Water-Rock Interaction, Kharaka & Maest (eds) © 1992 Balkema, Rotterdam. ISBN 90 5410 075 3

Using atomic force microscopy to study the structure, topography and dissolution of albite surfaces

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ABSTRACT: The application of atomic force microscopy (AFM) to the study of the structure and reactions on albite feldspar surfaces is illustrated with three examples. Images taken in air of a freshly cleaved surface show that the (010) plane is composed of en-echelon ring structures, where each ring shares an 'edge' with an adjacent ring. These rings most probably are composed primarily of oxygen atoms. Although we have not observed step and terrace structures at the atomic scale, our images show that the (010) plane has a high density of steps, with step heights ranging from approximately 25 to 50 Å. We also have had preliminary success imaging surfaces in aqueous solutions. Real time imaging of a freshly-cleaved surface in contact with a pH 2 solution shows the rapid dissolution of a surface layer in just a few minutes. We hypothesize that this represents the hydrolysis of a mechanically disturbed, highly strained near surface layer. These preliminary results point to the enormous potential offered by AFM in the study of surfaces and surface reactivity of silicate minerals.

1 INTRODUCTION

Since WRI-6, the study of mineral surfaces has undergone a giant leap forward with the recent development of scanning probe microscopy. The two most advanced and commonly used techniques within this new field are scanning tunneling microscopy (STM) and atomic force microscopy (AFM), invented by Binnig and coworkers (Binnig et al., 1982; 1986). These two closely related techniques can provide three dimensional surface images at nm to Å scale resolution. These new microscopies also have the advantage of permitting real time imaging of surface processes in a variety of environments, such as in air, in vacuum, or in aqueous solutions. Imaging of surface microtopography at atomic scale resolution is made possible by raster scanning a very fine tip across a surface and employing an ultrasensitive method for registering height deflections. The different nature of the interactions that induce deflections of the tip differentiate the two techniques; STM is dependent on a tunneling current between the tip and a surface atom, and is thus limited to conductor and semi-conductor surfaces. AFM is based on a physical force between the tip and the surface, and therefore permits the imaging of both conducting and non-conducting surfaces (for a detailed discussion, see Hansma et al., 1988).

As is well known now, the surface of a mineral is the key to understanding its reactivity. Interfacial processes, such as dissolution, precipitation, adsorption, and catalysis all depend on the atomic-scale structure, morphology, and chemical composition of a surface (see discussion by Hochella, 1990). To date, most mineralogically-oriented surface studies have used STM, primarily because this technique predates AFM by several years. With the development of AFM, several nonconducting minerals have also been imaged. Most of the early studies were restricted to graphite and phyllosilicates, a few of the more recent studies have imaged nonsilicates, such as carbonates (Manne et al., 1991; Drake et al., 1992).

The difficulty in obtaining high resolution images of structurally complex tectosilicates is borne out by the paucity of such studies. A recent study by Gratz et al. (1991) studied the development of etch pits on quartz crystals. Hochella et al. (1990) imaged the surface microtopography of albite feldspar. Both of these studies did not achieve atomic-scale resolution, only surface features on the order of several tens of nm were resolvable. Another recent study of albite by Drake and Hellmann (1991) showed molecular scale resolution of surface atom groups. Nonetheless, atomic scale resolution images, where individual atoms are distinquishable, have yet to be demonstrated for a complex silicate mineral surface.

The research results presented below are based on AFM images of albite surfaces. We chose to work with albite since it is a common silicate mineral with a good thermodynamic and crystallographic data base. The overall goal of the research we are pursuing is to understand the interrelationship between surface structure and reactivity. The observations which we describe below serve to briefly illustrate how AFM images can be used to gain a better understanding of surface structure, microtopography, and surface processes.

2 EXPERIMENTAL RESULTS

For this study we utilized one 'parent' sample of Amelia albite (Wards Scientific Establishment). In each case a newly cleaved (010) surface was examined; no surface cleaning or other pretreatment was performed. All images were taken with a NanoScope II contact mode AFM made by Digital Instruments (for more detail, see Ruger and Hansma, 1990); the optical lever design that is utilized is described in Meyer and Amer (1988) and Alexander et al. (1989). Imaging forces in air and solution ranged from 10-100 nN using 120 µm Si_3N_4 cantilevers. The size of the scan areas was 1 x 1 µm.

2.1 Surface structure

Figure 1 is a non-filtered, planefit 50 x 50 Å image of a (010) surface in air. The image shown did not change as a function of time, the same image is essentially reproducible from sample to sample. The grey scale on the righthand side of the image corresponds to elevation in nm, where the light and dark areas represent topographic highs and lows, respectively. The faintly visible rays drawn parallel to the light and dark bands form an included angle of 117°, this is very close to the value of ß (116°) formed by the *ac* net in the (010) plane. The sinuous, corrugated pattern created by the light and dark areas represents interconnected, en-echelon ring structures. Each ring shares a 'side' with an adjacent ring. The ring apices are characterized by bulbous, node-like structures, which also tend to have the highest elevations. The slight irregularity of the ring structures is either an imaging artifact, or possibly a function of the differential heights of the atoms comprising the rings.

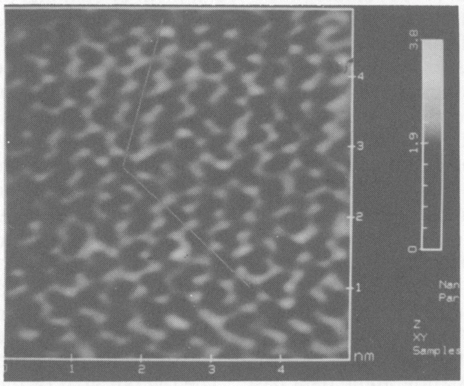

Fig. 1. A nonfiltered, planefit image of the (010) surface. Height grey scale to the right.

The feldspar structure is based primarily on 6-fold rings composed of SiO_4 and AlO_4 tetrahedra, forming what is typically called a double crankshaft chain. Due to the fact that 32 atoms out of a total of 52 atoms per unit cell are oxygens, and that the ionic radius of oxygen is fairly large (~1.2 Å), the probability is very high that the tip *predominantly* interacts with oxygen atoms. For this reason, we assume that the images represent rings of oxygen atoms. Due to the complex structure of albite, we cannot be sure that we have actually imaged individual atoms; it is far more likely that we see groups of closely spaced (oxygen?) atoms.

In an attempt to determine whether the surface structure is a simple termination of the bulk structure, Drake and Hellmann (1991) superimposed a projection of the albite *ac* net (at the same scale) onto a 2DFFT filtered image of a 25 x 25 Å area. The projection is based on X-ray and neutron diffraction data (Harlow and Brown, 1980). The superposition of the atoms is a relatively close match; non-matching atoms, as discussed by Drake and Hellmann, are possibly due to instrumental error, the choice of projection slice thickness, or other factors. The relatively good match of the projection onto the AFM image suggests that albite surfaces do not reconstruct upon cleavage in air.

2.2 Microtopography

Surface topography and morphology play a very important role in influencing the reactivity of a surface. Adsorption reactions, for example, are energetically favored to occur at step and kink sites, as has been shown in numerous metal-adsorbate studies. Based on surface thermodynamics, the reactivity of a surface is related to surface energy. The surface energy of any given surface is simply the energy per unit area needed to cleave and create a new surface (this neglects such phenomena as adsorption, reconstruction, relaxation, etc). Surface energy can be derived from the following expression: $\gamma = E(Z_S/Z)\, N_S$, where γ is the surface energy, E is the bulk cohesive energy, Z_S/Z is the fraction of bonds broken per surface atom, and N_S is the number of atoms per surface area (Zangwill, 1988). The terms E and N_S can be evaluated based on thermodynamic and crystallographic data, and Z_S/Z can be estimated from surface topography information. This is based on the premise that atoms residing at a step have a greater number of bonds broken than do atoms on flat surfaces. In general, an increase in the number of steps per unit area of surface increases the surface energy. Another similar and equally useful calculation involves the determination of the surface energy of a vicinal plane, which is dependent on knowledge of step heights and terrace spacing (see Zangwill, 1988). These variables can be estimated from AFM images.

From the two examples above, we show how surface microtopography and morphology influence the energy of a particular surface, and by inference, the reactivity, as well. Surface information, such as step heights, terrace widths, and overall step densities are measurable from AFM images. From our observations of multiple samples, the presence of step and terrace structures is ubiquitous to all albite surfaces.

Fig. 2 is a typical example of a surface profile on a nonfiltered, planefit image. The corresponding profile which traverses the image perpendicular to the steps shows the ability of AFM to resolve surface topography and morphology at a nm scale. From the profile, measurements indicate that individual steps range in height from approximately 25 to 50 Å, terrace lengths are quite variable, ranging up to 100-200 nm. We cannot be sure whether smaller terraces, separated by monatomic steps, are present. This may be the case for the sloped vicinal surfaces shown by the profile. Based on our images, the resolution of step heights is approximately 5-10 Å. It should be noted that estimates of step heights may have significant error due to z piezocalibration problems. We also note that the above discussion does not include dislocations and their effect on surface energy and reactivity.

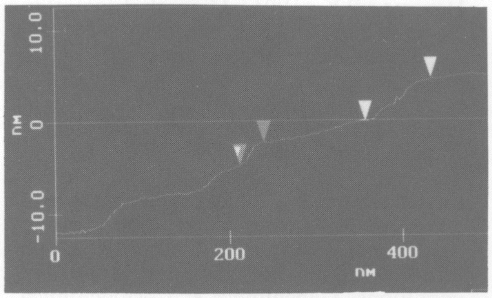

Fig. 2. A profile of a traverse perpendicular to step and terrace structures. Step heights range from 25 to 50 Å.

2.3 Surface dissolution

In mineral dissolution studies, the beginning stages of hydrolysis almost always are marked by elevated rates of dissolution. This has been attributed to either a diffusion-limited reaction mechanism or a surface reaction phenomenon. In the latter case, it has been postulated that this is due to the rapid dissolution of a surface phase, either in the form of surface fines or a mechanically disturbed surface layer (see discussion by Petrovich, 1981). Our observations of feldspar surfaces that have not undergone any grinding, but simply cleavage from a parent sample, show the large scale presence of surface fines. Thus, the rapid dissolution of surface fines, due to their high surface energies, should in part be responsible for observed high rates of initial hydrolysis. However, the dissolution of surface fines is not the only explanation for this phenomenon, as we show below.

We carried out some preliminary experiments with a fluid cell. A freshly cleaved surface was immersed in a pH 2 solution (HCl/H_2O); surface images were recorded on a real time basis. Within the time span of about 10 minutes, we observed the dissolution of a surface layer; the images are shown in Fig. 3. The forward time sequence of the images is from left to right, top to bottom; each image represents $(1.35\ \mu m)^2$. The thickness of the dissolving layer is estimated to be on the order of several tens of nm. The dissolution process was characterized by the coalescence of two dissolution fronts which were parallel or sub-parallel to visible surface steps. Towards the final stages of dissolution of this layer, only a few isolated islands remained; these islands eventually also disappeared. The step and terrace structure observed after the rapid dissolution of the surface layer exactly duplicated the initially observed step structure. Continued observation of the interface in contact with the pH 2 solution over a period of several hours resulted in no apparent change to the surface and the step structure. It is reasonable to suggest that the observed phenomenon represents the preferential hydrolysis of a high energy, mechanically disturbed near surface layer.

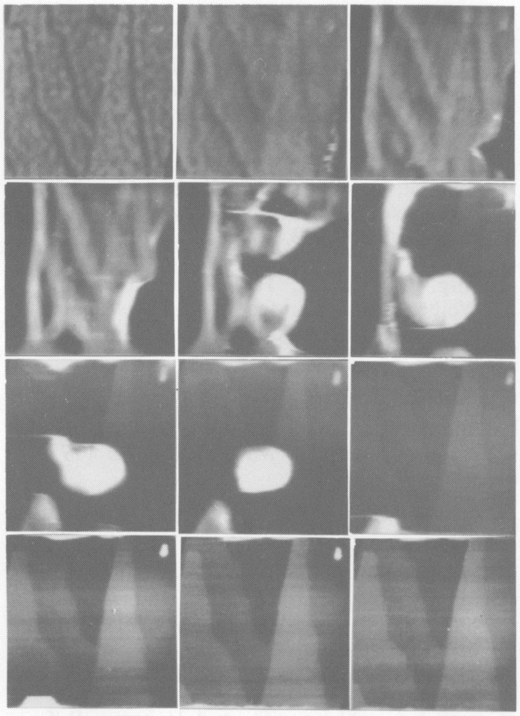

Fig. 3. A time series sequence of images showing the in-situ hydrolysis of a near surface layer within the first few minutes of contact with a pH 2 solution. Imaged area is $(1.35\ \mu m)^2$.

3 CONCLUSIONS

The brief description above of some of our most recent results concerning the structure and microtopography of albite shows the potential that AFM has for studying surfaces at the molecular scale. Based on the known bulk structure of albite, it is reasonable to assume that the ring structures observed in the AFM images are primarily due to tip-oxygen atom interactions. If the images do indeed show oxygens, then it is these same oxygen atoms that serve as adsorbtion sites for hydrolysis reactions. The observed in-situ hydrolysis process of what appears to be a mechanically disturbed near surface layer demonstrates that dynamic processes can actually be studied in detail by AFM. With further advances in AFM capabilities, leading hopefully to better resolution, we should in the not-to-distant future be able to better unravel the interrelationship between surface structure and reactivity. This in turn should lead to a more fundamental understanding of the mechanisms of surface processes.

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