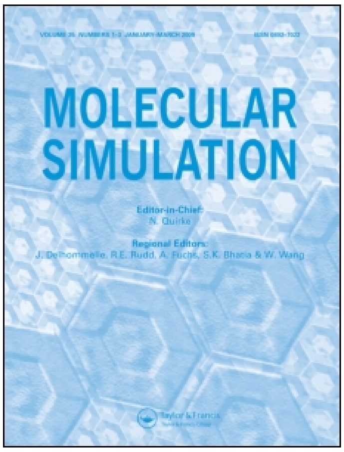

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Where the bulk terminates: Experimental evidence for restructuring, chemibonded OH - and H + , adsorbed water and hydrocarbons on calcite surfaces

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WHERE THE BULK TERMINATES: EXPERIMENTAL EVIDENCE FOR RESTRUCTURING, CHEMIBONDED OH^- AND H^+, ADSORBED WATER AND HYDROCARBONS ON CALCITE SURFACES

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Better understanding of mineral surface reactivity can improve control of crystal growth and dissolution which is central to biomineralisation, design of advanced materials and preventing transport of toxic substances in the environment. Some experimental observations of fundamental processes on calcite using high-resolution techniques (AFM, XPS, TOF-SIMS, LEED) are summarised. Surfaces, cleaved in ultrahigh vacuum (UHV) in the absence of reactive species, relax. Cleavage in air results in hydration and hydrolysis, covering the surface with chemisorbed CaOH and CO_3H. Water adsorbed from air promotes recrystallisation on apparently dry surfaces. Organic components can inhibit dissolution and precipitation; even in the cleanest laboratory, surfaces have at least a monolayer of hydrocarbons. On commercial calcite powders contaminated by organic additives during manufacture, we do not see layer-by-layer and atom-by-atom growth or dissolution and behaviour contradicts the theoretical models developed from macroscopic experiments with these materials. Instead, steps are rounded and many atomic layers high.

Keywords: Calcite; $CaCO_3$; Surface atomic structure; Solid solution interface; Surface processes; Hydrolysis species

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INTRODUCTION

For more than a 100 years, scientists have measured macroscopic properties in solution and described them with empirical models in the hope of finding the key to controlling crystal growth and dissolution. Conceptual models derived from whole-system behaviour have brought us closer to understanding surface processes, but the averaging inherent in the macroscopic approach masks individual processes that may be critical to a thorough understanding of what happens at the molecular level. Now, experimental techniques with resolution in the Ångström range and mathematical modelling based on atomic behaviour offer us the possibility to attack the question from the fundamental level. The dissolution and growth of $CaCO_3$ takes place with rates of reaction that make it possible to observe on laboratory time-scales and the solution concentrations of dissolved constituents are relatively easy to analyse with standard methods. Therefore, the $CaCO_3$ system is a convenient one for studying the fundamental chemical processes that determine crystal growth and dissolution and the factors that inhibit or enhance these processes.

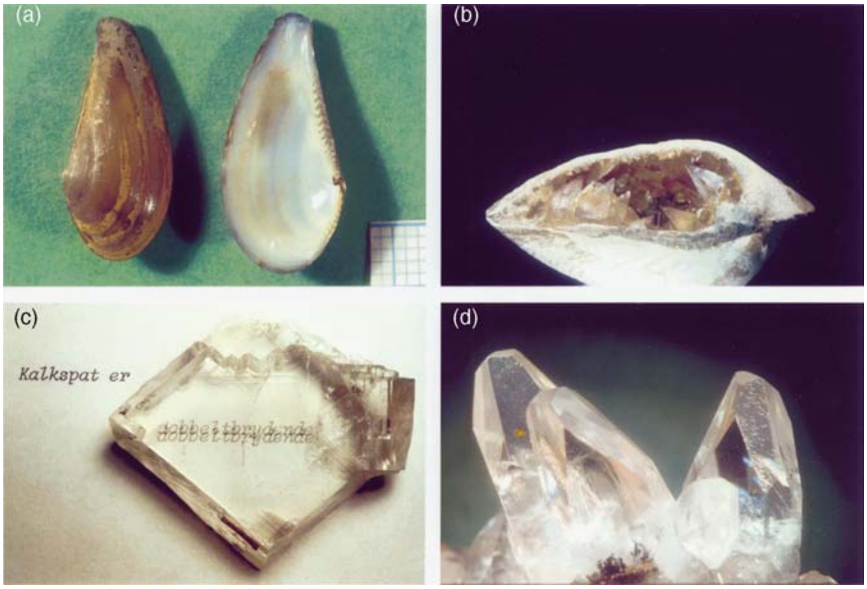


FIGURE 1 $CaCO_3$ can take a number of forms depending on the pressure, temperature and solution conditions during crystal growth. (a) A mollusc shell composed of aragonite. The animal makes a template of organic molecules that inhibits calcite and promotes aragonite because layers of fibrous aragonite make a stronger shell. The mother of pearl is also aragonite but its crystals are platy. (b) A fossil mollusc shell of aragonite with calcite crystals inside. (c) Calcite cleavage rhomb, a common form; (text means, “calcite is double-refracting”). (d) Calcite scalenohedra, another common form.

Calcium carbonate is present in almost all geological environments, but it has numerous forms (Fig. 1). Aragonite is preferred by many marine organisms for building shells because its orthorhombic crystal structure favours the formation of long, thin crystals which, when packed together in bundles, form a strong and elastic material. Calcite, the hexagonal (trigonal) polymorph, is the more stable phase, but crystal habit can vary. The rhomb and the scalenohedron are common, but the crystal growth form depends on the formation conditions such as temperature, pressure, and solution composition. Exactly how and why certain forms are favoured remains unclear, but a cooperative effort between fundamental modelling and experiments can help.

Modelling of mineral surface processes in the past was limited to empirical fitting of macroscopic parameters with a basis in physical relationships. Surfaces were conceived of as plates with net charge. The constant capacitance/electrical double-layer model (described by Stumm and Morgan [1], Sposito [2] and references therein) taught us much about adsorption on oxide surfaces. Refinements added more layers ([3,4] and references therein) or more than one type of site (for example by Hiemstra and colleagues [5,6]). A surface speciation model for calcite was proposed by van Cappellen *et al.* [7] and extended for other carbonate minerals by Pokrovsky and colleagues [8,9] but application of adsorption theory in the $CaCO_3-H_2O$ system is difficult because of moderately high solubility and fast dissolution rates. Monte Carlo simulations have been used, especially to describe dissolution [10,11]. Some of the first *ab initio* modelling of calcite gave a better idea of atomic bonding relationships ([12–15] and many others) and as the database of atom interaction parameters and computing power grew, the size and complexity of systems that could be treated increased. More recent studies ([16–21] and many others) have treated bulk and surfaces under simulation conditions that allow direct comparison with experiment.

The purpose of this article is not to review these modelling studies, but rather to summarise some experimental evidence from the work of our group on the calcite system that might contribute to bridging the gap between simulations and what we observe. High-resolution, surface-sensitive techniques offer new insight into behaviour at the solid/fluid (gas and liquid) interface and provide data that can be used to calibrate mathematical models. We can offer modellers the experimental data they ask for to help push the limits of understanding further and modellers can help us by testing the validity of the conceptual models we derive from observation. Eventually, the goal is to be able to predict behaviour in systems that are awkward, dangerous or impossible for us to experiment upon, such as for example, over geologic time or under extreme pressure, temperature or chemical conditions or because of toxicity or radioactivity. The interplay between modelling and experiment has the power to offer much more than double the returns of each community working alone. Here, information gathered from a number of separate investigations on calcite is assembled into a coherent story that can hopefully serve as a basis for modelling. Detailed reports of these studies already have been or are in the process of being published elsewhere, so experimental conditions, analytical parameters, and the complete scientific arguments for data interpretation can be found in the references cited.

Understanding of the laws that control crystal growth and dissolution are central to answering a number of questions of relevance to science and society. Crystal form can be controlled by organisms which create specific molecules that bind to surfaces and inhibit or enhance growth in certain directions. Growth and degradation of bones, teeth, and shells are examples; better understanding could improve medical treatment. If we could reliably predetermine crystal form, we would have the key to controlling material structure and the production of biominerals of other new materials with specific properties. We would be better able to control scaling in pipes, which would also contribute to reducing bacterial activity in drinking water, and we would be in a better position to predict the fate of heavy metals, toxic organic compounds, and radionuclides in environmental systems. In order to approach the level of understanding needed for predicting behaviour in natural or engineered systems however, we need to consider simplified systems. We must determine the several individual processes that spontaneously occur at mineral surfaces and discover how the interface behaves in response. When calcite is cleaved or at a growing surface, the surface, which is a termination of the bulk structure, does not resemble that within the mineral. Relaxation or restructuring adjusts atomic position of the outermost atoms, interaction with water satisfies dangling charge, liquid water from solution or that adsorbed from the atmosphere reacts with the surface, and omnipresent hydrocarbons are adsorbed and modify the interaction. For each of these scenarios, experimental evidence is presented and the process is discussed.

MATERIALS AND METHODS

Calcite

Single crystals of Iceland spar calcite from Chihuahua, Mexico, supplied by Ward's Scientific, were used for all experiments to ensure consistency. Trace element substitution in this natural material is less than 1%. Unfortunately, it is difficult to find natural crystals that are purer. Synthetic powder of higher purity is available, but even the purest of commercial compounds have some trace components and single crystals large enough to cleave are not available. Samples of Iceland spar calcite are often many centimetres across, making it possible to cleave fresh, flat faces, which is a necessity for analysis with some of the high-resolution techniques. Iceland spar from other localities often has higher defect density and trace element concentration, making experimental results less reproducible. For experiments with solution, deionised water, freshly washed glass vessels and reagent (analytical) grade chemicals were used. Details about sample preparation can be found in Refs. [22,23].

Techniques

Several methods that offer complementary data have been used; these include high-resolution, surface-sensitive techniques as well as classical, wet-chemistry methods. Morphology and surface structure can be observed using atomic force microscopy (AFM). This technique uses a sharp tip to feel the change in net forces interacting between tip and sample, as the sample is rastered beneath it by a piezoelectric scanner. Very small voltages applied to the semiconducting ceramic scanner cause movements on the order of fractions of a nanometre. Force differences sensed by the tip are recorded as a function of position resulting in images with atomic-scale resolution. Experiments are possible *in situ*, under solution, in controlled gas or in air. Eggleston [24] presents an introduction to AFM and other members of the scanning probe microscope (SPM) family.

Surface structure can also be investigated using low energy electron diffraction (LEED). Diffraction patterns from the top two or three atomic layers of a single crystal yield reciprocal lattice spacing for the surface unit cell that is sometimes different than expected from a projection of the bulk structure. More details about LEED as a technique are found in Clarke [25].

Chemical information from the near-surface is provided by several techniques. Infrared spectroscopy (IR) reveals the energies at which certain pairs of atoms absorb energy. More information about this technique is available in McMillan and Hofmeister [26]. X-ray photoelectron spectroscopy (XPS) offers chemical identity and bonding structure. Lateral resolution can range from several micrometres to a millimetre or so but most of the information from an insulator such as calcite comes from the top few nanometres. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) produces spectra with mass resolution of better than 1‰ over several thousand mass units and chemical maps can be made with lateral resolution as low as a micrometre. Analysed material is ejected mostly from the top two or three atomic layers making the technique much more surface sensitive than XPS, but information about bonding is not accessible. These two techniques require ultrahigh vacuum (UHV) but experience shows that a sample's history is recorded, at least to some degree, in the bonds with material that was at the solid/fluid interface. More information about XPS can be found in Hochella [27] and about TOF-SIMS, in Benninghoven *et al.* [28].

The net charge on a particle surface contributes to defining its behaviour in solution and its ability to adsorb and give up components. The solution conditions where net charge is neutral can be determined by electrokinetic mobility experiments, where colloidal-size particles ($\leq 1\,\mu$m) are observed to move between two oppositely charged plates while solution composition is changed. Data from these types of experiments are traditionally modelled using the electrical double layer (EDL) theory, with the purpose of describing adsorption behaviour. More information can be found in Sposito [2] and Stumm and Morgan [1]. Electrokinetic experiments on calcite are discussed by Brady and House [29] and reported for calcite by a number of researchers ([30–34] and others).

SURFACE PROCESSES

Restructuring in the Absence of Water

The overall aim of the investigations of the calcite surface was to determine the fundamental processes that add together to produce the behaviour we see in nature. If we can model each of these processes, we will have come a long way toward modelling growth and precipitation. The most fundamental was to explore the difference between bulk and surface structure by observing behaviour in UHV where the very low partial pressure of reactive gas species allows the possibility of observing a fresh surface before it reacts appreciably. The purpose of the experiments was to determine the extent of relaxation or restructuring on the termination of bulk calcite.

Samples were thoroughly cleaned with solvents, acid and eventually distilled water to decrease surface contamination as far as possible [22]. The UHV chamber with the sample inside was set to "bake-out", where temperature is raised above 100°C in order to evaporate adsorbed water vapour while being pumped at UHV conditions for 24 h. The procedure was run twice to ensure a minimum of adsorbed water, hydrocarbons and other contaminants on the calcite surface and in the vacuum chamber. Pressure was 10^{-10} mbar when the sample was cleaved. At this pressure, it would take about an hour for the surface to be covered by a monolayer of material if the sticking coefficient is assumed to be unity meaning that all material that comes by diffusion through the vacuum to the surface remains there. In practise, the sticking coefficient is less than 1 so it takes more than an hour to produce one adventitious layer.

The first XPS spectra, completed within 20 min of cleavage, showed absolutely no adventitious hydrocarbon on the surface (Fig. 2a). Peaks representing electrons from the components of calcite were as expected [22], but a very small

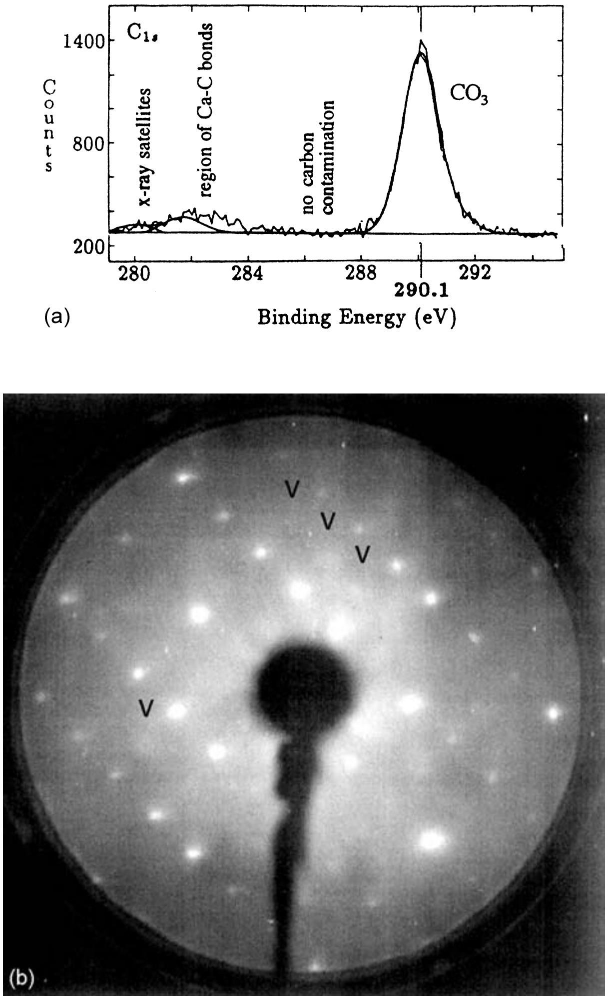


FIGURE 2 (a) XPS spectrum from calcite fractured in UHV and collected over the binding energy range for C_{1s} electrons. The main peak at 290.1 eV represents photoelectrons ejected from C in CO_3 groups. There is no carbon contamination. In the region where carbide bonds are expected, is observed a very small peak near 283 eV, slightly above the X-ray satellites. (b) LEED pattern from a calcite surface fractured in vacuum. The bright spots represent the expected pattern from the surface unit cell. The weak, diffuse spots (arrows) indicate a 2 × 1 superstructure.

carbon peak was observed in the region where carbide bonds are found (Fig. 2a). In the ultra-clean environment, there is an absence of other material to react with the broken bonds at the cleaved surface and this peak suggests that the outermost layer relaxes allowing increased interaction between Ca and C. Other samples baked and cleaved in the same way were also analysed with LEED. Weak maxima representing a 2×1 superstructure are observed (Fig. 2b; arrows). Such a pattern could be interpreted as evidence that CO_3 groups are twisted and that Ca–O octahedra are deformed. Results from preliminary attempts to model a cleaved calcite surface using force-field energy minimisation were consistent with a conceptual model where the top-most layer relaxes into the bulk and the CO_3 groups twist so that they make a slightly higher angle to the surface (unpublished work together with Jordan Alexander, then at Oslo University).

XPS offered no evidence of the presence of H_2O, CO_2 or OH on the in-vacuum fractured surface. Peaks representing these species would have appeared as small shoulders on the high binding energy flanks of the main O and C peaks. It is not possible to analyse for H directly by XPS. However, there was evidence of adsorbed H, manifested in the form of a small shoulder at slightly higher binding energy than the CO_3 peak (observed at 291.1 eV), in the location where one expects CO_3H (at 295.5 eV, Fig. 2a). Observing the effects of hydrogen is not a surprise; it makes up a high proportion of vacuum gas at UHV because it can easily pass through even the high quality niobium stainless steel of UHV chambers and it is not easily removed by most vacuum pumps. It is logical that hydrogen would react with the reactive surface.

When the in-vacuum fractured sample was exposed to air, subsequent analysis showed that the carbide peak disappeared, an adventitious hydrocarbon peak appeared, and the CO_3H peak increased in size. The carbide peak was absent on all calcite samples that had been cleaved in air before the entry into the UHV chamber, but on these samples, the CO_3H peak was always present. These observations confirm that the Ca–C interaction is unique to the UHV environment where other species for reaction are lacking. Interaction with air results in a different bonding environment, suggesting that reaction with some component in air is more energetically favourable than relaxation for stabilising the surface. More details of these studies can be found in Refs. [22,35].

Hydrolysed Water Behaving As OH and H

Calcite surfaces cleaved in air and put into UHV within 5 min of fracture provide no evidence of adsorbed CO_2 or H_2O with either XPS or TOF-SIMS. However, TOF-SIMS demonstrates that OH, O and H can be ejected from the top atomic layers even after the sample has been in UHV for several hours (Fig. 3). There are no peaks in the XPS binding energy region where H_2O would be expected (at about 534.5 and 292.5 eV, Fig. 4) but peaks are observed at energies representing OH and H attached to Ca and CO_3, respectively. This evidence suggests that water adsorbs to the highly reactive surface immediately after fracture and the layer in contact with the surface is hydrolysed. The peaks show an absence of "water" bonding character because in the UHV chamber, the adsorbed water is evaporated but OH and H feel more strongly attached as hydrolysis species. This

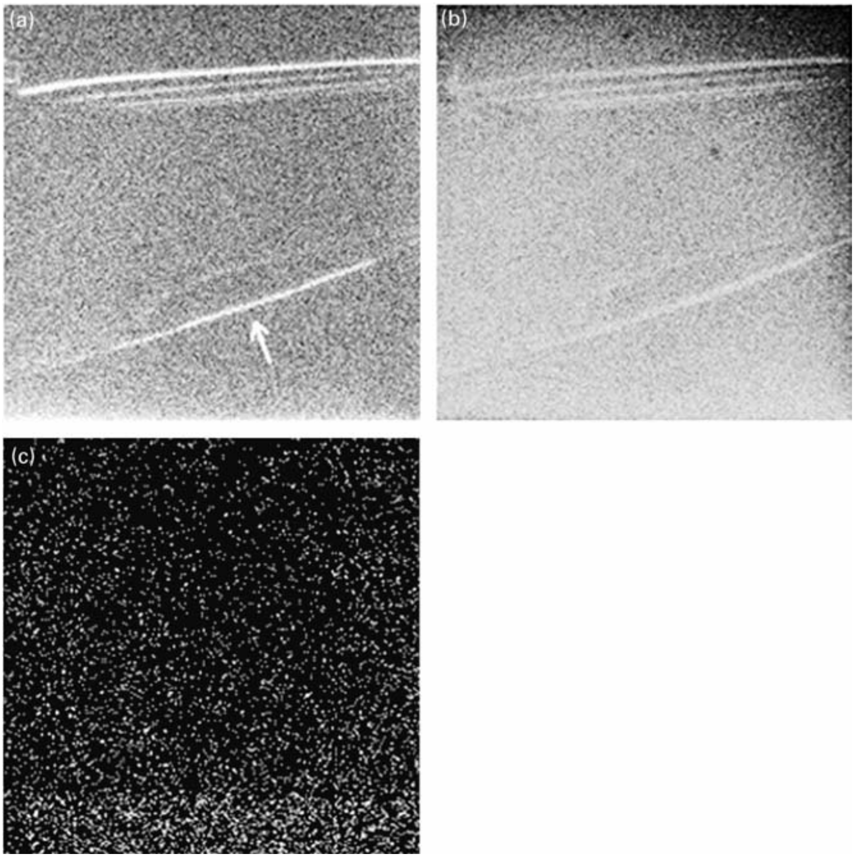


FIGURE 3 TOF-SIMS chemical maps from a freshly cleaved calcite surface. (a) H, (b) O and (c) C. Light colours represent highest intensity; there is only background intensity for C because it leaves the surface mostly as CO_2, which is neutral and therefore not accessible to detection. Intensities of H and O are high, indicating significant surface coverage. The map for OH looks the same. The bright lines (as at arrow) outline step edges, which are also covered by hydrolysis species. They are brighter because the steps lie roughly perpendicular to the detector's line of sight, allowing the surface species along these edges to produce higher intensity.

is not to say that interaction between OH and H is completely non-existent, but the strength of the bonds linking them to the surface is strong enough for their character to be observed. Other qualitative evidence for relative bonding strength is provided by observing behaviour with time. Attachment of OH and H is strong enough to resist storage in UHV for many hours; CaOH and CO_3H peaks remain, meaning that OH and H are not able to evaporate from the surface as water

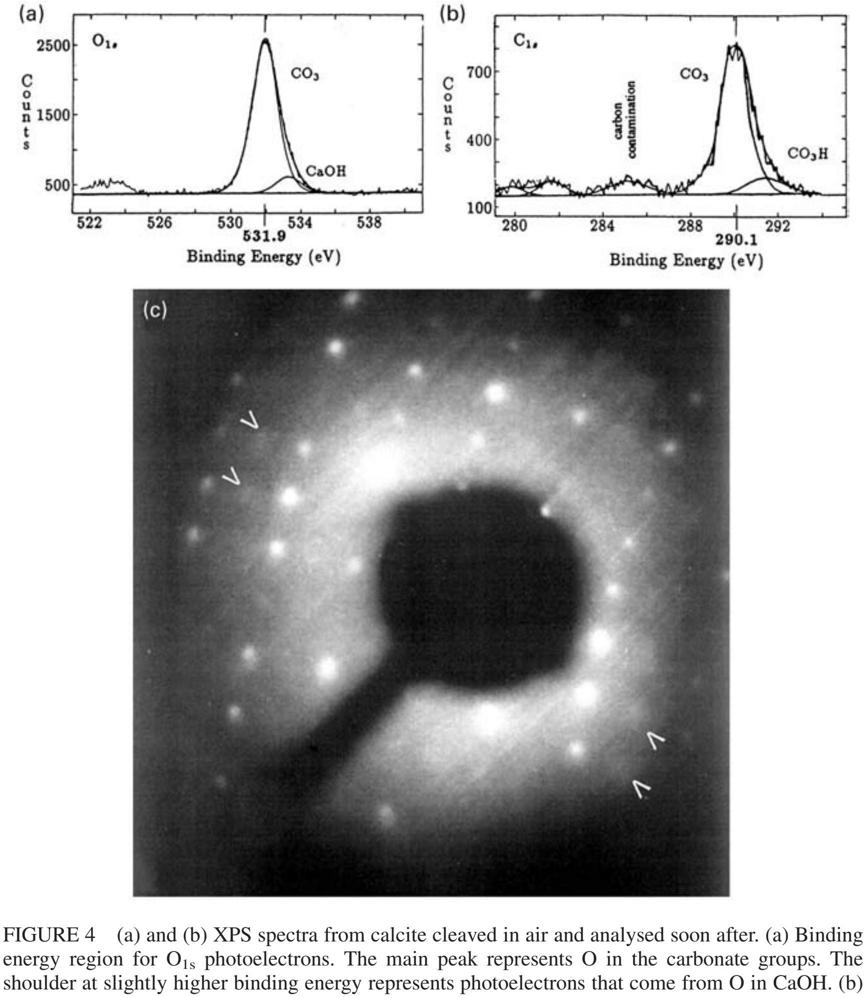


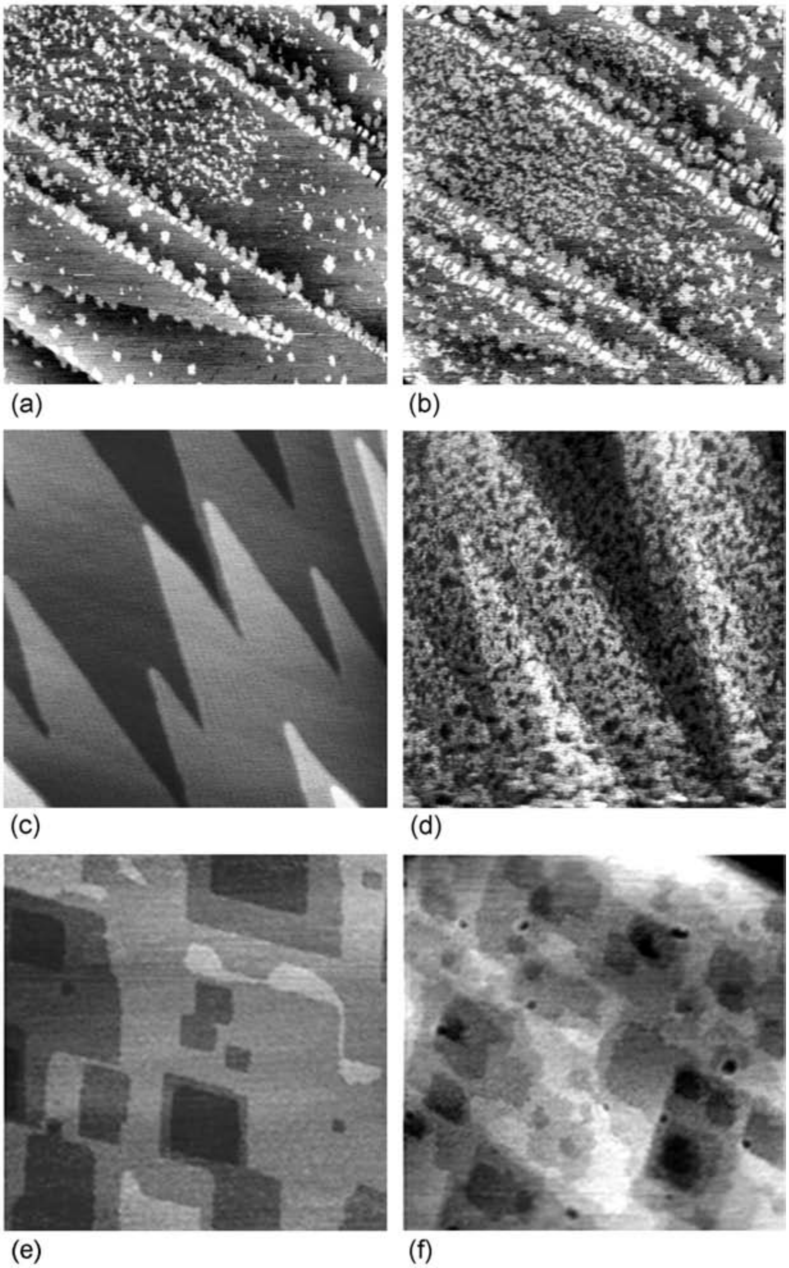
FIGURE 4 (a) and (b) XPS spectra from calcite cleaved in air and analysed soon after. (a) Binding energy region for O_{1s} photoelectrons. The main peak represents O in the carbonate groups. The shoulder at slightly higher binding energy represents photoelectrons that come from O in CaOH. (b) The region representing C_{1s} photoelectrons. The main peak results from CO_3; the shoulder, from CO_3H. The peak near 284.5 eV results from hydrocarbons that came from air. (c) LEED pattern for calcite cleaved in air. The expected surface unit cell makes the bright spots. The weak, diffuse spots (arrows) indicate a 2 × 1 superstructure.

vapour. However, long exposure to the X-ray beam does result in lost peak intensity both for the hydrolysis shoulders and for the C and O main peaks. In the energy of the X-ray beam, the $CaCO_3$ surface is broken down to CaO; CO_2 escapes as a gas.

LEED patterns from samples cleaved in air also show a 2×1 superstructure suggesting that production of hydrolysis species also promotes the twisting of CO_3 groups and distortion of Ca-octahedra (Fig. 4c). Preliminary modelling efforts with force-field minimisation show that when the surface is hydrated, CO_3 groups do twist, but in contrast to their behaviour in UHV, they rotate toward the surface plane, or flatten (unpublished work together with Jordan Alexander, then at Oslo University).

There are several other bits of evidence for the existence of hydrolysis species on calcite. Samples of otavite ($CdCO_3$), a carbonate mineral with crystallographic dimensions almost identical with calcite yield XPS spectra with shoulder peaks representing CdOH and CO_3H. However, bentonite, a swelling clay that has a high affinity for water, offers no XPS evidence that adsorbed water or hydrolysis species have survived UHV or analytical conditions. High-resolution AFM images also show a 2×1 superstructure during imaging in air or under water, supporting evidence for a restructured surface also outside the UHV environment. Furthermore, because of the dynamic and interactive nature of AFM imaging, one can probe the sample and watch its response. Scanning over the atomic rows at a variety of angles results in images with a variety of appearances, which one can only interpret as the result of interaction with something that lies somewhat loosely on the surface so that its position can be shifted by the tip. This is consistent with the interpretation that the tip images the uppermost OH from surface Ca-octahedra, which are constrained by only one bond to Ca.

Recent IR experiments on calcite exposed to various conditions of humidity (together with Simon Redfern, Cambridge) reveal undeniable peaks for OH vibrations. Finally, a number of electrokinetic experiments prove that OH and H are not potential-determining ions for calcite in solution as they are for oxides, which implies that on calcite, OH and H are strongly bound to the surface. Instead, the calcite-forming ions, Ca^{2+}, CO_3^{2-} and HCO_3^- have been observed to be potential determining, meaning that they attach weakly enough and they can detach when solution conditions are changed. Easy loss and attachment of the calcite-forming ions occurs during dissolution and precipitation, but under conditions where the system is at equilibrium, their easy loss and attachment can only be explained by adsorption on top of a layer of OH and H bonded as hydrolysis species. Further details on the studies summarised in this section are found in Refs. [22,35–38].


(a)
(b)
(c)
(d)
(e)
(f)

Presence of Water and Its Behaviour As a Solvent

Although we cannot see it, all mineral surfaces in air are covered with a thin film of water that they have adsorbed from the atmosphere. The thickness of the film varies depending on relative humidity. We can see its effects by the way the AFM tip behaves during approach to a surface and withdrawal from it. X-ray standing wave reflectivity on calcite in one particular experiment showed a water layer at least 20 monolayers thick [39]. Even though surfaces in air appear dry and stable, evidence of dissolution and reprecipitation in air is clear from the high-resolution of AFM images.

Observations at highly local scale ($< 1\ \mu$m) allow us actually to see dynamic equilibrium at work. Figure 5a,b shows two images of the same calcite surface with 20 min lapse in time. During exposure to air with about 50% relative humidity, holes form spontaneously in the middle of terraces (particularly visible at the lower right corner) and step edges are eroded (lower left corner) *at the same time as* new calcite precipitates on top of terraces and out from step edges. At high humidity, the surface is highly dynamic. Figure 5c,d shows a fresh surface soon after cleavage and the same surface 8 h later. The triangles that result from pressure cleavage and the step heights of one monolayer (3 Å) are preserved, but the surface is completely recrystallised. Even in the dry air of a dessicator, where humidity is less than 5%, there is enough water on the surface to allow recrystallisation, though the process proceeds at a slower rate and produces calcite that is more ordered and with fewer defects. Figure 5e, is taken from a freshly cleaved calcite sample that had been exposed for 1 min only to solution. The remaining droplet was blown away and the sample was imaged immediately. The short dissolution event resulted in one to several monolayer deep etch pits with straight edges. After 18 days storage (Fig. 5f), holes have begun to fill in and the pit edges have become rounded. Implications of this spontaneous recrystallisation process are that materials, such as adsorbed components, can

FIGURE 5 AFM images of dry calcite surfaces during exposure to air. Light colour represents levels that are closer to the viewer; dark, further away. (a) and (b) Taken from the same site 15 and 35 min after cleavage in air with ~50% relative humidity. Image width is 10 μm and the steps are one monolayer high (3 Å). The effects of dynamic equilibrium are visible. Holes form on the terraces (especially visible at lower right corner) and step edges are eroded whereas immediately adjacent, material is accumulated. (c) Taken within 5 min of cleavage and then (d) the same surface at a slightly different site, after 8 h exposure to air with humidity of about 40%. Image width is 1 μm. Step heights are preserved but the surface is completely recrystallised. (e) Taken after exposure of a fresh cleavage surface to solution for 1 min and immediately dried, and then (f) the same sample (different site) imaged after 18 days storage in a desiccator where humidity was less than 5%. Material from the straight edge etch pits on the fresh samples is dissolved and reprecipitated so that holes fill in and edges become irregular.

be incorporated into the near-surface bulk by burial. More details about the dynamic nature of calcite surfaces exposed to air are presented in Refs. [35,40].

Adsorbed Organic Compounds

Any surface exposed to air or water is covered almost immediately by a layer of adventitious carbon; this is an organic material that simply comes to the surface from the surroundings. Even samples cleaved in air and put into the UHV chamber after a few minutes have a peak of adventitious carbon that is equivalent to one or two molecular layers. An example is the peak at about 285 eV in Fig. 4b. Adventitious carbon can form a diffuse, physisorbed layer on surfaces that moves easily out of the way during dissolution or growth, or it can bind with surface sites and inhibit these processes. An example is shown in Fig. 6. Dissolution was initiated on a fresh calcite surface by deionised water contaminated by organic material from silicon tubing. Pinning prevented movement of step edges making rounded terraces and caused formation of numerous kinks. Sometimes calcite dissolved behind the attached material making peninsula-shaped protrusions and

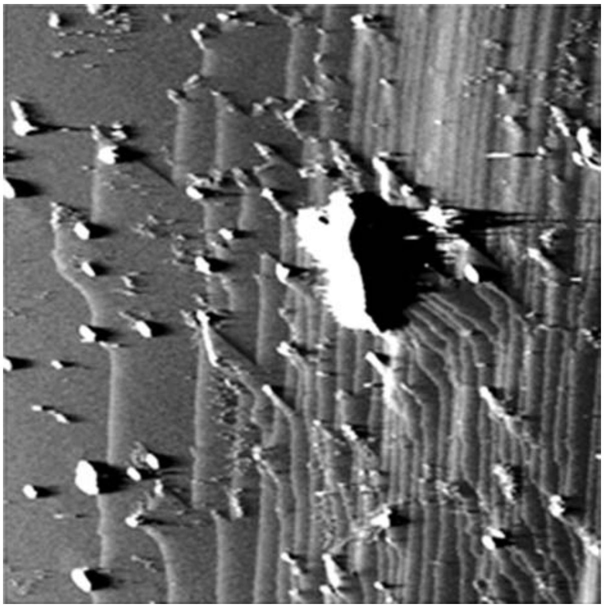


FIGURE 6 An AFM image of calcite that has been exposed for several minutes to distilled water contaminated by silicon tubing. This is a deflection mode image which highlights the change in slope so right-facing edges appear in shadow, and left-facing edges, light. The water dissolved the steps, which retreated toward the right side. Organic contamination pinned step edges so they could not retreat regularly. A very large particle near the middle blocked many steps behind it (to its right).

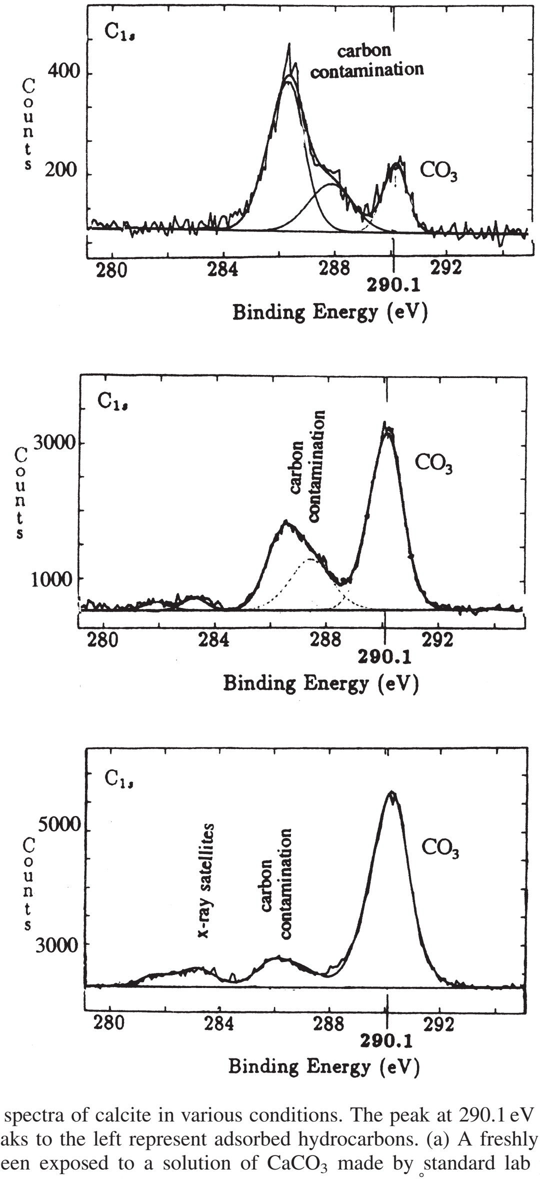


FIGURE 7 XPS spectra of calcite in various conditions. The peak at 290.1 eV represents the CO_3 groups and the peaks to the left represent adsorbed hydrocarbons. (a) A freshly cleaved surface of calcite that had been exposed to a solution of $CaCO_3$ made by standard lab practice. The peak representing carbon contamination dominates (approximately 28 Å thick). (b) Commercial calcite powder. Organic inhibitors were added during production of the powder to enhance nucleation and inhibit crystal growth to ensure a fine, homogeneous powder. The hydrocarbon contamination on this surface is approximately 15 Å thick. (c) After treatment, the amount of contamination is nearly as low as on a sample cleaved in air and analysed immediately (Fig. 4b). Here, the layer is about 3 Å thick.

islands. When the contaminant finally desorbed, edges retreated as on uncontaminated areas. In a similar way, crystal growth can be disrupted by organic components so that less favoured faces become prominent. A trick adopted by organisms to control the shape of shells, bones, and teeth is to make organic molecules that selectively block certain sites. In order to investigate the effects of organic material on surface processes, it is necessary to define a baseline by defining what a clean system is.

Our current conceptual model of dissolution is the ordered, progressive removal of steps, atom-by-atom and layer-by-layer. Similarly, the conceptual model for precipitation is the ordered, progressive addition of material. These models have been derived from the results of years of macroscopic experiments using standard practice in laboratories that we consider clean. Namely, they have used: commercial powder or ground mineral samples; distilled or deionised water with high resistivity stored in clean plastic bottles; glassware washed by standard practise with detergent, acid wash and final rinse of deionised water and stored in closed cupboards for several weeks before use; and solutions that are often filtered through polycarbonate filters in plastic holders and stored in bottles with plastic or parafilm covers. An XPS spectrum for a sample of freshly cleaved calcite that was exposed for only 1 min to a solution of $CaCO_3$ made by standard lab practice is presented in Fig. 7a. The small peak to the right at 290.1 eV binding energy results from the CO_3 of the calcite. The very large peak represents organic hydrocarbon, which is equivalent to retreat of a layer about 28 Å thick of contamination. This spectrum can be compared to the sample of freshly cleaved

FIGURE 8 SEM image of a sample of commercial calcite powder as it came from the bottle. The faces of the crystallites appear smooth and regular.

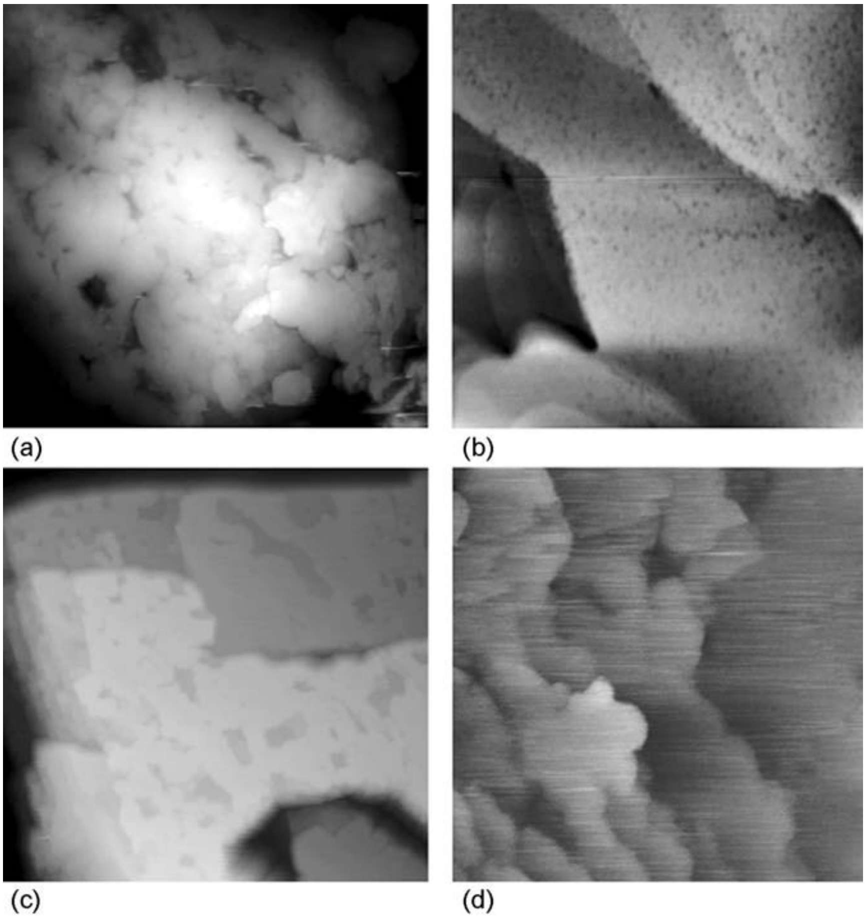


FIGURE 9 AFM images of commercial calcite powder as received (a) and (b) and after treatment (c) and (d). Before treatment (corresponding to Figs. 7b and 8), the surface at high-resolution is very rough. The height range in (a) is 4500 Å from light to dark, which can be compared to that for Fig. 5, where maximum range is 12–15 Å. The edges are rounded and irregular, tell-tale signs of the presence of reactive organic material during growth. (a) Image width is 6 μm. Step edges are rounded and the concept of a terrace is difficult to imagine. (b) Image width is 1 μm. Terraces are full of holes that are 2 or 3 or more atomic layers deep. Step edges are rounded and step heights are always more than one atomic layer, and often are many. After treatment, the terraces are flatter but edges are still rounded and steps are still many atomic layers tall. (c) Image width is 1.5 μm. The holes in the terrace in the middle of the image are about 60 atomic layers deep and the terrace lies about 90 layers above the next. (d) Image width is 400 nm; step height is occasionally 3 Å or one monolayer, but is more frequently several.

calcite that was exposed only to air, Fig. 4b. The extra contamination came from the solution that we believed to be clean.

One can decease such contamination by preparing solutions immediately before use, using centrifugation rather than filtration, not exposing the deionised water or solutions to any plastic storage or transfer vessel and washing glassware and deionising the water immediately before use. However, a significant proportion of the hydrocarbons responsible for the peak in Fig. 7a are derived from the commercial calcite powder itself (Fig. 7b). They result from organic compounds that are added during the manufacturing process to inhibit growth of large crystals and enhance nucleation so as to produce a fine-grained, homogenous powder. These organic compounds remain on the powder and unknowingly, are included into experiments. The commercial calcite powder looks smooth and regular with flat surfaces at micrometre scale (Fig. 8). However, at nanometre resolution, terraces are far from flat and step edges are many, many atomic layers high (Fig. 9a,b). This is dramatically different from the appearance of clean freshly cleaved calcite (Fig. 5c). Treating the powder before use [23] can remove a significant proportion of the hydrocarbon (Fig. 7c) and restores behaviour to something more normal (Fig. 9c,d), but even after treatment, the effects of organic carbon are still observable: terrace edges are still curved and steps are more than one or two atomic layers high.

So we are faced with a contradiction. Macroscopic investigations made in standard lab conditions have unknowingly been performed in the presence of significant amounts of adventitious carbon. However, results from these studies have been used to develop conceptual models, which propose that crystals grow and dissolve by atom-by-atom and layer-by-layer addition and removal of material. High-resolution evidence on calcite shows that, in these contaminated systems, step edges are curved, terraces are irregular and step edges are much more than one atomic layer high. Layer-by-layer and atom-by-atom addition and removal are the exception rather than the rule. On this topic, there is certainly work to be done, both experimentally and in the development of a conceptual model that explains inhibition and growth on crystalline surfaces.

Some information about contamination on calcite is presented in Ref. [22], but a full article is in preparation [23]. An investigation of surface atomic structure in the cleanest system possible will hopefully be published within the year [41].

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References

[1] Stumm, W. and Morgan, J.J. (1981) Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd ed. (Wiley, Toronto).

[2] Sposito, G. (1984) The Surface Chemistry of Soils (Oxford University Press, New York).

[3] Davis, J.A., James, R.O. and Leckie, J.O. (1978) "Surface ionization and complexation at the oxide/water interface", *J. Colloid Interface Sci.* **63**, 480–499.

[4] Davis, J.A., Hayes, K.F., (1986) In: Geochemical Processes at Mineral Surfaces (ACS Symposium Series, Washington, DC) **323**.

[5] Hiemstra, T., van Riemsdijk, W.H. and Bolt, G.H. (1989) "Multi-site proton adsorption modelling at the solid/solution interface of (hydr)oxides: A new approach. I. Model description and evaluation of intrinsic reaction constants", *J. Colloid Interface Sci.* **133**, 91–104.

[6] Hiemstra, T. and van Riemsdijk, W.H. (1991) "Physical–chemical interpretation of primary charging behavior of metal (hydr)oxides", *Colloids Surf.* **59**, 7–25.

[7] Van Cappellen, P., Charlet, L., Stumm, W. and Wersin, P. (1993) "A surface complexation model of the carbonate mineral-aqueous solution interface", *Geochim. et Cosmochim. Acta* **57**, 3505–3518.

[8] Pokrovsky, O.S., Schott, J. and Thomas, F. (1999) "Processes at the magnesium-bearing carbonate solution interface: I—A surface speciation model for magnesite", *Geochim. et Cosmochim. Acta* **63**, 863–880.

[9] Pokrovsky, O.S., Schott, J. and Thomas, F. (1999) "Dolomite surface speciation and reactivity in aquatic systems", *Geochim. et Cosmochim. Acta* **63**, 3133–3143.

[10] Liang, Y., Baer, D.R., McCoy, J.M., Amonette, J.E. and Lafemina, J.P. (1996) "Dissolution kinetics at the calcite–water interface", *Geochim. et Cosmochim. Acta* **60**, 4883–4887.

[11] McCoy, J.M. and Lafemina, J.P. (1997) "Kinetic Monte-Carlo investigation of pit formation at the $CaCO_3$ (10–14) surface–water interface", *Surf. Sci.* **373**, 288–299.

[12] Dove, M.T., Winkler, B., Leslie, M., Harris, M.J. and Salje, E.K.H. (1992) "A new interatomic potential model for calcite: Applications to lattice dynamics studies, phase transition and isotope fractionation", *Am. Mineral.* **77**, 244–250.

[13] Catti, M., Pavese, A., Apra, E. and Roetti, C. (1993) "Quantum mechanical Hartree-Fock study of calcite ($CaCO_3$) at variable pressure and comparison with magnesite ($MgCO_3$)", *Phys. Chem. Miner.* **20**, 104–110.

[14] Mao, Y. and Siders, P.S. (1997) "Molecular Hartree-Fock model of calcium carbonate", *Theochem. J. Mol. Struc.* **419**, 173–184.

[15] Thackeray, D.J. and Siders, P.D. (1998) "Molecular-orbital and empirical-potential descriptions of $CaCO_3$", *J. Chem. Soc., Faraday Trans.* **94**, 2653–2661.

[16] Titiloye, J.O., Parker, S.C. and Mann, S. (1993) "Atomistic simulation of calcite surfaces and the influence of growth additives on their morphology", *J. Cryst. Growth* **131**, 533–545.

[17] de Leeuw, N.H. and Parker, S.C. (1997) "Atomistic simulation of the effect of molecular adsorption of water on the surface structure and energies of calcite surfaces", *J. Chem. Soc., Faraday Trans.* **93**, 467–475.

[18] de Leeuw, N.H. and Parker, S.C. (1998) "Modeling the competitive adsorption of water and methanoic acid on calcite and fluorite surfaces", *Langmuir* **14**, 5900–5906.

[19] de Leeuw, N.H., Parker, S.C. and Harding, J.H. (1999) "Molecular dynamics simulation of C-crystal dissolution from calcite steps", *Phys. Rev. B: Condens. Matter* **60**, 13792–13799.

[20] Fisler, D.K. and Cygan, R.T. (1998) "Cation diffusion in calcite: Determining closure temperatures and the thermal history for the Allan-Hills-84001 Meteorite", *Meteor. Planet. Sci.* **33**, 785–789.

[21] Wright, K., Cygan, R.T. and Slater, B. (2001) "Structure of the (10–14) surfaces of calcite, dolomite and magnesite under wet and dry conditions", *Phys. Chem. Chem. Phys.* **3**, 839–844.

[22] Stipp, S.L. and Hochella, Jr, M.F. (1991) "Structure and bonding environments at the calcite surface as observed with X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED)", *Geochim. et Cosmochim. Acta* **55**, 1723–1736.

[23] Stipp, S.L.S. "What is a clean surface?—Organic carbon, its influence on calcite surface morphology and a treatment method for removing it" (in preparation).

[24] Eggleston, C.M. (1994) "High resolution scanning probe microscopy: tip-surface interaction, artifacts and applications in mineralogy and geochemistry", In: Nagy, K.L. and Blum, A.E., eds, Scanning Probe Microscopy of Clay Minerals (Clay Minerals Society), pp 1–90.

[25] Clarke, L.J. (1985) Surface Crystallography: An Introduction to Low-Energy Electron Diffraction (Wiley, New York).

[26] McMillan, P.F. and Hofmeister, A.M. (1988) "Infrared and Raman spectroscopy", In: Hawthorne, F.C., ed, Spectroscopic Methods in Mineralogy and Geology (Mineralogical Society of America, Washington, DC) Reviews in Mineralogy **18**, pp 99–159.

[27] Hochella, Jr, M.F. (1988) "Auger electron and X-ray photoelectron spectroscopies", In: Hawthorne, F.C., ed, Spectroscopic Methods in Mineralogy and Geology (Mineralogical Society of America, Washington, DC) Reviews in Mineralogy **18**, pp 573–637.

[28] Benninghoven, A., Rüdenauer, F.G. and Werner, H.W. (1987) Chemical Analysis (Wiley, Chichester).

[29] Brady, P.V. and House, W.A. (1996) "Surface-controlled dissolution and growth of minerals", In: Brady, P.V., ed, Physics and Chemistry of Mineral Surfaces (CRC Press, Boca Raton), pp 225–306.

[30] Somasundaran, P. and Agar, G.E. (1967) "The zero point of charge of calcite", *J. Colloid Interface Sci.* **24**, 433–440.

[31] Foxall, T., Peterson, G., Rendall, H.M. and Smith, A.L. (1979) "Charge determination at calcium salt/aqueous solution interface", *J. Chem. Soc., Faraday Trans. 1* **75**, 1034–1039.

[32] Siffert, B. and Fimbel, P. (1984) "Parameters affecting the sign and the magnitude of the electrokinetic potential of calcite", *Colloids Surf.* **11**, 377–389.

[33] Amankonah, J.O. and Somasundaran, P. (1985) "Effects of dissolved mineral species on the electrokinetic behavior of calcite and apatite", *Colloids Surf.* **15**, 335–353.

[34] Thompson, D.W. and Pownall, P.G. (1989) "Surface electrical properties of calcite", *J. Colloid Interface Sci.* **131**, 74–82.

[35] Stipp, S.L.S. (1999) "Toward a conceptual model of the calcite surface: Hydration, hydrolysis and surface potential", *Geochim. et Cosmochim. Acta* **63**, 3121–3131.

[36] Stipp, S.L.S., Hochella, Jr, M.F., Parks, G.A. and Leckie, J.O. (1992) "Cd^{2+} uptake by calcite, solid-state diffusion, and the formation of solid-solution: Interface processes observed with near-surface sensitive techniques (XPS, AES and LEED)", *Geochim. et Cosmochim. Acta* **56**, 1941–1951.

[37] Stipp, S.L.S., Eggleston, C.M. and Nielsen, B.S. (1994) "Calcite surface structure observed at micro-topographic and molecular scale with Atomic Force Microscopy (AFM)", *Geochim. et Cosmochim. Acta* **58**, 3023–3033.

[38] Stipp, S.L.S., Konnerup-Madsen, J., Franzreb, K., Kulik, A. and Mathieu, H.-J. (1998) "Spontaneous movement of ions through calcite at standard temperature and pressure", *Nature* **396**, 356–359.

[39] Chiarello, R.P., Wogelius, R.A. and Sturchio, N.C. (1993) "*In situ* synchrotron X-ray reflectivity measurements at the calcite–water interface", *Geochim. et Cosmochim. Acta* **57**, 4103–4110.

[40] Stipp, S.L.S., Gutmannsbauer, W. and Lehmann, T. (1996) "The dynamic nature of calcite surfaces in air", *Am. Mineral.* **81**, 1–8.

[41] Stipp, S.L.S., Eggleston, C.M. and Refson, K. "A more versatile conceptual model for describing crystal surface reactivity" (in preparation).