Structure of the $(10\bar{1}4)$ Surfaces of Calcite, Dolomite, and Magnesite under Wet and Dry

Conditions

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ABSTRACT

Atomistic computer simulation methods have been employed to model the structure of the $(10\bar{1}4)$ surfaces of calcite, dolomite and magnesite. Our calculations show that under vacuum conditions, calcite undergoes the greatest degree of surface relaxation with rotation and distortion of the carbonate group accompanied by movement of the calcium ion. The magnesite surface is the least distorted of the three carbonates, with dolomite being intermediate to the two end members. When water molecules are placed on the surface to produce complete monolayer coverage, the calcite surface is stabilized and the amount of relaxation is substantially reduced. In contrast, the dolomite and magnesite surfaces are destabilized by hydration as indicated by a significant increase in the surface energies relative to the dry surface.

INTRODUCTION

Knowledge of the structure of mineral surfaces at the atomic level is of fundamental importance when considering processes such as growth, dissolution and sorption of impurities. Over the past two decades improvements in surface science techniques such as surface probe microscopy (SPM), x-ray photoelectron spectroscopy (XPS) and x-ray adsorption fine-structure (XAFS) have led to an increase in our understanding of mineral surface behavior. However, these methods are unable to give detailed structural and dynamic information on the relaxed structure of the surface at the atomic level. By using computer simulation techniques in combination with experiment it is possible to develop more realistic models of mineral surfaces and hence gain a greater insight into those processes of interest.

The surface reactivity of calcite, and the related carbonate minerals dolomite and magnesite, is a key factor in the chemical control of aquatic environments, in diagenesis, in the cycling and entrapment of metal contaminants, the biogeochemical cycle of carbon, and in a variety of industrial processes. Calcite is the most commonly occurring of the carbonate minerals and its surfaces, the $(10\bar{1}4)$ in particular, have been extensively studied by a range of surface analytical techniques. For example, Stipp and Hochella (1991) used a combination of XPS and low energy electron diffraction (LEED) to study calcite surfaces under exposure to air and aqueous solutions, while Liang et al (1996) employed atomic force microscopy (AFM) to study relaxations of the surface under hydrous conditions. Both studies indicate only minimal relaxation of the surface when

exposed to aqueous fluids through rotation of the CO_3 group. Fenter et al. (2000) proposed a model based on high resolution x-ray reflectivity whereby the $(10\bar{1}4)$ calcite surface, when covered by a monolayer of H_2O relaxes by rotation and tilting of the carbonate groups down towards the surface. However, there remains some uncertainty as to the detailed atomic structure of the calcite surface at the mineral-fluid interface. Computational studies by de Leeuw and Parker (1997, 1998) and by de Leeuw et al (1999) have provided insights into the structure and relative stability of a range of calcite surfaces under both wet and dry conditions which are in good general agreement with experimental data.

By contrast, very little is known of the surface structure of the related minerals dolomite and magnesite at the atomic level although there is considerable interest in their chemical reactivity. Both are common in the geological past yet form only in small quantities in modern marine environments. Surface complexation models have been developed for dolomite (e.g. Brady et al 1996, Pokrovsky et al 1999a) and for magnesite (Pokrovsky et al 1999b) in order to understand more fully the mechanisms of dissolution and growth under a range of pH conditions. In addition, computational studies by Tittiloye et al (1998) have calculated the energetics and stability of dolomite surfaces. The aim of the present study is to investigate the detailed surface structure of the $(10\bar{1}4)$ perfect cleavage surfaces of calcite, dolomite and magnesite under both hydrous and anhydrous conditions using atomistic computer simulation methods. We utilize the interatomic potential set of Fisler et al. (2000) that was developed for the accurate simulation of the structure and properties of the rhombohedral carbonate phases.

2. COMPUTATIONAL METHODS

Atomistic simulation methods are based on the Born model of solids where interatomic potential functions are defined to model the long- and short-range forces acting between atoms or ions in the solid. The effects of oxygen ion polarizability on the system are included by use of the shell model (Dick and Overhauser 1956) while directionality of the bonding is described by three-body and four-body terms. Simulations are carried out using standard energy minimization schemes in which the energy of the system is calculated with respect to all atomic coordinates. Thus the equilibrium positions of the ions are evaluated by minimizing the lattice energy until all forces acting on the crystal are removed. A more comprehensive review of atomistic simulation methods can be found in Cormack (1999).

For the calculation of surface structures, the most commonly used approach is to treat the crystal as planes of atoms which are periodic in two dimensions. Surfaces are modeled by considering a single block, whereas two blocks together simulate the bulk, or a more complex interface. The simulation block is divided into two regions, a near-surface region, Region 1, comprised of those atoms adjacent to the surface or interface, and an outer region, Region 2. The atoms in Region 1 are allowed to relax to their minimum energy configuration, while the ions of Region 2 are held fixed at their bulk equilibrium positions. The specific surface energy is defined as the energy per unit area required to form the crystal surface relative to the bulk. The surface energy (γ) is therefore given by:

$$\gamma = \frac{U_s - U_b}{A} \quad (1)$$

where U_s refers to the energy of Region 1 for the surface, U_b refers to the energy of an equivalent number of bulk atoms and A is the surface area. The lower the surface energy, the more stable the surface will be.

In the present study we use the surface simulation code MARVIN (Gay and Rohl 1995) and the potential parameter set for carbonates derived by Fisler et al. (2000) which is able to accurately reproduce the structure and properties of calcite, magnesite and dolomite. In addition, water is described by the potentials of de Leeuw and Parker (2000) and calcite/water interactions by a modified form of the de Leeuw and Parker (1997) potential. All potential parameters are given in Table 1. All surface calculations were performed on a two-dimensional repeating simulation cell containing 600 ions where the $(10\bar{1}4)$ surface was bounded by the $(\bar{1}014)$ and $(\bar{1}2\bar{1}0)$ planes. Other calculations of bulk properties were carried out using the General Utility Lattice Program (GULP) of Gale (1997).

3. RESULTS

3.1 The anhydrous surface

The structure of the anhydrous $(10\bar{1}4)$ surfaces was simulated for all three carbonate minerals, which essentially mimics the dry expected conditions under a

vacuum environment. The detailed structure for the calcite surface is shown in Figure 1 and illustrates the manner in which the surface has reconstructed to accommodate dangling bonds produced on cleavage. The molecular CO_3 group can be thought of as having three different oxygen types, one above the plane (O1) which in the topmost layer (L1) is underbonded, one in the plane (O2) and one below (O3). The whole group has rotated (Figure 1a) and distorted in a convex manner with O1 and O2 bending down towards the bulk while in the second layer, the sense of distortion is concave, with O2 and O3 tilting upwards (Figure 1b). The central C atoms move down by only $0.04\text{\AA}$ in L1. The movements described above are most pronounced for the top two layers which form a convex/concave pair, although a total of five layers were needed in Region 1 before the system converged to the bulk structure. This is illustrated in Figure 2a, which gives the calculated torsional angles for the relaxed CO_3 group as a function of depth through the five effective surface layers down to the bulk. The dihedral or torsion angle is measured across the O-C-O-O position and indicates the out-of-plane distortion of the planar group. Additionally, the Ca position moves in the plane of the surface during relaxation. In the top layer (L1), the Ca moves down by $-0.75\text{\AA}$ and in plane by $-0.71\text{\AA}$ while in L2, the movement is $0.16\text{\AA}$ up and $0.52\text{\AA}$ in plane, in the opposite sense to the layer above. In the bulk, Ca is octahedrally coordinated to oxygen with a calculated Ca - O distance of $2.37\text{\AA}$ but in the top layer the octahedron is truncated and in L2 is very distorted giving Ca - O distances ranging from $2.35 - 2.73\text{\AA}$ as shown in Figure 3a. The surface of calcite retains its (1×1) symmetry for these various reconstructions.

The surfaces of dolomite and magnesite also show some distortion of the carbonate group, but to a lesser extent than that exhibited in calcite. Variation in torsion angles for the CO_3 groups and in cation – O octahedral distances are shown in Figures 2 and 3 respectively while the structure of the three surfaces can be compared in Figure 4. As in calcite, movement occurs in the opposite sense for alternate layers. Of the three carbonates considered, magnesite is the most rigid and exhibits the least distortion on relaxation with Mg moving only 0.36Å in L1 and 0.43Å in L2 from the bulk positions, compared to 1.05Å and 0.55Å in L1 and L2 respectively for Ca in calcite. This type of behavior reflects differences in the bulk moduli of the three carbonates, where magnesite is the least compressible and calcite the most (Fisler et al. 2000) Similarly, the CO_3 groups exhibit less rotation and less deviation in dihedral angles in magnesite (Figure 2). The greatest distortion in magnesite occurs in L2 where the smallest dihedral angle is 8% less than the 180° or planar value observed in the bulk. In calcite the greatest deviation is 11.5% and occurs in L1. Dolomite appears to exhibit a mixed behavior with respect to these distortions, part way between the two end members with each of the cations. The movement of Ca and Mg away from their initial bulk positions in L1 is 0.70Å and 0.97Å respectively. Distortions of the carbonate groups are also different depending on whether the group is associated with a Ca or Mg ion (Figure 2b). The calculated relaxed surface energies for the dry ($10\bar{1}4$) surfaces of calcite, dolomite and magnesite are given in Table 2.

3.2 The hydrated surface

The surfaces of calcite, dolomite and magnesite were hydrated by placing a single water molecule on the surface, and by covering with a complete monolayer of water. The molecules were initially placed at a distance of 2.4 Å above the surface Ca or Mg, the optimum height for calcite found by de Leeuw and Parker (1997). The surface and water molecules were then allowed to relax to their minimum energy configuration. The variation in CO₃ group torsional angles for the relaxed calcite surface with a monolayer of water are shown in Figure 5. The hydrated surface shows very little difference from the bulk below L2, and the degree of relaxation in L1 and L2 is substantially reduced compared to the dry surface. Ca moves from its bulk position by only 0.26 Å in L1 when water is present compared to 1.05 Å for the dry surface. The water molecules lie almost flat on the surface (hydrogens angled slightly upwards) and have an average Ca – O_w distance of 2.57 Å. This value is in excellent agreement with the experimental X-ray reflectivity data for the calcite-water system (Fenter et al., 2000). A similar geometry was found for the water layer on magnesite where the average Mg – O_w distance is longer at 2.94 Å. Dolomite exhibits mixed behavior, with Ca – O_w and Mg – O_w distances of 2.57 Å and 2.78 Å respectively, where the hydrogens of water molecules above Ca are again angled slightly upwards. The structure of each of the three hydrated surfaces is shown in Figure 6.

The hydration energies are calculated by comparing the energy of the surface with n adsorbed water molecules, to a bare surface plus n water molecules in the gas phase. Since we wish to consider liquid water on the surface, when calculating hydrated surface

energies, we must add the energy for $\text{H}_2\text{O}_{(l)}$ rather than $\text{H}_2\text{O}_{(g)}$. These values were calculated for a single molecule (for $\text{H}_2\text{O}_{(g)}$) and for a periodic array of molecules whose density was set to the experimental density of water (for $\text{H}_2\text{O}_{(l)}$) using the potential parameters in Table 1. The energy difference between liquid and gas is then the condensation energy, which we compute as -39 kJmol^{-1} and compares reasonably well with the experimental value of -44 kJmol^{-1} (Johnson 1982). The surface energy for the hydrated surface is obtained by:

$$\gamma_{wet} = \frac{U_{s,wet} - (U_b + U_w)}{A} \quad (2)$$

where $U_{s,wet}$ represents the potential energy of the relaxed hydrated surface and U_w the potential energy of the n water molecules ($\text{H}_2\text{O}_{(l)}$). Calculated hydration energies per water molecule and wet surface energies are presented in Table 2 and further illustrate the way in which water stabilizes these surfaces by significantly reducing the degree of relaxation experienced and hence the surface energy. Our calculations show that the dry calcite surface is the least stable, and hence most reactive, and dolomite the most stable. However, when hydrated, calcite is stabilized relative to dolomite and magnesite.

4. DISCUSSION

In the bulk carbonate structures, each metal cation is octahedrally coordinated by six oxygens, each from a different CO_3 group. Formation of the $(10\bar{1}4)$ surface leads to a configuration with only five-coordinated metal cation present at the surface and therefore the surface must restructure to compensate. This under-coordination causes the

cation to displace into the surface towards the bulk and the CO_3 groups to distort and tilt as shown in Fig. 1b for calcite. The magnitude of these atomic movements in the top surface layer is such that subsequent layers also need to reorganize, down to a depth of at least 4 layers. When water is added to the surface, then the cation is able to coordinate to the water oxygen thus forming a stable octahedron. This much more favorable configuration stabilizes the surface and significantly reduces the surface energy and degree of relaxation in the top layer, which in turn means that the layers beneath experience less strain and hence less need to reorganize. For the hydrated surfaces, the bulk configuration is reached at three layers below the surface rather than the five layers required under dry conditions.

There are some differences in how the water molecules are configured on the $(10\bar{1}4)$ surface for the energy minimization simulations for each of the three carbonate phases. As indicated in Figure 6a, the water molecules for the saturated monolayer configuration on calcite are arranged above each calcium ion and form a two dimensional hydrogen-bonded network among themselves on the surface. The water molecules are slightly angled above the surface plane with the hydrogen atoms pointing away from the surface. The mean Ca-O_w distance of 2.57 Å is slightly greater than the bulk Ca-O distance of 2.37 Å. In contrast, the hydrated magnesite $(10\bar{1}4)$ surface exhibits water lying flatter on the surface but at a mean distance of 2.94 Å. This distance is substantially greater than the bulk Mg-O distance of 2.13 Å. The extension of the Mg-O_w bond is related to the smaller magnesite unit cell and Mg polyhedra (Figure 6c), and to the strong network of hydrogen bonding among the surface water molecules. This

arrangement prevents any stabilization of the hydrated magnesite relative to the dry $(10\bar{1}4)$ surface (see Table 2).

The hydration of the $(10\bar{1}4)$ surface of dolomite involves the coordination of water molecules to both calcium and magnesium surface ions. Figure 6b shows that the relaxed dolomite surface structure with alternating magnesium and calcium sites is now large enough to accommodate water molecules more closely to the magnesium site. The mean Mg-O_w distance is 2.78 Å and the water molecules now occur at a slight angle to the surface. The calcium polyhedra are significantly large to help the water molecules access the magnesium sites. However, in contrast to the $(10\bar{1}4)$ surface of calcite, the energetics for both dolomite and magnesite simulations suggest a destabilization of the surfaces with hydration.

It is important to point out that the energies associated with our surface simulations are based on an accurate set of interaction potentials that have successfully and accurately modeled the bulk behavior of carbonate phases and water systems. Hydration and surface energies are sensitive to the values obtained for the isolated water molecule and liquid water assemblage, respectively. For this reason, no experimental values for the water energies are incorporated into the energy calculations; only values obtained directly from our simulations based on the potentials of Table 1 are used. Small variations in the energy terms are critical in this analysis as the hydration and surface energies involve taking differences in large energy values. Although potential-based empirical models cannot accurately predict all aspects of a bulk or surface system, we

feel that the observed *trends* in the reported energies are correct in modeling the *relative* behavior of the carbonate surface structures.

Our results for the dry $(10\bar{1}4)$ surface of calcite are consistent with the XPS and LEED data of Stipp (1999) which has been interpreted in terms of a restructuring at the surface by the rotation and downward relaxation of the CO_3 groups. There have been a number of studies which have looked at the structure of the $(10\bar{1}4)$ surface of calcite in contact with aqueous fluids. Fenter et al (2000) have used data from x-ray reflectivity experiments to produce a model of the surface water interface in which the top two layers of the surface are relaxed. In this model, the adsorbed monolayer of H_2O has a height of $2.5 \pm 12 \text{ \AA}$ relative to the surface Ca positions which is in excellent agreement with our predicted height of $2.57 \text{ \AA}$ relative to the same position. AFM images of the wet calcite surface (Liang et al. 1996) show different heights for the surface CO_3 groups leading to a loss of the (1×1) symmetry, although we find no evidence to support this in our calculations.

The simulations of de Leeuw and Parker (1997) show a similar geometry of the hydrated calcite surface to those presented here, although the values of surface energy and hydration energy differ somewhat. These authors use the carbonate potential of Pavese et al (1996) and a different water potential (de Leeuw et al 1996) in their calculations. Because the surface energies are essentially dependent on the potential parameters used, it is not surprising that our reported energies are different. However, trends shown by the energies should be the same if both parameter sets are valid and

indeed we find that this is the case. The results of our calculations and those of de Leeuw and Parker (1997) both show that the $(10\bar{1}4)$ surface energy of calcite is reduced on hydration by a monolayer of water.

Comparison of our results for magnesite and dolomite with experiment is much more problematic, since the surface structure of these minerals has not been so extensively studied. Pokrovsky et al (1999a ,b) have investigated the surface speciation and reactivity of both dolomite and magnesite under hydrous conditions and consider $M-OH_2$ speciation (where M is Ca or Mg) to be important for both systems at moderate pH values. However, no structural models have been proposed for these hydrated surfaces. The computational study by Tittiloye et al (1998) compared calcite and dolomite surfaces and found that the anhydrous dolomite $(10\bar{1}4)$ surface had a higher surface energy than that for calcite, the opposite of the results presented here. This may be due to differences in the Mg – O potential used or to differences in the size of the simulation cell or a combination of factors. The potentials used in the present study were derived to be fully transferable between different carbonate minerals (Fisler et al. 2000) and the region 1 size was fully converged, thus we feel confident that our results are consistent within the limitations of the models employed.

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Table 1. Potential parameters used in this study. O_L denotes a lattice oxygen, O_w a water oxygen. Intra and inter refer to O core-O core intramolecular and O shell-O shell intermolecular interactions respectively.

Species	Core charge	Shell charge		
Ca	+2			
Mg	+2			
H	+0.4			
C	+1.343539			
O _L	1.018487	-2.133		
O _w	1.25	-2.05		
Buckingham $A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}r^{-6}$	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å ⁻⁶)	Cut-off (Å)
O _L - O _L (intra)	4030.30	0.2455		2.5
O _L - O _L (inter)	79158.60	0.1983	21.844	15.0
Ca - O _L	2154.06	0.2891		10.1
Mg - O _L	1039.59	0.2893		10.1
O _w - H	396.27	0.25	10.0	20.0
Ca - O _w	1694.037	0.2891		10.1
Mg - O _w	0.2891			10.1
O _L - O _w	60599.94	0.1983	21.844	10.1
O _L - H	396.27	0.230		10.1
Morse $D\{[1-\exp(-a(r-r_0)^2)]-1\}$	D (eV)	a (Å ⁻¹)	r_0 (Å)	
C - O _L	5.0	2.5155	1.2025	1.3
O _w - H	6.203713	2.22003	0.92376	1.2
Spring $\frac{1}{2}k_2r^2 + \frac{1}{2}k_4r^4$	k_2 (eV Å ⁻²)	k_4 (eV Å ⁻⁴)		
O _L core-shell	32.194	10000.0		
O _w core-shell	209.45			
Three-body $\frac{1}{2}k_2(\theta-\theta_0)^2 + \frac{1}{6}k_3(\theta_0)^3 + \frac{1}{12}k_4((\theta-\theta_0)^4$	k_2 (eV rad ⁻²)	θ_0		
O _L -C-O _L	1.7887	120		
O _w -H-O _w	4.19978	108.69		
Torsion $k(1+\cos(n\phi-\phi_0))$	k (eV)	n		
O _L -C-O _L -O _L	0.1510	-2		
Lennard-Jones $A r^{-m} - B r^{-n}$	A	B		
O _w - O _w	39344.98	42.15		20.0

Table 2. Hydration energies (per molecule) for monolayer coverage on carbonate surfaces, and wet and dry surface energies.

	E_{hyd} (kJmol ⁻¹)	γ_{dry} (Jm ⁻²)	γ_{wet} (Jm ⁻²)
Calcite	-39.5	0.322	0.315
Dolomite	-27.2	0.247	0.348
Magnesite	-30.1	0.256	0.338

Figure captions.

Figure 1. The structure of the relaxed $(10\bar{1}4)$ surface of calcite seen from above (a), and from the side with $(\bar{1}2\bar{1}0)$ in the plane of the paper (b). The thin black lines and dots represent the bulk unrelaxed positions of the carbonate groups and Ca ions respectively.

Figure 2. Calculated torsional angles of the CO_3 groups as a function of layer depth for (a) calcite, (b) dolomite and (c) magnesite where filled circles represent CO_3 associated with Ca and open circles with Mg.

Figure 3. Ca – O (filled circles) and Mg - O (open circles) octahedral distances as a function of layer depth in (a) calcite, (b) dolomite and (c) magnesite.

Figure 4. Comparison of the structure of calcite, dolomite and magnesite relaxed $(10\bar{1}4)$ surfaces viewed from the side with $(\bar{1}014)$ in the plane of the paper. Black lines and dots show the bulk unrelaxed structure as in Figure 1.

Figure 5. Comparison of torsional angles for the wet and dry surface of calcite.

Figure 6. Structure of the hydrated surfaces of calcite (a), dolomite (b) and magnesite(c) showing the completion of the CaO_6 and MgO_6 octahedra.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6