

## LETTER

### Sorption of trace metals on calcite: Applicability of the surface precipitation model

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**Abstract**—Published sorption isotherm data of  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$  on calcite are adequately described by the surface precipitation model which was originally developed by FARLEY *et al.* (1985) for the sorption of cations on metal oxides. In addition to monolayer adsorption, the model accounts for the formation of a surface phase with a composition that is described by a solid solution having as end members the sorbent calcium carbonate mineral and a pure carbonate precipitate of the sorbing trace metal. The model thus specifies a continuum between adsorption and precipitation. This feature is supported in the literature by observations on the reaction kinetics and the amount of surface coverage during trace metal sorption on calcite. The apparent adsorption constants of these trace metals, as derived from the model, can be ranked according to the degree to which their ionic radii match the ionic radius of  $\text{Ca}^{2+}$ .

#### INTRODUCTION

CALCITE, BEING THE MOST abundant carbonate mineral, occurs in a variety of geochemical environments such as soils and freshwater and marine sediments. Despite its abundance, relatively little is known about its surface chemistry and its interactions with trace metals at the solid/solution interface (MORSE, 1986). Detailed knowledge of these processes may prove very useful because they record the chemical environment in which calcium carbonate has been formed. For instance, the cadmium content of benthic foraminifera has been used by BOYLE (1986) to reconstruct paleophosphate levels and paleo-oceanic circulation. Manganese and zinc have been used successfully as tracers for modelling carbonate diagenesis (PINGITORE, 1978). Furthermore, it has been shown that the aqueous solubility of trace metals can be governed by interaction with carbonate minerals (THOMSON *et al.*, 1986; MIDDELBURG *et al.*, 1987). However, a more fundamental mechanistic approach to interactions between carbonate mineral surfaces and trace metals is clearly required.

SOMASUNDARAN and AGAR (1967) were the first to describe the surface chemistry of calcite in terms of surface complexation reactions. On the basis of thermodynamical calculations on the system calcite/aqueous solution/atmosphere they suggest that  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$  and  $\text{OH}^-$  are the potential determining ions.

Although many sorption studies have been done with hydrous metal oxides and clay minerals, there have been relatively few experimental studies on the sorption of trace metals on calcite (HEYDEMANN, 1959; MCBRIDE, 1979, 1980; JURINAK and BAUER, 1956; KITANO *et al.*, 1976; FRANKLIN and MORSE, 1982,

1983; KORNICKER *et al.*, 1985). Most of the studies on calcite show remarkable agreement as regards observations on the kinetics of the sorption processes: an initial rapid uptake of the trace metal followed by a period of relatively slow removal from solution. The rapid sorption step is generally ascribed to an adsorption reaction, whereas the slow uptake, at relatively high concentrations, is commonly thought to represent (solid solution) precipitation on the calcite surface. It was also observed by MCBRIDE (1980) and JURINAK and BAUER (1956) that sorption isotherms showed surface saturation followed by increased sorption at higher equilibrium concentrations.

The most direct evidence for initial rapid adsorption and subsequent nucleation and precipitation on the calcite surface at higher concentrations was given by MCBRIDE (1979). From measurements of surface area and unit cell size McBride calculated that the adsorption density of  $\text{Mn}^{2+}$  on calcite was higher than could be explained by the number of adsorption sites available. Electron Spin Resonance (ESR) data indicated that no discrete new phase formed at low  $\text{Mn}^{2+}$  surface concentrations, but that at high concentrations  $\text{MnCO}_3$  was nucleated on the calcite surface. It was suggested by MCBRIDE (1979) that the sorption process was continuous from chemisorption to precipitation.

Because sorption data for cations on metal oxides do not show saturation in adsorption density at monolayer surface coverage but show a continuous increase, FARLEY *et al.* (1985) postulated that the sorption process could be depicted more accurately by allowing for a continuum between adsorption reactions and precipitation. These authors therefore proposed a model that is conceptually similar to the BET-isotherm which describes a continuum between monolayer gas ad-

sorption and ultimate condensation of the gas. By analogy, the model accounts for a continuum between adsorption and a precipitation reaction which is described by the formation of a surface phase whose composition varies continuously between that of the original solid and a pure precipitate of the sorbing cation.

The obvious coincidence between the underlying principles of the 'surface precipitation model' of FARLEY *et al.* (1985) and the experimental observations reported in the literature on the sorption of trace metals on calcite, inspired us to try and apply the model to these data. In this paper we present the results of our modelling efforts on the sorption of  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$  on calcite, using data of MCBRIDE (1980), MCBRIDE (1979), JURINAK and BAUER (1956), and KORNIKER *et al.* (1985), respectively.

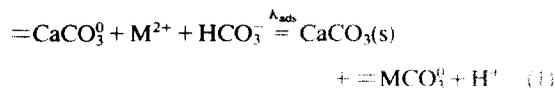
In a very recent paper, to which our attention was drawn during review, DAVIS *et al.* (1987) propose a mechanism for the sorption of Cd on calcite, which is supported by a unique combination of Cd sorption and Ca isotopic exchange experiments. This two-step mechanism is very similar to the mechanism which forms the basis of the model of FARLEY *et al.* (1985): the first step involves a fast adsorption reaction followed by diffusion of  $\text{Cd}^{2+}$  into a surface layer of hydrated  $\text{CaCO}_3$  that overlies crystalline calcite. The second step is solid solution formation in new crystalline material which grows from the disordered mixture of Cd and Ca carbonate in the hydrated surface layer.

#### FORMULATION OF THE MODEL IN TERMS OF TRACE METAL/CALCITE INTERACTION

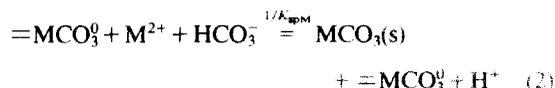
The concept of the surface precipitation model is discussed in detail by FARLEY *et al.* (1985) in connection with the sorption properties of cations on metal oxides. If we extend this concept to sorption of cations on carbonates, the sorption process can be summarized briefly as follows (for clarity, we use the term 'adsorption' only for monolayer coverage of the surface, whereas 'sorption' is used to denote all processes that transfer a cation from solution to the solid phase): when a cation adsorbs on the surface of a carbonate mineral, a second carbonate surface is created which permits a further transfer of both the sorbing cation and cations of the sorbent mineral to the solid phase. Therefore, in addition to monolayer adsorption, the model allows for the formation of a surface phase with a composition that is described by a solid solution having as end members the sorbent calcium carbonate mineral and a pure carbonate precipitate of the sorbing cation. An alternative suggestion put forward by DAVIS *et al.* (1987) is that the solid solution grows from a disordered mixture of Cd and Ca carbonate in a hydrated surface layer that overlies crystalline calcite; the existence of this surface layer was proposed by MUCCI *et al.* (1985). This alternative does not affect the validity of the 'surface precipitation model' as formulated here.

In the mathematical model for the surface precipitation concept metals at the carbonate/water interface are treated as surface species, whereas metals which are not in direct contact with the solution, but separated by the adsorption monolayer, are treated as solid species. The surface precipitation reactions for the sorption of trace metals on calcium carbonate can then be written as follows:

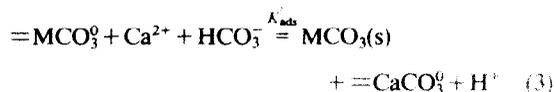
Adsorption of  $\text{M}^{2+}$  on  $\text{CaCO}_3(\text{s})$ :



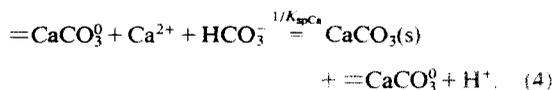
Precipitation of  $\text{M}^{2+}$ :



Adsorption of  $\text{Ca}^{2+}$  on  $\text{MCO}_3(\text{s})$ :



Precipitation of  $\text{Ca}^{2+}$ :



The surface symbol = is used here to indicate bonds of the metal at the adsorption monolayer. Since only three of these four expressions are independent,  $K'_{\text{ads}}$  can be written as  $1/K_{\text{ads}}K_{\text{spM}}K_{\text{spCa}}$ .

As formulated in Eqn. (1), the mechanism of trace metal adsorption causes some  $\text{CaCO}_3(\text{s})$  to dissolve [reverse of Eqn. (4)] in order to neutralize the resulting proton. This approach is in accordance with that of MCBRIDE (1979), who suggested that the release of  $\text{Ca}^{2+}$  during adsorption of  $\text{Mn}^{2+}$  was not the result of direct ion displacement but was effected by a proton transfer according to Eqns. (1) and (4).

The mole balances for the model can be written as follows:

$$\text{TOTM} = [\text{M}^{2+}] + [= \text{MCO}_3^{\text{I}}] + [\text{MCO}_3(\text{s})] \quad (5)$$

$$\text{TOTCa} = [\text{Ca}^{2+}] + [= \text{CaCO}_3^{\text{I}}] + [\text{CaCO}_3(\text{s})] \quad (6)$$

$$S_T = [= \text{CaCO}_3^{\text{I}}] + [= \text{MCO}_3^{\text{I}}] \quad (7)$$

where  $S_T$  represents the total concentration of surface sites for cation binding. For a particular pH the surface precipitation model can be expressed in the form of a 'BET-like' sorption isotherm (FARLEY *et al.*, 1985):

$$\Gamma_{\text{M}} = \frac{(B-1)[\text{M}^{2+}]\{S_T/\text{TOTCa}(1 - [\text{M}^{2+}]/[\text{M}^{2+}]_s) + (1/(B-1) + [\text{M}^{2+}]/[\text{M}^{2+}]_s)\}}{([\text{M}^{2+}]_s - [\text{M}^{2+}])\{1 + (B-1)[\text{M}^{2+}]/[\text{M}^{2+}]_s\}} - \frac{[\text{Ca}^{2+}]_s[\text{M}^{2+}]}{\text{TOTCa}[\text{M}^{2+}]_s} \quad (8)$$

where  $B = K_{\text{ads}}K_{\text{spM}}$ ;  $[M^{2+}]_s = K_{\text{spM}}\{H^+\}/[HCO_3^-]$   
 $= K_{\text{spM}}\{H^+\}^2/K_1K_H P_{CO_2}$ ;  $[Ca^{2+}]_s = K_{\text{spCa}}\{H^+\}/[HCO_3^-]$   
 $= K_{\text{spCa}}\{H^+\}^2/K_1K_H P_{CO_2}$  ( $K_1$ ,  $K_H$ ,  $P_{CO_2}$  are the first  
 acidity constant of the carbonate system, the Henry's  
 law constant of the carbonate system, and the partial  
 pressure of  $CO_2$ , respectively); and

$$\Gamma_M = \frac{[MCO_3^0] + [MCO_3(s)]}{\text{TOTCa}},$$

indicating total moles of  $M^{2+}$  sorbed per mole of total  
 calcium.

#### APPLICATION OF THE SURFACE PRECIPITATION MODEL TO ISOTHERM DATA

As was mentioned earlier, we applied the surface  
 precipitation model to published laboratory data on  
 the sorption of  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ , and  $Co^{2+}$  on calcite  
 (MCBRIDE, 1980; MCBRIDE, 1979; JURINAK and  
 BAUER, 1956; and KORNICKER *et al.*, 1985, respec-  
 tively). In all of these studies an aqueous phase was  
 used, consisting of the metal chloride solution without  
 further background electrolyte, except for  $Zn^{2+}$  where  
 the ionic strength was kept constant at 0.01 M with  
 NaCl. Equilibration times were 24 hrs, 24 hrs, 6 hrs,  
 and 3–8 hrs for the isotherm data of  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  
 and  $Co^{2+}$ , respectively. It should be noted at this point  
 that the laboratory experiments from which the avail-  
 able sorption data were derived were not designed for  
 modelling purposes. Except for the data on  $Mn^{2+}$  and  
 $Cd^{2+}$  (MCBRIDE, 1979, 1980), the applied concentra-  
 tion range of the sorbing metal, the type of calcite, the  
 equilibration time, and the values for pH and TOTCa,  
 are all different for each trace metal. No attempts were  
 made to control the pH. In spite of these restrictions  
 and because of the absence of a more consistent set of  
 data, we feel that the data are adequate for testing the  
 applicability of the surface precipitation model.

We applied the model to the isotherm data using  
 the adsorption constant ( $K_{\text{ads}}$ ) and the solubility prod-  
 uct of the trace metal carbonate ( $K_{\text{spM}}$ ) as fitting pa-  
 rameters. The total number of surface sites available  
 for cation binding ( $S_T/\text{TOTCa}$ ) was estimated from  
 the double-logarithmic isotherm plots (see FARLEY  
*et al.*, 1985) and found to be in agreement with the ad-  
 sorption maxima observed or calculated by MCBRIDE  
 (1979, 1980), JURINAK and BAUER (1956) and KOR-  
 NICKER *et al.* (1985). A sensitivity analysis showed that  
 the use of different values for  $K_{\text{spM}}$  did not affect the  
 optimum isotherm fit in the concentration range where  
 adsorption dominates, and different values for  $K_{\text{ads}}$  had  
 no effect on the concentration range of dominant solid  
 solution precipitation. Values for  $K_H$ ,  $K_1$ , and  $P_{CO_2}$  for  
 the carbonate system were taken from STUMM and  
 MORGAN (1981) and for  $K_{\text{spCa}}$  from PLUMMER and  
 BUSENBERG (1982).

The isotherm fits of the surface precipitation model  
 for the sorption of  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ , and  $Co^{2+}$  on  
 calcite are shown in Fig. 1. The apparent constants for  
 adsorption and for solid solution precipitation which

were used in the model [*i.e.*, in the 'B' term of Eqn.  
 (8)], the total concentration of surface sites ( $S_T$ ), and  
 the TOTCa and pH values are indicated. For the  $Co^{2+}$   
 experiments, neither the exact TOTCa value (only the  
 upper and lower limits) nor the pH was given. We  
 estimated the pH value to be 8.4, by assuming equi-  
 librium with calcite and atmospheric  $CO_2$ . We ob-  
 served that for the experimental conditions the second  
 term of Eqn. (8) was negligible and that consequently  
 only the  $S_T/\text{TOTCa}$  ratio was significant. This was ver-  
 ified by model calculations for  $Co^{2+}$  using both the  
 upper and lower limits of the TOTCa values given by  
 KORNICKER *et al.* (1985). During the calculations, the  
 pH was kept constant at the values listed in Fig. 1,  
 although MCBRIDE (1979, 1980) observed a lowering  
 of the pH at high adsorption density. JURINAK and  
 BAUER (1956) and KORNICKER *et al.* (1985) did not  
 monitor the pH during their experiments.

The isotherm fits of the surface precipitation model  
 (Fig. 1) show that the model provides a good description  
 of the sorption process of these four trace metals on  
 calcite, despite the differences in experimental condi-  
 tions. The apparent adsorption constants of  $Cd^{2+}$ ,  
 $Mn^{2+}$ ,  $Zn^{2+}$ , and  $Co^{2+}$  ( $10^{1.43}$ ,  $10^{0.65}$ ,  $10^{0.08}$ , and  
 $10^{-0.40}$ , respectively) follow the sequence expected from  
 their ionic radii and from the similarity of these radii to  
 the ionic radius of  $Ca^{2+}$  ( $r = 0.99 \text{ \AA}$ ):  $Cd^{2+}$  (0.97  $\text{\AA}$ ) >  
 $Mn^{2+}$  (0.80  $\text{\AA}$ ) >  $Zn^{2+}$  (0.74  $\text{\AA}$ ) >  $Co^{2+}$  (0.72  $\text{\AA}$ )  
 (WEAST, 1981). It is reasonable to expect that (valences  
 being equal) the affinity of the metal for the calcite  
 surface will increase with the degree to which the ionic  
 radius of the metal matches that of  $Ca^{2+}$ . The appar-  
 ent adsorption constants of  $Cd^{2+}$ ,  $Mn^{2+}$ , and  $Co^{2+}$   
 are also consistent with their distribution coefficients in  
 calcite, as determined by LORENS (1981). At the slowest  
 rate of calcite precipitation, during recrystallization  
 (near or at calcite saturation), LORENS (1981) found:  
 $D_{Cd}$  ( $10^{1.85}$ ) >  $D_{Mn}$  ( $10^{1.71}$ ) >  $D_{Co}$  ( $10^{0.92}$ ). It  
 should be mentioned here that the model assumes sorp-  
 tion under equilibrium conditions with respect to calcite  
 solubility. Otherwise, the incorporation of trace metal  
 into calcite may be controlled by kinetic factors, as  
 was shown by LORENS (1981).

On the basis of the present data, it is not possible  
 to make a valid comparison between the apparent sol-  
 ubility products of the trace metal carbonates (Fig. 1)  
 and literature values. As was stated above, the pH was  
 not controlled in any of the experimental studies. A  
 change in the pH is expected whenever the trace metal  
 carbonate—instead of calcite—controls the equilib-  
 rium composition of the solution (STUMM and MOR-  
 GAN, 1981). MCBRIDE (1979, 1980) did indeed observe  
 a pH decrease at high surface coverage, *i.e.*, during  
 solid solution precipitation. The fact that the pH was  
 kept constant during the model calculations might thus  
 have influenced the apparent solubility products. Note  
 also that we assumed the formation of an ideal solid  
 solution, whereas the carbonate system under consid-  
 eration shows non-ideal solid solution behaviour  
 (LIPPMANN, 1980). In the latter situation,  $K_{\text{spM}}$  is a

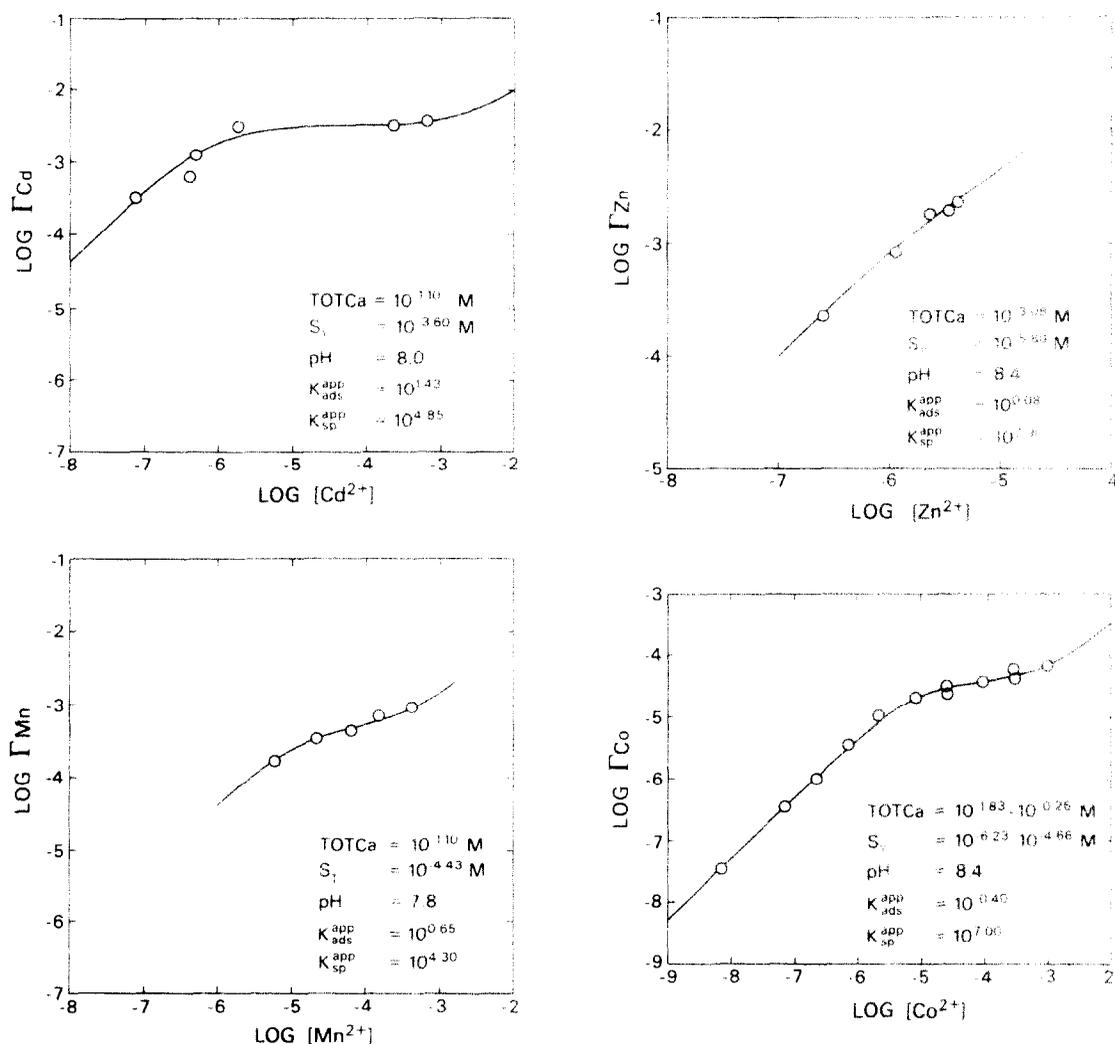


FIG. 1. Isotherm fits of the surface precipitation model for the sorption of Cd<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> on calcite. Data from MCBRIDE (1980); MCBRIDE (1979); JURINAK and BAUER (1956) and KORNICKEK *et al.* (1985), respectively.  $\Gamma_M$  indicates total moles of M<sup>2+</sup> sorbed per mole of total calcium.

function of the trace metal concentration in the solid. This may cause a variation of several orders of magnitude in  $K_{spM}$  values (MIDDELBURG *et al.*, 1987). Consequently, the solubility products are to be regarded as fitting parameters (FARLEY *et al.*, 1985).

DZOMBAK and MOREL (1986), in a paper subsequent to that of FARLEY *et al.* (1985), included a second (weaker) binding site in the 'surface precipitation model.' Assuming ideal solid solution behaviour in their hydrous metal oxide system, they were able by means of this extension to use published  $K_{spM}$  values and therefore required no additional fitting parameter. Adequate data concerning trace metal sorption on calcite (especially at high sorbate/sorbent ratios) to test this approach are not available at present. Provided additional data of sufficient quality become available, future modelling efforts might benefit from the inclusion of a second (adsorption) surface site in the 'surface precipitation model.'

## CONCLUSIONS

The sorption of Cd<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, and Co<sup>2+</sup> on calcite has been shown to be adequately described by the surface precipitation model of FARLEY *et al.* (1985). The underlying principles of the model, which allows for a continuum between adsorption and precipitation, are supported by observations on the reaction kinetics and the amount of surface coverage during trace metal sorption on calcite. The need for such a model was recently expressed by MORSE (1986) after a thorough review of the literature.

The apparent adsorption constants of these trace metals, as derived from the model, can be ranked according to the degree to which their ionic radii match the ionic radius of Ca<sup>2+</sup>. The available laboratory data which were used to test the applicability of the model do not fully meet the criteria necessary to justify the derivation of more generally valid modelling constants

for adsorption and solid solution precipitation. There is evidently a need for a consistent set of data on trace metal sorption on carbonate minerals. To obtain these data it will be necessary to do laboratory experiments which include long equilibration times (of the order of days), a wide range of dissolved metal concentrations (up to high sorbate/sorbent ratios) and surface saturations, and in which a constant pH is maintained throughout the experiments. When used in conjunction with such a consistent data base, from which we can derive constants of more general validity, the surface precipitation model will extend our knowledge of the mechanistics of the interactions between trace metals and carbonate minerals.

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