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VICINAL FACES ON SYNTHETIC GOETHITE OBSERVED BY ATOMIC FORCE MICROSCOPY

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Abstract—In this paper atomic force microscopy-studies are reported suggesting the existence of vicinal faces on the (100) plane of artificially grown goethite. Goethite crystals are commonly regarded to have boundary planes of (100), (010) and (001) faces. In contradiction to these theoretical models TEM and SEM images exhibit (110) and (021) faces to be dominating. These goethite particles consist of many crystallographic coherent domains so that the existence of dislocations on the surfaces has to be assumed. These sites on the surfaces may serve as a nucleation site for the formation of steps. The vicinal faces on the (100) face found with the AFM are (021) faces. They influence the growth velocity of the (100) face to such a degree, that this face vanishes and only (110) faces remain as stable boundary surfaces. The (021) faces are also stable, but have the highest growth rate among the faces considered.

Key Words—Atomic Force Microscopy, Crystal Growth, Goethite.

INTRODUCTION

In recent years models of the sorption behavior of ions such as phosphate and heavy metals oxyhydroxides recognized the importance of the morphology of these oxyhydroxide crystals (Hiemstra et al. 1989a, 1989b). Therefore a detailed study was undertaken to obtain more information of the surfaces of these oxyhydroxides.

Goethite (α-FeOOH) is one of the most common oxide minerals within soil. It accounts for the brown to yellow color of many soils, even though it may be present in only small quantities. Goethite crystallizes usually into acicluar needles, elongated in the crystallographic c-axis (spacegroup # 62, Pbnm setting). The most common faces are (110) faces and (021) faces (Schwertmann and Cornell 1991), but (100) faces are not entirely excluded. Due to the needle-like morphology, (021) faces seem to be the fastest growing faces compared to the other faces, forming the surface of the goethite crystal.

Among different theories of crystal growth from solution (Bennema 1974), the growth theory of Burton, Cabrera, and Frank (Burton et al. (1951), BCF theory) gave valuable insight into the growth behavior of crystal faces. They introduced spirals due to screw-dislocations as a nonvanishing source of steps. The presence of steps on the faces influence the growth velocity and therefore, the habitus of a crystal.

For this study an atomic force microscope (AFM) (Binning et al. 1986; Wickramasinghe 1989) was used to investigate the surface morphology of goethite crystals. This novel technique has the opportunity of giving direct insight into the topography and mechanical properties of surfaces. It can be used under ambient conditions, for example, under water or at room temperature. Usually no vacuum or special preparation procedures for example, metal coating, are needed. It is even possible to image cells *in vivo* with a resolution of about 50 nm (Radmacher et al. 1992; Fritz et al. 1994). Atomic resolution can be obtained from hard and flat samples, such as minerals. The whole instrument is available commercially and can be used quite easily.

A crucial detail for AFM work is the sample preparation. The common method is the adsorption of the material onto mica. Here we present a similar method. Instead of mica we used natural quartz crystals (rock crystal) that have grown into hexagonal prisms. This gives the opportunity of having, not only a flat and parallel surface, but also fixed particles. The preparation method is based on the work of Scheidegger et al. (1993). In their work, crystobalite sand was coated with goethite for chemical exchange columns. Experiments with regularly available glass slides for light microscopy and different oxyhydroxides yield the same satisfying results. This work will give some answers to the questions concerning the morphology of the goethite crystals.

MATERIALS AND METHODS

The goethite was produced following the procedure of Schwertmann and Cornell (1991). Exactly 180 ml of 5 M KOH solution was added to 100 ml of 1 M $Fe(NO_3)_3$ solution under vigorous stirring. Immediately the red brown suspension was diluted to 2 liter with double distilled water and held in a closed polyethelene flask at 68 °C for 2 mo under moderate stirring with a magnet stirrer. The yellowish suspension was centrifuged, washed and freeze-dried.

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Characterization of the product was carried out with a Guinier-Camera with monochromatic Co-Kα1 radiation (λ = 0.17889 nm). The diffractograms were recorded from 19–83 °2θ with 0.02 °2θ steps and 4 s counting time. Si-metal was added as an internal standard. Mean coherence lengths (MCL) were calculated after Klug and Alexander (1974) using a computer program written by Stanjek (1991).

Specific surface area was obtained with a Autosorb 1 volumetric adsorption device from Quantachrome Corp. using nitrogen as adsorptive at 77.3 K. The molecular cross-sectional area was assumed to be 0.162 nm^2. The sample was outgassed at 25 °C for 7 h until the residual pressure in the sample cell was stable at 2 Pa (=15 mTorr). Thirteen points from the partial pressure range of 0.001 to 0.3 p/p_0 (p_0 saturation pressure) were used for the calculation of the BET surface area.

Particle size and morphology was examined with a Zeiss EM 10A transmission electron microscope (TEM) operating at 100 kV.

The AFM used was a Nanoscope III from Digital Instruments, Santa Barbara, CA, with conventional Si_3N_4-Cantilevers. Some basic principles of the AFM-technique are reviewed by Binning et al. (1986), Wickramasinghe (1989) and Wickramasinghe (1990). Details of the instrument are described by Anonymous (1993).

Because the AFM is a novel instrument, which is not routinely used in mineralogy so far, we offer a brief description of some basic principles. A very sharp tip is brought close to the surface of the sample mounted onto a piezo tube. During scanning of the sample in the xy-direction, the forces occurring between the tip and the surface cause the spring-like cantilever to deflect. This deflection is monitored via the reflection of a laser beam, which is focused on a split photo diode. A topographic or frictional image of the surface is obtained by correlating the xy-position with the deflection signal of the photo diode. There are several imaging modes. The most important are the "deflection" and the "height-mode". While scanning of the sample, the z-position of the piezo or of the sample can be held constant. In this case ("deflection mode"), the needle moves up and down. Conversely, if the z-position is controlled by a feed-back circuit, the bending of the spring can be kept constant ("height mode"). The interesting signal is the feed-back itself. It can be interpreted to be proportional to the height of surface steps, but due to the limited feedback speed, details of the topography may be smoothed out.

Small prisms of quartz crystals (3–5 mm long and 1–2 mm in diameter) were sonicated in 6 M HCl for 20 min, then washed with double distilled water. 10–30 mg sample of goethite was suspended into 25 ml 0.01 M $NaNO_3$ solution and the pH was adjusted to 5. The suspension and the quartz crystal were shaken overnight and then ovendried at 75 °C. The same procedure was applied to the glass slides, except the suspension was shaken for only one h.

Scheidegger et al. (1993) showed that the interaction between goethite and quartz crystal is not solely of an electrostatical nature. At the suspension pH of 5, the surface of the rock crystal (point of zero charge, PZC $\approx$ 2) is negatively charged and the surface of the goethite (PZC $\approx$ 8) is positively charged. Therefore, goethite particles are absorbed onto the surface of the rock crystal. The close match of the two surface structures might support the formation of Si-O-Fe bonds, which were observed by Scheidegger et al. (1993). Scanning a goethite particle in an AFM for 5 min under high forces split the particle into two parts without moving the remainder of the particle. Particles on regular glass slides could not be moved during scanning. Conversely, goethite crystals coated with silica could be moved over the glass slide surface.

RESULTS AND DISCUSSION

XRD and Morphology

No phase other than goethite was detected from the diffractogram. The unit cell parameters are a = 0.4605 nm, b = 0.9956 nm and c = 0.3023 nm, which correspond well with the values from JCPDS card 29-713 Berry et al. 1980, a = 0.4608 nm, b = 0.9956 nm, c = 0.30215 nm. The mean coherence length (MCL) calculated from the (020), (040) and (060) reflections are 42.3 nm and from the (110), (220) and (330) reflections are 43.5 nm. Therefore, the MCL in the direction of the a-axis is 18.3 nm and in the direction of the b-axis is 39.5 nm.

The goethite particles are heterogeneous in both size and shape (Figure 1). Mostly they are 2 μm long and approximately 0.5 μm wide needles, which consist of smaller needle-like subunits (multidomainic). Some of these large needles are star-shaped particles (twins on (021) faces) and some appear to be single crystals. There are also 2 μm long and very narrow needles that are approximately 50 nm in width. Using these particle sizes (2.0 μm, 0.5 μm and 0.1 μm) for the estimation of the specific surface area gives a value of 5.9 m^2/g. This is reasonable compared to the measured value of 7.9 m^2/g, indicating the presence of smaller particles. The BET-C constant is low with a value of 26.

AFM Images

Figure 2 and Figure 3 show the deflection mode images. These are closeups of what we interpreted as the single (?) crystal which is marked with an arrow in Figure 1. The deflection mode amplifies the stepped appearance of the goethite faces. One can see the stepped surface of the (100) face. Indexing of the different faces was achieved by measuring the angles be-

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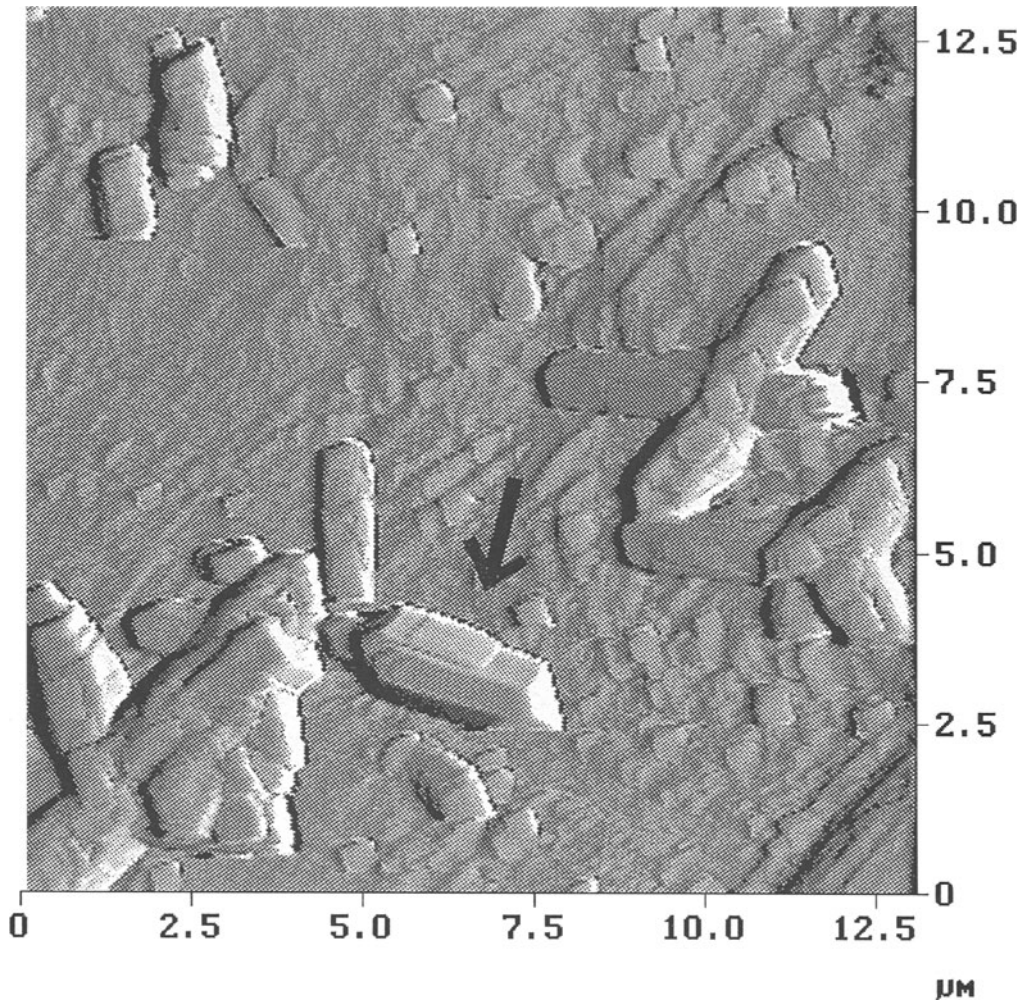


Figure 1. Deflection mode image of the goethite sample. Most of the particles are star shaped and multidomainic. The single (?) crystal further examined in Figures 2 and 3 is marked with an arrow.

tween adjacent faces. The smaller steps on the (100) face are (021) faces with a mean height of approximately 1.2 nm, corresponding to approximately 3 unit cell heights. These (021) faces are so numerous that the constituent face can be considered to be a vicinal face (Wilke 1988). If steps are formed fine enough, smooth surfaces can be pretended, for example, fine steps of (100) and (010) faces can simulate a (110) face in a cubic system.

The ends of the needles are bounded by (121) faces. The macrostep heights in Figure 2 are from left to right, 266 nm, 32 nm and 16 nm.

A very interesting feature can be seen in Figure 3. The steps all seem to proceed from right to left, which implies that the crystal is only growing in this direction. In this spacegroup (#62, with the Pbnm setting), a mirrorplane perpendicular to the crystallographic c-axis (parallel to the elongation), suggests equal behavior both in the c and $\bar{c}$ direction.

The parallel rills running along the (110) face suggest a layer-like growth of the crystals. This is supported by the impression of Figure 2, but so far no cleavage plane for the (100) plane has been reported.

The main feature of the BCF-theory (Burton et al. 1951) is the existence of screw-dislocations as a source of steps. But stepped surfaces will also be produced when the supersaturation is high (Bennema 1974). Thus far, no data on the critical concentrations have been published. No screw-dislocations have been found on the crystal-faces. The rectangular area on the right end of the crystal (Figure 3, arrow) is flat on the sub-nm scale. But as can be seen from the mean coherence length, these particles consist of many smaller crystals. Assuming a mean length of 2 µm and a width

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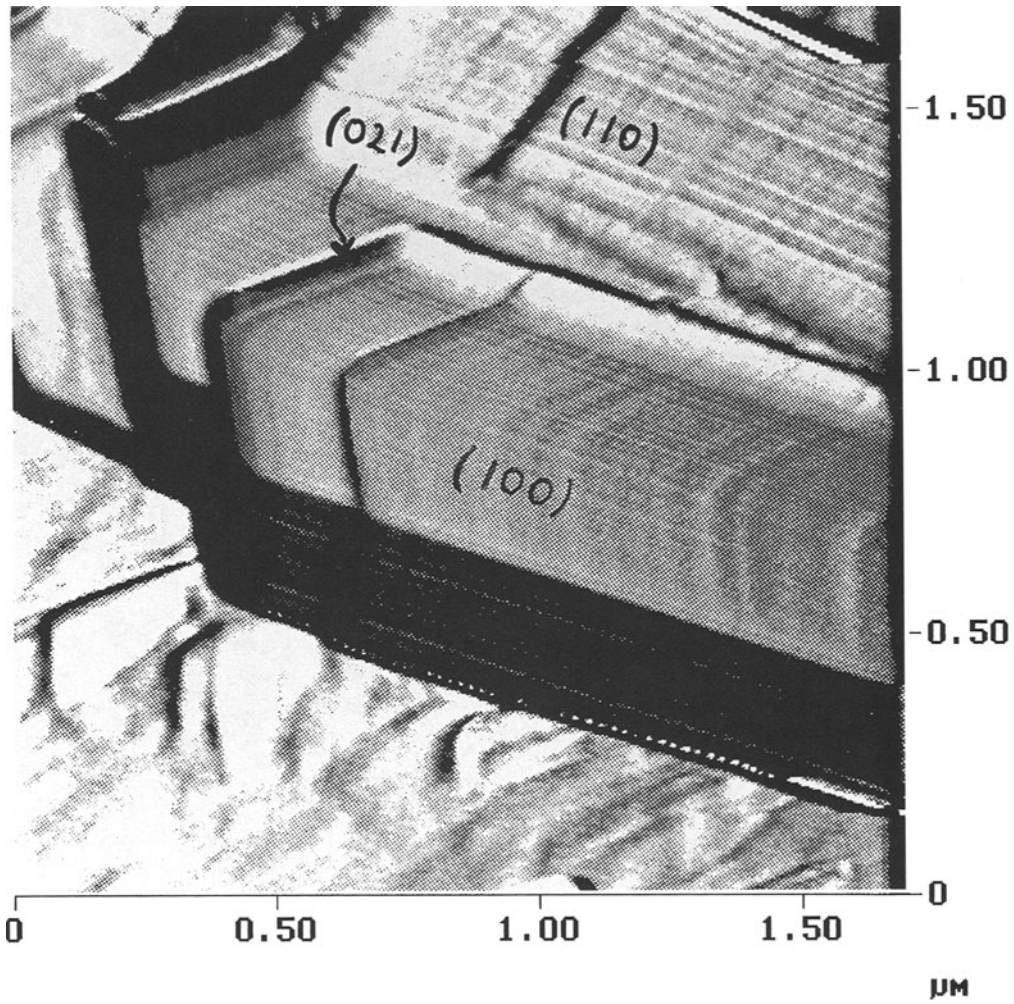


Figure 2. Deflection mode image a single (?) crystal of goethite. The faces are marked with their Miller indices. Macro- and microsteps proceeding from the right to the left of the crystal. Step heights are stated in the text.

of 0.5 µm for the stepped (100) face, one calculates from the MCLs that approximately 1400 crystal units build up this face. So there is evidence that these domain boundaries may be sites of dislocations, which can serve as a source for step formation.

But this is only an estimation for the upper limit of the amount of domain boundaries. The MCL is a property of the bulk sample (powder XRD) and therefore, no precise data for the the crystal in Figures 2 and 3 is available.

Distances between steps and terraces are not equidistant. There might be asymmetric diffusion fields to the left and the right of the steps, leading to different catchment areas (Schwoebel and Shipsey 1966, Schwoebel-effect). But, dislocations are present that influence the step velocity. Therefore, steps may coalesce to form macrosteps, which have a lower step velocity (Janssen-vanRosmalen 1977). These steps should be higher the more distant they are from the seed area of the steps.

Mussard and Goldsztaub (1972) report a higher growth velocity for stepped surfaces. This is in agreement with the observation of the (110) faces as the dominating surface of goethite crystals. The stepped (100) face will therefore vanish or grow out and (110) faces will remain.

Consideration of an atomic model of the structure of the (021) plane shows that the (021) plane cuts through the middle of the O-OH octahedra and supports the incorporation of an Fe-atom. This forces O's to complete the Fe coordination and create new halves of octahedra. Their center of gravity is displaced by c/2 (c-axis parameter) in the (001) direction. This again favors the incorporation of an Fe atom and new halved octahedra are created, forming the identical initial structure, but two more layers of Fe and O atoms

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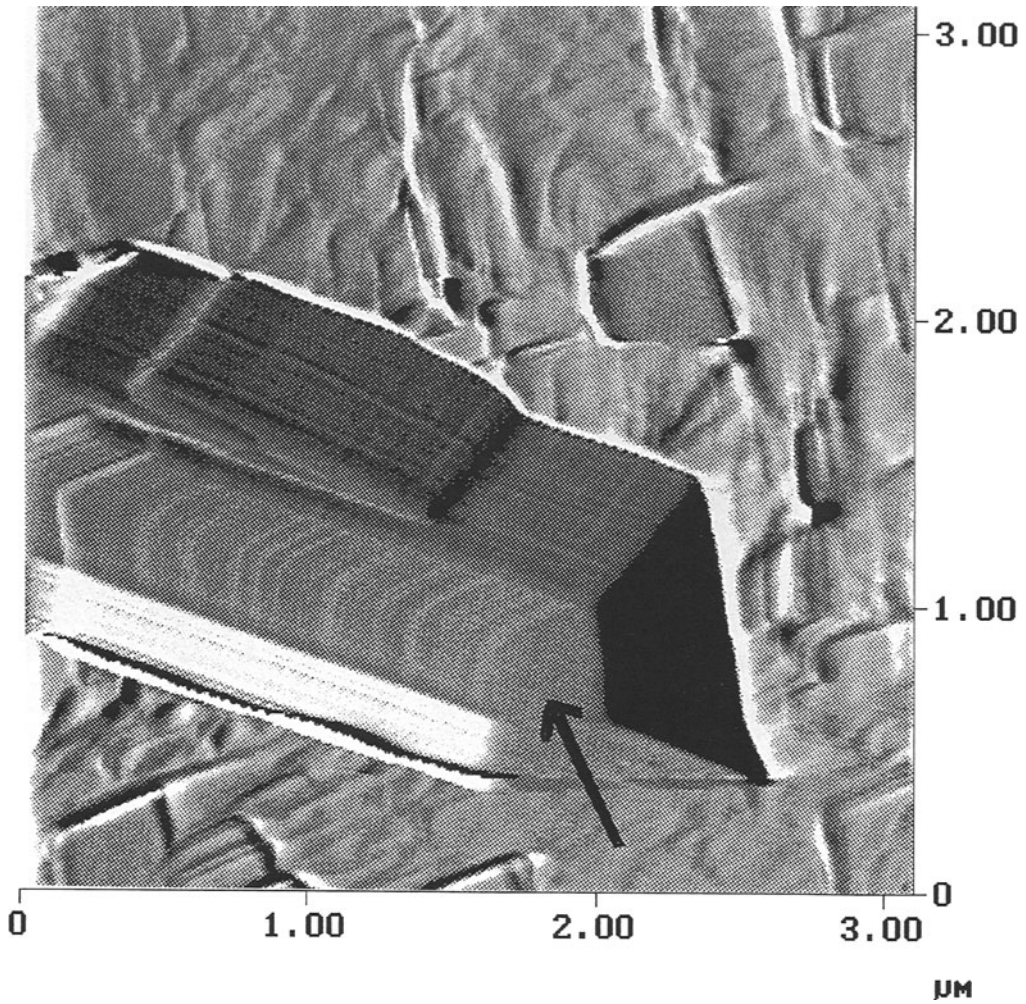


Figure 3. Deflection mode image of a single (?) crystal of goethite. Note the V-shaped steps on the (100) face running only in one direction from right to left. The rectangular area on the right end of the crystal (arrow) is flat on the sub-nm scale.

have been added in the direction perpendicular to the (021) plane. Again the relative slow growing (110) face bounds the (021) plane in the (110) direction.

CONCLUSIONS

Low index faces are considered the dominating faces that bound the crystals (Kleber 1990). The existence of vicinal faces, consisting of (021) faces and (100) faces, is the reason that the low index face (100) is not the dominating face or is even absent on many goethite crystals. The source of these steps are not screw-dislocations as needed in the BCF-theory. Whether concentrations in the solution meet such supersaturation conditions that stepped or very rough surfaces have to form, can not be stated. Goethite particles consist of many crystallographic coherent domains. The existence of dislocations on the surfaces has to be assumed. These sites on the surfaces may serve as a nucleation site for the formation of steps.

The elongation in the crystallographic c-axis can be explained by structural considerations of the (021) plane. This structure supplies the growing crystal with the maximum number of high affinity sites for Fe-atoms, and therefore promotes the growth in the (001) direction.

Our experimental findings are not fully consistent with the theoretical models considering the (100), (010) and (001) faces as the dominating ones, found in literature. Our results suggest the existence of (021) vicinal faces and therefore, the dominance of the (110) faces.

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