

The surface chemistry of carbonates, a new approach

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ABSTRACT: The Charge Distribution-MultiSite Ion Complexation (CD-MUSIC) model was applied to describe the surface chemistry of calcite. Protonation reactions and proton affinity constants were predicted and the resulting surface model was compared to the existing Surface Complexation (SC) model. The CD-MUSIC model approach results in a surface charge pH-dependence that fits the point of zero proton charge (pH_{ZPC}) values as reported from electrophoretic measurements.

1 INTRODUCTION

Carbonates play an important role in regulating the chemistry of aquatic environments from lakes to oceans, aquifers to hydrothermal systems, and soils to sediments under oxic to anoxic conditions. Through mineral surface processes such as dissolution, precipitation and adsorption, carbonates affect the biogeochemical cycles of Ca, Mg, Fe and C, major components of carbonate minerals, as well as H, P and trace elements such as radionuclides.

In order to understand and describe the reactivity of the carbonate–water interface, Van Cappellen et al. (1993) proposed a Surface Complexation model for divalent metal carbonates. This model is based on the modeling of experimentally determined surface charge curves from acid/base titrations of rhodochrosite (MnCO_3) and siderite (FeCO_3) suspensions and on data from electrokinetic and flotation studies of calcite (CaCO_3) suspensions. The model was validated by comparison to spectroscopic measurements of the surface group concentrations over a large pH range (3 to 12; Chiarello et al. 1993; Pokrovsky et al. 2000). Table 1 summarizes the parameters from the SC model for carbonate mineral surfaces.

However, as Van Cappellen et al. pointed out, the model represents a first-order description of the chemistry of the carbonate–aqueous solution interface, and does not take into account surface site heterogeneities. In the present study, an alternative model has been developed, describing the surface reactivity based on crystallographic data using the CD-MUSIC model approach (e.g. Hiemstra & Van Riemsdijk 1996). In the CD-MUSIC model, the bond valence theory is used to describe the basic

charging of mineral surfaces (Hiemstra et al. 1989a,b). Initially developed and refined for simple metal (hydr)oxides (Hiemstra et al. 1989a,b, Hiemstra & Van Riemsdijk, 1996, Hiemstra et al. 1996), it has recently been applied successfully to the more complex phyllosilicates (Tournassat et al., in press). Here, it will be applied to theoretically describe the surface charge pH dependence of carbonate minerals. The CD-MUSIC model is then compared to the SC model, which shall be used to describe radionuclide sorption processes at the calcite surface.

2 METHOD

The surface chemistry model is based on ideal, unrelaxed surfaces and therefore should be considered as a preliminary description of the actual surface, as the composition of the solution will affect the surface characteristics. Nevertheless, XPS and LEED studies (Stipp & Hochella 1991) have shown the presence of an ordered calcite surface at least 1 nm thick that is very similar to the bulk lattice. Hence, approximating the calcite surfaces based on the distances and bond angles present within the bulk structure is a valid first-order approach. Koretsky et al. (1998) tested five different methods to calculate the number of surface sites on each surface of various minerals and compared the results for each method to available experimental estimates. Estimates based on the number of broken bonds gave the best agreement with site densities determined using the tritium exchange method. In this method, each broken bond on a near-surface atom

Table 1. Surface complexation model for calcite. LogK values are at 25°C, 1 atm, $I = 0$ (Van Cappellen et al. 1993).

Surface reactions	logK
$\equiv\text{CO}_3^- + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}^0$	+4.9
$\equiv\text{CO}_3\text{Ca}^+ + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}^0 + \text{Ca}^{2+}$	+2.8
$\equiv\text{CaO}^- + \text{H}^+ \leftrightarrow \equiv\text{CaOH}^0$	+17
$\equiv\text{CaOH}^0 + \text{H}^+ \leftrightarrow \equiv\text{CaOH}_2^+$	+12.2
$\equiv\text{CaOH}^0 + \text{CO}_2 \leftrightarrow \equiv\text{CaHCO}_3^0$	6.0
$\equiv\text{CaOH}^0 + \text{CO}_2 \leftrightarrow \equiv\text{CaCO}_3^- + \text{H}^+$	-2.6

Table 2. Protonation reactions and proton affinities predicted from applying the CD-MUSIC model to calcite.

Type	Surface reactions	logK
Face	$\equiv\text{CO}_3^{-1/3} + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}^{+2/3}$	+4.4
Edge	$\equiv\text{CO}_3^{-2/3} + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}^{+1/3}$	+4.4
Corner	$\equiv\text{CO}_3^- + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}^0$	+4.4
	$\equiv\text{CO}_3\text{H}^0 + \text{H}^+ \leftrightarrow \equiv\text{CO}_3\text{H}_2^+$	-7.5
Face	$\equiv\text{CaO}^{-5/3} + \text{H}^+ \leftrightarrow \equiv\text{CaOH}^{-2/3}$	+25.0
	$\equiv\text{CaOH}^{-2/3} + \text{H}^+ \leftrightarrow \equiv\text{CaOH}_2^{+1/3}$	+13.1
Edge	$\equiv\text{CaO}^{-4/3} + \text{H}^+ \leftrightarrow \equiv\text{CaOH}^{-1/3}$	+25.0
	$\equiv\text{CaOH}^{-1/3} + \text{H}^+ \leftrightarrow \equiv\text{CaOH}_2^{+2/3}$	+13.1
Corner	$\equiv\text{CaO}^- + \text{H}^+ \leftrightarrow \equiv\text{CaOH}^0$	+25.0
	$\equiv\text{CaOH}^0 + \text{H}^+ \leftrightarrow \equiv\text{CaOH}_2^+$	+13.1

was considered as a surface reactive group. This method will be followed here to calculate the site densities for carbonate surfaces. The calculated site densities and stoichiometries will be compared to experimentally determined values reported in the literature.

To determine the surface structures, the calcite mineral structure was taken from Diamond[®]. The orientation of cleavage and growth planes are well established experimentally (e.g. Reeder & Grams 1987; Stipp & Hochella 1991; Chiarello et al. 1993; Paquette & Reeder 1995; Pokrovsky et al. 2000; Elzinga & Reeder 2002). Additionally, atomistic simulation methods have been used to calculate and compare the surface structure and energies of various surfaces of calcite (Titiloye et al. 1998). The calcium and carbonate-terminated {1014} surface of calcite is the most stable crystal plane and will dominate the predicted equilibrium morphology. Therefore, the surface site types for calcite will be derived from an ideal cleavage rhombohedron with {1014} faces and carbonate groups at the corners (e.g., Fig. 1). Surface sites present on other important faces, as shown by sector zoning, shall be explored. In the CD-MUSIC model, the site types are constrained by the crystal structure, so they are not free fitting parameters within the model. The formal charges and proton affinities of the sites have been calculated using the CD-MUSIC model (Hiemstra & Van Riemsdijk 1996, Hiemstra et al. 1996). For the surface charge pH-dependence calculations (Fig. 2), a size of 0.04 μm for the rhombohedra was assumed.

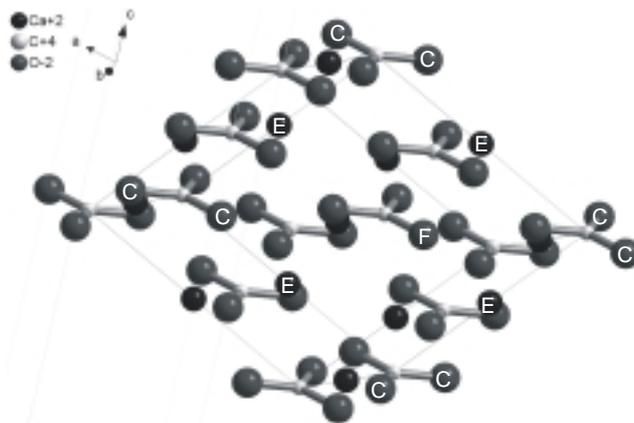


Figure 1. Sketch of the cleavage rhombohedron of calcite, consisting of {1014} faces. Rib lengths are 6.399 Å. For one face, the corner (C), edge (E) and face (F) sites are indicated for the oxygen in CO_3 and the calcium in $\equiv\text{CaO}$ groups.

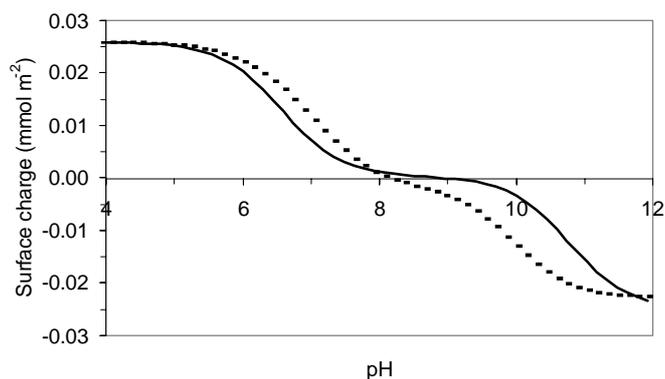


Figure 2. Preliminary surface charge pH-dependence calculated by the CD-MUSIC model (black line), compared to the surface charge pH-dependence calculated by the SC model (dashed line). The calcite surface charge was calculated using either the SC parameters or the CD-MUSIC parameters in the constant capacitance model in MINEQL+. Modeling was performed with the following conditions: specific surface area = 55 $\text{m}^2 \text{g}^{-1}$, morphology = ideal cleavage rhombohedra; capacitance $k = 30 \text{ F m}^{-2}$, $I = 0.032 \text{ M}$; $[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = 10^{-3} \text{ M}$. For the CD-MUSIC curve, corner sites were used as representing all sites with respect to actual charges, and for calcium and carbonate sorption, the SC reactions were used.

3 RESULTS AND DISCUSSION

The protonation reactions and the proton affinity constants predicted using the CD-MUSIC model are listed in Table 2. The formal charges for $\equiv\text{CO}_3$ and $\equiv\text{CaO}$ vary depending on their position at the surface. This is due to a difference, with position, in coordination of the surface carbon or calcium to the bulk lattice. As can be seen in Table 2, the protonation affinities of the $\equiv\text{CO}_3$ and $\equiv\text{CaO}$ groups do not vary with position, in contrast to what has been observed, for example, for goethite (Hiemstra & Van Riemsdijk 1996, Hiemstra et al. 1996). This is due to the constant mono-coordination of the oxygen within the $\equiv\text{CO}_3$ and $\equiv\text{CaO}$ groups to either calcium or carbon, independent of surface site position. Since the coordination of the oxygen does not change with site position, its proton affinity does not change.

Comparison of the proton affinities from the SC model (Table 1) and the predicted proton affinities from the CD-MUSIC model (Table 2) shows that the affinities are close for the first protonation step of the $\equiv\text{CO}_3$ group and the second of the $\equiv\text{CaO}$ group. For the first protonation step of the $\equiv\text{CaO}$ group, the affinities do not agree. However, the large proton affinity of the $\equiv\text{CaO}$ group in both models indicates that, within the pH range 2–12, the deprotonated $\equiv\text{CaO}$ group is insignificant.

To facilitate comparison of the two models, the surface charge pH dependence of calcite was calculated using both models. The resulting curves are depicted in Figure 2. For calcite, no acid/base titration data are known at present. Electrophoretic measurements indicate a pH_{ZPC} varying from 7 to 10.8 (e.g. Somasundaran & Agar 1967; Mishra 1978; Amankonah & Somasundaran 1985; Thompson & Pownall 1989; Cicerone et al. 1992). The SC model was fit to a pH_{PZC} of 8.2 (Mishra 1978), using the surface site density as calculated from crystallography (Van Cappellen et al. 1993). In contrast, the CD-MUSIC model gives a prediction of the surface charge, based on crystallographic information and the proton affinity calculations, that is in good agreement with the previously reported pH_{ZPC} values. In fact, the surface charge curve from the CD-MUSIC model is flat around pH_{ZPC} , which may be an explanation of the large range of pH_{ZPC} observed in electrophoretic measurements.

It must be noted that the CD-MUSIC model presented here is a preliminary model. Ongoing work on the model encompasses including the sorption reactions of carbonate and calcium, which are also potential-determining ions for the pristine calcite surface. Also, the model will be applied to other carbonate minerals, such as rhodochrosite, for which surface acid/base titration data are available, to test the model approach. Furthermore, data on radionuclide adsorption onto calcite are being reviewed and shall be described using the model. The importance of specific adsorption on various faces shall be discussed.

4 CONCLUSIONS

The predicted proton affinities of the calcite surface by the preliminary CD-MUSIC model approach results in a surface charge pH-dependence that fits the pH_{ZPC} values as reported from electrophoretic measurements. The flat surface charge curve around observed pH_{ZPC} values may be an explanation of the large range of pH_{ZPC} values reported in literature.

The proton affinities of the surface sites do not vary with position at the surface, due to the constant mono-coordination of the surface oxygen atoms to either calcium or carbon. The formal charges of the surface $\equiv\text{CO}_3$ and $\equiv\text{CaO}$ groups do vary with posi-

tion due to the change in coordination of these groups to the bulk lattice.

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