

Atomistic Simulations of the $(10\bar{1}4)$ Surface of Carbonate Minerals

Kate Wright¹, Randall T. Cygan², and Ben Slater¹

¹Royal Institution of Great Britain,
London, W1X 4BS, U.K.

²Geochemistry Department, Sandia National Laboratories,
Albuquerque, NM 87185-0750, U.S.A.

ABSTRACT

Atomistic simulation methods have been used to model the structure of the $(10\bar{1}4)$ surfaces of calcite, dolomite, and magnesite under dry and wet conditions. The potential parameters for the carbonate and water species contain shell terms to model the polarizability of the oxygen atoms. These static calculations show that the surfaces undergo relaxation leading to the rotation and distortion of the carbonate groups with associated movement of cations. The dry surface energies are 0.322, 0.247, and 0.256 Jm⁻² for calcite, dolomite, and magnesite respectively. The influence of water on the surface structure and energies has been investigated for monolayer coverage. When fully hydrated with a monolayer of water, the surface energy for calcite is reduced indicating a stabilization of the surface with hydration. The extent of carbonate group distortion is greater for the dry surfaces compared to the hydrated surfaces, and for the dry calcite relative to that for dry magnesite.

INTRODUCTION

The morphology and atomistic description of calcite surfaces and those of related carbonate minerals (for example, magnesite and dolomite) is needed for an improved understanding of materials and geochemical processes. Calcite (CaCO₃) has been incorporated in numerous industrial applications, is of considerable interest in diagenetic processes and related oil production issues, can selectively entrap contaminant metals from the environment, and more recently has been examined with regard to biomineralization and the engineering of materials for a variety of new applications. Although numerous experimental and spectroscopic studies of calcite morphology and surface structure have been completed [1-3], there is no accurate atomistic model of the calcite surface. Even less is known of the structure of the dolomite and magnesite surfaces. Several recent theoretical studies have developed an atomistic treatment of calcite [4-6] and dolomite [4] which has been used to assess the relative stability of different surfaces and to predict external morphology. The aim of the present study is to develop a detailed model of the common $(10\bar{1}4)$ cleavage surface of calcite, dolomite (CaMg(CO₃)₂), and magnesite (MgCO₃), and evaluate the differences of surface relaxation for the vacuum surface and that modified by water.

THEORETICAL APPROACH

Our theoretical treatment of the $(10\bar{1}4)$ surface of the carbonate phases is based on an ionic model of atomic interaction that incorporates an electrostatic energy term, a Buckingham

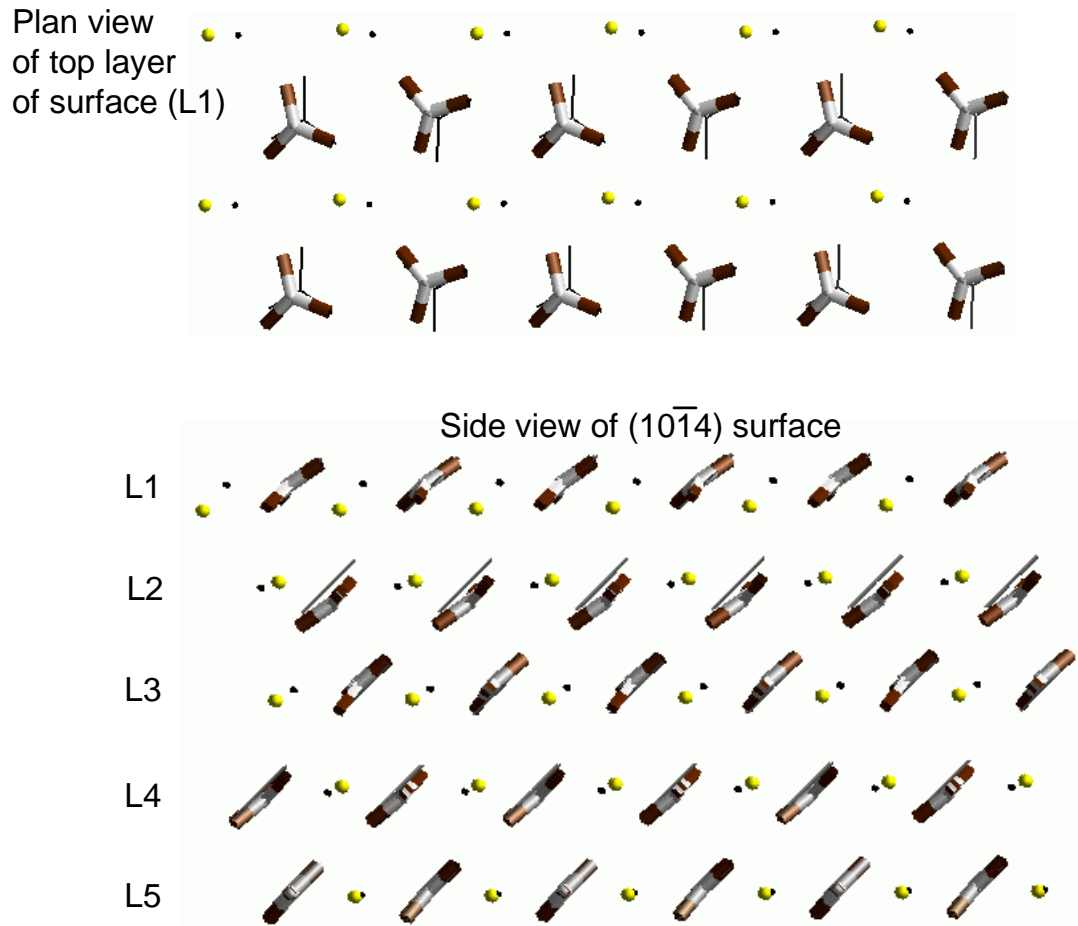


Figure 1. Plan and side views of the $(10\bar{1}4)$ surface of calcite as obtained using a shell model with full structural relaxation and energy minimization. The black lines for the carbonate groups and black dots for the calcium ions correspond to the bulk structure of calcite.

potential for the repulsive and van der Waals (attractive) short range interactions, and harmonic bond and bond angle terms to describe the covalent nature of the C-O bonds associated with the planar carbonate anion groups. Additionally, a shell model is used to describe the polarization of oxygen atoms [7] that will be important in controlling the relaxation response of the carbonate surface. We use the energy parameters obtained from a recent theoretical study of the bulk structures of calcite and several other metal carbonate phases [8]. Beyond the accurate simulation of bulk structures, the parameter set reproduces the bulk moduli (pressure derivatives), the calcite-aragonite transition, and the vibrational spectrum of calcite. We also incorporate a water model and water-carbonate interactions that have been previously used to simulate the $(10\bar{1}4)$ calcite surface [5].

Surface calculations were performed using the MARVINS code that calculates the surface energy for a given surface slice based on a multiple region approach [9]. The near surface environment of the carbonate $(10\bar{1}4)$ surface is represented by up to five layers that are allowed to be fully relaxed (free translation of all atomic coordinates) during the optimization of the total energy. A second region lies below this upper region and is constrained to the observed

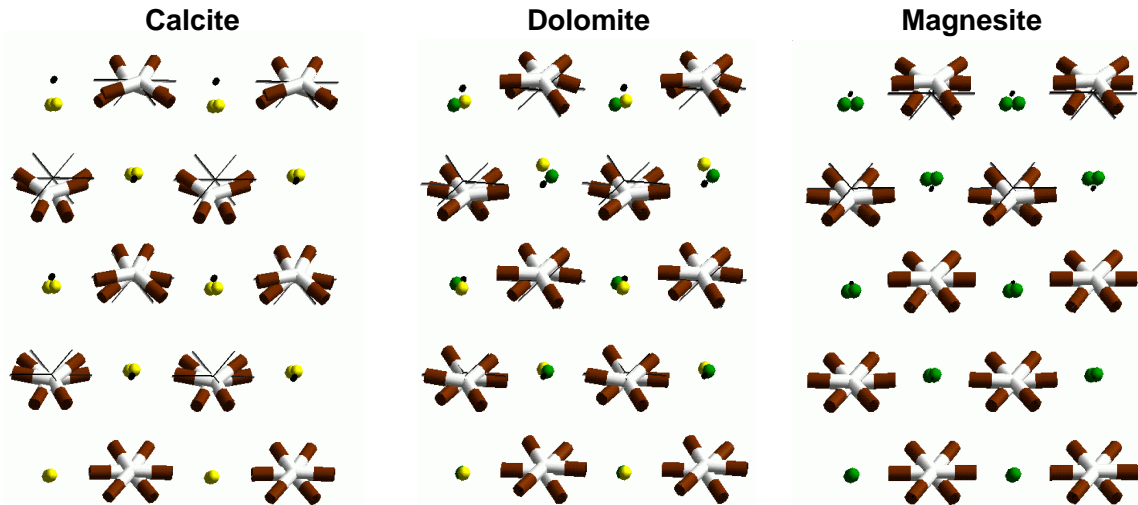


Figure 2. Comparison of relaxed $(10\bar{1}4)$ surfaces for three carbonate compositions based on energy minimized structures with surface in contact with vacuum. The black lines for the carbonate groups and black dots for the metal ions correspond to the observed bulk structures.

carbonate bulk structure. The MARVINS code incorporates a two-dimensional Ewald summation and optimization algorithm to obtain the minimum energy and surface structure. Simulations of wet surfaces are performed by the addition of a finite number of water molecules to the vacuum region above the upper carbonate surface region.

RESULTS AND DISCUSSION

The optimized structure for the $(10\bar{1}4)$ surface of calcite as exposed to vacuum is presented in Figure 1. We determined that the choice of a five layer model for the upper surface region is sufficient for simulating the relaxation of the surface atoms. The positions of the fifth layer atoms are equivalent to those for the bulk calcite structure. The simulated calcite surface exhibits significant rotation and distortion of the carbonate groups accompanied by a displacement of the calcium ions downward from the surface. The second surface layer shows similar carbonate distortion but the calcium ions are significantly less displaced. The carbonate groups exhibit alternating layers of concave downward and concave upward distortions from the surface. Ultimately, the degree of distortion and displacement is reduced with depth. Surface structures for the $(10\bar{1}4)$ surfaces of dolomite and magnesite are presented in Figure 2 along with that of calcite for comparison. The magnesite surface structure exhibits less carbonate group distortion and displacement of the magnesium ions than that observed for the calcite simulation. Relaxation of the magnesite surface appears to be relatively shallow; the observed bulk structure is obtained by the fourth layer. The mixed metal structure of dolomite exhibits a surface structure that has both carbonate group distortion and metal ion displacement, with the magnesium moving more in the topmost surface plane than calcium, but less in subsequent planes. The rotation of carbonate groups is significantly less than that observed for calcite.

The surfaces of calcite, dolomite, and magnesite were hydrated by placing a single water molecule on the surface and by covering with a monolayer of water. The molecules were



Figure 3. Simulation result for relaxed $(10\bar{1}4)$ surface of calcite with a monolayer of water.

initially placed above the surface calcium or magnesium at an initial distance of 2.4 \AA above the cation, and the carbonate surface and water were allowed to relax to their minimum energy configuration. Results for the simulation of the hydrous $(10\bar{1}4)$ calcite surface are presented in Figure 3. The hydrated surface shows almost no difference from the bulk below the third layer while the degree of relaxation in the top two layers is substantially reduced compared to the dry surface. Water molecules nearest the calcite surface ultimately associate themselves with the calcium ions in order to complete the octahedral coordination of the metal ion with oxygens. Figure 4 provides a comparison of the variation of the torsional angle for the carbonate groups (O-C-O-O) as a function of layer position. Results are presented for both the dry and wet calcite surfaces. The greatest distortion occurs in the first layer for both simulations, but the trend with depth is vastly different with the wet surface exhibiting the bulk structural value by the fourth layer. A similar pattern emerges for the wet surfaces of dolomite and magnesite, where water stabilizes these surfaces by reducing the extent of surface relaxation and the surface energy. In the dry case, the surface energies are 0.322 , 0.247 and 0.256 Jm^{-2} for calcite, dolomite, and magnesite respectively, and when fully hydrated with a monolayer of water, these energies are reduced to 0.315 , 0.348 and 0.338 Jm^{-2} . The relative values for the surface energies suggest that the calcite surface is stabilized upon hydration while the corresponding surfaces for dolomite and magnesite are destabilized.

The results of our simulations of calcite are consistent with available experimental data [2,3] and with earlier simulations [4-6]. No comparable experimental data are available for dolomite or magnesite, although we are confident that the model used here is able to accurately reproduce the structure of these surfaces.

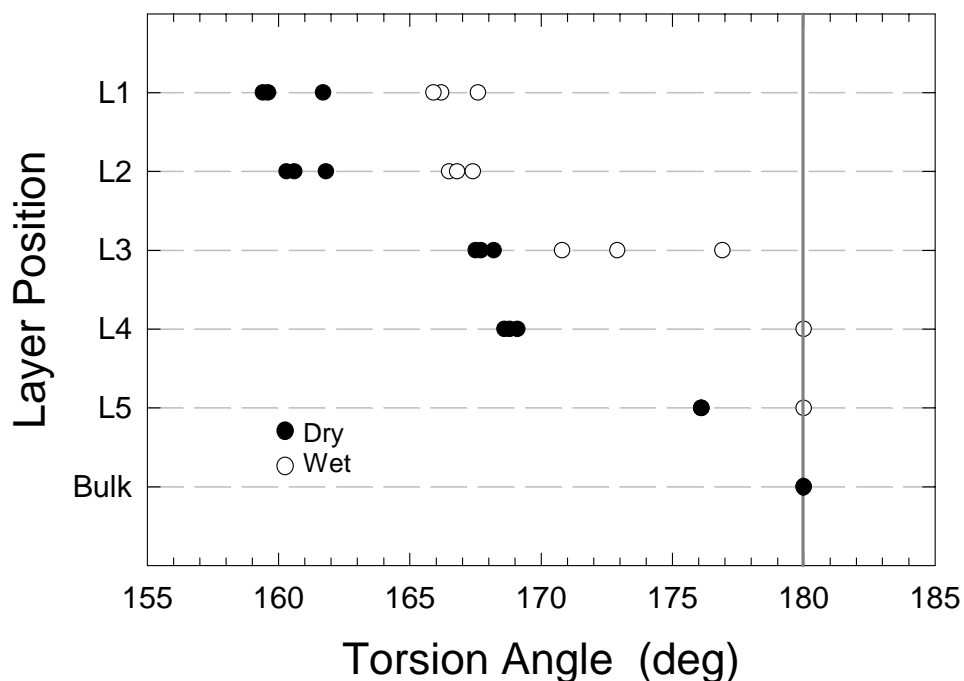


Figure 4. Variation of the torsional angle for the carbonate groups as a function of layer depth for the simulated $(10\bar{1}4)$ calcite surface in contact with vacuum (filled circles) and with a monolayer of water (open circles).

CONCLUSIONS

Due to the limitations associated with experimental and spectroscopic observations, it is important to develop an atomistic model to help understand the energy and structural variations of calcite and other carbonate surfaces. We have developed a theoretical model that provides a description of the structure of the calcite, dolomite, and magnesite $(10\bar{1}4)$ surfaces. Surface relaxation occurs via carbonate group distortion and rotation, and combined with metal ion displacement, helps to reduce the surface energy. Simulations of the calcite surface in the presence of water indicate a significant reduction of distortion and surface energy.

Our future work involves collaboration with experimentalists at Argonne National Laboratory who are advancing the use of synchrotron sources for the analysis of mineral-water interfaces. In addition, we will extend our model to include a significant layer of water on the surfaces of these materials and assess the effects of temperature by running molecular dynamics simulations. In combination with accurate spectroscopic determinations of dry and wet carbonate surfaces, this theoretical approach will help to fully evaluate the structure and reactivity of an industrial and environmentally important class of materials.

ACKNOWLEDGMENTS

We would like to thank P. V. Brady for useful discussions regarding the applications of this study. This work was supported by the U.S. Department of Energy, Office of Basic Energy

Sciences, Geosciences Research Program, under contract DE-AC04-94AL85000 with Sandia National Laboratories. K. Wright is funded by the Royal Society under their University Research Fellowship program.

REFERENCES

1. P. van Cappellen, L. Charlet, W. Stumm and P. Wersin, *Geochim. Cosmochim. Acta*, **57**, 3505 (1993).
2. S. L. S. Stipp, *Geochim. Cosmochim. Acta*, **63**, 3121 (1999).
3. L. Cheng, N. C. Sturchio and M. J. Bedzyk, *Phys. Rev. B*, **61**, 4877 (2000).
4. J. O. Titiloye, N. H. de Leeuw and S. C. Parker, *Geochim. Cosmochim. Acta*, **62**, 2637 (1998).
5. N. H. de Leeuw and S. C. Parker, *J. Chem. Soc. Faraday Trans.*, **93**, 467 (1997).
6. N. H. de Leeuw, S. C. Parker and J. H. Harding, *Phys. Rev. B*, **60**, 13792 (1999).
7. B. G. Dick and A. W. Overhauser, *Physical Review*, **112**, 90 (1958).
8. D. K. Fidler, J. D. Gale and R. T. Cygan, *Am. Mineral.*, **85**, 217 (2000).
9. D. H. Gay and A. L. Rohl, *J. Chem. Soc. Faraday Trans.*, **91**, 925 (1995).