_{Sr}$  values from this investigation with other studies which used different solution compositions. It was observed that for the same precipitation rate,  $D_{Sr}$  values for experiments based on Mg<sup>2+</sup>-containing solutions in the laboratory and Lake Constance water in the field were approximately an order of magnitude higher than experiments using Mg<sup>2+</sup>-free solutions. It was postulated that the large increase in  $D_{Sr}$  values in these solutions when compared to  $D_{Sr}$  values from Mg-free experiments was caused by the high saturation states resulting from magnesium and phosphorus inhibition of calcite precipitation. When combined into a single data set,  $D_{Sr}$  values for all studies were much more strongly correlated with saturation state than precipitation rate. The dependence of  $D_{Sr}$  values on saturation state may be due to its effect on step migration rates during precipitation. Step migration rates increase as saturation states increase, with a concomitant decrease in selectivity of one cation over another during the precipitation process.

## CHAPTER 1 INTRODUCTION

#### 1.1 Background

A fundamental understanding of the processes which control the partitioning of trace metals between the solid and aqueous phases in natural waters is necessary in order to accurately predict the mobility of toxic metals at waste disposal sites and effluent discharge points. Most conceptual and computational contaminant transport models consider only adsorption and pure phase precipitation as mechanisms for retarding contaminant migration. At low and trace levels of metals in natural waters, the prediction of metal partitioning between the solid and aqueous phases has relied primarily on surface adsorption models. At higher levels of metals in natural waters, precipitation of trace metals is expected only when the concentration of the metal ion in the aqueous phase is above the level necessary for saturation with respect to a pure solid phase. For example,  $Cd^{2+}$  would not be expected to precipitate as a carbonate solid phase until the solution was slightly supersaturated with respect to pure  $CdCO_{3(s)}$ . Thus when precipitation as  $CdCO_{3(s)}$  is ruled out, it has often been assumed that low levels of  $Cd^{2+}$  can only partition to the solid phase by adsorption reactions.

There is increasing evidence that the above approach is not correct. It has long been established that ions can partition into common mineral phases during deposition, resulting in mineral phases with chemical compositions which are seldom, if ever, pure (Garrels and Christ, 1965). The high temperatures found in many geologic environments favor this partitioning process. Recent evidence suggests that this process may also be important at near surface temperatures (Davis *et al.*, 1987; Fuller

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and Davis, 1987; Stipp *et al.*, 1992). The partitioning of ions into mineral solids results in the formation of a solid solution. A solid solution is a single crystalline phase where one ion has substituted for another in a crystal lattice. For example, a  $CdCO_{3(s)}/CaCO_{3(s)}$  solid solution is formed when  $Cd^{2+}$  ions substitute for some of the  $Ca^{2+}$  ions in the crystal lattice (Figure 1.1). The solid solution phase formed by this substitution is represented by  $Ca_{1-x}Cd_xCO_{3(s)}$ , where x represents the fraction of "Ca sites" which are occupied by cadmium.

The partitioning of ions to solid solution phases can have a significant impact on their mobilities in natural waters. Contaminant transport predictions which do not include the solid solution partitioning process risk overestimating the mobility of contaminants. Continuing with the above example, the mobility of  $Cd^{2+}$  would be overestimated because precipitation of  $Cd^{2+}$  in a  $Ca_{1-x}Cd_xCO_{3(s)}$  solid solution phase is possible at aqueous concentrations of  $Cd^{2+}$  below saturation with respect to pure  $CdCO_{3(s)}$ . The effect of solid solution formation on the aqueous solubility of metals will be discussed in more detail in Section 2.2.4.

#### **1.2 Calcite-Metal Interactions in Natural Waters**

Calcite was selected as the mineral phase (or adsorbent) in this study because of its prevalence in both ground water and surface water environments. The partitioning of metals to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions has implications for metal mobility in a variety of natural water systems.

Ground water in nearly all sedimentary terrains is in contact with carbonate minerals during at least a part of its flow path (Freeze and Cherry, 1979). Calcite is the most abundant carbonate mineral. Calcite dissolution and precipitation kinetics is fast relative to flow rates and paths such that ground waters are often saturated with respect to calcite. Therefore, the incorporation of trace metals into calcite via adsorption and subsequent solid solution formation may play a major role in retarding the migration of metal contaminants in ground water.

Calcite precipitation and dissolution is of major importance in controlling the pH and aqueous composition of many lake waters. The lowering of dissolved  $CO_2$  levels

# **Calcite Lattice**



**Figure 1.1** Schematic representation of solid solution formation. A  $Ca_{1-x}Cd_xCO_3$  solid solution is formed by the substitution of Cd for Ca in the calcite lattice.

by algal consumption and/or increases in temperature of lake surface waters can cause these waters to become increasingly oversaturated with respect to calcite. This can cause calcite to precipitate as a fine suspension of particles, often referred to as a "whiting event." Metal ions may be removed from solution by the precipitation of a  $Ca_{1-x}Me_xCO_{3(s)}$  solid solution, but may redissolve when calcite particles sediment into deeper lake waters which are often undersaturated with respect to calcite. Thus, the solid solution partitioning of a metal ion to calcite may have major implications for metal cycling in lakes.

Finally, since virtually all surface seawater is supersaturated with respect to calcite (Morse and Mackenzie, 1990), the formation of  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions has implications for marine systems. For example, it has been suggested that a  $Ca_{1-x}Sr_xCO_{3(s)}$  solid solution may control the aqueous concentrations of  $Sr^{2+}$  in the oceans (Schindler, 1967). In addition, the Sr/Ca ratio of calcites has been used to provide clues as to the  $Sr^{2+}$  concentration of paleo-ocean waters and the amount of recrystallization that a calcite sample has undergone.

#### **1.3 Objectives**

As noted above, a better understanding of metal partitioning to  $Ca_{1-x}Me_xCO_{3(s)}$ solid solutions can greatly improve our knowledge of the behavior of divalent cations in natural waters. However, assessing the solid solution partitioning that is occurring in a given natural system is not an easy undertaking, as such partitioning has been found to be dependent on both solution composition and precipitation rate (Morse and Bender, 1990). Therefore, since calcite precipitation and dissolution reactions occur over a wide range of rates and solution compositions, a single partitioning coefficient which describes the solid solution partitioning behavior of a metal to calcite cannot be used.

It is the objective of this work to better define how solid solution partitioning of metals to calcite depends on precipitation rate and solution composition, with a particular emphasis on determining solid solution partitioning behavior under equilibrium conditions. However, since calcite precipitation reactions often occur in nature at relatively fast rates, non-equilibrium partitioning is also of interest. From the above considerations, the goals of this work are to:

 $\cdot$  determine the equilibrium partitioning of Cd^{2+}, Sr^{2+}, Ba^{2+}, and Zn^{2+} to

Ca<sub>1-x</sub>Me<sub>x</sub>CO<sub>3(s)</sub> solid solutions;

 $\cdot$  establish the non-equilibrium partitioning behavior of  $Sr^{2+}$  to  $Ca_{1-x}Sr_{x}CO_{3(s)}$  solid solutions;

 $\cdot$  study the mechanisms responsible for the non-equilibrium partitioning of metals to Ca<sub>1-x</sub>Me<sub>x</sub>CO<sub>3(s)</sub> solid solutions;

 $\cdot$  apply the non-equilibrium partitioning results to existing data on the partitioning of Sr<sup>2+</sup> to calcite during lake whiting events; and

 $\cdot$  evaluate the effects of the formation of CaMe<sub>x</sub>CO<sub>3(s)</sub> solid solutions on the retardation of divalent metal ions in ground water systems.

## CHAPTER 2 PARTITIONING TO SOLID SOLUTION PHASES: THEORY AND REPRESENTATION

#### 2.1 Introduction

As noted in Chapter 1, the association of an element with a mineral may occur by several processes: surface adsorption, solid solution formation and pure phase precipitation. The chemical composition of a mineral almost always deviates from that of the pure mineral phase, indicating that adsorption or solid solution formation has occurred. (Contamination by other mineral phases is another possibility that won't be considered here.) Surface adsorption can be thought of as a two dimensional process, whereby "foreign" ions are held by the attraction of surface atoms. Solid solutions are single crystalline phases with a composition that can vary from sample to sample, and may not be homogenous within any given sample. Solid solution formation occurs primarily by the substitution of one ion for another in the crystal structure (Figure 1.1). The following discussion is primarily directed at the theory and representation for solid solutions formed under equilibrium and non-equilibrium conditions and the implications solid solution formation has on the solubility of trace elements in solution. Lastly, the experimental determination of metal ion partitioning to solid solutions is discussed.

#### 2.2 Thermodynamic Equilibrium

The partitioning of a generic metal ion,  $Me^{2+}$ , to a  $Ca_{1-x}Me_xCO_{3(s)}$  solid solution can be thought of as being formed by the mixing of the two solids,  $CaCO_{3(s)}$  and

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MeCO<sub>3(s)</sub>. The mixing of two solids always will tend to occur when the free energy of mixing,  $\Delta G_{mxg}$ , is less than zero, where

$$\Delta G_{mxg} = \Delta H_{mxg} - T \Delta S_{mxg} . \qquad (2-1)$$

The enthalpy of mixing,  $\Delta H_{mxg}$ , embodies the chemical interactions which can either favor ( $\Delta H_{mxg} < 0$ ) or oppose mixing ( $\Delta H_{mxg} > 0$ ). The entropy of mixing,  $\Delta S_{mxg}$ , is a measure of the change in the degree of disorder which occurs on mixing. Since mixtures are always less ordered than pure solids,  $\Delta S_{mxg}$  is always greater than zero and thus favors mixing. The molar free energy of mixing,  $\Delta \bar{G}_{mxg}$ , for the mixing of MeCO<sub>3(s)</sub> in calcite is (Pankow, 1991):

$$\Delta \overline{G}_{mxg} = X_{MeCO_{3(s)}} RT \ln a_{MeCO_{3(s)}} + X_{CaCO_{3(s)}} RT \ln a_{CaCO_{3(s)}}, \qquad (2-2)$$

where:  $X_{MeCO_{3(s)}}$  is the mole fraction of MeCO<sub>3(s)</sub>;  $X_{CaCO_{3(s)}}$  is the mole fraction of CaCO<sub>3(s)</sub>;  $a_{CaCO_{3(s)}}$  is the solid phase activity of CaCO<sub>3(s)</sub>; and  $a_{MeCO_{3(s)}}$  is the solid phase activity of MeCO<sub>3(s)</sub>.

The solid phase activities of  $MeCO_{3(s)}$  and  $CaCO_{3(s)}$  are defined as

$$a_{MeCO_{3(i)}} = X_{MeCO_{3(i)}} \zeta_{MeCO_{3(i)}}, \qquad (2-3)$$

$$a_{CaCO_{3(n)}} = X_{CaCO_{3(n)}} \zeta_{CaCO_{3(n)}}, \qquad (2-4)$$

where:  $\zeta_{MeCO_{3(s)}}$  is the solid phase activity coefficient of MeCO<sub>3(s)</sub>; and

 $\zeta_{CaCO_{3(a)}}$  is the solid phase activity coefficient of CaCO<sub>3(s)</sub>.

Substitution of Equations 2-3 and 2-4 into Equation 2-2 yields the following expression for the molar free energy of mixing:

$$\Delta \overline{G}_{mxg} = X_{MeCO_{3(n)}} RTln X_{MeCO_{3(n)}} + X_{MeCO_{3(n)}} RTln \zeta_{MeCO_{3(n)}} + X_{CaCO_{3(n)}} RTln X_{CaCO_{3(n)}} + X_{CaCO_{3(n)}} RTln \zeta_{CaCO_{3(n)}} .$$

$$(2-5)$$

The molar enthalpic contribution to mixing is embodied in the terms containing the solid phase activity coefficients,  $\zeta$ . The entropic contribution to the molar free energy of mixing is represented by the remaining terms. The molar enthalpic and entropic expressions are as follows:

$$\Delta \overline{H}_{mxg} = X_{MeCO_{3(s)}} RTln \zeta_{MeCO_{3(s)}} + X_{CaCO_{3(s)}} RTln \zeta_{CaCO_{3(s)}}, \qquad (2-6)$$

$$-T\Delta \overline{S}_{mxg} = X_{MeCO_{3(s)}} RTln X_{MeCO_{3(s)}} + X_{CaCO_{3(s)}} RTln X_{CaCO_{3(s)}} .$$
(2-7)

The entropic contribution to the molar free energy of mixing is easily calculated as it requires only a knowledge of  $X_{MeCO_{yn}}$  and  $X_{CaCO_{yn}}$  for the solid solution phase considered. The enthalpic contribution is more difficult to evaluate as it requires a knowledge of the  $\zeta$  values. The  $\zeta$  values are a measure of the affinity of the Me<sup>2+</sup> and  $Ca^{2+}$  for the lattice cation position relative to that in the  $MeCO_{3(s)}$  and  $CaCO_{3(s)}$  lattices, respectively. As a crystal grows from an aqueous solution, competition between ions at the crystal surface occurs for positions in the crystal lattice. If Me<sup>2+</sup> has a greater affinity for the MeCO<sub>3(s)</sub> lattice than the CaCO<sub>3(s)</sub>, then  $\zeta_{MeCO_{va}}$  will be greater than unity (more often the case). If  $Me^{2+}$  prefers the CaCO<sub>3(s)</sub> lattice to the MeCO<sub>3(s)</sub> then the  $\zeta_{MeCO_{10}}$  will be less than unity. Similar statements can be made for Ca<sup>2+</sup> partitioning to  $MeCO_{3(s)}$  and  $CaCO_{3(s)}$ . In general, ions which most closely resemble the lattice ions of the crystal will have solid phase activity coefficient values close to 1.0, and will be easily incorporated. The magnitude of chemical interactions, and therefore  $\zeta_{MeCO...}$ , will depend on the similarity of the lattice position of Me<sup>2+</sup> in  $MeCO_{3(s)}$  to that of  $Ca^{2+}$  in  $CaCO_{3(s)}$ . The properties of the  $Me^{2+}$  and  $Ca^{2+}$  ions which are of importance in determining the similarity of these lattice positions are: the ionic

radii; ionic charge; electronegativity; and the crystal class of the carbonate formed. Table 2.1 provides a list of these properties for the metal ions of interest in this study.

#### 2.2.1 Ideal Mixing

Ideal mixing occurs when the crystal being formed can accommodate both ions equally well. In this case, both  $\zeta$  values are equal to unity. Since under ideal conditions it is assumed there are no chemical interactions as the result of ion substitution,  $\Delta \bar{G}_{mxg}$  then becomes equal to only the entropic terms so that

$$\Delta \overline{G}_{mxg} = \Delta \overline{G}_{mxg,ideal} = X_{MeCO_{3(s)}} RTln X_{MeCO_{3(s)}} + X_{CaCO_{3(s)}} RTln X_{CaCO_{3(s)}} .$$
(2-8)

Strictly speaking, solid solutions are never ideal. However, similar ionic radii, charges, and electronegativities for the two ions improve the likelihood that the assumption of ideality closely approximates actual conditions.

#### 2.2.3 Non-Ideal Mixing

In most cases, ion substitution creates significant chemical interactions and may not be accurately approximated by ideal conditions. Therefore, it is necessary to consider both the entropic and enthalpic contributions to  $\Delta \bar{G}_{mxg}$ , *i.e.* 

$$\Delta \overline{G}_{mxg} = \Delta \overline{G}_{mxg,ideal} + X_{MeCO_{3(a)}} RTln \zeta_{MeCO_{3(a)}} + X_{CaCO_{3(a)}} RTln \zeta_{CaCO_{3(a)}} .$$
 (2-9)

The solid phase activity coefficients in Equation 2-9 above are in general dependent on  $X_{MeCO_{340}}$ . As more Me<sup>2+</sup> is incorporated into the calcite lattice, the solid becomes more like MeCO<sub>3(s)</sub>. Thus, it is expected that as  $X_{MeCO_{340}}$  increases, the non-ideal chemical interactions which occur as the result of Me<sup>2+</sup> substitution decrease. Accordingly, the  $\zeta_{MeCO_{340}}$  will approach unity as  $X_{MeCO_{340}}$  approaches unity. One possible set of equations to describe the dependence of the solid phase activity coefficients on the mole fraction are Guggenheim's (1937) expansion,

| Cation           | Electronegativity <sup>a</sup> | Ionic Radius <sup>b</sup> ( <b>Å</b> ) | Mineral      | Formula           | Crystal Class | -log K <sub>s,0</sub> |
|------------------|--------------------------------|--|--------------|-------------------|---------------|-----------------------|
| Ca <sup>2+</sup> | 1.0                            | 1.00                                   | Calcite      | CaCO <sub>3</sub> | Rhombohedral  | 8.48°                 |
| Cd <sup>2+</sup> | 1.7                            | 0.95                                   | Otavite      | CdCO <sub>3</sub> | Rhombohedral  | 12.1 <sup>d</sup>     |
| Zn <sup>2+</sup> | 1.6                            | 0.74                                   | Smithsonite  | ZnCO <sub>3</sub> | Rhombohedral  | 10.8°                 |
| Sr <sup>2+</sup> | 1.0                            | 1.31                                   | Strontianite | SrCO <sub>3</sub> | Orthorhombic  | 9.27 <sup>f</sup>     |
| Ba <sup>2+</sup> | 0.9                            | 1.47                                   | Witherite    | BaCO <sub>3</sub> | Orthorhombic  | 8.56 <sup>g</sup>     |

Table 2.1: Cation and corresponding carbonate mineral properties.

<sup>a</sup> Pauling (1960) <sup>b</sup> Shannon (1976)

<sup>c</sup> Plummer and Busenberg (1982)

<sup>d</sup> Stipp et al. (1993)

<sup>e</sup> Schindler et al. (1969)
<sup>f</sup> Busenberg et al. (1984)
<sup>g</sup> Busenberg and Plummer (1986)

$$\ln \zeta_{MeCO_{3(t)}} = X_{CaCO_{3(t)}}^{2} [a_{0} - a_{1} (3X_{MeCO_{3(t)}} - X_{CaCO_{3(t)}})...] , \qquad (2-10)$$

$$\ln \zeta_{CaCO_{3(a)}} = X_{MeCO_{3}}^{2} [a_{0} + a_{1} (3X_{CaCO_{3}} - X_{MeCO_{3}})...] .$$
 (2-11)

The first two terms  $(a_0 \text{ and } a_1)$  of the above expansion series are generally sufficient to represent the dependence of  $\zeta$  values on composition (Glynn and Reardon, 1990). If only the  $a_0$  term is necessary to describe the solid phase activity coefficient dependence on mole fraction, then a regular solid solution is said to occur, and the solid phase activity coefficient functions are symmetrical with respect to mole fraction.

#### **Dilute Solid Solutions**

Dilute solid solutions occur when the substitution of Me<sup>2+</sup> for Ca<sup>2+</sup> in the crystal structure is sufficiently small that  $X_{CaCO_{3(n)}}$  and  $\zeta_{CaCO_{3(n)}}$  are essentially unity. Dilute solid solutions are important in environmental applications when trace metals encounter an abundant solid phase. In this case, the substitution of the trace metal for the lattice ion may be limited such that the activity of the major phase (CaCO<sub>3(s)</sub> in the example above) remains essentially unity. The system can often be further simplified because  $\zeta_{MeCO_{3(n)}}$  is at the same time generally insensitive to small changes in the  $X_{MeCO_{3(n)}}$ , and can be considered constant with respect to solid phase composition.

#### 2.2.4 Solubility Relationships

The above discussions have focused on the thermodynamic reasons for solid solution formation. This section is concerned with the effect solid solutions have on the solubilities of trace metal ions. The formation of a solid solution affects the activity of the solid phase which in turn affects its solubility. Aqueous solution equilibrium with respect to a  $Ca_{1-x}Me_xCO_{3(s)}$  solid solution is described by

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$$IAP_{MeCO_{3(s)}} = \{Me^{2+}\}\{CO_{3}^{2-}\} = K_{s0,MeCO_{3(s)}}a_{MeCO_{3(s)}}, \qquad (2-12)$$

$$IAP_{CaCO_{3(r)}} = \{Ca^{2+}\}\{CO_{3}^{2-}\} = K_{s0,CaCO_{3(r)}} a_{CaCO_{3(r)}}, \qquad (2-13)$$

where: *IAP* is the ion activity product;

{Me<sup>2+</sup>} is the aqueous activity of Me<sup>2+</sup>; {Ca<sup>2+</sup>} is the aqueous activity of Ca<sup>2+</sup>;  $K_{s0,MeCO_{3(s)}}$  is the solubility constant for MeCO<sub>3(s)</sub>; and

$$K_{s0,CaCO_{11}}$$
 is the solubility constant for CaCO<sub>3(s)</sub>.

For dilute solid solutions,  $a_{CaCO_{34n}}$  is nearly unity and Equation 2-13 is essentially equivalent to that for pure CaCO<sub>3(s)</sub>. Therefore, dilute solid solutions only significantly affect the aqueous solubility of the minor substituent, Me<sup>2+</sup>.

#### Pure Phase Precipitation

For precipitation of pure  $MeCO_{3(s)}$ ,  $a_{MeCO_{3(s)}}$  is equal to unity. From Equation 2-12, the precipitation of  $MeCO_{3(s)}$  may only occur when the ion activity product is equal to or greater than  $K_{s0,MeCO_{3(s)}}$ . The value of  $\{Me^{2+}\}$  saturated with respect to pure  $MeCO_{3(s)}$  is given by

$$\{Me^{2^+}\} = \frac{K_{s0,MeCO_{3(s)}}}{\{CO_3^{2^-}\}} .$$
 (2-14)

Thus, if only pure solids are considered, aqueous activities of Me<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> which result in ion activity products below  $K_{s0,MeCO_{y0}}$  do not result in precipitation.

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#### Solid Solution Precipitation

Precipitation of  $Me^{2+}$  in a  $Ca_{1-x}Me_xCO_{3(s)}$  phase is possible at an aqueous activity of  $Me^{2+}$  below that described by Equation 2-14. The {Me<sup>2+</sup>} value in equilibrium with a  $Ca_{1-x}Me_xCO_{3(s)}$  solid solution is given by

$$\{Me^{2^+}\} = \frac{K_{s0,MeCO_{3(n)}}a_{MeCO_{3(n)}}}{\{CO_3^{2^-}\}} .$$
(2-15)

Solid solutions formed under equilibrium conditions always decrease the solubility of a solid relative to the pure phase precipitation case discussed above. The two terms which affect the value of  $a_{MeCO_{MR}}$  and therefore the solubility of {Me<sup>2+</sup>} are  $\zeta_{MeCO_{y_0}}$  and  $X_{MeCO_{y_0}}$ . The value of  $X_{MeCO_{y_0}}$  is always less than unity in a solid solution and tends to decrease the aqueous solubility of the metal ion. The value of  $\zeta_{MeCO_{10}}$  is usually greater than unity and thus usually tends to increase the aqueous solubility of the metal ion. As noted above, similarity of the substituent, Me<sup>2+</sup> to the dominant lattice ion, Ca<sup>2+</sup>, reduces the chemical interactions which occur and therefore favors a solid phase activity coefficient value that is near 1. The aqueous solubility of ions with physical properties similar to that of the dominant lattice ion are reduced more relative to pure phase precipitation than ions with properties significantly different from the dominant lattice ion. For example, cadmium and calcium have similar ionic radii whereas barium is much larger than calcium. It can be expected that the solid phase activity coefficient for cadmium substitution in calcite is much closer to 1 than for barium substitution in calcite.

Trace metal ion partitioning to a solid solution phase can result in significant retardation of divalent metal ions in ground water systems which are undersaturated with respect to pure  $MeCO_{3(s)}$ . For example, from examination of Equation 2-15, the value of  $\{Me^{2+}\}$  in equilibrium with a  $Ca_{0.9}Me_{0.1}CO_{3(s)}$  ideal solid solution would be 10 times less than the  $\{Me^{2+}\}$  in equilibrium with pure  $MeCO_{3(s)}$ . Therefore, if a contaminant solution containing  $Me^{2+}$  enters a calcite-saturated water body, a solid

solution containing  $Me^{2+}$  would form at a value of  $\{Me^{2+}\}$  that is below that necessary to form pure  $MeCO_{3(s)}$ . In certain cases, the value of  $\{Me^{2+}\}$  may be controlled by minor substitution in calcite, and a solid solution containing mostly  $Me^{2+}$  may never form.

#### 2.3 Distribution Coefficients

Metal partitioning between the aqueous and solid solution phases is often described for both experimental and natural systems by a distribution coefficient,  $D_{Me}$ , which is defined for metal ion Me<sup>2+</sup>, partitioning into calcite as follows:

$$D_{Me} = \frac{\frac{X_{MeCO_{3(i)}}}{[Me^{2+}]}}{\frac{X_{CaCO_{3(i)}}}{[Ca^{2+}]}},$$
(2-16)

where  $[Ca^{2+}]$  and  $[Me^{2+}]$  represent the calcium and metal ion concentrations, respectively. If equilibrium is assumed, then by substitution using Equations 2-12 and 2-13, the equilibrium distribution coefficient,  $D_{Me,eq}$  is defined as

$$D_{Me,eq} = \frac{K_{s0,CaCO_{3(s)}} \gamma_{Me^{2*}} \zeta_{CaCO_{3(s)}}}{K_{s0,MeCO_{3(s)}} \gamma_{Ca^{2*}} \zeta_{MeCO_{3(s)}}}, \qquad (2-17)$$

where the two  $\gamma$  values represent the solution phase activity coefficients.

Equation 2-17 illustrates that  $D_{Me,eq}$  is dependent on three factors: the ratio of the solubility constants of the pure end members; a solution interaction factor; and a solid interaction factor. The solution interaction factor represents the effect of the solution composition on the distribution coefficient and is given by the ratio of the solution phase activity coefficients. Solution phase activity coefficients are primarily dependent on the ionic charge of the ion and the ionic strength of the solution. In the systems considered here, the ionic charge of both the substituent and the lattice ion are the same. Therefore, the solution phase activity coefficients will usually be approximately equal, and thus cancel from Equation 2-17. The solid phase interaction

factor is given by the ratio of the solid phase activity coefficients, which are the major unknowns in Equation 2-17.

In the case of a dilute solid solution, the degree of substitution of Me<sup>2+</sup> for Ca<sup>2+</sup> in calcite is small such that  $\zeta_{CaCO_{3(a)}}$  can assumed to be equal to unity, so that

$$D_{Me,eq} \approx \frac{K_{s0,CaCO_{3(a)}}}{K_{s0,MeCO_{3(a)}}} \zeta_{MeCO_{3(a)}}$$
 (2-18)

If  $D_{Me,eq}$  can be determined experimentally, then  $\zeta_{MeCO_{3kn}}$  can be calculated from Equation 2-18. Under ideal conditions, both of the solid phase activity coefficients will be unity, and  $D_{Me,eq}$  simply equals the ratio of the solubility constants.

#### 2.4 Experimental Determination of Metal Partitioning to Solid Solutions

Metal partitioning to solid solution phases has been examined using both precipitation and dissolution experiments. There is considerable uncertainty regarding the accuracy of the  $D_{Me}$  values calculated from laboratory investigations. The following section describes the factors which have limited the usefulness of previous investigations into the partitioning of metals to solid solution phases.

#### 2.4.1 The Determination of $D_{Me}$ and $D_{Me,eq}$ from Precipitation Experiments

Distribution coefficients calculated from precipitation experiments are often used to estimate solid solution/aqueous solution partitioning of ions in natural systems. The applicability of  $D_{Me}$  values calculated in many of these investigations has often been hampered by the formation of heterogeneous solids. Any change in the composition of the solid phase that is formed during the course of an experiment complicates the study of metal partitioning to solid solution phases. When accurate  $D_{Me}$  values have been obtained, rate effects have made the application of these values to equilibrium conditions suspect. The formation of heterogeneous solids and the effects of precipitation rate are discussed in more detail in the following sections.

#### 2.4.1.1 Heterogeneous Solid Formation

Any precipitation experiment which allows the solution phase composition to vary will result in the formation of a heteregeneous solid. For example, many precipitation experiments have been conducted using the free drift method: a supersaturated solution is allowed to approach equilibrium and the aqueous concentration of the trace metal is allowed to vary. As the reaction proceeds, the aqueous concentration of both  $Me^{2+}$  and  $Ca^{2+}$  decrease but usually not by equal percents. For example, if the  $D_{Me}$  value is much greater than 1, the initial layer of solid that is formed will be enriched in  $Me^{2+}$  relative to the solution, causing the solution to become depleted in  $Me^{2+}$  relative to  $Ca^{2+}$  (Figure 2.1). If the distribution coefficient remains constant, the next layer will then have a lower concentration of  $Me^{2+}$  as a result of the lower solution phase  $Me^{2+}/Ca^{2+}$  ratio. The overall result is solution and solid phase compositions which change constantly as precipitation proceeds. In this type of system, it is difficult to determine the composition of the solid phase which is in equilibrium with the solution at each time interval. To interpret this type of data, the Doerner-Hoskins (1925) distribution coefficient,  $\lambda$ , is often used. The value  $\lambda$  relies on the initial and final aqueous concentrations to determine metal partitioning according to

$$\ln \frac{[Me_{initial}^{2+}]}{[Me_{final}^{2+}]} = \lambda \ln \frac{[Ca_{initial}^{2+}]}{[Ca_{final}^{2+}]} .$$
(2-19)

A derivation of Equation 2-19 is provided by McIntire (1963). The Doerner-Hoskins approach assumes that the  $D_{Me}$  value is constant during the course of the experiment, and that no recrystallization occurs. There are two main limitations to this approach: in many instances the assumption of a constant  $D_{Me}$  may not be valid; and even if  $D_{Me}$  can be assumed to be constant, the  $D_{Me}$  value determined is not necessarily equal to  $D_{Me,eq}$ . (Only when the degree of initial supersaturation is infinitely small will  $\lambda \approx D_{Me,eq}$  (McIntire, 1963).) The assumption of a constant  $D_{Me}$  is likely to be valid only when the initial and final solution compositions are not







(b) Time  $t + \triangle t$ .

**Figure 2.1** For  $D_{Me} > 1$ , heterogeneous solid solution forms in response to a decrease in the  $[Me^{2+}]/[Ca^{2+}]$  ratio as the reaction proceeds. See text for details.

significantly different. Large changes in the solution phase composition may result in variable  $D_{Me}$  values as the reaction proceeds due to changes in both the solid phase concentration ratio of Me<sup>2+</sup> and Ca<sup>2+</sup> and the rate of precipitation. For example, as the reaction proceeds in a free drift experiment, the saturation state decreases, causing the precipitation rate to decrease. This decrease in precipitation rate will likely result in a change in the  $D_{Me}$  value as the reaction proceeds. Experiments which maintain a nearly constant aqueous composition will produce nearly homogeneous solids and can be used to determine  $D_{Me}$  values. A  $D_{Me}$  value obtained in this manner may equal the corresponding  $D_{Me,eq}$  if the precipitation rate is low.

#### 2.4.1.2 Precipitation Rate Effects on $D_{Me}$

The formation of a solid solution from an aqueous solution with a nearly constant aqueous composition can result in the formation of a homogeneous solid and allows for the determination of  $D_{Me}$  for those conditions. It cannot be assumed, however, that the measured value of  $D_{Me}$  will equal  $D_{Me,eq}$ : the rate of precipitation has been shown to influence the partitioning of metal ions into calcite solid solutions (Lorens, 1981). Depending on the metal ion, kinetic influences can cause either an increase or a decrease in the  $D_{Me}$  value:  $D_{Me}$  values approach unity as the precipitation rate is increased, reflecting a decrease in ion selectivity at high rates.

A decrease in ion selectivity as precipitation rates increase results in the formation of metastable solids. A metastable solid is defined as a solid which precipitates from an aqueous solution in spite of the fact that there is at least one solid phase which has a lower solublity and is thus more stable. Metastable solids are not in equilibrium with the solution from which they precipitated but form because the kinetics of precipitation are too fast to allow for equilibrium to be achieved between the solid and the solution. For example, Plummer and Busenburg (1987) observed that homogeneous stoichiometric strontian aragonites formed from a highly supersaturated solution would recrystallize while aging in the solutions. The initial solid was apparently metastable. Because the solution was initially highly supersaturated, it was

likely to be oversaturated with respect to solid solutions with a range of compositions. The initial solid did not represent an equilibrium solid with respect to the solution but formed because the kinetics of precipitation were faster than that of the equilibrium solid.

The formation of metastable solids during precipitation reactions requires an analysis of rate effects on the value of  $D_{Me}$  for the experimental system considered. Rate effects may be evaluated by examining the partitioning of Me<sup>2+</sup> at different precipitation rates.  $D_{Me}$  values which remain constant as the precipitation rate is decreased can be argued to approximate the corresponding  $D_{Me,eq}$  value.

2.4.2 The Determination of Solid Solution Equilibria From Dissolution Experiments

While  $D_{Me}$  values are normally obtained with precipitation experiments, dissolution experiments have also been used to evaluate solid solution/aqueous solution equilibria. If equilibrium can be assumed, solid phase activity coefficients can be calculated from these experiments and subsequently inserted into Equation 2-17 to calculate a  $D_{Me,eq}$  value, if desired. Unfortunately, dissolution reactions often result in the formation of heterogeneous solids.

The dissolution of a solid solution is often congruent. Congruent dissolution proceeds until the solution is in equilibrium with a solid solution phase which is enriched in the less soluble end member. At this point a secondary solid enriched in the less soluble end member may precipitate on the initial solid, and the dissolution occurs incongruently. The aqueous solution may then achieve equilibrium with this secondary solid and not the initial solid, resulting in a partial equilibrium condition (Figure 2.2).

Partial equilibrium occurs in a system which is in equilibrium with respect to at least one reaction, but not in equilibrium with others. With regard to the dissolution of a solid solution, the aqueous solution achieves equilibrium with a surface coating, however the "initial" solid is not in equilibrium with the solution or the surface coating. The "initial" solid may become reactive by solid state diffusion (a slow



Figure 2.2 Partial equilibrium condition. Solution is in equilibrium with surface coating and not the initial solid. See text for details.

process), or if the coating is not complete, by reaction with the solution. In either case, the aqueous solution/solid solution equilibria changes as more of the initial solid reacts. Useful information on equilibrium partitioning to the solid solution phase can be obtained, provided that: 1) it can be assumed that the initial solid is non-reactive; and 2) the solid phase composition of the secondary phase can be estimated. This secondary phase may be very thin and may not be homogeneous, thus making an estimate of its composition difficult. While, dissolution in a presaturated solution may minimize the amount of coating which forms (Königsberger *et al.*, 1991), it will not eliminate this effect. The formation of secondary solids during dissolution has made the determination of equilibrium parameters from dissolution experiments suspect. It is not that equilibrium, albeit partial, is not achieved, but that the composition of the solid phase controlling the equilibrium is difficult to determine.

#### 2.4.3 Summary

Several considerations must be taken into account when designing an experiment to evaluate the equilibrium partitioning of ions into a solid solution. There are two major concerns: that the solid and aqueous phases be easily characterized and do not change appreciably during the course of the experiment; and that the reaction rate effects on ion partitioning to the solid solution phase be evaluated. Due to the formation of surface coatings, dissolution experiments do not result in easily characterized solid phases. Precipitation experiments using methods which produce overgrowths of a known composition from a solution of nearly constant composition are therefore preferable to dissolution experiments. If  $D_{Me,eq}$  values are to be obtained, precipitation rate effects on the  $D_{Me}$  values obtained in laboratory experiments must be evaluated to assure that the solids produced are in equilibrium with the solution and do not represent a metastable condition.

## CHAPTER 3 COPRECIPITATION OF DIVALENT CATIONS INTO CALCITE: BATCH EXPERIMENTS

#### 3.1 Background

The incorporation of "foreign" cations into a crystal lattice during precipitation is often an important process controlling trace metal transport in ground and surface waters. However, this process is rarely considered in conceptual and computational geochemical models due to the limited knowledge of the solid solution/aqueous solution equilibria for most systems of interest. Calcite (hexagonal calcium carbonate) was selected as the "adsorbent" for this investigation because it is abundant, and many natural waters are saturated with respect to this mineral. The solid solution partitioning behavior of trace metals with calcite provides insight into: paleo-water chemistry, diagenesis reactions, and metal transport. As discussed in Chapter 2, solid solution partitioning behavior is often described by the distribution coefficient,  $D_{Me}$ :

$$D_{Me} = \frac{X_{MeCO_{3(n)}}/[Me^{2^{+}}]}{X_{CaCO_{3(n)}}/[Ca^{2^{+}}]}$$
(3-1)

Much of the early work done on carbonate solid solutions was aimed at trying to determine the aqueous composition of paleo-waters. Experimentally- or empirically-derived  $D_{Me}$  and  $X_{MeCO_{3(n)}}$  values for carbonate solids have been used to estimate metal ion concentrations of the solutions at the time of crystallization.  $D_{Me}$  values have also been used to provide estimates of the amount of calcite recrystallization which has occurred. This was accomplished by comparing  $D_{Me}$  values

for natural calcite with experimentally-determined equilibrium distribution coefficient values,  $D_{Me,eq}$ . The effect of solid solution partitioning on the contaminant transport of metal ions in natural waters (*e.g.*, retardation in ground water) has received attention only recently (*i.e.*, Davis *et al.*, 1987; Jensen, 1993).

The application of laboratory-derived  $D_{Me}$  values to natural systems requires that the experimental conditions accurately represent the natural environment. Morse and Bender (1990) have noted that many factors affect experimental  $D_{Me}$  values, including temperature, precipitation rate, solution composition, and solid composition. Morse and Bender (1990) suggest that experimentally-derived  $D_{Me}$  values should be used with caution, particularly when applied to systems where the precipitation rate is not well known. Indeed, the incorporation of metal ions into the calcite crystal lattice is very dependent on the precipitation rate (Lorens, 1981). Therefore, experimentally-derived  $D_{Me}$  values may only be representative of natural precipitation reactions which occur at similar rates. Calcite precipitation rates in the natural environment vary from relatively fast, such as biogenic deposition in the oceans and during "whiting" events in lakes, to slower reactions such as aragonite/calcite transformations. Many important reactions (e.g., recrystallization reactions in both ground and surface water) occur at relatively slow rates when compared to those used in many laboratory investigations. It was the intent of this work to determine the precipitation rate dependence of divalent cation partitioning into calcite and to ultimately provide estimates of the  $D_{Me,eq}$ values which are applicable to systems characterized by slow reaction rates.

#### **3.2 Previous Experiments**

Previous experiments have been directed primarily at determining the nature of solid solution/aqueous solution partitioning during the biogenic deposition of marine calcites. Two general experimental procedures have been employed. The  $CO_2$  evolution method involves the slow release of  $CO_2$  from the reaction vessel. This causes the pH to rise and the solution to become supersaturated with respect to calcite. The precipitation rate is controlled by the  $CO_2$  release rate. The compositions of the

solid and solution vary during the course of the experiment. In the **constant composition method**, precipitation is induced by the controlled addition of titrants. The rate of precipitation is determined by the rate of titrant addition and the surface area of reactive solids (*i.e.*, calcite). This method has the advantage of maintaining a nearly constant precipitation rate and aqueous composition, resulting in the formation of a solid overgrowth having an approximately homogeneous composition.

#### 3.2.1 Strontium Experiments

There have been several investigations of strontium coprecipitation with calcite, primarily to improve estimates of the strontium composition of paleo-waters. Figure 3.1 provides a summary of the range of  $D_{Sr}$  values obtained in the investigations discussed below. Precipitation rate has long been recognized as a factor controlling cation partitioning to calcite (e.g., see Kinsman and Holland, 1969). A detailed examination of the precipitation rate dependence of cation partitioning into calcite was carried out by Lorens (1981). Lorens (1981) examined the effect of precipitation rate on the incorporation of Sr<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, and Mn<sup>2+</sup> into calcite using a constant composition method. Lorens (1981) found that  $D_{Sr}$  increased as the precipitation rate was increased over several orders of magnitude. Values for  $D_{Sr}$  ranged from 0.027 at low growth rates to 0.1 at high rates.

Mucci and Morse (1983) conducted constant composition experiments to evaluate the effect of precipitation rate and solution composition on the incorporation of  $Sr^{2+}$ and  $Mg^{2+}$  into calcite. The value of  $D_{Sr}$  was observed to increase from 0.20 to 0.34 as  $X_{MgCO_{3(n)}}$  increased. It has been suggested that an increase in  $D_{Sr}$  as a function of  $Mg^{2+}$ concentration may be an indirect effect of precipitation rate since  $Mg^{2+}$  in solution inhibits calcite precipitation (Apitz, 1991). Although Mucci and Morse (1983) observed no dependence of  $D_{Sr}$  on the precipitation rate, their experiments covered a relatively limited range (from approximately 1 to 15 nmoles/mg-min).

The application of experimentally-derived  $D_{Sr}$  values to natural systems requires consideration of the precipitation rates in the natural system of interest. The


Figure 3.1 The ranges of  $D_{Sr}$  values measured in the investigations of Lorens (1981), Holland (1966), Katz et al. (1972), Kitano et al. (1971), Pingitore and Eastman (1986), Apitz (1991), and Mucci and Morse (1983).

precipitation rates of natural calcite vary widely: from slowly-recrystallizing abiotic marine calcites at rates on the order of  $10^{-8}$  nmole/m<sup>2</sup>-min (calculated from Apitz (1991)) to cave deposits formed by CO<sub>2</sub> outgassing at precipitation rates on the order of  $10^5$  nmoles/m<sup>2</sup>-min (Herman and Lorah, 1988). Holland (1966) conducted CO<sub>2</sub> evolution experiments in a Mg<sup>2+</sup>-free solution and arrived at a  $D_{Sr}$  value of 0.14 at 25°C. This value is consistent with the  $D_{Sr}$  value which can be calculated based on the composition of cave deposits and the water from which they precipitated (Holland *et al.*, 1964).

Holland's (1966)  $D_{sr}$  value of 0.14 is also in agreement with the Sr content of biotic marine low magnesian calcites (e.g., Bender *et al.*, 1975) and was previously thought to represent the equilibrium partitioning of Sr<sup>2+</sup> to marine calcites. Abiotic marine calcites form at lower precipitation rates and, therefore,  $D_{sr}$  values calculated for these calcites may be more representative of equilibrium conditions. Apitz (1991) calculated  $D_{sr}$  values for basally-lithified ridge flank (abiotic) calcites by assuming that these limestones were recrystallized in unaltered seawater. The pore water composition was corrected to account for changes in seawater composition during the course of deposition. Using the most recrystallized samples, the  $D_{sr}$  value for these limestones was taken to be 0.026 ±0.003. The precipitation rate for recrystallizing basal limestone is slow (on the order of 4 x 10<sup>-8</sup> nmoles/min) so equilibrium partitioning of strontium into calcite was expected (Apitz, 1991). The aragonite-calcite transformation also occurs at low rates relative to biogenic calcite precipitation. Katz *et al.* (1972) examined the behavior of strontium during this transformation and found  $D_{sr}$  to vary from 0.055 at 40°C to 0.058 at 98°C.

The effect of the aqueous concentration of strontium on partitioning into calcite was examined by Pingitore and Eastman (1986). Pingitore and Eastman used the  $CO_2$  evolution method and obtained  $D_{Sr}$  values which depended upon the  $Sr^{2+}/Ca^{2+}$  ratio in the solution. Below a molar ratio of  $10^{-3}$ ,  $D_{Sr}$  values between 0.10 and 0.20 were observed, and above that ratio a value of 0.06 was observed. Although the  $D_{Sr}$  value increased with precipitation rate, a quantitative relationship between  $D_{Sr}$  and

precipitation rate was not presented. The CO<sub>2</sub> evolution method was also used by Kitano *et al.* (1971) to spontaneously nucleate coprecipitates. They determined a  $D_{sr}$  value of 0.08 ±0.02 for their lowest precipitation rates.

Precipitation rate differences may be the main factor responsible for variations in strontium partitioning to calcites precipitated from both natural waters and from experimental systems. The dependence of  $D_{Sr}$  on the precipitation rate underscores the need to determine  $D_{Sr}$  (and other  $D_{Me}$ ) values at rates which are applicable to the systems investigated. For example, Holland's (1966) value of 0.14 may adequately describe relatively fast reactions such as primary precipitation by organisms and cave deposits. However, it will not adequately describe slower reactions such as calcite recrystallization reactions in ocean water or ground water.

# 3.2.2 Barium

All of the relatively few investigations into barium partitioning to calcite have used the CO<sub>2</sub> evolution method. Kitano *et al.* (1971) spontaneously nucleated coprecipitates and found that in all runs, both  $D_{Ba}$  and the precipitation rate decreased as the reaction proceeded. A  $D_{Ba}$  value of 0.1 was obtained from the late stages (lowest precipitation rates) of their experiments. An increase in the stirring rate resulted in an increase in the  $D_{Ba}$  values obtained. Pingitore and Eastman (1986) used seed material to facilitate precipitation and obtained  $D_{Ba}$  values of 0.04 ±0.01 over a wide range of barium concentrations at an approximate precipitation rate of 220 nmole/mg-min. The lower value for  $D_{Ba}$  obtained by Pingitore and Eastman (1986) versus the value of 0.1 obtained by Kitano *et al.* (1971) may be due to lower average precipitation rates caused by the seeding of the reaction vessel in the former experiments. Pingitore and Eastman (1985) also found that barium partitioning during the transformation of aragonite to calcite was consistent with their experimentally-determined  $D_{Ba}$  value of 0.06 ±0.01.

### 3.2.3 Zinc

Few investigations into the partitioning of zinc into calcite have been conducted. Lorens (1978, 1981) used a constant composition method to examine the precipitation of radiolabeled zinc with calcite. Lorens calculated distribution coefficient values using total zinc in solution and not the concentration of the free ion. These values generally ranged from 50 to 130. These values were converted to  $D_{Zn}$  values as defined in Equation 3.1 using the % free metal reported by Lorens (1978, 43% free zinc, 100% free calcium); the range of  $D_{Zn}$  values calculated is 115 to 300. Zinc partitioning into calcite was not found to be as strongly dependent on precipitation rates as was the case for the other metals examined (Sr<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup>).

#### 3.2.4 Cadmium

Lorens' (1978, 1981) distribution coefficient values for cadmium were converted to the free ion form shown in Equation 3.1, and generally ranged from 500 at high precipitation rates (140 nmoles/mg-min) to 1500 at lower precipitation rates (3 nmoles/mg-min). Davis *et al.* (1987) conducted cadmium adsorption experiments with calcite and suggested that solid solution formation may be responsible for the slow but constant rate of cadmium uptake observed after an initial 24 hour period. An average  $D_{Cd}$  value of 1510 ±300 was calculated from the rates of Cd<sup>2+</sup> adsorption and Ca<sup>2+</sup> isotopic exchange during this period.

### **3.3 Experimental Objective**

The objective of this research was to determine the equilibrium values of the solid solution / aqueous solution distribution coefficients at precipitation rates which were sufficiently low that the  $D_{Me}$  measured would no longer be dependent on the precipitation rate. Solid phase composition data, in conjunction with aqueous composition data, was used to determine metal partitioning into calcite and its dependence on precipitation rate. To evaluate solid solution / aqueous solution equilibria, it was necessary to determine the composition of the solid phase which was

in equilibrium with the solution. In order to produce easily characterized solid phases, coprecipitates were formed using the constant composition method.

## **3.4 Experimental Procedure**

A constant composition method similar to that of Mucci (1981) was used to precipitate the carbonate solid solutions. Figure 3.2 provides a schematic representation of the experimental setup. For each experiment, 400 mL of 0.22 M NaCl was maintained at 25°C in a water-jacketed beaker. The solution was maintained at approximately 1 atmosphere partial pressure of  $CO_2$ . Sufficient calcite was then added to the reaction vessel to equilibrate the solution with respect to calcite and to provide seed material to facilitate precipitation. The solution was stirred with a Nalgene "floating" stir bar assembly to prevent grinding of calcite against the bottom of the reaction vessel. The aqueous composition of the solution was maintained and precipitation induced by the titration of 0.5 M Na<sub>2</sub>CO<sub>3</sub> and 0.5 M CaCl<sub>2</sub> using a dual syringe pump outfitted with either one mL or ten mL gastight syringes. The addition of the titrants caused the solution pH to rise and become increasingly oversaturated with respect to calcite (up to point A in Figure 3.3). Simultaneously, the precipitation rate for calcite increased with the degree of oversaturation until the precipitation rate equaled the titration rate. From this point on, the solution composition remained nearly constant, as the rates of calcium and alkalinity lost to precipitation became equal to the rates of calcium and alkalinity addition by titration. The precipitation rate of experiments was varied by changing the rate of titration. The procedure used to maintain  $\{Me^{2+}\}\$  nearly constant depended on the metal investigated.

#### 3.4.1 Method For Barium and Strontium

For metals with expected distribution coefficients much less than 1, the following procedure was used. Once a steady state precipitation rate was achieved by the titration of  $0.5 M \text{ Na}_2\text{CO}_3$  and  $0.5 M \text{ CaCl}_2$ , approximately 2 mL of MeCl<sub>2</sub> solution at an appropriate concentration was added to the reaction vessel to achieve the desired metal solution concentration (Figure 3.3). The addition of titrants and the



Figure 3.2 A schematic of the apparatus used in the experiments discussed in Chapter 3.



Figure 3.3 Illustration of pH vs. time plot for strontium and barium constant composition experiments. See text for details.

coprecipitation of metal with calcite was continued at the same rate as before. Due to the low distribution coefficient, the change in concentration of Me in solution as the result of precipitation remained negligible throughout the experiment. The solution was sampled with a syringe just after the metal was added and again at the end the experiment. Each solution sample was immediately passed through a 0.45  $\mu$ m filter and acidified, then analyzed for calcium and metal concentration by atomic absorption spectroscopy (AAS).

The moles of calcium precipitated during the time period from just after the addition of  $MeCl_2$  (time *T1*) to the end of the experiment (time *T2*) was determined from the following calcium mass balance calculation:

$$mols_{precip, T1 to T2} = mols_{soln,T1} + mols_{titrated, T1 to T2} - mols_{soln,T2}$$
(3-2)

where:  $mols_{precip, T1 to T2}$  is the moles of Ca precipitated from time T1 to T2

 $mols_{soln,Tl}$  is the moles of Ca in solution at time Tl

 $mols_{soln,T2}$  is the moles of Ca in solution at time T2

mols<sub>titrated,T1-T2</sub> is the moles of Ca titrated into the solution from time T1 to T2. At the end of the experiment the entire solution was passed through a 0.45 µm filter. The rinsing of precipitates to remove adsorbed Me<sup>2+</sup> was considered. If solids were not rinsed, a portion of the Me<sup>2+</sup> in the solid fraction would have been due to adsorption and not solid solution precipitation. However, if the solids were rinsed with deionized water, dissolution of a portion of the surface coating would have occurred. Therefore, solids were rinsed with a calcite saturated solution, thus minimizing the dissolution of the surface coatings while still removing adsorbed metal. (By comparing  $D_{Sr}$  and  $D_{Ba}$  values for fractions which were rinsed and not rinsed, it was determined that adsorption had only a small impact on measured  $D_{Me}$  values.)

The solids were then baked at 105 °C for over 24 hours, then weighed. A portion of the precipitate was dissolved in 6 M HCl and diluted for determination of calcium and partitioning metal by AAS. The amount of Me in the precipitate included both that in the surface precipitate as well as that in the original seed material. This is

emphasized through the use of the subscript "total" in the equation below. The mole fraction of Me in the surface precipitate,  $X_{MeCO_{3(n)},sp}$ , was determined by correcting the total solid phase composition for the Me contribution of the initial seed material, as follows:

$$\left\{\frac{g Me}{g CaCO_{3(s)}}\right\}_{sp} = \frac{\left\{\frac{g Me}{g CaCO_{3(s)}}\right\}_{total}}{F_{sp}} - F_{seed} \left\{\frac{g Me}{g CaCO_{3(s)}}\right\}_{seed}, \quad (3-3)$$

$$X_{MeCO_{3(s)},sp} = \left\{ \frac{g Me}{g CaCO_{3(s)}} \right\}_{sp} \left\{ \frac{100 g CaCO_{3(s)}}{mole CaCO_{3(s)}} \right\} \left\{ \frac{1 mole MeCO_{3(s)}}{AW of Me} \right\}, \quad (3-4)$$

where:  $F_{seed}$  is the seed fraction of the solid phase (by weight); and

 $F_{sp}$  is the surface precipitate fraction of the solid phase (by weight). The distribution coefficient was calculated from the aqueous and surface precipitate composition according to

$$D_{Me} = \frac{X_{MeCO_{3(a)}, sp} / [Me^{2+}]}{X_{CaCO_{3(a)}, sp} / [Ca^{2+}]} .$$
(3-5)

### 3.4.2 Method for Zinc

When the above procedure was used for zinc, the addition of  $ZnCl_2$  altered the steady state precipitation condition. In particular, zinc inhibited calcite precipitation and caused both the pH and the calcite saturation state to increase. To achieve a steady state condition sooner, the above procedure was modified by adding the  $ZnCl_2$  solution as soon as the titration of 0.5 *M* Na<sub>2</sub>CO<sub>3</sub> and 0.5 *M* CaCl<sub>2</sub> was initiated.

Additions of zinc during the course of the experiment were required to maintain a nearly constant  $\{Zn^{2+}\}$  value. For the purposes of the following calculation, "initial" aqueous concentrations of zinc and calcium include the contribution of any zinc and calcium titrated into the solution prior to the conclusion of the experiment. The distribution coefficient,  $\lambda$ , was determined using the "initial" and final  $\{Ca^{2+}\}$  and  $\{Zn^{2+}\}$  values and the Doerner-Hoskins equation, which is:

$$\lambda_{Zn} = \frac{\ln\left[[Zn_{init}]/[Zn_{final}]\right]}{\ln\left[[Ca_{init}]/[Ca_{final}]\right]} .$$
(3-6)

## 3.4.3 Method for Cadmium

For a metal with distribution coefficients greater than 1, use of the above procedures would lead to a rapid decrease in the aqueous metal concentration due to preferential partitioning into the solid phase. The following modifications to the above procedure maintained nearly constant metal concentrations in solution. As before, precipitation was induced by the titration of solutions of Na<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub>. After a constant precipitation rate was achieved, the CaCl<sub>2</sub> solution was replaced with a 0.5 *M* Ca<sub>1-x</sub>Cd<sub>x</sub>Cl<sub>2</sub> solution. The 0.5 *M* Na<sub>2</sub>CO<sub>3</sub> and 0.5 *M* Ca<sub>1-x</sub>Cd<sub>x</sub>Cl<sub>2</sub> solutions were titrated at a fixed rate from a dual syringe pump into the solution. The solution was sampled periodically and analyzed for aqueous calcium and cadmium concentrations by AAS. The pH of the solution was monitored.

The addition of  $CdCl_2$  to the  $CaCl_2$  syringe led to a steady state condition for which the cadmium concentration in solution remained constant. Initially, the mole fraction of cadmium in the titrant exceeded that of the precipitate, causing the cadmium concentration of the solution to increase (E to F, Figure 3.4). The cadmium concentration of the solution continued to increase until the mole fraction of metal in the titrant solution was equal to that of the precipitate (point F, Figure 3.4). From this point on, the { $Cd^{2+}$ } value remained nearly constant: the rate of cadmium addition was approximately equal to the rate of cadmium precipitation (F to G, Figure 3.4). The mole fraction of Cd in the precipitate during the steady state portion of the experiment



**Figure 3.4** Illustration of pH *vs.* time plot for cadmium constant composition experiments. Line E-F-G refers to the concentration of Cd in solution, [Cd]. See text for details.

was assumed to be equal to its mole fraction in the titrant solution. The distribution coefficient was determined from the aqueous concentrations of calcium and cadmium during the steady state portion of the experiment ( $\{Ca^{2+}\}_{ss}$  and  $\{Cd^{2+}\}_{ss}$ ) and the mole fractions of the titrant using the equation below:

$$D_{Cd} = \frac{X_{CdCl_{s}, titrant} / [Cd^{2*}]_{ss}}{X_{CaCl_{s}, titrant} / [Ca^{2*}]_{ss}}$$
(3-7)

# 3.5 Results

The aqueous compositions, precipitation rates, and distribution coefficients for the strontium and barium experiments are shown in Tables 3.1 and 3.2, respectively. As before, the term T1 refers to the time of  $SrCl_2$  (or  $BaCl_2$ ) addition to the reaction vessel. The term T2 refers to the end of the experiment. (All of the figures in this chapter were prepared using data for time T2.) Each steady state precipitation rate was normalized to the amount of reactive solid present. Because the amount of reactive solid varied from T1 to T2, the precipitation rate also varied. Precipitation rate information for the strontium and barium experiments at both T1 and T2 are shown in Tables 3.1 and 3.2. Table 3.3 presents the data from the zinc experiment. The details of the cadmium experiment are provided in the Appendix and are summarized in Table 3.4. Aqueous speciation calculations for all experiments were performed using MINTEQA2 (Allison *et al.*, 1991).

#### 3.5.1 Strontium

The  $D_{sr}$  vs. precipitation rate plot is shown in Figure 3.5. The precipitation rate ranged from 0.3 to over 400 nmoles/mg-min. At precipitation rates above 30 nmoles/mg-min, the distribution coefficient increased with precipitation rate. The distribution coefficient remained nearly constant at precipitation rates below 30 nmoles/mg-min, with a mean value of 0.021 and a 99% confidence interval from 0.018 to 0.024. Since the  $D_{sr}$  value remained effectively constant over a several order of

| SAMPLE | [Ca]<br>@ <i>T1</i> | [Ca]<br>@ 72 | [Sr]<br>@ <i>T1</i> | [Sr]<br>@ <i>T</i> 2 | рН<br>@ <i>Т1</i> | рН<br>@ <i>Т</i> 2 | DURATION<br>T1-T2<br>minutes | PRECIP. 1<br>nmoles/<br>@ T1 | RATE<br>(mg-min)<br>@ T2 | DISTRIBUT<br>COEFF.<br>@ T1 | ION<br>@ T2 |
|--------|---------------------|--------------|---------------------|----------------------|-------------------|--------------------|------------------------------|------------------------------|--------------------------|-----------------------------|-------------|
| Q      | 548                 | 546          | 5.8                 | 5.6                  | 5.97              | 6.08               | 1080                         | 3.4                          | 2.5                      | 0.024                       | 0.025       |
| R      | 629                 | 588          | 13                  | 13                   | 6.12              | 6.09               | 1500                         | 4.7                          | 2.8                      | 0.055                       | 0.051       |
| S      | 540                 | 451          | 23                  | 23                   | 6.12              | 6.18               | 3360                         | 3.6                          | 1.6                      | 0.026                       | 0.022       |
| U      | 614                 | 583          | 32                  | 31                   | 6.12              | 6.14               | 1110                         | 6.2                          | 3.7                      | 0.019                       | 0.018       |
| v      | 502                 | 374          | 18                  | 14                   | 6.11              | 6.03               | 960                          | 10.4                         | 6.8                      | 0.023                       | 0.022       |
| X      | 599                 | 583          | 151                 | 149                  | 6.10              | 6.08               | 440                          | 4.0                          | 3.4                      | 0.030                       | 0.030       |
| Y      | 636                 | 571          | 51                  | 49                   | 6.15              | 6.15               | 60                           | 70.2                         | 40.4                     | 0.066                       | 0.061       |
| Z      | 716                 | 800          | 53                  | 55                   | 6.33              | 6.45               | 5.7                          | 557.3                        | 423.0                    | 0.130                       | 0.140       |
| 1ª     | 517                 | 522          | 53                  | 53                   | 6.04              | 6.07               | 2430                         | 0.3                          | 0.3                      | 0.015                       | 0.016       |
| 3      | 535                 | 504          | 57                  | 53                   | 6.08              | 6.03               | 2660                         | 1.4                          | 1.0                      | 0.019                       | 0.019       |
| 4      | 728                 | 745          | 49                  | 48                   | 6.20              | 6.27               | 18                           | 222.3                        | 158.7                    | 0.087                       | 0.092       |
| 5      | 648                 | 700          | 51                  | 50                   | 6.10              | 6.14               | 28                           | 52.8                         | 46.0                     | 0.059                       | 0.066       |

Table 3.1: Aqueous composition (total concentrations in mg/L reported), precipitation, and distribution coefficient data for strontium experiments.

<sup>a</sup>Titrants used in this experiment were 0.05 M Na<sub>2</sub>CO<sub>3</sub> and 0.05 M CaCl<sub>2</sub>.

| SAMPLE          | [Ca]<br>@ T1 | [Ca]<br>@ 72 | [Sr]<br>@ T1 | [Sr]<br>@ <i>T</i> 2 | pH<br>@ <i>T1</i> | рН<br>@ <i>Т</i> 2 | DURATION<br>T1-T2<br>minutes | PRECIP.<br>nmoles/<br>@ T1 | RATE<br>/(mg-min)<br>@ <i>T</i> 2 | DISTRIBUTIC<br>COEFF.<br>@ T1 ( | )N<br>@ <i>T</i> 2 |
|-----------------|--------------|--------------|--------------|----------------------|-------------------|--------------------|------------------------------|----------------------------|-----------------------------------|---------------------------------|--------------------|
| 6               | 845          | 842          | 47           | 43                   | 6.23              | 6.26               | 28                           | 310.0                      | 166.0                             | 0.097                           | 0.106              |
| 7               | 695          | 763          | 57           | 53                   | 6.21              | 6.27               | 34                           | 178.2                      | 111.0                             | 0.058                           | 0.068              |
| 8b⁵             | 574          | 539          | 38           | 35                   | 6.42              | 6.33               | 130                          | 21.2                       | 19.1                              | 0.090                           | 0.091              |
| 9 <sup>b</sup>  | 643          | 602          | 61           | 52                   | 6.15              | 6.41               | 1065                         | 6.0                        | 3.7                               | 0.023                           | 0.026              |
| 10 <sup>b</sup> | 614          | 583          | 32           | 31                   | 6.29              | 6.32               | 397                          | 3.3                        | 2.9                               | 0.034                           | 0.035              |
| 11              | 734          | 656          | 60           | 57                   | 6.08              | 6.06               | 120                          | 43.7                       | 28.6                              | 0.037                           | 0.034              |
| 17              | 479          | 492          | 93           | 92                   | 6.05              | 6.12               | 1030                         | 2.8                        | 2.2                               | 0.022                           | 0.023              |
| 18              | 702          | 697          | 60           | 59                   | 6.16              | 6.11               | 140                          | 25.8                       | 18.9                              | 0.021                           | 0.022              |
| 26              | 744          | 551          | 55           | 42                   | 6.08              | 6.12               | 35                           | 351.5                      | 157.6                             | 0.123                           | 0.119              |

Table 3.1 (continued): Aqueous composition (total concentrations in mg/L reported), precipitation, and distribution coefficient data for strontium experiments.

<sup>b</sup>Column experiments.

|        | [Ca] | [Ca] | [Ba] | [Ba] | ъЦ          | ъН   | DURATION PRECIP. RATE |       | DISTRIBUT | ION         |       |
|--------|------|------|------|------|-------------|------|-----------------------|-------|-----------|-------------|-------|
| SAMPLE | @ T1 | @ T2 | @ T1 | @ T2 | @ <i>T1</i> | @ T2 | minutes               | @ T1  | @ T2      | @ <i>T1</i> | @ T2  |
| 13     | 531  | 543  | 14.1 | 14.1 | 6.07        | 6.14 | 960                   | 3.2   | 2.5       | 0.022       | 0.022 |
| 14     | 574  | 595  | 14.1 | 14.3 | 6.18        | 6.17 | 54                    | 55.2  | 42.5      | 0.024       | 0.024 |
| 15     | 650  | 703  | 14.0 | 14.0 | 6.20        | 6.25 | 27                    | 89.7  | 72.2      | 0.029       | 0.031 |
| 16     | 499  | 493  | 15   | 15   | 6.00        | 6.01 | 2520                  | 1.0   | 0.8       | 0.015       | 0.015 |
| 19     | 933  | 976  | 11   | 11   | 6.16        | 6.22 | 17                    | 322.6 | 208.4     | 0.045       | 0.047 |
| 20     | 650  | 697  | 16   | 16   | 6.06        | 6.09 | 165                   | 15.9  | 12.7      | 0.012       | 0.012 |
| 21     | 756  | 882  | 16   | 16   | 6.19        | 6.28 | 5                     | 308.0 | 266.9     | 0.045       | 0.053 |
| 22     | 603  | 608  | 15   | 16   | 6.02        | 6.09 | 3960                  | 2.4   | 1.2       | 0.010       | 0.010 |
| 23     | 758  | 759  | 12   | 12   | 6.02        | 6.02 | 1020                  | 18.8  | 6.4       | 0.003       | 0.003 |
| 24     | 510  | 561  | 9.3  | 9.5  | 6.06        | 6.20 | 65                    | 54.4  | 40.2      | 0.017       | 0.019 |
| 25     | 550  | 660  | 9.3  | 8.2  | 6.10        | 6.20 | 8.5                   | 453.1 | 327.1     | 0.011       | 0.015 |
| 28     | 579  | 634  | 19   | 18   | 6.04        |      | 3865                  | 0.7   | 0.6       | 0.010       | 0.011 |
| 29     | 623  | 669  | 9.8  | 10.4 | 6.07        | 6.07 | 1110                  | 3.5   | 2.5       | 0.020       | 0.020 |
| 30     | 664  | 643  | 22   | 21   | 6.04        | 6.07 | 5460                  | 1.8   | 0.9       | 0.008       | 0.008 |

Table 3.2: Aqueous composition (total concentrations in mg/L reported), precipitation rate and distribution coefficient data for the barium experiments.



Figure 3.5  $D_{Sr}$  vs. precipitation rate plot for the strontium batch experiments conducted in this study.

magnitude change in precipitation rate, it is believed that 0.021 ±0.003 represents the value of  $D_{Sr,eq}$  for the range of aqueous compositions considered.

Figure 3.6 is a plot of the  $X_{SrCO_{Max}}$  vs.  $[Sr^{2+}]/[Ca^{2+}]$  ratio in solution for samples precipitated at rates below 30 nmoles/mg-min. Since the  $[Ca^{2+}]$  did not vary much between experiments, changes in the  $[Sr^{2+}]/[Ca^{2+}]$  ratio in solution are largely due to variations in the  $[Sr^{2+}]$  in solution. With the exception of sample X, the correlation corresponding to a  $D_{Sr}$  value of 0.021 provides a good fit to the data, indicating that  $D_{Sr}$  is largely independent of the  $[Sr^{2+}]/[Ca^{2+}]$  ratio in solution. The increased value of  $X_{SrCO_{Max}}$ (and hence  $D_{Sr}$ ) for sample X may have been due to the precipitation of trace amounts of strontianite as this was the only sample which was precipitated from a solution oversaturated with respect to strontianite. Although an X-ray diffraction analysis of sample X did not detect strontianite, with such a low distribution coefficient, only a trace amount of strontianite would be necessary to cause this difference. Thus, the value for  $D_{Sr,eq}$  of 0.021 ±0.003 appears to be applicable over the range of  $Sr^{2+}$ concentrations considered as long as supersaturation with respect to strontianite does not occur.

As discussed in Chapter 1, for the partitioning of trace levels of  $Sr^{2+}$  into calcite, at equilibrium the value  $D_{Sr}$  is related to the activity coefficient  $\zeta_{SrCO_{3(r)}}$  in the calcite by

$$D_{Sr} = D_{Sr,eq} = \frac{K_{S0, CaCO_{3(r)}}}{K_{S0, SrCO_{3(r)}} \zeta_{SrCO_{3(r)}}}.$$
 (3-8)

 $K_{s0}$  values for calcite and strontianite of  $10^{-8.48}$  (Plummer and Busenberg, 1982) and  $10^{-9.27}$  (Busenberg *et al.*, 1984), respectively, are used in the following calculation. For  $D_{Sr,eq} = 0.021 \pm 0.003$ ,  $\zeta_{SrCO_{367}}$  is calculated to be 294 with a 99% probability range from 257 to 342. If the two-suffix Margules approach is assumed, having been used successfully to describe the solid phase activity coefficient dependence on mole fraction in other cases, we have



**Figure 3.6** Mole fraction of  $SrCO_{3(s)}$  for the precipitate vs. the aqueous  $[Sr^{2+}]/[Ca^{2+}]$  ratio. Line shows trend for  $D_{Sr}$  value of 0.021.

$$\ln \zeta_{SrCO_{3(r)}} = a_0 X_{CaCO_{3(r)}}^2$$
 (3-9)

The  $\zeta_{SrCO_{3(a)}}$  value of 294 corresponds to a value of 5.7 for the parameter  $a_0$ . (The 99% confidence interval is 5.5 to 5.8).

## 3.5.2 Barium

A plot of  $D_{Ba}$  vs. precipitation rate is shown in Figure 3.7. Precipitation rates ranged from less than 1 to over 300 nmoles/mg-min. The  $D_{Ba}$  value generally increased when the precipitation rate exceeded 50 nmoles/mg-min. Below this precipitation rate,  $D_{Ba}$ , appeared to level off with a mean value of 0.012 ±0.005 at the 99% confidence level. It is believed that 0.012 ±0.005 represents the equilibrium  $D_{Ba}$ since it does not appear that this value will markedly change with further reductions in the precipitation rate. This value should apply to systems characterized by slow precipitation rates, e.g., systems which are at or near saturation with respect to calcite.

For the equilibrium partitioning of trace levels of  $Ba^{2+}$  into calcite, the value of  $D_{Ba}$  is related to  $\zeta_{BaCO_{ac}}$  by

$$D_{Ba} = D_{Ba,eq} = \frac{K_{s0, CaCO_{3(e)}}}{K_{s0, BaCO_{3(e)}} \zeta_{BaCO_{3(e)}}} .$$
(3-10)

Using a  $K_{s0}$  value for witherite (BaCO<sub>3</sub>) of 10<sup>-8.56</sup> (Busenberg and Plummer, 1986), for  $D_{Ba,eq} = 0.012 \pm 0.005$ ,  $\zeta_{BaCO_{360}}$  is calculated to be 100 with a 99% probability range from 71 to 172. A  $\zeta_{BaCO_{360}}$  value of 100 corresponds to a value of 4.6 for the parameter  $a_0$  in the two-suffix Margules equation. (The 99% confidence interval is 4.3 to 5.1)

## 3.5.3 Zinc

The results of the zinc experiment are shown in Table 3.3. Samples were taken approximately twice a day for a two week period. As indicated in Table 3.3, this



Figure 3.7  $D_{Ba}$  vs. precipitation rate plot for the barium experiments conducted in this study.

method was successful at maintaining the aqueous concentration of zinc at a nearly constant level. The titration rate during this experiment was approximately 0.09 mL/hr. Figure 3.8 is a plot of pH *vs.* time. The pH increased from 6.04 to approximately 6.32 before levelling off. From day 9 (216 hours) to the end of the experiment, the pH remained constant indicating that the precipitation was approximately equal to the titration rate. The "steady state" pH was much higher than in the  $Sr^{2+}$  or  $Ba^{2+}$  experiments conducted at the same titration rate due the inhibiting effect of  $Zn^{2+}$  on calcite precipitation.

An X-ray diffraction analysis of the precipitate identified the presence of both aragonite and calcite (Figure 3.9). The aragonite peaks were observed to be of greater intensity, suggesting that the majority and possibly all of the surface precipitate was aragonite. It was therefore not possible to identify the proportion of zinc solid solution partitioning which involved calcite. An overall  $D_{Zn}$  value of 0.8 for partitioning into both solid phases was calculated for the period from day 9 to the end of the experiment using Equation 3-6. The precipitation rate during this period was between 3 and 19 nmole/mg-min. No further experiments of this type were conducted due to the formation of aragonite and the resulting uncertainty regarding the solid phase responsible for partitioning.

### 3.5.4 Cadmium

Complete data sets for each of the cadmium experiments are provided in the Appendix. The duration, titration volume, aqueous composition, pH, the steady state interval and distribution coefficient values are included in that data set. The main premise of these experiments was that a steady state condition was attained when the  $X_{CdCO_{340}}$  of the precipitate became equal to that of the titrant. Figures 3.10 through 3.18 plot [Cd<sup>2+</sup>] vs. time for each of the cadmium experiments as exhibited by nearly state condition was indeed achieved in each of the experiments as exhibited by nearly constant [Cd<sup>2+</sup>] in spite of continued titration of the Ca<sub>1-x</sub>Cd<sub>x</sub>Cl<sub>2</sub> solution. As expected, the [Cd<sup>2+</sup>] increased initially, but in all cases the [Cd<sup>2+</sup>] eventually leveled



Figure 3.8 A plot of pH vs. time for the zinc experiment.

| SAMPLE | TIME  | рН   | Ca <sup>2+</sup> | Zn <sup>2+</sup> | Ca <sup>2+</sup> | Zn <sup>2+</sup> | DISTR. |
|--------|-------|------|------------------|------------------|------------------|------------------|--------|
| #      | HOURS |      | moles/L          | moles/L          | moles/L          | moles/L          | COEFF  |
|        |       |      |                  |                  | (+TITR.)         | (+TITR.)         | D-H    |
| E-1    | 0.0   | 6.04 |                  |                  | 0.011            | 0.000027         |        |
| E-3    | 2.5   | 6.03 | 0.010            | 0.000030         | 0.012            | 0.000033         | -2.92  |
| E-4    | 19.5  | 6.09 | 0.010            | 0.000028         | 0.0108           | 0.000030         | 1.19   |
| E-5    | 23.5  | 6.08 | 0.012            | 0.000035         | 0.0138           | 0.000035         | 1.31   |
| E-6    | 40.5  | 6.10 | 0.013            | 0.000033         | 0.0137           | 0.000034         | 1.12   |
| E-7    | 47.0  | 6.10 | 0.012            | 0.000027         | 0.0134           | 0.000032         | 1.35   |
| E-8    | 65.7  | 6.15 | 0.014            | 0.000033         | 0.0164           | 0.000033         | 0.70   |
| E-9    | 90.0  | 6.18 | 0.019            | 0.000028         | 0.0206           | 0.000029         | -1.28  |
| E-10   | 112.7 | 6.24 | 0.018            | 0.000031         | 0.0188           | 0.000031         | -0.70  |
| E-11   | 119.7 | 6.23 | 0.015            | 0.000025         | 0.017            | 0.000027         | 1.06   |
| E-12   | 137.7 | 6.26 | 0.019            | 0.000031         | 0.0196           | 0.000031         | 1.15   |
| E-13   | 142.2 | 6.27 | 0.016            | 0.000026         | 0.0177           | 0.000026         | 0.84   |
| E-14   | 160.7 | 6.28 | 0.016            | 0.000023         | 0.0166           | 0.000025         | 1.01   |
| E-15   | 166.8 | 6.28 | 0.022            | 0.000033         | 0.0238           | 0.000034         | 1.02   |
| E-16   | 184.7 | 6.26 | 0.021            | 0.000030         | 0.0221           | 0.000030         | 1.05   |
| E-17   | 191.2 | 6.27 | 0.022            | 0.000040         | 0.0224           | 0.00004          | 32.02  |
| E-18   | 191.7 | 6.27 | 0.025            | 0.000033         | 0.0253           | 0.000033         | -1.77  |

| SAMPLE | TIME  | рН   | Ca <sup>2+</sup> | Zn <sup>2+</sup> | Ca <sup>2+</sup> | Zn <sup>2+</sup> | DISTR. |
|--------|-------|------|------------------|------------------|------------------|------------------|--------|
| #      | HOURS |      | moles/L          | moles/L          | moles/L          | moles/L          | COEFF  |
|        |       |      |                  |                  | (+TITR.)         | (+TITR.)         | D-H    |
| E-19   | 192.2 | 6.27 | 0.022            | 0.000031         | 0.0235           | 0.000031         | 0.36   |
| E-20-1 | 209.7 | 6.32 | 0.026            | 0.000032         | 0.0258           | 0.000032         | 0.40   |
| E-20-2 | 209.7 | 6.32 | 0.025            | 0.000031         | 0.0257           | 0.000031         | 1.60   |
| E-21   | 214.7 | 6.33 | 0.027            | 0.000028         | 0.0287           | 0.000028         | -2.91  |
| E-22   | 239.2 | 6.34 | 0.028            | 0.000029         | 0.0312           | 0.000030         | -1.18  |
| E-23   | 278.7 | 6.33 | 0.031            | 0.000030         | 0.0333           | 0.000030         |        |
| E-24   | 303.7 | 6.34 | 0.031            | 0.000028         | 0.0332           | 0.000028         | 1.13   |
| E-25   | 329.2 | 6.35 | 0.032            | 0.000024         | 0.0321           | 0.000024         | 3.73   |
| E-26   | 333.0 | 6.32 | 0.029            | 0.000023         | 0.0295           | 0.000023         | 0.15   |
| E-27   | 335.5 | 6.30 | 0.028            | 0.000023         | 0.0282           | 0.000023         | -0.10  |



Figure 3.9 X-ray diffraction pattern for the solids collected at the conclusion of the zinc experiment. The symbols A and C denote aragonite and calcite peaks, respectively.

off. The nearly constant aqueous concentrations of cadmium with respect to time are important for two reasons: (1) as discussed above, they demonstrate that a steady state condition was reached, and (2) it supports the conclusion that solid solution formation and not adsorption was responsible for the partitioning of cadmium to calcite.

The precipitation rate,  $X_{CdCl_{1}, titr.}$ ,  $X_{CdCO_{3un'}, mb}$ ,  $D_{Cd, titr.}$ , and  $D_{Cd, mb}$  values for all of the cadmium experiments are shown in Table 3.4.  $X_{CdCO_{3un'}, mb}$  is an estimate of the  $X_{CdCO_{3un}}$  precipitated during the steady state portion of the experiment and was calculated using mass balance equations on calcium and cadmium. The similarity of the values of  $X_{CdCl_{1}, titr.}$  and  $X_{CdCO_{3un'}, mb}$  supports the assumption that a steady state condition was indeed reached in each case.  $D_{Cd, titr.}$  values were calculated for each sampling event during the experiment using Equation 3-7. Each  $\overline{D}_{Cd, titr.}$  value presented in Table 3.4 is an average of the  $D_{Cd, titr.}$  values obtained during the steady state portion of an experiment. The  $\overline{D}_{Cd, mb}$  values were determined in the same manner except that  $X_{CdCO_{3un'}, mb}$  was used to represent  $X_{CdCO_{3un'}}$ . Little difference between the  $D_{Cd, titr.}$  values and the  $D_{Cd, mb}$  values are observed indicating that the steady state assumption was valid and that  $X_{CdCl_2, titr.}$  adequately represents  $X_{CdCO_{3un'}}$  precipitated during each defined steady state interval. From this point on  $\overline{D}_{Cd}$  refers to the value  $\overline{D}_{Cd, titr.}$  as defined above.

 $\bar{D}_{Cd}$  values are plotted *vs.* precipitation rate in Figure 3.19.  $\bar{D}_{Cd}$  values decrease as the precipitation rate increases. With the exception of the results from experiment 43, at low precipitation rates (< 0.5 nmoles/mg-min), little variation of  $\bar{D}_{Cd}$  as a function of precipitation rate is observed. The apparent lack of dependence of  $\bar{D}_{Cd}$  on precipitation rate indicates that equilibrium partitioning may have occurred. Therefore, an average of these data points, 1240 ±240, provides a reasonable estimate of  $D_{Cd,eq}$ . Table 3.4: Precipitation rates,  $X_{CdCl_2, titr.}$ ,  $X_{CdCO_{3(n)}, mb}$ , and  $\overline{D}_{Cd}$  values are presented for the cadmium coprecipitation experiments.  $X_{CdCl_2, titr.}$  is the mole fraction of CdCl<sub>2</sub> which was used as a titrant during the experiment.  $X_{CdCO_{3(n)}, mb}$  is the mole fraction of CdCO<sub>3</sub> precipitated during the steady state portion of the experiment and was calculated via mass balance equations on cadmium and calcium.  $\overline{D}_{Cd}$  values were calculated using both  $X_{CdCl_2, titr.}$  and  $X_{CdCO_{3(n)}, mb}$  to represent the  $X_{CdCO_{3(n)}}$  of the precipitate.

| Experiment<br># | Precipitation<br>Rate (Min.)<br>nmoles/(mg-<br>min) | Precipitation<br>Rate (Max.)<br>nmoles/(mg-<br>min) | $X_{CdCl_2, \ titrant}$ | $X_{CdCO_{3(s)}, mb}$ | $ar{D}_{\mathit{Cd, titr.}}$ | $ar{D}_{\mathit{Cd, mb}}$ |
|-----------------|---|---|-------------------------|-----------------------|------------------------------|---------------------------|
| 32              | 0.4   | 0.9   | 0.063                   | 0.060                 | 1069                         | 1015                      |
| 33              | 1.3   | 2.3   | 0.063                   | 0.061                 | 861                          | 832                       |
| 37              | 12  | 28  | 0.063                   | 0.072                 | 239                          | 275                       |
| 38              | 28  | 99  | 0.063                   | 0.049                 | 201                          | 154                       |
| 39              | 0.6   | 0.8   | 0.170                   | 0.199                 | 2006                         | 2456                      |
| 40              | 0.12  | 0.15  | 0.063                   | 0.060                 | 1294                         | 1229                      |
| 42              | 0.05  | 0.06  | 0.063                   | 0.055                 | 1486                         | 1286                      |
| 43              | 0.014   | 0.015   | 0.063                   | 0.071                 | 3041                         | 3466                      |
| 46              | 0.012   | 0.013   | 0.063                   | 0.059                 | 1123                         | 1047                      |



Figure 3.10 Plot of total cadmium in solution, [Cd], vs. time for experiment 32.



Figure 3.11 Plot of total cadmium in solution, [Cd], vs. time for experiment 33.



Figure 3.12 Plot of total cadmium in solution, [Cd], vs. time for experiment 37.



Figure 3.13 Plot of total cadmium in solution, [Cd], vs. time for experiment 38.



Figure 3.14 Plot of total cadmium in solution, [Cd], vs. time for experiment 39.



Figure 3.15 Plot of total cadmium in solution, [Cd], vs. time for experiment 40.



Figure 3.16 Plot of total cadmium in solution, [Cd], vs. time for experiment 42.



Figure 3.17 Plot of total cadmium in solution, [Cd], vs. time for experiment 43.



Figure 3.18 Plot of total cadmium in solution, [Cd], vs. time for experiment 46.


Figure 3.19  $D_{Cd}$  vs. precipitation rate plot for the cadmium experiments.

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As discussed earlier for barium and strontium, for the partitioning of trace levels of cadmium into calcite,  $D_{Cd,eq}$  is related to  $\zeta_{CdCO_{cd}}$  by

$$D_{Cd} = \frac{K_{s0, CaCO_{3(s)}}}{K_{s0, CdCO_{3(s)}} \zeta_{CdCO_{3(s)}}}$$
(3-11)

Using a  $K_{s0}$  value for otavite (CdCO<sub>3</sub>) of 10<sup>-12.1</sup> (Stipp *et al.*, 1993), and a  $D_{Cd,eq}$  value of 1240 ±240,  $\zeta_{CdCO_{3(n)}}$  is calculated to be 3.4 with a 99% probability range from 2.8 to 4.2. A  $\zeta_{CdCO_{3(n)}}$  value of 3.4 corresponds to a value of 1.4 ±0.2 for the parameter  $a_0$  in the two-suffix Margules equation.

# 3.6 Discussion

# 3.6.1 Solid Solution Theory

The substitution of one cation for another in the crystal structure is dependent upon several equilibrium and non-equilibrium effects. Non-equilibrium effects are caused by rate dependent processes, such as precipitation or dissolution, which result in a solid solution/aqueous solution system which changes composition as it approaches equilibrium. The experiments discussed above illustrate the importance of precipitation rate on the non-equilibrium partitioning of divalent cations into calcite.

At high precipitation rates, a  $D_{Me}$  value will approach unity, reflecting a decrease in metal ion selectivity. The mechanisms which may be responsible for this effect will be discussed in Chapter 4. At low precipitation rates, the  $D_{Me}$  value is expected to approach the equilibrium value. The extent of partitioning at equilibrium is expected to be dependent upon several factors, including: ionic radius, ionic charge, electronegativity, end member solubility, and crystal class. Table 2.1 provides this information for Ba<sup>2+</sup>, Sr<sup>2+</sup>, Cd<sup>2+</sup> and Ca<sup>2+</sup> and their respective carbonate phases. As discussed in Chapter 2, ideal solid solution occurs when the substituent exhibits no preference between the end member phases (*i.e.*, Cd<sup>2+</sup> into CdCO<sub>3</sub> vs. Cd<sup>2+</sup> into CaCO<sub>3</sub>). In the absence of experimental or empirical data, ideal solid solution has been assumed to represent metal partitioning behavior in solid solution/aqueous solution systems (*i.e.*, Griffioen, 1994). The extent to which a substituent will behave ideally is likely to depend upon the similarity of its properties listed in Table 2.1 to that of calcium in calcite. Under ideal mixing conditions, Equation 2-18 becomes:

$$D_{Me,ideal} = \frac{K_{s0, CaCO_{3(r)}}}{K_{s0, MeCO_{3(r)}}} .$$
(3-12)

Thus, for ideal solid solutions, the value of  $D_{Me}$  depends only upon the solubility differences between the two end members.  $D_{Me,ideal}$ ,  $D_{Me,eq}$ ,  $\zeta_{MeCO_{3(e)}}$ , and  $a_0$  values for Cd<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> equilibrium partitioning into calcite are given in the Table 3.5.

| Cation           | $D_{Me,ideal}$ | D <sub>Me,eq</sub> | ζ <sub>MeCO<sub>3(s)</sub></sub> | <i>a</i> <sub>0</sub> |
|------------------|----------------|--------------------|----------------------------------|-----------------------|
| Cd <sup>2+</sup> | 4170           | 1240 ±240          | 2.8-4.2                          | 1.2-1.6               |
| Sr <sup>2+</sup> | 6.2            | 0.021 ±0.003       | 257-342                          | 5.5-5.8               |
| Ba <sup>2+</sup> | 1.2            | 0.012 ±0.005       | 71-172                           | 4.3-5.1               |

Table 3.5: Parameters for Cd<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> partitioning to calcite.

The  $D_{Ba,eq}$  and  $D_{Sr,eq}$  values obtained in this investigation are more than two orders of magnitude smaller than the corresponding  $D_{Me,ideal}$  values. The  $D_{Ba,ideal}$  and  $D_{Sr,ideal}$  values are greater than unity and indicate that in the absence of non-ideality effects,  $Sr^{2+}$  and  $Ba^{2+}$  would prefer the solid solution phase. In fact, the  $D_{Ba,eq}$  and  $D_{Sr,eq}$  values are much less than unity, and  $Ba^{2+}$  and  $Sr^{2+}$  prefer to partition into the aqueous phase due to non-ideality effects. This type of behavior for the substitution of  $Ba^{2+}$  and  $Sr^{2+}$  for  $Ca^{2+}$  in calcite is consistent with the properties listed in Table 2.1.  $Sr^{2+}$  and  $Ba^{2+}$  have ionic radii which are much larger than  $Ca^{2+}$ . In addition,  $Sr^{2+}$  and  $Ba^{2+}$  prefer to form orthorhombic carbonate crystals and therefore may be less likely to partition into calcite, which has a rhombohedral structure. The  $D_{Cd,eq}$  value estimated in this study is within an order of magnitude of the  $D_{Cd,ideal}$  estimate and the  $\zeta_{CdCO_{340}}$  value of 2.8-4.2 indicates only relatively weak non-ideality. The fact that Cd<sup>2+</sup> exhibits close to ideal behavior when substituting for Ca<sup>2+</sup> in calcite is not surprising since the ionic radii are similar and the crystal classes of otavite and calcite are the same (Table 2.1).

# 3.6.2 Comparison of Measured $D_{Me,eq}$ Values to Previous Data

#### 3.6.2.1 Strontium

The vast majority of previous investigations have reported  $D_{sr}$  values in excess of the  $D_{sr,eq}$  value determined in this study (Figure 3.1). Only the experimental and empirical investigations obtained at low precipitation rates compare favorably with these results. Lorens (1981) obtained  $D_{sr}$  values of approximately 0.03 from his lowest precipitation rate experiments and a  $D_{sr}$  value of 0.027 ±0.011 from recrystallization experiments. However, Lorens' (1981) lowest precipitation rate experiments continued to show a dependence of  $D_{sr}$  on precipitation rate, indicating that equilibrium partitioning was not achieved. Interestingly, it appears that equilibrium partitioning conditions were reached at a higher precipitation rate in this investigation than in Lorens' (1981) work. This may be the result of faster Ostwald ripening in this investigation due to the lower pH (6.0-6.2 as compared to 7.3-7.5) and thus higher calcite solubility.

Empirical  $D_{sr}$  values calculated from slowly recrystallized calcite may provide an independent check on the assumption that equilibrium conditions were reached. Apitz (1991) examined basally-lithified limestones which were formed at low rates such that  $Sr^{2+}$  uptake by calcite may have been characterized by equilibrium conditions. The empirical  $D_{sr}$  value calculated for those limestones of 0.026 ±0.003 is very similar to the  $D_{sr.eq}$  of 0.021 ±0.003 of this investigation.

## 3.6.2.2 Barium

Investigations into the partitioning of Ba<sup>2+</sup> into calcite are limited. None of the prior experiments were conducted at constant precipitation rates and solution compositions. Only a qualitative assessment of the precipitation rate dependence of  $D_{Ba}$  was provided by Kitano *et al.* (1971). The best previous estimate of equilibrium partitioning was provided by Pingitore and Eastman (1986). Their  $D_{Ba}$  value of 0.04 ±0.01 was from solids precipitated at a rate of 220 nmoles/(mg-min). This value is consistent with results of this investigation, as it plots with the data in this investigation. However, lower rates were required to attain the  $D_{Ba,eq}$  value obtained here.

#### 3.6.2.3 Cadmium

Lorens (1981) and Davis *et al.* (1987) have both examined the partitioning of cadmium into calcite at low precipitation or recrystallization rates.  $D_{Cd}$  vs. precipitation rate data from this study, Lorens (1981), and Davis *et al.* (1987) are shown in Figure 3.20.

Lorens' (1981) experimental procedure was similar to the procedure used in this investigation, with two notable exceptions: the solution concentrations of cadmium were not maintained constant by titration; and substantially less precipitate was laid down. As has been discussed in Section 2.4.1.1, not maintaining constant cadmium concentrations can lead to the formation of heterogeneous solids. Lorens' (1981) may have, in fact, avoided this problem by allowing only small amounts of precipitate to form before terminating the experiment. On the other hand, limiting the amount of precipitate which forms increases the relative effect of adsorption on the observed value of  $D_{Cd}$ .

The data from Lorens'(1981) investigation plots generally along the trend observed in this study. The fact that Lorens'(1981) data plots slightly higher than the data obtained here, may due to an adsorption effect on his measured  $D_{Cd}$  values. Experiments in this study were conducted at rates up to two orders of magnitude



**Figure 3.20**  $D_{Cd}$  vs. precipitation rate plot for data from this study, Lorens (1981), and Davis *et al.* (1987).

slower than Lorens (1981), possibly allowing for the attainment of equilibrium partitioning in this work and not in the experiments conducted by Lorens (1981).

Davis *et al.* (1987) examined the partitioning of cadmium to calcite in saturated solutions over time. Precipitation was not induced by titration. Solid solution formation during recrystallization was postulated as a mechanism for the slow uptake of cadmium by calcite. Since precipitation was not induced, the amount of precipitate formed was small and no direct evidence of solid solution was presented. The data from Davis *et al.* (1987) generally agree with an extrapolation of the data from this study, thus supporting the argument that the partitioning of cadmium to calcite observed by Davis *et al.* (1987) was due to the formation of a solid solution. Furthermore, most of the  $D_{Cd}$  values obtained by Davis *et al.* (1987) plot in the estimated region (1000-1500) of equilibrium partitioning. The general agreement of this data with our  $D_{Cd, eq}$  value adds to the validity of this estimate as the recrystallization rates observed by Davis *et al.* (1987) are an additional two orders of magnitude lower than the slowest experiments in this study.

## 3.6.3 Comparison of $D_{Sr,eq}$ to Miscibility Gap Data

Miscibility gap information from natural samples can be used to approximate the thermodynamic mixing parameters for solid solutions. If a regular solid solution is assumed, the relationship between  $a_0$  and the miscibility gap  $X_m$  is (Lippmann, 1980)

$$\ln (1-X_m) - \ln X_m = a_0 (1-2X_m) . \tag{3-13}$$

Lippmann used the data from several natural calcite and strontianite samples analyzed by Harder (1963) to estimate that  $X_m = 0.005$ . This value for the miscibility gap corresponds to  $a_0=5.3$  which compares favorably with the  $a_0$  value of 5.7 calculated from the  $D_{Sr,eq}$  value determined in this investigation.

# 3.6.4 Application of $D_{Sr}$ Values to Marine Calcites

The majority of the previous work done in the area of partitioning of strontium into calcite has been carried out for marine systems, which are often supersaturated with respect to calcite. The suitability of Holland's (1966) 0.14 value for  $D_{Sr}$  to marine low magnesian calcites probably reflects the fast precipitation rates which occur under organic deposition conditions. As these calcites recrystallize, the Sr content of the calcite will decrease as the solid solution/aqueous solution system approaches equilibrium. Accordingly, the Sr/Ca molar ratios of marine calcites have been observed to decrease as a function of burial and age (Apitz, 1991). By using an estimate of  $D_{Sr,eq}$ , several investigators (*i.e.*, Baker *et al.*, 1982; Delaney, 1989) have used this change in Sr content of calcites to determine the amount of recrystallization which has taken place. The  $D_{Sr,eq}$  value presented in this work will aid future assessments of recystallization.

# 3.6.5 Metal Transport in Natural Waters

Ground waters are often at or near equilibrium with respect to calcite. Therefore, it is likely that the rate of precipitation (or recrystallization) will be slow when compared to the biogenic deposition of marine calcites and is more likely to be represented by the equilibrium values determined in this investigation. Therefore, it is suggested that solid solution partitioning of strontium and barium to calcite for the ground water environment may be described by the  $D_{Sr}$  and  $D_{Ba}$  values of 0.021 ±0.003 and 0.012 ±0.005, respectively.

The migration of a contaminant relative to the average linear velocity of the water is described by the retardation factor,  $R_{i}$ .

$$R_{f} = \frac{v}{v_{c}} = 1 + \frac{\rho_{b}}{n} K_{d} , \qquad (3-14)$$

where:

v is the average linear velocity of the ground water;  $v_c$  is the velocity of the contaminant in ground water;  $\rho_b$  is the bulk mass density in g/cm<sup>3</sup>; and

## n is the aquifer porosity.

The term  $K_d$  is referred to as a distribution coefficient, and is defined as

$$K_{d} = \frac{\text{mass of contaminant in/on the solid per unit mass of solid}}{\text{concentration of solute in solution}}$$
(3-15)

 $K_d$  and  $R_f$  values have been used primarily to describe the retardation of contaminants by adsorption reactions. Solid solution partitioning also retards contaminant transport. Thus, the calculation of  $R_f$  values for solid solution precipitation will help illustrate the potential effect of this process on contaminant transport. Assuming a dilute solid solution,  $K_d$  values for solid solution partitioning can be calculated from  $D_{Me}$  values from the following equation:

$$K_{d} = \frac{D_{Me}}{[Ca^{2+}]} \frac{mols \ CaCO_{3(s)} \ precip.}{g \ of \ solid} \frac{1000 \ mL}{L} .$$
(3-16)

A retardation factor for solid solution partitioning can be calculated using Equation 3-14. The extent to which solid solution partitioning affects the retardation of contaminants in natural waters depends upon the  $D_{Me}$  value and the number of moles of solid solution precipitated per gram of solid. A convenient way to examine the effect of the amount precipitated on  $R_f$  is to consider solid solution precipitation (or recrystallization) in terms of the number of monolayers of calcite that are involved in solid solution/aqueous solution partitioning of the contaminant. Based on Möller and Sastri's (1974) estimate of 5 x 10<sup>14</sup> Ca atoms per square centimeter and a surface area of 0.8 m<sup>2</sup>/g, one monolayer of calcite contains 6.6 µmoles of Ca atoms per gram. Lorens (1981) has estimated that 25 monolayers of recrystallization occurred in saturated solutions over a four day period. Table 3.6 presents the retardation factors which have been calculated from  $D_{Me}$  values determined in this investigation for both one and 25 monolayer recrystallization of calcite.

 $Cd^{2+}$ , due to its similarity with  $Ca^{2+}$ , is significantly retarded by solid solution reactions with calcite. Conversely,  $Sr^{2+}$  and  $Ba^{2+}$  do not partition strongly into calcite.

Table 3.6:  $K_d$  and  $R_f$  values, calculated from  $D_{Me}$  values determined in this investigation, are presented for both 1 and 25 monolayers of calcite precipitation or recrystallization.

| CATION    | PRECIP. RATE  | $D_{Me}$ | 1 MONC  | LAYER       | 25 MONC | <b>JLAYERS</b> |
|-----------|---------------|----------|---------|-------------|---------|----------------|
|           | (nmol/mg-min) |          | $K_{d}$ | $R_{\rm f}$ | $K_{d}$ | R              |
| Cadmium   | 0.1           | 1300     | 850     | 5400        | 21,000  | 135,000        |
|           | 40            | 200      | 130     | 6,900       | 3,300   | 21,000         |
| Strontium | 1             | 0.02     | 0.013   | 1.08        | 0.33    | 3.08           |
|           | 500           | 0.14     | 0.09    | 1.58        | 2.31    | 15.6           |
| Barium    | 1             | 0.01     | 0.007   | 1.04        | 0.17    | 2.04           |
|           | 300           | 0.09     | 0.059   | 1.37        | 1.49    | 10.3           |

However, the 25 monolayer case suggests that retardation by solid solution may be important if the amount of calcite precipitated is high. Also  $Sr^{2+}$  and  $Ba^{2+}$  partitioning into calcite may be high in cases where a contaminant plume has produced calcite supersaturated ground water with resulting high precipitation rates. In conclusion, the effect of solid solution on metal retardation in a natural system depends upon: the  $Me^{2+}$  affinity for the solid solution phase under equilibrium conditions (expressed by  $D_{Me,eq}$ ); the precipitation rate of the system and its effect on  $D_{Me}$  values; and the number of monolayers precipitated or recrystallized.

#### 3.7 Summary

The solid solution partitioning of  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Cd^{2+}$ , and  $Zn^{2+}$  into calcite was examined using a constant composition method. For the cadmium experiments, a new method was developed which allows the aqueous concentration of  $Cd^{2+}$  to be maintained at a constant level during the course of the experiment in spite of its strong partitioning to calcite. The precipitation rate dependence of  $Me^{2+}$  partitioning into calcite was determined. Estimates of the  $D_{Me,eq}$  values were obtained from experimental data which appeared independent of precipitation rate. This data was evaluated in the context of previous investigations into calciton partitioning into calcite as well as its implications for the transport of  $Cd^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  in ground water.

#### **CHAPTER 4**

# FACTORS INFLUENCING SOLID SOLUTION PARTITIONING OF STRONTIUM INTO CALCITE: DISCUSSION OF PARTITIONING MECHANISMS

### 4.1 Introduction

In order to apply laboratory-derived distribution coefficients to natural systems it is helpful to consider which factors cause major changes in observed  $D_{Me}$  values. It has been established in Chapter 3 and in other investigations that precipitation rate has a major affect on the partitioning of divalent cations into calcite. Several other system parameters, such as aqueous composition and  $P_{co_2}$ , may also influence this partitioning (Morse and Bender, 1990; Burton and Walter, 1991). The objectives of this chapter are to evaluate the effects of system parameters on  $D_{Me}$  values, and to consider possible mechanisms for cation partitioning. The approach taken to accomplish the first objective is to evaluate the experimental results presented in Chapter 3 and compare these results to those of previous investigations. The observed dependencies of  $D_{Me}$  values on system parameters is then used to provide insights into the mechanisms responsible for cation partitioning into calcite.

## 4.2 Concentration Gradient Effects

Measured  $D_{Me}$  values are calculated using the concentrations of calcium and the partitioning metal in the bulk solution. Therefore, the presence of a concentration gradient between the mineral surface and the bulk solution will be a source of artifact when measuring  $D_{Me}$  values. During surface precipitation, ions are removed from the aqueous solution at the mineral surface. If precipitation is to continue, a concentration

gradient must develop, with concentrations higher in the bulk solution than at the mineral surface. At steady state, the diffusive flux of ions to the surface J, is equivalent to the loss of ions due to precipitation (expressed in nmoles/m<sup>2</sup>-min) and is described by Fick's first law

$$J = -D \frac{dC}{dx}$$
(4-1)

where x is the distance from the surface, D is the aqueous phase diffusion coefficient, C is the concentration of an ion which is precipitating (e.g.,  $Ca^{2+}$ ). The concentration gradient can be approximated as

$$\frac{dC}{dx} \approx \frac{C_{surf} - C_{bulk}}{\delta}$$
(4-2)

where  $C_{surf}$  and  $C_{bulk}$  are the aqueous concentrations of the metal in question at the surface and in the bulk solution, respectively, and  $\delta$  is the effective diffusion layer thickness.

Figure 4.1 presents a schematic representation of the concentration gradient from the calcite surface out to the bulk solution. If the precipitation rate is slow, only a small gradient is necessary to create the diffusive flux of ions to the surface needed to keep pace with the rate of ion removal from the aqueous solution by precipitation. In this case it can be assumed that  $C_{surf} = C_{bulk}$ . Conversely, if the precipitation rate is fast, then the rate of precipitation may be controlled solely by the diffusive transport of ions to the surface and a significant gradient may develop.

Increasing the rate of stirring in a solution during precipitation has been suggested as a convenient way to evaluate if diffusion-controlled precipitation reactions are occurring. As the rate of stirring increases, the value of  $\delta$  often decreases, thus causing the diffusion-controlled precipitation rate to increase. Therefore, if the rate of precipitation and the  $D_{Me}$  values are sensitive to the rate of stirring, then a diffusion effect is suggested.



Figure 4.1 Schematic of the concentration gradient of precipitating ions from the mineral/water interface out to the bulk solution. The term  $\delta$  represents the effective diffuse layer thickness. See text for details.

Experiments were conducted in this study at different stirring rates and significant changes in either precipitation rates or  $D_{Me}$  values were not observed. This suggests that in this work, the rates of precipitation were not diffusion limited and significant concentration gradients likely did not occur. However, an insensitivity of precipitation rate to stirring speed is not conclusive proof that the growth rate is not diffusion controlled. First, at relatively high stirring speeds the diffusion layer thickness may only decrease slightly in response to increased stirring (Janssen-van Rosmalen *et al.*, 1975), and second, when small micron-sized crystals are used as seed material (as they were in this work), they may move with the solution, allowing the diffusion layer thickness to be unaffected by the rate of stirring (Nielsen, 1984).

Convincing evidence regarding the magnitude of the concentration gradients that are possible at the surface of precipitating minerals can be obtained by determining the maximum possible concentration gradient for calcium in the experiments discussed in Chapter 3. The value of  $C_{surf}$  must be calculated to determine the magnitude of the concentration gradient. Rearrangement of Equations 4-1 and 4-2, yields

$$C_{surf} = C_{bulk} - \frac{\delta J}{D} .$$
 (4-3)

To estimate the value of  $\delta$  for a spherical particle falling by gravity through an aqueous solution, Nielsen (1980) derived that

$$\delta = (5.74) r^{0.145} (\Delta \rho)^{-0.285}$$
(4-4)

where r is the particle radius in  $\mu$ m and  $\Delta \rho$  is density difference between the solid and the solution. Using a particle radius of 2.5  $\mu$ m and  $\rho$  value for calcite of 2.71 g/cc, a  $\delta$  value of 5.6  $\mu$ m is calculated. Equation 4-4 likely provides an upper estimate of the diffusion layer thickness for the particles due to the vigorous stirring of the solutions in this study.

In order to evaluate if sizeable concentration gradients were attained in this study, the gradient required to sustain the fastest precipitation rate utilized was calculated. Precipitation rates were expressed in nmoles/mg-min in Chapter 3. Using

a specific surface area of 0.6 m<sup>2</sup>/g (based on particle radius and an equation derived by Walter (1983)), the precipitation rates given in Chapter 3 were converted to µmoles/m<sup>2</sup>-min. Experiment Z had a precipitation rate of approximately 930 µmoles/m<sup>2</sup>-min and a bulk solution concentration of calcium of 800 mg/L. Using a value of 10<sup>-9</sup> m<sup>2</sup>/s for *D*, and  $\delta = 5.6$  µm, the surface concentration of calcium calculated from Equation 4-3 is 796 mg/L. This represents the maximum gradient possible for this set of experiments since an upper estimate for  $\delta$  and the largest precipitation rate were used in this calculation. A similar calculation was made to determine the concentration gradient for Sr<sup>2+</sup>. A precipitation rate for Sr<sup>2+</sup> of 3.72 µmoles/m<sup>2</sup>-min was calculated by multiplying the precipitation rate for Ca<sup>2+</sup> by the  $X_{SrCO_{360}}$  (0.004 for Experiment Z). The bulk solution concentration of Sr<sup>2+</sup> was 53 mg/L. The surface concentration of Sr<sup>2+</sup> calculated from Equation 4-3 is 52.7 mg/L, virtually equivalent to the bulk solution concentration.

It is clear from these calculations that the effect of  $Ca^{2+}$  and  $Sr^{2+}$  concentration gradients on measured  $D_{Sr}$  values in this investigation are negligible and can be neglected. In addition, these small gradients indicate that the precipitation rate is probably not diffusion controlled but is instead controlled by surface processes. This conclusion is consistent with results obtained by Nancollas and Reddy (1971) and Brown *et al.* (1993).

# 4.3 Effect of $p_{CO_2}$ on $D_{Sr}$ Values

Burton and Walter (1991) have suggested that the  $p_{CO_2}$  of a solution has an effect on the incorporation of Mg<sup>2+</sup> into calcite. They observed that  $D_{Mg}$  values increased from 0.013 at 10<sup>-1</sup> atm to 0.024 at 10<sup>-4.5</sup> atm. The significance of  $p_{CO_2}$  on Sr<sup>2+</sup> partitioning to calcite can be examined by comparing the investigation of Lorens (1981) which was conducted at a  $p_{CO_2}$  of approximately 10<sup>-2</sup> atm with the results of this study which were conducted at a  $p_{CO_2}$  of 1 atm.  $D_{Sr}$  values determined in both investigations are plotted versus precipitation rate in Figure 4.2. While the  $D_{Sr}$  values measured by Lorens (1981) are somewhat higher at high precipitation rates, the difference between the two investigations narrows at low rates, indicating that the estimates of  $D_{Sr,eq}$  value for both systems are nearly the same. The somewhat higher  $D_{Sr}$  values observed by Lorens may be due to the higher pH in his study (7.3-7.5 versus 6.0-6.2). At higher pH values more  $Sr^{2+}$  is adsorbed and thus may have a greater likelihood of becoming incorporated in the crystal structure via trapping by the next layer of crystallization. This non equilibrium mechanism of cation incorporation will be discussed in greater detail in Section 4.7.

## 4.4 Precipitation Rate Effects

Precipitation rate effects on the partitioning of cations into calcite have been observed in several investigations.  $D_{sr}$  dependence on precipitation rate has been noted by both Lorens (1981) and in this study by evaluating  $Sr^{2+}$  partitioning to calcite over a wide range in precipitation rates. Mucci and Morse (1983) evaluated the effect of  $Mg^{2+}$  on  $Sr^{2+}$  partitioning to calcite over a more narrow range of precipitation rates.  $D_{sr}$  values determined in all three investigations are plotted in Figure 4.3. The data from Mucci and Morse (1983) are segregated according to the amount of  $Mg^{2+}$ (represented by the Mg:Ca ratio) present in the solution.

Figure 4.3 shows that the data from the Mg-free studies of Lorens (1981) and from this investigation are similar, while the data from Mucci and Morse (1983) for  $Mg^{2+}$ -containing solutions plot approximately an order of magnitude higher. Even over the limited range of precipitation rates examined by Mucci and Morse (1983), a precipitation rate effect is observed when the data sets for the different Mg:Ca ratios are plotted separately.

# 4.5 Mg<sup>2+</sup> Effect on Sr<sup>2+</sup> Partitioning to Calcite

From the previous section it is clear that the presence of magnesium in solution affects the relationship between  $D_{Sr}$  values and the precipitation rate. Two possible causes of this effect are: 1) the incorporation of Mg<sup>2+</sup> distorts the crystal lattice in a



Figure 4.2  $D_{Sr}$  vs. precipitation rate plot for the data from this study and from Lorens (1981).



**Figure 4.3**  $D_{s_r}$  vs. precipitation rate plot for the data from this study, Lorens (1981), and Mucci and Morse (1983). Mucci and Morse (1983) data are segregated according to the [Mg]/[Ca] ratio of the solution.

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way that allows more  $Sr^{2+}$  to partition into it; and/or 2) the role of  $Mg^{2+}$  as an inhibitor of calcite crystallization causes a higher state of disequilibrium when compared to a Mg-free solution at the same precipitation rate. (As will be discussed in Section 4.7, a higher state of disequilibrium may cause more  $Sr^{2+}$  to become incorporated due to faster step advance across the crystal surface.)

The crystal lattice distortion argument, presented by Mucci and Morse (1983), postulates that as the smaller  $Mg^{2+}$  ion becomes incorporated into the calcite lattice, cationic sites greater than  $Ca^{2+}$  are created. These larger sites would then be more able to accommodate the larger  $Sr^{2+}$  ion. Since Mucci and Morse (1983) were unable to directly identify this distortion of the calcite crystal lattice, indirect approaches are necessary to consider the validity of this hypothesis. The approach taken here is to evaluate the effect of saturation state on  $D_{Sr}$  values for a constant [Mg]/[Ca] ratio in solution. The saturation state,  $\Omega$ , is used to express the degree to which a solution is saturated with respect to a mineral phase. For calcite, the saturation state is defined as

$$\Omega = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{s0,CaCO_3}}.$$
(4-5)

Since the amount of  $Mg^{2+}$  incorporated in the calcite lattice is not positively correlated with saturation state, then no increase in lattice distortion effects should occur. As such, plotting the  $D_{Sr}$  data from Mucci and Morse (1983) versus saturation state for each [Mg]/[Ca] ratio in the aqueous solution may help distinguish the effects of saturation state from those caused by  $Mg^{2+}$  incorporation into the calcite lattice. Figure 4.4 shows the  $D_{Sr}$  data from Mucci and Morse (1983) segregated according to amount of  $Mg^{2+}$  present in solution and plotted against saturation state. It would not be expected that  $D_{Sr}$  values for the same [Mg]/[Ca] ratio in the aqueous solution would depend strongly on saturation state if crystal lattice distortion was the process responsible for the incorporation of  $Sr^{2+}$  into calcite. However, the increase in  $D_{Sr}$ values as the [Mg]/[Ca] ratio in the aqueous solution is increased can be largely explained by extrapolation of the  $D_{Sr}$  - saturation state trend observed at lower saturation states. This observation suggests that lattice distortion due to  $Mg^{2+}$  substitution is not the cause of the positive correlation between  $Sr^{2+}$  incorporation and the concentration of  $Mg^{2+}$  in solution.

An analysis of  $D_{Sr}$  values from other investigations also suggests that the lattice distortion hypothesis may not be valid. A lattice distortion effect should cause  $D_{Sr,eq}$  to vary as a function of the amount of magnesium incorporated into the lattice. The  $D_{Sr,eq}$  value observed by Apitz (0.026 ±0.003, 1991) for abiotic marine calcites generally agrees with the values for  $D_{Sr,eq}$  determined in this study (0.021 ±0.003) in spite of the difference in  $X_{MgCO_{10}}$  in the calcite precipitated (up to 3% MgCO<sub>3(s)</sub> for abiotic marine calcites versus essentially 0% in this study). Furthermore, Apitz (1991) did not find any correlation between the amount of magnesium incorporated into the calcite lattice and the  $D_{sr}$  values determined. These observations suggest that  $D_{sr}$ values are more closely related to the state of disequilibrium (*i.e.*, saturation state) rather than the amount of Mg incorporated in the crystal structure. The agreement between the  $D_{Sr,eq}$  values from this study and Apitz (1991) suggests that the calcite precipitated by Mucci and Morse (1983) exhibited greater partitioning of Sr<sup>2+</sup> to calcite because of the high saturation states during precipitation. However, if these calcites were permitted to equilibrate in solution, the above evidence suggests that as the calcites recrystallize at much lower saturation states, much of the Sr<sup>2+</sup> would be excluded from the solid phase.

#### 4.6 Saturation State Effect

As the saturation state of an aqueous solution increases from unity (or decreases from unity in the case of dissolution), the aqueous solution achieves a higher state of disequilibrium with respect to calcite. Therefore, saturation state may be a useful indicator of the non-equilibrium partitioning of metals to calcite. Figure 4.5 presents a plot of  $D_{Sr}$  values versus saturation state for all three of the above-mentioned investigations (this study; Mucci and Morse, 1983; and Lorens, 1981). A comparison of Figures 4.3 and 4.5 demonstrates the stronger relationship between  $D_{Sr}$  and saturation state than between  $D_{Sr}$  and precipitation rate. A good trend is observed in



Figure 4.4  $D_{sr}$  vs. saturation state plot for the data from Mucci and Morse (1983). Data are segregated according to the [Mg]/[Ca] ratio of the solution.



**Figure 4.5**  $D_{Sr}$  vs. saturation state plot for the data from this study, Lorens (1981), and Mucci and Morse (1983). Mucci and Morse (1983) data are segregated according to the [Mg]/[Ca] ratio of the solution.

spite of the differences in aqueous composition between the three investigations. This indicates that saturation state may be a more robust indicator of strontium partitioning into calcite than is the precipitation rate.

The following equation was used in order to fit the data shown in Figure 4.5:

$$D_{Sr} = D_{Sr,\max} \frac{A \Omega}{1 + (A \Omega)}$$
(4-6)

where A is a fitting constant,  $\Omega$  is the saturation state, and  $D_{Sr,max}$  is the maximum possible value of  $D_{Sr}$ . It has been observed by several investigators that  $D_{Me}$  values approach one as saturation states increase. Indeed, stoichiometric precipitation ( $D_{Me} =$ 1) has been observed during spontaneous nucleation reactions conducted at very high saturation states. Therefore, a  $D_{Sr,max}$  value of unity is appropriate. The best fit line for this data corresponds to an A value of 0.042 and is plotted along with the 90% confidence limits in Figure 4.6. The correlation coefficient for this non-linear fit is 0.85.

# 4.7 Mechanism for Sr<sup>2+</sup> Incorporation into Calcite

#### 4.7.1 Crystal Growth Theory

#### 4.7.1.1 General

Background information on crystal growth is necessary to adequately describe the possible mechanisms of  $Sr^{2+}$  partitioning to calcite. A brief review of crystal growth theory is presented below. For a more detailed discussion see Ohara and Reid (1973).

Ions which will eventually precipitate must first adsorb to the surface. The ions may then diffuse across the surface to a suitable incorporation site. The types of sites available for incorporation are illustrated in Figure 4.7. Flat areas of a crystal surface are not energetically favored because ions are bonded in only one direction (Figure 4.7, position A). Ions which are attached to edge faces are more energetically favored because they are bonded to both a step face and the surface (Figure 4.7, position B). Kink sites on steps are even more favorable as they are bonded in three directions (Figure 4.7, position C). As ions become incorporated along the step, the step edge



Figure 4.6  $D_{sr}$  vs. saturation state plot for the data from this study, Lorens (1981), and Mucci and Morse (1983). The solid line is the best fit to the data using equation 4.6.



Figure 4.7 Illustration of a crystal surface, depicting growth on a terrace (A), edge face (B), and kink site (C).

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migrates across the surface. So, the general process of crystal growth involves: 1) adsorption to the surface; 2) surface diffusion to a step face or kink site; and 3) step migration across the surface.

Ohara and Reid (1973) present several crystal growth theories which generally fall into three categories: 1) two dimensional growth; 2) surface diffusion and dislocation; and 3) mass transfer limited growth. The following discussion focusses only on the first two theories since it was determined in Section 4.2 that crystal growth was probably not mass transfer limited. Crystal growth theories are usually concerned with two processes: the formation of new steps; and the advancement of these steps across the surface.

#### 4.7.1.2 Step Formation

Two-dimensional growth theory differs from surface diffusion and dislocation growth theory principally in how each theory handles the generation of new steps. Two-dimensional growth requires the formation of nuclei on the surface, which form when growth units form into clusters. If these clusters are greater than a critical size they form stable nuclei for crystal growth. Along the edges of these nuclei are steps upon which crystal growth can proceed. Growth clusters which are smaller than the critical nucleus are not stable and are unlikely to lead to growth steps. An equation which has been suggested by Ohara and Reid (1973) to describe the dependence of the nuclei formation rate, I, on system parameters is

$$I = C_1 \sqrt{\ln (\Omega)} \exp \left[ \frac{-C_2}{T^2 \ln (\Omega)} \right]$$
(4-7)

where  $C_1$  and  $C_2$  are positive constants which are dependent upon system parameters such as molecular volume, step height, and interfacial free energy, and T is temperature in degrees Kelvin. From Equation 4-7 it is apparent that the rate of nuclei formation increases as the saturation state of the solution increases. The growth rate determined from the rate of nuclei formation by this mechanism is extremely small at low saturation states (Zhang and Nancollas, 1990). It has also been observed that at low saturation states, the growth rate predicted by this method of step creation is not sufficient to match measured growth rates (Ohara and Reid, 1973).

The fact that the nucleation of steps is too slow to account for the growth rates observed at low saturation states gave rise to the surface diffusion and dislocation model of Burton, Cabrera and Frank (1951). This model, referred to as the BCF model, relies on the formation of steps at screw dislocation sites. Screw dislocations are structural defects caused by the formation of a screw axis which is not normally present in the crystal structure. In this way, steps are perpetuated, and remain present even at low saturation states when the formation of stable nuclei on the surface is unlikely.

### 4.7.1.3 Step Migration

Once steps are formed, crystal growth occurs by the diffusion of ions to kink sites on steps. The incorporation of these ions leads to the migration of steps across the surface. The predicted rate of migration of steps differs with the model selected, from infinitely fast in the monomolecular growth theory to a zero spreading velocity in the polynuclear 2-D nucleation model. Intermediate cases are more likely, with step migration rates which are dependent on the saturation state and other system parameters. One possible equation to describe the dependence of the straight step velocity  $v_s$  on system parameters was presented by Ohara and Reid (1973) and is

$$v_{\rm s} = K_1 (\Omega - 1) \tanh [K_2 / (T \ln \Omega)],$$
 (4-8)

where  $K_1$  and  $K_2$  are functions involving surface diffusivities, kink spacing, and other parameters which relate solute surface concentrations near a step to the concentration of unincorporated ions on the step. Values for  $K_1$  and  $K_2$  are not easily obtained, so the determination of the step velocity is problematic. As expected, Equation 4-8 indicates that step velocity is dependent upon saturation state. An increase in step migration rate with increases in saturation state was observed in experiments conducted by Dunning and Albon (1958). The presence of inhibitors affects the relationship between step velocity and saturation state. Inhibitors, such as magnesium and phosphate species, are thought to retard crystal growth by adsorbing to and inactivating kink sites on the calcite surface (Reddy and Wang, 1980). Crystal growth continues in areas where the distance between adsorbed inhibitors is greater than the radius of the critical size two-dimensional nucleus,  $\rho_c$ . However, as the step squeezes between the adsorbed inhibitors, the radius of curvature of the step,  $\rho$ , decreases. As  $\rho$  decreases, the step velocity,  $\nu$ , also decreases as a result of the increase in surface free energy with curvature. A relationship suggested by Ohara and Reid (1973) to express the dependence of the step velocity on the radius of curvature is

$$v = v_s (1 - \rho_c / \rho)$$
 (4-9)

The use of this function is complicated by the dependence of  $\rho_c$  on saturation state, with  $\rho_c$  values decreasing as the saturation state increases. From Equation 4-9, it is apparent that as the amount of inhibitor increases,  $\rho$  values increase, and the step velocity decreases.

# 4.7.2 Mechanisms for the Incorporation of $Sr^{2+}$ into Calcite

Most previous investigations have focused on the dependence of  $D_{Me}$  values on the rate of precipitation. As discussed in Section 4.6, this work has found that  $D_{Sr}$ values are dependent upon saturation state, and not as directly on precipitation rate. This observation may provide some clues as to the mechanism responsible for the incorporation of divalent cations into calcite under non-equilibrium precipitation conditions. A mechanism which is sensitive to changes in saturation state is indicated.

As noted above, the rate of formation of two-dimensional nuclei is dependent on saturation state and may play a role in  $Sr^{2+}$  incorporation. The incorporation of greater amounts of  $Sr^{2+}$  during two-dimensional nucleation may occur because there are less steric constraints when  $Sr^{2+}$  adsorbs and becomes incorporated on a flat surface rather than at a kink site. When inhibitors are present, crystal growth by step migration is reduced, possibly allowing the formation of new steps by two-dimensional nucleation

to play a greater role in crystal growth. Two-dimensional nuclei formation as a possible method of  $Sr^{2+}$  incorporation is applicable only at high saturation states, since two-dimensional nucleation probably does not occur at low saturation states. Given the uncertainty regarding the validity of this method of step formation, particularly at low saturation states, this mechanism for  $Sr^{2+}$  incorporation is less appealing than a process involving step migration.

As discussed in Section 4.7.1.2, the migration of steps across the surface is likely to be dependent upon the saturation state of the solution. Therefore, as the saturation state increases, the step migration rate also increases. This may result in an increased amount of  $Sr^{2+}$  incorporated into the calcite lattice. Mechanistically,  $Sr^{2+}$  may initially become incorporated into a monolayer of crystallization. Before the next layer is put down, the steric constraints caused by the substitution of the larger  $Sr^{2+}$  ion for  $Ca^{2+}$ are minimized because the lattice is able to distort in the direction facing the solution (Figure 4.8a). In this way, the crystal structure may be able to accommodate more  $Sr^{2+}$  than if it were part of a 3-dimensional lattice. As the step on the next layer forms and is laid down on top of the previous layer, the steric constraints of ion substitution increases. If the rate of step advance is slow enough,  $Sr^{2+}$  can be excluded from the underlying layer (Figure 4.8b). As the saturation state increases, the rate of decking over increases, and  $Sr^{2+}$  may not be able to leave the solid phase quickly enough, and remains incorporated in the crystal lattice.

This "decking over" process can occur either by the formation of nuclei on the surface or more likely by the advance of steps across the surface. The rate at which "decking over" occurs would be dependent on the rate of nuclei formation, and/or the rate of migration of steps across the surface. The likelihood of both of these processes are positively correlated with saturation state. The dependence of  $D_{sr}$  values on saturation state supports the suggestion that  $Sr^{2+}$  is being incorporated by a decking over mechanism.

Scanning electron microscope (SEM) images of calcite overgrowths precipitated at high rates in this study show numerous multilayer steps on the surface (Figures 4.9). This is in stark contrast to the near absence of visible steps present on samples



Figure 4.8 Illustration of a possible mechanism for the partitioning of strontium to calcite from an aqueous solution. See text for details.

precipitated at low rates (Figure 4.10). A comparison between the crystal surfaces at low and high precipitation rates is provided in the high magnification images shown in Figure 4.11. These images indicate that crystal growth occurred on several layers simultaneously at high rates, increasing the likelihood that  $Sr^{2+}$  may have been trapped by a decking over process.

An evaluation of the  $D_{Sr}$  - saturation state relationship in the context of the decking over mechanism is warranted. For simplicity, increases in the radius of curvature due to the presence of inhibitors and its resulting effect on step migration rates are neglected in the following discussion. In Section 4.6, an empirical equation was fitted to the  $D_{Sr}$  - saturation state relationship. If increases in the rate of migration of steps was responsible for the increased incorporation of  $Sr^{2+}$  into calcite, then Equation 4-8 may help describe the  $D_{Sr}$  - saturation state relationship. A linear relation between  $D_{Sr}$  and step velocity is assumed, where:

$$D_{sr} = K_3 v_s$$
 (4-10)

An equation relating  $D_{Sr}$  to saturation state can then be written as

$$D_{\rm sr} = K_4 \; (\Omega - 1) \; \tanh \; [K_2 \; / \; (T \; \ln \; \Omega)] \; , \qquad (4-11)$$

where  $K_4$  is equal to the product of  $K_1$  and  $K_3$ . This equation would probably not apply to systems where precipitates are formed from solutions with high saturation states (*i.e.*, >100) where spontaneous nucleation may occur. A best fit line using Equation 4-11 is shown in Figure 4.12. The best fit values of  $K_2$  and  $K_4$  were determined to be 184 and 0.12, respectively. The goodness of this fit ( $r^2$ =0.86) using the step velocity relation, while not a rigorous test of this hypothesis, is encouraging.

#### 4.8 Conclusions

The effect of several system parameters on the incorporation of  $Sr^{2+}$  into calcite was examined. Major conclusions from this analysis are as follows.



**Figure 4.9** Scanning electron microscope images of calcite overgrowths precipitated at high rates. Top image is sample is of sample 4, bottom image is of sample Z.

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**Figure 4.10** Scanning electron microscope images of calcite overgrowths precipitated at low rates. Top image is sample is of sample 42, bottom image is of sample U.





**Figure 4.11** Scanning electron microscope images of calcite overgrowths. Top image is of sample 42, which was precipitated at 0.06 nmol/(mg-min), and bottom image is of sample 4, precipitated at 160 nmol/(mg-min).

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**Figure 4.12**  $D_{sr}$  vs. saturation state plot for the data from this study, Lorens (1981), and Mucci and Morse (1983). The solid line is the best fit using equation 4.11. See text for details.
• Concentration gradients from the surface to the bulk solution created during the precipitation experiments conducted in Chapter 3 were found to be minimal, with a negligible effect on measured  $D_{Sr}$  values. This suggests that surface reactions control the rate of precipitation, in agreement with prior investigations into the kinetics of calcite reactions (Nancollas and Reddy, 1971; Brown *et al.*, 1993).

• From a comparison between the results of this study and those of Lorens (1981), it was observed that changes in  $p_{co_2}$  resulted in only small changes in measured  $D_{Sr}$  values. This effect decreased as the precipitation rate decreased, indicating that  $D_{Sr,eq}$  values are unaffected by changes in  $p_{co_2}$ .

• The positive correlation between  $D_{sr}$  values and precipitation rate discussed in Chapter 3 was found to be consistent with the results obtained in previous investigations. However, for similar precipitation rates, the presence of Mg<sup>2+</sup> in solution resulted in higher  $D_{sr}$  values. Evidence was presented which suggested that lattice distortion was not responsible for this effect.

• It was suggested that saturation state is a better indicator of  $Sr^{2+}$  partitioning into calcite, possibly due to its effect on the rate of step migration. An equation relating  $D_{Sr}$  values to step velocity was successfully fitted to experimental results, supporting the hypothesis that  $Sr^{2+}$  is incorporated by a decking over mechanism involving step migration.

# CHAPTER 5 APPLICATION OF LABORATORY-DERIVED DISTRIBUTION COEFFICIENTS: LAKE CONSTANCE

#### 5.1 Background

Sedimentation processes can have a significant effect on the cycling of elements in lake and ocean waters. The partitioning of metals between solid and aqueous phases prior to and during sedimentation, through processes such as precipitation, adsorption, and desorption, makes a significant contribution to changes in the chemistry of lake waters. During the vegetative period, calcite has been shown to be a major component of the sedimenting particles in hard-water lakes. Therefore, solid solution partitioning into calcite may be an important process controlling the aqueous concentration of trace metals in these lakes.

A discussion of the factors which affect the precipitation of calcite in lakes is provided in the next section. This discussion is followed by a description of Lake Constance and its sedimentation fluxes of calcium and strontium. Data from Lake Constance are used to calculate  $D_{Sr}$  values and precipitation rates. The chapter ends with a comparison between these field values and experimentally-derived values determined in this and other investigations.

## 5.2 Calcite Precipitation In Lakes

An understanding of the rates and mechanisms of calcite precipitation is needed to accurately apply laboratory-derived distribution coefficients to lake systems. Several factors contribute to the precipitation of calcite in lakes. An important factor which directly and indirectly drives calcite precipitation is the elevated temperatures of near surface waters during spring and summer. Increased surface water temperatures reduce calcite solubility, and can also lead to spring and summer algal blooms if the lake has sufficient nutrients.

#### 5.2.1 Temperature Effects

During the winter, lake water temperatures do not vary appreciably with depth; this period is referred to as the period of homothermy. As air temperatures rise in the spring, the water temperature of the surface waters increases. The lower density of these warmer near surface waters can cause the lake to become thermally stratified. The uppermost layer of water, referred to as the epilimnion, is warmer than deeper water and is well mixed by wind and wave action. The lowermost layer of water, the hypolimnion, is characterized by colder and relatively stagnant waters. The region between the epilimnion and hypolimnion, where temperatures drop off quickly through the thermocline, is referred to as the metalimnion.

The elevated temperatures of the epilimnion increase the degree of saturation of these waters with respect to calcite: calcite becomes less soluble with increased temperatures. Temperature has been found to be the primary factor responsible for calcite precipitation in Fayetteville Green Lake (Brunskill, 1969). However, temperature alone may often not be sufficient to induce calcite precipitation, and several authors have suggested that phytoplankton activity also plays an important role (*e.g.*, Kelts and Hsü, 1978; Stabel, 1985).

## 5.2.2 Effect of Phytoplankton Activity

An increase in phytoplankton activity often occurs when thermal stratification occurs in fertile lakes. Phytoplankton activity causes several changes in the chemistry of lakes, all of which favor the formation of calcite. Indeed, phytoplankton consume  $CO_2$  as well as phosphorus, and may act as nucleation sites for calcite precipitation.

#### 5.2.2.1 $CO_2$ Consumption

Phytoplankton consume  $CO_2$ , and thereby cause the pH of near surface waters to increase. This increase in pH causes epilimnion lake water to become increasingly saturated with respect to calcite. As discussed in Chapter 4, the saturation state,  $\Omega$ , is used to express the degree to which a solution is saturated with respect to a mineral phase. For calcite, the saturation state is defined as

$$\Omega = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{s0,CaCO_1}} .$$
 (5-1)

A saturation state greater than 1 indicates that the solution is oversaturated with respect to the mineral phase. The pH increase caused by  $CO_2$  consumption results in the conversion of  $HCO_3^{-1}$  to  $CO_3^{2^-}$ . It is the increase in  $\{CO_3^{2^-}\}$  that causes the saturation state of calcite to increase. Saturation states greater than 15 were recorded within the top ten meters of Lake Constance in 1981 (Stabel, 1985).

#### 5.2.2.2 Role of Phosphorus

As has been discussed in Chapter 3, phosphorus in low concentrations has been found to inhibit the crystallization of calcite (Reddy and Nancollas, 1973; House, 1987). The inhibition of calcite crystallization by phosphorus allows the calcite saturation state to rise in response to increases in temperature and pH. Kuchler-Krischum and Kleiner (1990) have observed that calcite crystals were present in Lake Constance only after phosphorus concentrations decreased to concentrations less than 10 micrograms per liter. The removal of phosphorus by phytoplankton may allow the supersaturated epilimnion waters to precipitate calcite unimpeded.

#### 5.2.2.3 Nucleation of Calcite by Algae

Stabel (1986) has suggested that calcite precipitation is initiated by heterogeneous nucleation on the cell walls of certain algal species. This conclusion was based on the fact that calcite supersaturation maxima were not found to be in phase with maximum particulate fluxes of calcium. Stabel (1986) observed that a time lag of one week

occurred between the maximum degree of calcite supersaturation and the maximum calcite settling flux. However, the maximum calcite precipitation events were found to be associated with the maximum populations of certain algae species. It was suggested by Stabel (1986) that calcite precipitation was induced by heterogeneous nucleation by certain algal species.

While Kuchler-Krischun and Kleiner (1990) found no time lag between the maximum saturation state and the maximum settling flux of calcite, they did observe that calcite precipitation was associated with peaks in the population of a certain algal species (*Stephanodiscus hantzchii*). Both Stabel (1985) and Kuchler-Krischun *et al.* (1990) found, via scanning electron microscopy, that calcite crystals were associated with algae. This finding supports the hypothesis that calcite precipitation was heterogeneously nucleated by algae.

### 5.3 Sedimentation of Calcium and Strontium in Lake Constance

The water chemistry and sedimentation processes of Lake Constance have been studied extensively, making this lake an ideal system in which to apply laboratory-derived distribution coefficients. Lake Constance is a large and deep lake at the northern fringe of the Alps with a surface area of 538 km<sup>2</sup>, and a maximum depth of 252 meters. The lake has been fertilized heavily in the last three decades and is seasonally stratified. The sedimentation process of the lake is dominated by the annual cycle of calcite precipitation. In the spring and summer, algal blooms consume  $CO_2$  and water temperatures increase causing the epilimnion to become increasingly oversaturated with respect to calcite, ultimately leading to the precipitation and sedimentation of calcite.

Stabel *et al.* (1986) collected sediment samples during the period of January 1985 to March 1986 using sedimentation traps. The traps were set at a depth of 20 meters, which was the maximum depth of the euphotic zone. (The euphotic zone is the region of lake water where light penetration is sufficient for photosynthesis to occur.) Sedimentation rates for strontium and calcium were calculated from the analysis of these samples and were found to be highly correlated. It was suggested that the correlation between strontium and calcium sedimentation rates indicates that coprecipitation of strontium with calcite was a significant sink of strontium in Lake Constance. Stabel *et al.* (1986) conducted coprecipitation experiments using filtered lake water to test this hypothesis and found significant incorporation of strontium by calcite.

In a more thorough investigation during 1986, the seasonal fluctuations in the concentration of strontium and calcium in the water as well as the sinking material collected below the euphotic zone were determined for Lake Constance (Stabel, 1989). Two main periods of calcite formation (May and August) dominated the calcite sedimentation process. Stabel (1989) has suggested that calcite nucleation was initiated by *Asterionella formosa* in May, and *Fragilaria crotonesis* in August. The calcium and strontium fluxes were again strongly correlated (Figure 5.1).

#### 5.4 Data Analysis

 $D_{sr}$  and precipitation rate estimates for sedimentation events in the euphotic zone are necessary to evaluate the applicability of the experimentally-derived  $D_{sr}$  to natural systems. Data from Stabel (1989) were used to obtain  $D_{sr}$  and precipitation rate estimates for the sedimentation events in Lake Constance in 1986.

## 5.4.1 $D_{sr}$ Estimates

 $D_{sr}$  values were calculated using data which was digitized from figures in Stabel (1989). The aqueous compositions of strontium and calcium were taken from Figure 4 of Stabel (1989), which plots the seasonal variations of the atomic ratios of Sr/Ca in the aqueous phase of the euphotic zone (0-20 meter depth). Since a complete analysis of the aqueous composition was not available, the aqueous solution could not be speciated and thus the  $[Sr^{2+}]/[Ca^{2+}]$  could not be determined. Due to the weak hydrolysis of these ions, the  $[Sr_{total}]/[Ca_{total}]$  is likely to closely approximate the  $[Sr^{2+}]/[Ca^{2+}]$  of the aqueous phase and thus was used to estimate this ratio.



Figure 5.1 Seasonal variability in the Ca and Sr contents of settling matter in Lake Constance (from Stabel 1989).

The  $X_{srCO_{360}}$  values for calcite precipitated during the course of 1986 were calculated from the seasonal variability plots of percent dry weight (% DW) of calcium and strontium of settling matter (Figure 7 of Stabel, 1989). Assuming that all of the solid calcium and strontium was bound as carbonate, the values of  $X_{srCO_3}$  were calculated according to

$$X_{SrCO_{3(r)}} = \frac{(\% DW Sr)/(MW Sr)}{\left[\frac{\% DW Ca}{MW Ca}\right] + \left[\frac{\% DW Sr}{MW Sr}\right]}.$$
(5-2)

The  $D_{Sr}$  values were then calculated from Equation 3-1. The seasonal variation of the  $D_{Sr}$  values is shown in Figure 5.2.

## 5.4.2 Precipitation Rate Estimates

Estimates of the calcite precipitation rate in Lake Constance were calculated from the calcite sedimentation fluxes. Calcite sedimentation fluxes, in nmoles/(m<sup>2</sup>-min), were obtained by digitization of Figure 5 in Stabel (1989). These values represent fluxes of calcite through the base of the euphotic zone. The calculation of precipitation rates are normalized to the surface area on which precipitation occurred. To convert the sedimentation fluxes into precipitation rates, an estimate of the surface area of calcite on which precipitated occurred was estimated from the amount of calcite present in the euphotic zone. This conversion was accomplished using

$$R = \frac{SR}{L \times S \times C} , \qquad (5-3)$$

where: L is the depth in meters of lake water in which calcite precipitated,

S is the specific surface area in  $m^2/g$ ,

SR is the sedimentation rate in nmoles/ $(m^2-min)$ ,

R is the precipitation rate in nmoles/( $m^2$ -min), and

C is the concentration of calcite particles in lake water in  $g/m^3$ .



Figure 5.2 Seasonal variation in calculated  $D_{Sr}$  values for Lake Constance in 1986.

An estimate of *L* can be obtained by examining the relationship between calcite saturation state and water depth. Stabel (1985) reported high calcite saturation states during spring and summer for lake waters from the surface to 10 meters in depth for Lake Constance in 1981. Between a 10 and 20 meter depth, lake water saturation states were usually less than 10 and often undersaturated with respect to calcite ( $\Omega < 1$ ). A 10 meter depth is a reasonable estimate of the depth over which precipitation occurred (*L* in Equation 5-3). Estimates of *S* and *C* were determined from the literature. The surface area responsible for heterogeneous calcite precipitation can be estimated from the average particle diameter and the amount of calcite present in Lake Constance. Kuchler-Krischum and Kleiner (1990) obtained an average calcite crystal diameter of 40 µm and an average calcite content (*C* in Equation 5-3) of 4.8 g/m<sup>3</sup> for Lake Constance. The specific surface area (*S* in Equation 5-3) of a 40 µm calcite crystal has been estimated to be approximately 0.06 m<sup>2</sup>/g (Walter, 1983).

The seasonal variation in precipitation rates calculated from Equation 5-3 is plotted in Figure 5.3. The largest source of uncertainty in the calculation of precipitation rates from sedimentation rates is the estimate of surface area available for calcite precipitation. Estimates of the surface area responsible for calcite precipitation are complicated by the fact that the concentration of suspended calcite and other solids in lake water which may nucleate calcite change during the course of the year.

Calcite can nucleate on pre-existing calcite and possibly algae. The amount of suspended particulate calcite and algae present in a given lake varies during the course of a year. It is expected that the estimate of 4.8 g/m<sup>3</sup> by Kuchler-Krischum and Kleiner (1990) for Lake Constance would generally be low during periods of high sedimentation and high during periods of low sedimentation. Consequently the precipitation rate (in nmole/(m<sup>2</sup>-min)) during the May and August algal blooms was likely to have been lower than estimated.

### 5.4.3 $D_{sr}$ vs. Precipitation Rate

Figure 5.4 plots the variation in  $D_{sr}$  as a function of precipitation rate. The  $D_{sr}$  values for calcite precipitated from Lake Constance do not vary appreciably with the precipitation rates calculated above. Most  $D_{sr}$  values range from 0.2 to 0.4, with a slight tendency for higher values at low precipitation rates.

#### 5.5 Discussion

Chapter 3 described a dependence of  $D_{Sr}$  on precipitation rate in laboratory experiments in the absence of inhibitors (*i.e.*, phosphorus, magnesium). At high precipitation rates,  $D_{Sr}$  values were found to increase as the precipitation rate increased. At low precipitation rates, a constant  $D_{Sr}$  was observed and it was suggested that this value was representative of equilibrium partitioning of  $Sr^{2+}$  into calcite. The  $D_{Sr}$  values and precipitation rates calculated for Lake Constance in the previous sections provide an opportunity to apply our laboratory-derived  $D_{Sr}$  values to a natural system.

Figure 5.5 plots  $D_{sr}$  values *vs.* precipitation rate for Lake Constance samples as well as those obtained in the laboratory during this investigation and during that of Lorens (1981).  $D_{sr}$  values for calcite precipitated from Lake Constance are an order of magnitude higher than those calculated from this investigation (Chapter 3) or from Lorens (1981). The possible reasons for this difference are discussed in the following sections:

5.5.1 Effect of Variable  $p_{co}$ 

When phytoplankton consume CO<sub>2</sub>, it is expected that the  $p_{CO_2}$  of the water will decrease. However, as discussed in Chapter 4,  $p_{CO_2}$  effects are not likely to be responsible for significant changes in the partitioning of Sr<sup>2+</sup> in calcite. Lorens (1981) conducted his investigation at a  $p_{CO_2}$  of approximately 10<sup>-2</sup> atmosphere and the experiments discussed in Chapter 3 were conducted at 1 atmosphere. In spite of the



Figure 5.3 Seasonal variability in the calculated  $D_{Sr}$  values and precipitation rates for Lake Constance in 1986.



Figure 5.4  $D_{Sr}$  vs. precipitation rate plot for Lake Constance in 1986.



**Figure 5.5**  $D_{sr}$  vs. precipitation rate plot for Lake Constance data calculated in Section 5.3, and experimental data from this study, Lorens (1981), and Stabel (1986).

two orders of magnitude difference in  $p_{co_1}$ , the changes in  $D_{Sr}$  were small. The partitioning of  $Sr^{2+}$  in calcite does not appear to be sensitive to changes in the  $p_{co_1}$ .

## 5.5.2 Magnesium Incorporation in the Calcite Lattice

It has been observed by Mucci and Morse (1983) that as the value of  $X_{MgCO_{3so}}$  for calcite precipitates increase, the  $D_{Sr}$  value increases. The relationship between  $D_{Sr}$ and  $X_{MgCO_{3so}}$  was described by Mucci and Morse (1983) using the following equation:

$$D_{Sr} = 0.146 + 1.833 X_{MeCO...}$$
(5-4)

Mucci and Morse (1983) suggested that since Mg<sup>2+</sup> has a smaller ionic radius than Ca<sup>2+</sup>, the incorporation of magnesium in the calcite lattice creates a larger lattice position for Sr<sup>2+</sup>. Thus if this mechanism occurs, dissolved magnesium present in Lake Constance may become incorporated into calcite during precipitation and result in higher  $D_{Sr}$  values than found in our experimental studies. However, dissolved magnesium concentrations are too low in Lake Constance to explain the increase in  $D_{Sr}$  values. Dissolved Mg:Ca ratios in Lake Constance in 1982 ranged from < 0.1 to 0.35 (Stabel, 1986), which from the  $D_{Mg}$  values reported by Mucci and Morse (1983) would result in a  $X_{MgCO_{360}}$  of less than 0.01. A maximum  $D_{Sr}$  value of approximately 0.16 is obtained from Equation 5-4 above. Since  $D_{Sr}$  values for Lake Constance range from 0.2 to 0.4, this mechanism does not appear to explain Sr<sup>2+</sup> partitioning to calcite in this lake. Moreover, as discussed in Chapter 4 of this study, the increase in  $D_{Sr}$  with  $X_{MgCO_{360}}$  observed by Mucci and Morse (1983) may be due more to the inhibitory effect of magnesium rather than its incorporation in the crystal lattice.

#### 5.5.3 Effect of Inhibitors

The prediction of  $Sr^{2+}$  partitioning into calcite based on precipitation rate is made more difficult by the presence of inhibitors. Lake Constance contains dissolved magnesium and phosphorus, both of which are inhibitors of calcite formation. As discussed in Section 4.7.1.3, inhibitors affect the relationship between  $D_{Sr}$  and precipitation rate via the inactivation of nucleation sites (*i.e.*, kink sites). Crystal growth occurs only where the distance between adsorbed inhibitors is sufficiently large. In these areas, the rate of step advancement across the surface is a function of the saturation state. A more accurate prediction of  $Sr^{2+}$  partitioning into calcite may be obtained using plots of experimentally derived  $D_{Sr}$  values versus saturation state.

An estimate of the saturation state of the near surface waters of Lake Constance is necessary to test the applicability of the  $D_{Sr}$  - saturation state relationship developed in Chapter 4. While data on the saturation state of the Lake Constance waters from which these calcites precipitated is currently not available, Stabel (1985) observed saturation states of 10 to greater than 15 for the top 10 meters of Lake Constance in 1981. Figure 5.6 is a plot of the best fit line and the 90% confidence intervals for the  $D_{Sr}$  and saturation state data from the experimental investigations described in Chapter 4, as well as the data range for the Lake Constance samples. This predicted range of  $D_{Sr}$  values from the saturation state of the near surface lake water agrees well with the  $D_{Sr}$  values calculated for Lake Constance (0.2-0.4) and is a much better estimate of  $Sr^{2+}$  partitioning than the precipitation rate dependence plots discussed earlier.

It is postulated that inhibition of calcite formation by phosphorus resulted in elevated saturation states which caused an increase in the rate of step advance at the remaining active sites and greater  $Sr^{2+}$  incorporation. If this mechanism occurs, it is expected that  $D_{Sr}$  values would be positively correlated with dissolved phosphorus concentrations. Figure 5.7 is a plot of the seasonal variation of the  $D_{Sr}$  and dissolved phosphorus. Peaks in  $D_{Sr}$  in the beginning of May and the middle of June are also periods of high dissolved phosphorus. A plot of  $D_{Sr}$  versus dissolved phosphorus is shown in Figure 5.8.  $D_{Sr}$  and phosphorus are positively correlated with a sample correlation coefficient (r) of 0.75, which is significant at the 1 % level. A higher degree of correlation was not expected since the saturation state (and hence the rate of step advance) was likely affected by other factors such as the pH and temperature.



**Figure 5.6**  $D_{sr}$  vs. saturation state graph showing the best fit to the experimental data shown in Figure 4.5 and the data range calculated for Lake Constance.



Figure 5.7 Seasonal fluctuations in the calculated  $D_{sr}$  values and dissolved phosphorus concentrations for the epilimnion of Lake Constance. Phosphorus data are from Kleiner and Stabel (1989).



**Figure 5.8** Plot of  $D_{sr}$  values vs. dissolved phosphorus concentrations for the epilimnion of Lake Constance. Phosphorus data are from Kleiner and Stabel (1989).

## 5.6 Summary

The solid solution partitioning of  $Sr^{2+}$  in calcite was examined for precipitation events which occurred in Lake Constance in 1986. The relationship between  $D_{Sr}$  and precipitation rate was determined from data in Stabel (1989). Experimentally-derived  $D_{Sr}$  versus precipitation rate plots did not successfully model  $Sr^{2+}$  partitioning to calcite in Lake Constance. It was suggested that this was due to the fact that the inhibitory effect of phosphorus alters the  $D_{Sr}$ -precipitation rate relationship. Lake Constance  $D_{Sr}$ values were in agreement with experimentally-derived  $D_{Sr}$  values when plotted versus saturation state. The results of this study support the hypothesis put forth in Chapter 4: saturation state may be a better indicator of  $Sr^{2+}$  partitioning into calcite than measured precipitation rates.

## CHAPTER 6 SUMMARY AND CONCLUSIONS

The solubilities of metals in ground waters, lakes and ocean waters are reduced by the formation of  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions relative to pure phase precipitation. Therefore, metal partitioning to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions may be an important process affecting the mobility of metals in natural waters. The application of experimental results on the partitioning of metals to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions to natural systems is complicated by the dependence of this process on both the precipitation rate and the solution composition.

The extent of  $Sr^{2+}$ ,  $Ba^{2+}$ , and  $Cd^{2+}$  partitioning to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions was determined over a range of precipitation rates using a constant composition method. This method maintained nearly constant precipitation rates and solution compositions during the course of each experiment. From these experiments,  $D_{Me}$ values were found to approach unity as the precipitation rates were increased. At low precipitation rates,  $D_{Sr}$  and  $D_{Ba}$  values did not vary appreciably as a function of precipitation rate, indicating that equilibrium partitioning had occurred.  $D_{Sr,eq}$  and  $D_{Ba,eq}$  values of 0.021 ±0.003 and 0.012 ±0.005 were determined from these low precipitation rate experiments. A  $D_{Cd,eq}$  value of 1240 ±240 was estimated based on low precipitation rate experiments and the results from recrystallization experiments conducted by Davis *et al.* (1987).

The effect of solution composition on the partitioning of metals to  $Ca_{1-x}Me_xCO_{3(s)}$ solid solutions was evaluated by comparing the  $D_{Sr}$  values measured in this investigation with experimentally- and empirically-derived  $D_{Sr}$  values measured in previous investigations which used different solution compositions.  $D_{Sr}$  values from experiments conducted in the presence of magnesium were approximately an order of magnitude higher than the  $D_{Sr}$  values obtained in Mg-free experiments conducted at the same precipitation rate. Empirically-derived  $D_{Sr}$  values for abiotic calcites precipitated from magnesium-containing solutions (seawater) were in agreement with the  $D_{Sr,eq}$  value obtained in the Mg-free experiments conducted in this study. The Ca<sub>1-x</sub>Sr<sub>x</sub>CO<sub>3(s)</sub> solid solutions precipitated in both cases were only slightly supersaturated with respect to calcite, in contrast to the magnesium-containing experiments, which were precipitated from solutions which had much higher saturation states due to the inhibitory effect of magnesium. It is concluded from these and other observations that saturation state is a better indicator of metal partitioning to Ca<sub>1-x</sub>Me<sub>x</sub>CO<sub>3(s)</sub> solid solutions than precipitation rate; possibly due to the effect of saturation state on the migration of steps across the surface of a crystal. Step migration rates increase as the saturation state of the solution increases.  $D_{Me}$  values approaching unity as the saturation state increases may be caused by a decrease in the ion selectivity of the crystal lattice as the step migration rate increases.

Experimentally-determined  $D_{sr}$  values were compared to the  $D_{sr}$  values calculated from data obtained during whiting events in Lake Constance in 1986. The  $D_{sr}$  values calculated for Lake Constance were consistent with the best fit of the  $D_{sr}$  - saturation state plot prepared from both Mg and Mg-free experimental data. When plotted versus precipitation rate, the  $D_{sr}$  values, like the magnesium experiments discussed above, were an order of magnitude higher than what was expected based on the  $D_{sr}$  values obtained from this study. An inhibitory effect was again indicated, possibly the result of the inhibition of calcite precipitation by the high concentrations of phosphorus in Lake Constance.

This investigation has increased the level of knowledge regarding the partitioning of metals to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions under both equilibrium and non-equilibrium conditions. The estimates of  $D_{Me,eq}$  determined in this study will likely be applicable to systems characterized by slow precipitation rates. When non-equilibrium conditions are expected, experimentally-derived  $D_{Me}$  - saturation state plots, coupled with knowledge of the saturation state of the natural water may be the best approach for predicting the partitioning of metals to  $Ca_{1-x}Me_xCO_{3(s)}$  solid solutions and its impact on metal mobility.

## CHAPTER 7 REFERENCES

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## **APPENDIX A**

## EXPERIMENTAL DATA FOR CADMIUM EXPERIMENTS

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| run#:               | 32             |           | f           | file:cd32tab | )       |              |               |              |
|---------------------|----------------|-----------|-------------|--------------|---------|--------------|---------------|--------------|
| X-CdCl2 o           | f titrant:     | 0.063     |             |              |         |              |               |              |
| X-CaCl2 of titrant: |                | 0.937     |             |              |         |              |               |              |
|                     |                |           |             |              |         |              |               |              |
|                     |                |           | Cumulative  | [Cd]         |         | [Ca]         |               |              |
| sample              | time           |           | CaCdCl2     | total        | [Cd2+]  | total        | [Ca2+]        | Distribution |
| #                   | hours          | pН        | titr. (mls) | mg/l         | moles/l | mg/l         | moles/l       | Coeff.       |
| 32-1                | 0.0            | 6.03      |             | 0.02         | 1.7E-08 | 523          | 0.0123        | 48839        |
| 32-2                | 2.3            | 6.03      | 0.1         | 0.55         | 4.6E-07 | 536          | 0.0126        | 1820         |
| 32-3                | 5.3            | 6.04      | 0.2         | 0.50         | 4.2E-07 | 529          | 0.0124        | 1976         |
| 32-4                | 8.8            | 6.04      | 0.4         | 0.49         | 4.1E-07 | 514          | 0.0121        | 1959         |
| 32-5                | 27.8           | 6.04      | 1.4         | 0.79         | 6.6E-07 | 492          | 0.0116        | 1163         |
| 32-6                | 71.8           | 6.04      | 3.0         | 0.72         | 6.0E-07 | 545          | 0.0128        | 1414         |
| 32-7                | 81.8           | 6.03      | 3.4         | 1.02         | 8.6E-07 | 532          | 0.0125        | 974          |
| 32-8                | 96.8           | 6.04      | 4.1         | 0.99         | 8.3E-07 | 488          | 0.0115        | 921          |
| 32-9                | 104.8          | 6.03      | 4.4         | 0.87         | 7.3E-07 | 522          | 0.0123        | 1121         |
| 32-10               | 120.3          | 6.01      | 5.2         | 0.86         | 7.2E-07 | 532          | 0.0125        | 1155         |
| 32-11               | 128.8          | 6.03      | 5.5         | 0.84         | 7.1E-07 | 533          | 0.0125        | 1185         |
| 32-12               | 144.0          | 6.02      | 6.2         | 1.05         | 8.8E-07 | 544          | 0.0128        | 968          |
| 32-13               | 144.0          | 6.03      |             | 1.06         | 8.9E-07 | 583          | 0.0137        | 1027         |
| 32-15               | 146.0          | 6.03      | 6.6         | 1.06         | 8.9E-07 | 532          | 0.0125        | 937          |
| 32-16               | 153.0          | 6.04      |             | 0.86         | 7.2E-07 | 555          | 0.0130        | 1205         |
| 32-17               | 168.0          | 6.05      | 7.2         | 0.79         | 6.6E-07 | 535          | 0.0126        | 1265         |
| 32-18               | 177.0          | 6.02      | 7.6         | 0.94         | 7.9E-07 | 547          | 0.0129        | 1087         |
| 32-19               | 241.0          | 6.06      | 10.5        | 1.01         | 8.5E-07 | 531          | 0.0125        | 982          |
| Moles prec          | ip during stea | dy state: |             |              |         | Steady-stat  | e D:          | 1069         |
| Ca:                 | 3.35E-03       |           |             |              |         | -            |               |              |
| Cd:                 | 2.13E-04       |           | X-Cd:       | 0.060        |         | Steady state | e interval: 7 | -19          |

file:cd32tab

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| n#:<br>CdCl2 of<br>CaCl2 of | 33<br>titrant:<br>titrant: | 0.063<br>0.937 | file:33dist                         |                         |                   |                       |                   |                        |
|-----------------------------|----------------------------|----------------|-------------------------------------|-------------------------|-------------------|-----------------------|-------------------|------------------------|
| ample<br>#                  | time<br>hours              | Hq             | Cumulative<br>CaCdCl2<br>titr.(mls) | [Cd2+]<br>total<br>mg/l | [Cd2+]<br>moles/I | [Ca]<br>total<br>mg/l | [Ca2+]<br>moles/l | Distribution<br>Coeff. |
| 33-1                        | 0.0                        | 6.06           | 0                                   | 0.08                    | 7.14E-08          | 508                   | 0.012065          | 11357                  |
| 33-2                        | 4.0                        | 6.10           | 0.2                                 | 1.08                    | 9.64E-07          | 525                   | 0.012469          | 869                    |
| 33-3                        | 6.5                        | 6.13           | 1.2                                 | 1.04                    | 9.29E-07          | 540                   | 0.012825          | 929                    |
| 33-4                        | 8.5                        | 6.09           | 1.5                                 | 1.30                    | 1.16E-06          | 518                   | 0.012303          | 713                    |
| 33-5                        | 23.5                       | 6.11           | 4.1                                 | 1.28                    | 1.14E-06          | 544                   | 0.01292           | 760                    |
| 33-7                        | 32.5                       | 6.10           | 5.6                                 | 1.41                    | 1.26E-06          | 564                   | 0.013395          | 715                    |
| 33-8                        | 55.5                       | 6.10           | 9.4                                 | 1.14                    | 1.02E-06          | 596                   | 0.014155          | 935                    |
| 33-9                        | 73.5                       | 6.10           | 11.9                                | 0.86                    | 7.68E-07          | 533                   | 0.012659          | 1108                   |
| es preci                    | p. during ste              | ady-state:     |                                     |                         |                   | Steady sta            | te D:             | 861                    |
| Ca:<br>Cd:                  | 5.42E-03<br>3.52E-04       |                | X-Cd:                               | 0.061                   |                   | Steady sta            | te interval:      | 2-9                    |

| run#:                    | 37                       |                | f                     | ile:cd37tal   | -0      |                   |         |              |
|--------------------------|--------------------------|----------------|-----------------------|---------------|---------|-------------------|---------|--------------|
| X-CdCl2 of<br>X-CaCl2 of | f titrant:<br>* titrant: | 0.063<br>0.937 |                       |               |         |                   |         |              |
| sample                   | time                     |                | Cumulative<br>CaCdCl2 | [Cd]<br>total | [Cd2+]  | [Ca]<br>total     | [Ca2+]  | Distribution |
| <b>'</b> #               | minutes                  | Hd             | titr.(mls)            | mg/l          | moles/  | mg/l              | moles/I | Coeff.       |
| 37-1                     | 0                        | 6.05           |                       | 0.16          | 1.4E-07 | 619               | 0.0161  | 7738         |
| 37-2                     | 47                       |                | 0                     | 0.20          | 1.8E-07 | 670               | 0.0159  | 5796         |
| 37-3                     | 137                      | 6.10           | 1.9                   | 21.63         | 1.9E-05 | 645               | 0.0153  | 53           |
| 37-4                     | 277                      | 6.13           | 4.8                   | 6.39          | 5.7E-06 | 857               | 0.0203  | 238          |
| 37-5                     | 344                      | 6.13           | 6.2                   | 5.92          | 5.3E-06 | 757               | 0.0180  | 227          |
| 37-6                     | 397                      | 6.13           | 7.3                   | 5.83          | 5.2E-06 | 841               | 0.0200  | 256          |
| 37-7                     | 437                      | 6.12           | 8.1                   | 5.88          | 5.2E-06 | <i><b>772</b></i> | 0.0183  | 233          |
| Moles prec               | ip. during ste           | ady state:     |                       |               | •1      | Steady state      | D:      | 239          |

239

| ady state D:         | ady state interval: 5-7 |
|----------------------|-------------------------|
| Ste                  | Ste<br>0.072            |
|                      | X-Cd:                   |
| luring steady state: | 7.34E-04<br>5.72E-05    |
| oles precip. (       | Ca:<br>Cd:              |

129

| run#:<br>X-CdCl2 o | 38<br>f titrant: | 0.063      | fil                                 | le: cd38tab           |                   |                       |                   |                        |
|--------------------|------------------|------------|-------------------------------------|-----------------------|-------------------|-----------------------|-------------------|------------------------|
| X-CaCl2 of         | f titrant:       | 0.937      |                                     |                       |                   |                       |                   |                        |
| sample<br>#        | time<br>minutes  | pН         | Cumulative<br>CaCdCl2<br>titr.(mls) | [Cd]<br>total<br>mg/l | [Cd2+]<br>moles/l | [Ca]<br>total<br>mg/l | [Ca2+]<br>moles/l | Distribution<br>Coeff. |
| 38-1               | 0                | 6.14       |                                     | 0.05                  | 4.5E-08           | 782                   | 0.0186            | 27495                  |
| 38-2               | 35               | 6.17       | 2.7                                 | 11.95                 | 1.1E-05           | 822                   | 0.0195            | 123                    |
|                    | 55               | 6.18       | 4.2                                 | 12.42                 | 1.1E-05           | 875                   | 0.0208            | 126                    |
| ж.                 | 85               | 6.18       | 6.7                                 | 9.96                  | 8.9E-06           | 943                   | 0.0224            | 169                    |
| 38-5               | 105              | 6.18       | 8.4                                 | 8.57                  | 7.7E-06           | 886                   | 0.0210            | 185                    |
| 38-6               | 130              | 6.17       | 10.1                                | 7.85                  | 7.0E-06           | 890                   | 0.0211            | 203                    |
| 38-7               | 150              | 6.17       | 11.8                                | 7.21                  | 6.4E-06           | 860                   | 0.0204            | 213                    |
| 38-8               | 175              | 6.17       | 13.8                                | 7.64                  | 6.8E-06           | 847                   | 0.0201            | 198                    |
| 38-9               | 198              | 6.16       | 15.7                                | 7.56                  | 6.7E-06           | 816                   | 0.0194            | 193                    |
| 38-10              | 218              | 6.16       | 17.2                                | 7.33                  | 6.5E-06           | 808                   | 0.0192            | 197                    |
| Moles prec         | ip. during ste   | ady state: |                                     |                       | :                 | Steady state          | D:                | 201                    |
| Ca:                | 4.15E-03         |            |                                     |                       |                   | Steady state          | interval: 6       | 5-10                   |
| Cd:                | 2.13E-04         |            | X-Cd:                               | 0.049                 |                   | -                     |                   |                        |

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| X-CdCl2 of titrant: 0.17   |                        |
|--|------------------------|
|  |                        |
| X-CaCl2 of titrant: 0.83   |                        |
| Cumulative[Cd][Ca]sampletimeCaCdCl2total[Cd2+]total[Ca2+#hourspHtitr.(mls)mg/lmoles/lmg/lmoles/l | Distribution<br>Coeff. |
| 39-1 0.0 6.05 0.00 0.0E+00   |                        |
| 39-2 3.0 6.04 0.2 1.59 1.4E-06 632 0.015   | 0 2166                 |
| 39-3 7.5 6.04 0.3 1.65 1.5E-06 684 0.016   | 2 2259                 |
| 39-4 16.5 6.05 1.0 1.92 1.7E-06 630 0.015  | 0 1788                 |
| 39-5 25.5 6.03 1.4 1.92 1.7E-06 636 0.015  | 1 1805                 |
| 39-6 42.5 6.04 2.2 1.75 1.6E-06 647 0.015  | 4 2014                 |
| Moles precip. during steady state: Steady state D:   | 2006                   |
| Ca: 6.80E-04 Steady state interval   | 2-6                    |
| Cd: 1.69E-04 X-Cd: 0.199   |                        |

| run#:      | 40    |  |
|------------|-------|--|
| X-CdCl2 o  | 0.063 |  |
| X-CaCl2 of | 0.937 |  |

file:cd40tab

|        |       |      | Cumulative | [Cd2+] |         | [Ca]  |         |              |
|--------|-------|------|------------|--------|---------|-------|---------|--------------|
| sample | time  |      | CaCdCl2    | total  | [Cd2+]  | total | [Ca2+]  | Distribution |
| #      | hours | pН   | titr.(mL)  | mg/l   | moles/l | mg/l  | moles/l | Coeff.       |
| 40-1   | 0.0   | 5.99 |            | 0.13   | 1.2E-07 | 620   | 0.0147  | 8530         |
| 40-2   | 3.0   | 6.01 | 0.1        | 0.24   | 2.1E-07 | 756   | 0.0180  | 5634         |
| 40-3   | 23.5  | 6.03 | 1.0        | 0.42   | 3.8E-07 | 599   | 0.0142  | 2551         |
| 40-4   | 55.5  | 6.05 | 3.4        | 0.63   | 5.6E-07 | 575   | 0.0137  | 1632         |
| 40-5   | 68.0  | 6.04 | 4.0        | 0.67   | 6.0E-07 | 576   | 0.0137  | 1538         |
| 40-6   | 75.5  | 6.04 | 4.3        | 0.54   | 4.8E-07 | 586   | 0.0139  | 1941         |
| 40-7   | 94.0  | 6.02 | 5.1        | 0.64   | 5.7E-07 | 561   | 0.0133  | 1568         |
| 40-8   | 102.0 | 6.05 | 5.4        | 0.73   | 6.5E-07 | 579   | 0.0138  | 1419         |
| 40-9   | 116.5 | 6.07 | 6.1        | 0.70   | 6.3E-07 | 559   | 0.0133  | 1428         |
| 40-10  | 124.5 | 6.06 | 6.5        | 0.68   | 6.1E-07 | 563   | 0.0134  | 1481         |
| 40-11  | 139.0 | 6.03 | 7.1        | 0.86   | 7.7E-07 | 514   | 0.0122  | 1069         |
| 40-12  | 141.0 | 6.03 | 7.2        | 0.71   | 6.3E-07 |       |         |              |
| 40-13  | 141.0 | 6.03 | 7.2        | 0.85   | 7.6E-07 | 550   | 0.0131  | 1157         |
| 40-14  | 148.0 | 6.03 | 7.5        | 1.01   | 9.0E-07 | 554   | 0.0132  | 981          |
| 40-15  | 168.5 | 6.05 | 8.4        | 0.7    | 6.3E-07 | 543   | 0.0129  | 1387         |
| 40-16  | 199.5 |      |            | 0.76   | 6.8E-07 | 567   | 0.0135  | 1334         |
| 40-18  | 238.0 | 6.09 | 11.5       | 0.69   | 6.2E-07 | 535   | 0.0127  | 1387         |
|        |       |      |            |        |         |       |         |              |

Moles precip during steady state:

τ.

Steady state D: 1294

Ca: 3.01E-03 Cd: 1.92E-04 X-Cd: 0.060 Steady state interval: 8-18

132
| run#:          | 42            |        | f          | ile:cd42tab | )       |             |         |              |
|----------------|---------------|--------|------------|-------------|---------|-------------|---------|--------------|
| X-CdCl2 of tit | rant:         | 0.063  |            |             |         |             |         |              |
| X-CdCl2 of tit | rant:         | 0.937  |            |             |         |             |         |              |
|                |               |        | Cumulative | [Cd]        |         | [Ca]        |         |              |
| sample         | time          |        | CaCdCl2    | total       | [Cd2+]  | total       | [Ca2+]  | Distribution |
| #              | hours         | pН     | titr.(mLs) | mg/l        | moles/l | mg/l        | moles/l | Coeff.       |
| 42-1           | 0.0           | 6.04   |            | 0.19        | 1.7E-07 | 590         | 0.0140  | 5554         |
| 42-2           | 21.5          | 6.02   | 0.9        | 0.31        | 2.8E-07 | 551         | 0.0131  | 3179         |
| 42-3           | 48.0          | 6.05   | 2.1        | 0.35        | 3.1E-07 | 569         | 0.0135  | 2908         |
| 42-4           | 77.0          | 6.06   | 3.3        | 0.51        | 4.6E-07 | 539         | 0.0128  | 1890         |
| 42-5           | 118.0         | 6.05   | 5.2        | 0.59        | 5.3E-07 | 513         | 0.0122  | 1555         |
| 42-6           | 142.0         | 6.04   | 6.3        | 0.64        | 5.7E-07 | 487         | 0.0116  | 1361         |
| 42-7           | 150.5         | 6.04   | 6.6        | 0.62        | 5.5E-07 | 503         | 0.0119  | 1451         |
| 42-9           | 174.0         | 6.06   | 7.6        | 0.57        | 5.1E-07 | 503         | 0.0119  | 1578         |
| Moles precip.  | during steady | state: |            |             | Ş       | Steady stat | e D:    | 1486         |

| loles precip | . during steady      | / state: |       | Steady state D:            |
|--------------|----------------------|----------|-------|----------------------------|
| Ca:<br>Cd:   | 1.23E-03<br>7.21E-05 | X-Cd:    | 0.055 | Steady state interval: 5-9 |

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| 43             |   | f   | ile: cd43ta  | b  |   |   |   |
|----------------|---|---|--|--|---|---|---|
| of titrant:    | 0.063   |   |  |  |   |   |   |
| f titrant:     | 0.937   |   |  |  |   |   |   |
|                |   | Cumulative  | [Cd]   |  | [Ca]  |   |   |
| time           |   | CaCdCl2   | total  | [Cd2+]   | total   | [Ca2+]  | Distribution  |
| hours          | pН  | titr.(mls)  | mg/l   | moles/l  | mg/l  | moles/l   | Coeff.  |
| 0              | 6.06  |   | 0.06   | 5.4E-08  | 579   | 0.0138  | 17259   |
| 44             | 6.19  | 0.51  | 0.40   | 3.6E-07  | 488   | 0.0116  | 2182  |
| 212            | 6.04  | 2.52  | 0.31   | 2.8E-07  | 900   | 0.0214  | 5192  |
| 284            | 6.02  | 3.39  | 0.28   | 2.5E-07  | <b>479</b>  | 0.0114  | 3060  |
| 332            | 6.03  | 3.97  | 0.29   | 2.6E-07  | 535   | 0.0127  | 3299  |
| 380            | 6.00  | 4.49  | 0.37   | 3.3E-07  | 479   | 0.0114  | 2315  |
| 388            |   | 4.58  | 0.25   | 2.2E-07  | 488   | 0.0116  | 3491  |
| ip. during ste | eady state:   |   |  |  | Steady state  | e D:  | 3041  |
| 4.69E-04       |   |   |  |  | Steady state  | e interval:   | 5-8   |
| 3.58E-05       | X-Cd:   | 0.071   |  |  | 2   |   |   |
|                | 43<br>of titrant:<br>f titrant:<br>time<br>hours<br>0<br>44<br>212<br>284<br>332<br>380<br>388<br>cip. during sta<br>4.69E-04<br>3.58E-05 | 43<br>of titrant: 0.063<br>of titrant: 0.937<br>time<br>hours pH<br>0 6.06<br>44 6.19<br>212 6.04<br>284 6.02<br>332 6.03<br>380 6.00<br>388<br>tip. during steady state:<br>4.69E-04<br>3.58E-05 X-Cd: | 43 f   of titrant: 0.063   f titrant: 0.937   ime CaCdCl2   hours pH   titr.(mls)   0 6.06   44 6.19   0 6.04   212 6.04 2.52   284 6.02 3.39   332 6.03 3.97   380 6.00 4.49   388 4.58 | 43 file: cd43tal   of titrant: 0.063   f titrant: 0.937 $Lime$ CaCdCl2   time CaCdCl2   hours pH   titr.(mls) mg/l   0 6.06   44 6.19   0 6.04   212 6.04   212 6.04   232 6.03   332 6.03   338 4.58   0.25   tip. during steady state:   4.69E-04   3.58E-05 X-Cd:   0.071 | 43file: cd43tabof titrant:0.063of titrant:0.937time<br>hoursCumulative<br>pH[Cd]<br>total<br>titr.(mls)06.06446.1906.042126.042126.042320.312846.023326.033990.282502.5E-073806.004.580.252.2E-073884.580.252.2E-07 | 43file: cd43tabof titrant:0.063f titrant:0.937time<br>hoursCumulative<br>pH[Cd]<br>titr.(mls)[Cd2+]<br>mg/l06.0606.0606.062126.042.520.312.846.023.390.282.5E-074793326.033.970.292.6E-075353806.004.580.252.2E-07488cip. during steady state:Steady stat4.69E-04<br>3.58E-05S.7Cd:0.071535 | 43file: cd43tabof titrant:0.063<br>0.937file: cd43tabf titrant:0.937Cumulative<br>CaCdCl2<br>titr.(mls)[Cd]<br>total<br>mg/l[Cd2+]<br>total<br>moles/l[Ca]<br>total<br>mg/l06.06<br>440.06<br>5.15.4E-08<br>0.40<br>3.6E-07579<br>488<br>488<br>0.011606.06<br>212<br>6.04<br>2.120.06<br>5.4E<br>0.40<br>3.6E-07579<br>488<br>488<br>0.0116106.06<br>4.49<br>3.32<br>4.580.06<br>0.25<br>0.31<br>2.2E-07579<br>479<br>479<br>479<br>479<br>488<br>0.0114ass6.00<br>4.49<br>4.580.25<br>0.25<br>2.2E-07Steady state<br>488<br>488<br>0.0116tip. during steady state:Steady state D:4.69E-04<br>3.58E-05<br>3.58E-05X-Cd:0.071 |

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| run#:              | 46 |       | file:cd46tab |
|--------------------|----|-------|--------------|
| X-CdCl2 of titrant | t: | 0.063 |              |
| X-CaCl2 of titrant | •  | 0.937 |              |

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|            |                 |            | Cumulative | [Cd2+] |         | [Ca]         |              |              |
|------------|-----------------|------------|------------|--------|---------|--------------|--------------|--------------|
| sample     | time            |            | CaCdCl2    | total  | [Cd2+]  | total        | [Ca2+]       | Distribution |
| #          | days            | pН         | titr.(mls) | mg/l   | moles/l | mg/l         | moles/l      | Coeff.       |
| 46-1       | 0.0             | 6.00       | 0.00       | 0.07   | 6.3E-08 | 570          | 0.0135       | 14563        |
| 46-2       | 4.8             | 6.00       | 0.49       | 0.17   | 1.5E-07 | 606          | 0.0144       | 6375         |
| 46-3       | 13.0            | 6.00       | 1.37       |        |         |              |              |              |
| 46-4       | 19.0            |            | 2.00       | 0.32   | 2.9E-07 | 602          | 0.0143       | 3365         |
| 46-5       | 24.0            | 6.03       | 2.52       | 0.63   | 5.6E-07 | 548          | 0.0130       | 1556         |
| 46-6       | 26.8            |            | 2.82       | 0.54   | 4.8E-07 | 545          | 0.0129       | 1805         |
| 46-7       | 35.1            | 6.05       | 3.69       | 0.38   | 3.4E-07 | 540          | 0.0128       | 2542         |
| 46-8       | 47.9            | 6.10       | 5.05       | 0.91   | 8.1E-07 | 544          | 0.0129       | 1069         |
| 46-9       | 54.0            | 6.05       | 5.69       | 0.78   | 7.0E-07 | 529          | 0.0126       | 1213         |
| 46-10      | 56.2            | 6.07       | 5.92       | 0.85   | 7.6E-07 | 543          | 0.0129       | 1143         |
| 46-11      | 60.0            | 6.09       | 6.32       | 0.91   | 8.1E-07 | 543          | 0.0129       | 1067         |
| Moles prec | ip. during stea | ady-state: |            |        | S       | Steady state | D:           | 1123         |
| Ca:        | 6.07E-04        |            |            |        | S       | Steady state | interval: 8- | 11           |
| Cd:        | 3.81E-05        |            | X-Cd:      | 0.059  |         | -            |              |              |

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## **APPENDIX B: SOLID PHASE CHARACTERIZATION**

Surface precipitates formed in the experiments discussed in Chapter 3 were examined by several methods to provide a better understanding of the nature of the solid solution/aqueous solution partitioning process. The objectives of this study were to determine: 1) the mineralogy of the precipitates; 2) the composition of the overgrowths formed and; 3) the size of the crystals and their surface morphologies.

### X-ray Diffraction

Surface precipitates from this study were examined by X-ray diffraction (XRD) to identify the mineral phases present. The mineralogy of the precipitates is of major importance in order to determine if Me<sup>2+</sup> had partitioned only to calcite and not to  $MeCO_{3(s)}$  or to aragonite (orthorhombic  $CaCO_{3(s)}$ ). (While, most of the solutions used in the experiments were undersaturated with respect to  $MeCO_{3(s)}$  phases, XRD analyses can provide direct evidence on the mineral phases present.) A Siemens D500 Diffractometer, with a Cu metal target which emitted CuK $\alpha_1$  and CuK $\alpha_2$  X-rays, was used to analyze the samples. Samples were packed into a holder and scanned from  $2\Theta = 20$  to  $2\Theta = 80$  or 90. The samples selected for analysis represented a range of experimental conditions (i.e., precipitation rate, pH). As discussed in Section 3.5.3, peaks corresponding to aragonite were detected in the analysis of Sample X (Figure 3.9). For all other samples, only peaks corresponding to calcite were detected. Diffraction patterns for three of these samples are shown in Figures B.1-B.3. These analyses support the conclusions that aragonite, witherite (BaCO<sub>3(s)</sub>), otavite (CdCO<sub>3(s)</sub>), strontianite (SrCO<sub>3(s)</sub>), and smithsonite (ZnCO<sub>3(s)</sub>) did not form in these experiments and that Me<sup>2+</sup> partitioning was to calcite.

#### Scanning Electron Microscopy

The size and morphology of the precipitates formed in the experiments discussed in Chapter 3 were examined using a Zeiss DSM-960 Scanning Electron Microscope (SEM). Representative images of the precipitates are shown in Figures 4.9, 4.10 and 4.11. A discussion regarding the surface morphology of the precipitates is provided in Section 4.7.2. The size of the precipitates generally ranged from 5 to 15  $\mu$ m. Energy dispersive X-ray microanalysis (EDX) was used to estimate the compositions of selected overgrowths. This method did not prove useful as the escape depth for X-ray emission ( $\approx 1 \mu$ m) generally exceeded the thickness of the overgrowth.

#### Transmission Electron Microscopy

The focus of the Transmission Electron Microscopy (TEM) study was to determine the compositional variations with depth from the surface of precipitates by examining them in cross section. To prepare the sample for analysis, approximately 1 mg of a precipitate was added to a sample tube. The tube was filled with LR White embedding medium (Pelco<sup>®</sup>), capped, and baked at 60 °C for 24 hours to polymerize the sample. The sample was sectioned into approximately 600 Å thick blocks using a microtome and placed on a sample grid, which was subsequently coated with carbon.

The sample was analyzed by TEM to obtain an image of the solid and by EDX to obtain compositional information. During EDX analysis, the sample is struck by electromagnetic radiation with sufficient energy to dislodge an inner shell electron. An outer shell electron fills this vacancy and X-rays are released with an energy equal to the difference between the two shells. The energy of the X-ray released is specific to the element (and orbitals) involved in this process and can therefore be used to determine the composition of the material analyzed.

An image of a cross section of a crystal from Experiment 37 is shown in Figure B.4a. Compositional information for the edge and the center of the crystal were estimated by EDX:

| Sample      | Analyte | Peak  | K-Factor | Atom % |
|-------------|---------|-------|----------|--------|
| 37 - Center | Ca-K    | 11355 | 1.00     | 98.9   |
| 37 - Center | Cd-L    | 146   | 2.47     | 1.1    |
| 37 - Edge   | Ca-K    | 4801  | 1.00     | 87.8   |
| 37 - Edge   | Cd-L    | 756   | 2.47     | 12.2   |

The terms Ca-K and Cd-L refer to the X-rays generated by the replacement of electrons in the K and L shells, respectively. A  $X_{cdCo_{300}}$  of 0.12 for the precipitate at the edge of the crystal from Sample 37 was estimated by EDX. This is approximately twice the value expected based on the mass balance calculations presented in Chapter 3. An overestimate of the K-factor may be responsible for this discrepancy. In any event, the results of the EDX analyses suggest that the center of the crystal has undergone little, if any, recrystallization.

Selected area diffraction (SAD) patterns were obtained for the center and the edge of the sample from Experiment 37. (The SAD pattern for the edge of Experiment 37 is shown in Figure B.4b.) SAD analysis can provide information on d-spacings for a discrete area of the sample. Changes in d-spacings as a result of Cd<sup>2+</sup> substitution in the crystal lattice were not detected by these analyses.



Figure B.1 X-ray diffraction pattern for precipitate from Experiment 11. Table provides  $2\Theta$  and d-spacing information for the identified peaks.

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| Sample: ZSER 26-Mac-1993 11:56:07 |          |        |        |        |        |        |        |
|-----------------------------------|----------|--------|--------|--------|--------|--------|--------|
| Data                              | file: ZS | ER RAW |        |        |        |        |        |
|                                   |          |        |        |        |        |        |        |
| Seq                               | 2theta   | d      | rel. I | Sea    | 2theta | d      | cel. T |
| 1                                 | 22.962   | 3.8701 | 11.8   | 2      | 29.331 | 3.0425 | 100.0  |
| 2                                 | 29.331   | 3.0425 | 100.0  | 5      | 39.372 | 2.2867 | 51.5   |
| з                                 | 31.375   | 2.8488 | 4.0    | -<br>- | 43,115 | 2.0964 | 20.3   |
| 4                                 | 35.908   | 2.4989 | 16.0   | 8      | 47.448 | 1.9146 | 18.9   |
| 5                                 | 39.372   | 2.2867 | 21.2   | ģ      | 48.430 | 1,8781 | 17.7   |
| 6                                 | 43.115   | 2.0964 | 20.3   | 4      | 35,908 | 2.4989 | 16.0   |
| 7                                 | 47.061   | 1,9294 | 7.8    | TT.    | 57,333 | 1.6058 | 12.0   |
| 8                                 | 47.448   | 1.9146 | 18.9   | 1      | 22.962 | 3,8701 | 11.8   |
| 9                                 | 48.430   | 1.8781 | 17.7   | 7      | 47.061 | 1.9294 | 7.8    |
| 10                                | 56.499   | 1.6275 | 4.7    | 18     | 64,609 | 1.4414 | 6,6    |
| 11                                | 57.333   | 1.6058 | 12.0   | 13     | 60.608 | 1,5266 | 6.4    |
| 12                                | 57.500   | 1.6015 | 5.7 ?  | 24     | 63.726 | 1,1543 | 6.1    |
| 13                                | 60.608   | 1.5266 | 6,4    | 12     | 57.500 | 1,6015 | 5.7 ?  |
| 14                                | 60.800   | 1.5222 | 5,4 ?  | 14     | 60.800 | 1.5222 | 5.4 ?  |
| 15                                | 61.333   | 1.5103 | 3.8    | 20     | 65.549 | 1.4230 | 4.7    |
| -16                               | 62,984   | 1,4746 | 3.5    | 10     | 56.499 | 1.6275 | 4.7    |
| 17                                | 63.153   | 1.4711 | 2.4    | з      | 31.375 | 2,8488 | 4.0    |
| 18                                | 64.609   | 1.4414 | 6.6    | 15     | 61.333 | 1.5103 | 3.8    |
| 19                                | 64.795   | 1.4377 | 3.6    | 19     | 64.795 | 1.4377 | 3.6    |
| 20                                | 65.549   | 1,4230 | 4.7    | 16     | 62,984 | 1.4746 | 3.5    |
| 21                                | 70.187   | 1.3399 | 1.9    | 22     | 77.118 | 1.2358 | 2.6    |
| 22                                | 77.118   | 1.2358 | 2.6    | 26     | 84.704 | 1.1434 | 2.4    |
| 23                                | 81,442   | 1.1808 | 2.3    | 25     | 83.948 | 1.1518 | 2.4    |
| 24                                | 83.726   | 1.1543 | 6.1    | 17     | 63,153 | 1.4711 | 2.4    |
| 25                                | 83.948   | 1.1518 | 2.4    | 23     | 81.442 | 1.1808 | 2.3    |
| 26                                | 84.704   | 1.1434 | 2.4    | 21     | 70.187 | 1.3399 | 1.9    |

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**Figure B.2** X-ray diffraction pattern for precipitate from Experiment Z. Table provides  $2\Theta$  and d-spacing information for the identified peaks.

Sample: CD33 Data file: CD33.RAW

| 9-Sep | -1993 | 14:46:06 | • |
|-------|-------|----------|---|
|-------|-------|----------|---|

| 5en | 2thats |        | 1 T    | <b>C</b> | Other  | -      |        |
|-----|--------|--------|--------|----------|--------|--------|--------|
| 264 |        |        | Let' T | Seq      | zuneta | 0      | LET' T |
| 1   | 22,728 | 3,9093 | 15.8   | 3        | 53.101 | 3.0661 | 100.0  |
| 2   | 27.148 | 3.2820 | 1.9    | 5        | 39.113 | 2.3012 | 27.3   |
| з   | 29.101 | 3.0661 | 100.0  | 9        | 48,226 | 1.8855 | 26.3   |
| 4   | 35.644 | 2.5169 | 25.1   | 4        | 35.644 | 2.5169 | 25.1   |
| 5   | 39.113 | 2.3012 | 27.3   | 6        | 42.868 | 2.1079 | 25.0   |
| 6   | 42.868 | 2.1079 | 25.0   | 8        | 47.232 | 1.9229 | 18.9   |
| 7   | 46.842 | 1.9379 | 11.9   | 1        | 22.728 | 3,9093 | 15.8   |
| 8   | 47.232 | 1.9229 | 18.9   | 11       | 57,100 | 1.6118 | 14.1   |
| 9   | 48.226 | 1.8855 | 26.3   | 7        | 46.842 | 1.9379 | 11.9   |
| 10  | 56.242 | 1.6343 | 4,6    | 15       | 64.376 | 1.4460 | 9.8    |
| 11  | 57,100 | 1.6118 | 14.1   | 12       | 60.390 | 1,5316 | 9.4    |
| 12  | 60.390 | 1.5316 | 9.4    | 10       | 56,242 | 1,6343 | 4.6    |
| 13  | 61.013 | 1.5174 | 4.4    | 13       | 61.013 | 1.5174 | 4.4    |
| 14  | 62.731 | 1.4799 | 3.9    | 16       | 72.608 | 1.3010 | 4.2    |
| 15  | 64.376 | 1.4460 | 9.8    | 14       | 62,731 | 1,4799 | 3.9    |
| 16  | 72.608 | 1.3010 | 4.2    | 18       | 76.012 | 1.2510 | 2.7    |
| 17  | 73.510 | 1.2873 | 2.1    | 17       | 73.510 | 1.2873 | 2.1    |
| 18  | 76.012 | 1.2510 | 2.7    | 2        | 27.148 | 3,2820 | 1.9    |









**Figure B.4** TEM image (top) and SAD pattern for a cross section of precipitate from Experiment 37. Magnification for TEM image is 40,000x.

# BIOGRAPHY

The author was born and raised on Staten Island, New York. He received his elementary education from the New York City public school system and his secondary education from Msgr. Farrell High School. Jim earned a B.A. degree in Geology from the State University of New York at Buffalo in 1982 and a M.S. degree in Geology from Arizona State University in 1985. His M.S. thesis work on brine migration in domal salt introduced him to many of the issues concerning the geologic isolation of nuclear waste. After working with the N. J. Department of Environmental Protection, this interest led to employment with the U.S. Nuclear Regulatory Commission as a geochemist on the Salt Repository Project. In the Fall of 1989, he was admitted to the Oregon Graduate Institute, where he earned his Doctor of Philosophy degree in 1994.

Jim was married to Rosemary DiCandilo in 1986. They have enjoyed their time in the Pacific Northwest, largely due to the friends they have made here and the fun they have had exploring the area. The author's roots stay with him, though, as he is still waiting for the Knicks to win and knows a good slice of pizza when he sees one (which isa't too often out here). Jim plans to continue his career as an aqueous geochemist working on the protection and restoration of surface water and ground water quality.

## **PUBLICATION**

Tesoriero A. J. and Knauth L. P. (1988) The distribution of trace water around brine leaks in the Avery Island Salt Mine: implications for the natural migration of water in salt. *Nuclear and Chemical Waste Management*, **8**, 189-197.