Observations of hydration, hydrolysis and recrystallization on calcite surface exposed only to air

S. L. S. Stipp
Geologisk Institut, Københavns Universititet, Øster Voldgade 10,
DK-1350 København K, Denmark

Although we often think of a mineral surface simply as a termination of the bulk's structure and composition, evidence shows that in many cases the surface behaves very differently than expected. Partial charges remaining at the interface of a solid must be delocalized by atomic rearrangement or satisfied by reaction with the environment. Lattice restructuring changes the physical geometry and local charge configuration of a surface, whereas adsorption can alter local geometry, charge distribution and chemical relationships. Each mineral's characteristic response to the disruption in atomic structure caused by a surface controls the compostion of the fluid in contact, be it solution, air or other gases.

In an aquifer, a waste dump, a water-treatment plant, a sedimentary basin or an ore-body, surfaces provide sites of uptake or release of trace components. Atomic-level understanding of how a surface's composition and structure differ from the bulk can help us test theoretical models and refine predictions for the mobility and fate of contaminants, diagenetic fluids or ore-forming species. The common occurance of calcite ($CaCO_3$) makes it a mineral of interest in many fields of Earth sciences and its relatively rapid rates of reaction make it an excellent choice for the fundamental study of surface processes.

Some recent work proved that the surface of calcite is not static in air (Stipp *et al.*, 1996). Even in the absence of a visible liquid phase, surfaces rearrange (Fig. 1). Cleavage faces that are atomically flat immediately after fracture become covered with new material that is several unit cells thick, over intervals of a few minutes to several days. In some places, pits form and terrace edges change shape whereas in other places, material grows out over the surface from small calcite particles that remain clinging after cleavage. The phenomenon was shown to be a function of the ambient humidity, but absolute mineralogical identification of the rearranged material remained uncertain.

The purpose of this short communication is to very briefly review previously published observations about the composition and structure of the calcite surface and to present new evidence concerning the identity of the rearranged material.

Previous work has shown that a calcite surface, fractured in air, satisfies its dangling bonds by reacting with water present as humidity. X-ray photoelectron spectroscopy (XPS) revealed increased concentrations of O at the surface relative to the bulk, and proved the presence of the hydrolysis species: $S\cdot$ CaOH and $S\cdot$ CO_3H (where $S\cdot$ represents the $CaCO_3$ surface) (Stipp and Hochella, 1991). Molecular-scale images taken with Atomic Force Microscopy (AFM) demonstrated that calcite surfaces are reconfigured as a result of hydration (Stipp *et al.*, 1994). Investigations of force relationships between tip and sample at various humidities has shown that a layer of water of varying thicknesses adsorbs from air onto the calcite surface (work in progress). This water layer explains what looks like dissolution and growth on surfaces that are exposed only to air (Stipp *et al.*, 1996).

New studies using Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) shows that the top few atomic layers of both fresh and air exposed calcite samples are composed of the elements expected for calcite, namely, Ca, C and O, but there is also evidence of H and OH in the secondary ion cloud, suggesting that these species are also abundant at the surface. On all samples that have been exposed to air for several hours to several days, surface rearrangement is clear in AFM images but TOF-SIMS shows that the surface concentration of all other elements is at background levels. Thus the composition of the reorganized material is defined; possibilities for the material's identity are limited to either an amorphous or a crystalline combination of Ca with carbonate, bicarbonate, hydroxyl or hydrate.

AFM images of many samples collected over a range of humidity conditions for periods of up to a couple of weeks show that material accumulates either slowly as a single layer in an ordered outgrowth on step edges (Fig. 1), or more rapidly

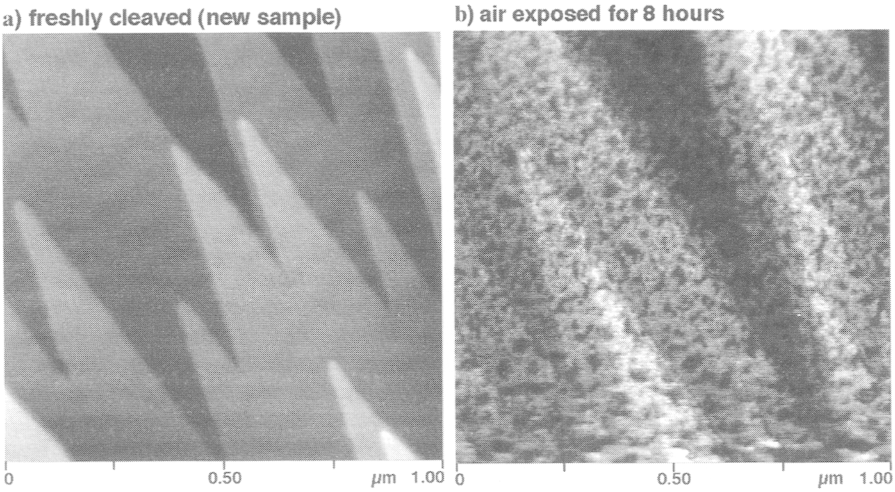

FIG. 1. AFM image of the calcite surface in air. The terraces are one unit cell high. Light surfaces are highest, dark are further away. (a) soon after cleavage. (b) after exposure to air for 8 hours. This sample has only been in contact with the humidity in air, never with liquid water.

and somewhat chaotically, spreading in several-layer thick accumulations across terraces. In many cases, epitaxial continuity with the underlying calcite lattice is obvious and holes where material is lacking often show a rhombohedral symmetry. Atomic resolution images of the accumulated material have indicated an ordered arrangement with a pattern that resembles that found on freshly cleaved terraces, but to date, these images have proven difficult to obtain and of poor resolution. Thus, the material is clearly crystalline, but the pseudomorphs of $CaCO_3$, namely vaterite and aragonite, and its hydrates, $CaCO_3{\cdot}H_2O$ and ikaite ($CaCO_3{\cdot}6H_2O$) have a lattice mismatch that makes them unlikely to grow directly on a calcite surface. Therefore, the structural evidence suggests that the reorganized material is recrystallized calcite.

However, the reorganized material has some subtle differences in physical properties when compared to the original cleaved surface. The material crystallized at the edges of steps often appears to be very slightly taller than the original terrace from which it grew. The accumulated material is more fragile to destruction when imaging force on the tip is increased, and until now it has not been possible to get clear images at atomic scale. The friction coefficients are sometimes different than those for surfaces of the original calcite. The new material, particularly that which accumulates rapidly as several unit-cell-thick layers, has many holes and irregularities that trend in the direction of the calcite rhombohedral structure. With time, some of the recrystallized material appears to settle to a lower height, holes fill in and step edge definition sharpens. All of these observations suggest that the defect density of the newly recrystallized material is significantly higher than the original cleavage surface and with time, some of these defects heal.

These observations are consistent with the following conceptual model:

After cleavage, the surface hydrates, water is hydrolyzed to satisfy the dangling bonds left by fracture, and a capillary layer of water adheres to the surface, with thickness depending on the humidity present in the air in contact. The solution reaches equilibrium with the calcite surface by dissolving material at step edges, at defects in terraces and from small calcite particles left by cleavage. When saturation is reached, the process called 'dynamic equilibrium' leads to precipitation of calcite at points where the surface free energy can be lowered, namely at step edges and defects on terraces. Ca and CO_3 move through the solution as hydrolyzed ions, and when they join the crystalline material, they bring their hydration and hydrolysis products with them. If precipitation rate is higher than dehydration rate, then the OH, H and H_2O, that are paired with the Ca and CO_3, remain entrained within the newly crystallized material, causing abundant defects in the lattice. With time and continued rearrangement, the newly recrystallized material dehydrates, some defects are healed and the material takes on the structure and composition of calcite.