

ON THE SURFACE PROCESSES OF CRYSTAL GROWTH AT LOW TEMPERATURES

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Abstract

This paper deals with some microscopic phenomena, which occur on crystal surfaces during growth from aqueous solutions. Since crystallisation and crystal-solution interactions are ubiquitous in nature, their study is of relevance for a better understanding of processes in mineralogy, environmental sciences and biomineralisation. By using Atomic Force Microscopy we have been able to image the evolution of surfaces during the growth of pure substances and solids with chemical variability (solid solutions), and also during dissolution-crystallisation reactions. In order to interpret, and in some cases predict, the crystal growth behaviour at a molecular scale we have taken into account the relationships between supersaturation, growth mechanisms and crystallographic features of the surfaces.

Key words: crystal growth, supersaturation, solid solution, replacement reactions, atomic force microscopy

1 INTRODUCTION

How crystals grow from a disordered medium has always been an intriguing question, and one studied from different points of view. Among the theories and models, which have constituted breakthroughs in the field of crystal growth must undoubtedly be mentioned the contributions of Kossel [1], Stranski [2] and Volmer [3] to the nucleation theory, the spiral growth mechanism proposed by Burton, Cabrera and Frank [4] and the Hartman-Perdok theory which relates crystal morphology to the existence of periodic bond chains (PBCs) in the structure [5]. All of these theories are strongly rooted in basic concepts and ideas about the microscopic nature of surfaces and, at the time they were published, direct observations of crystal faces during growth on a molecular level were very limited. However, the recent invention and development of surface science techniques (e.g., Atomic Force Microscopy (AFM), X-ray Photo Spectroscopy and Scanning Electron Microscopy), together with the development of computational methods for studying the structure of solid-liquid interfaces, has provided new tools to study the surface processes operating when crystals grow. Now it is possible, for example, to quantify directly the advancement of monomolecular growth steps and two-dimensional

nucleation kinetics and to follow *in situ* the motion of single growth spirals [6,7]. This allows us to test the validity and limits of the classical crystal growth theories, and gives us the possibility of observing new nanoscopic growth phenomena not predicted by these theories.

This paper summarises some recent investigations in the field of crystal growth conducted in collaboration with the Mineral Surface Group of Münster University. Firstly, the main results of our work on barite (BaSO_4) growth will be presented. This mineral represents a model example highly suitable for testing classical crystal growth theories. It has allowed us to describe and study the strong effect that crystallography can have on the growth behaviour of pure substances. Once we obtained a clear picture of the nanometric phenomena occurring on barite surfaces during their growth, we focused the investigations on the growth at a molecular scale when Sr is incorporated extensively into the barite structure, i.e., the formation of the $(\text{Ba,Sr})\text{SO}_4$ solid solution. The surface features resulting from the compositional variability of the solid phase clearly show the influence of composition on growth. Their characteristics can be explained by considering in detail the relationship between supersaturation and growth mechanisms. Finally, an example of surface processes during a dissolution-crystallisation reaction will be described.

All cases described here illustrate the innovative observations possible by the application of Atomic Force Microscopy in the field of mineral surface science. Such observations and their interpretation have not only a pure academic interest, but they can also contribute to a better understanding and control of mineral-forming processes, global geochemical cycles, environmental contamination and biomineralisation occurring on the Earth's surface.

2 MATERIALS AND METHODS

Experiments shown in this paper were conducted at 25°C using a Digital Instruments Multimode AFM equipped with a fluid cell (Fig. 1). An AFM consists essentially of a very sharp tip (ending in one single atom) with which a sample is scanned. From the deflection of a laser beam focussed on the tip, a computer determines the force between the tip and the surface during the scanning. The recorded force data allows images to be obtained in real time, with a vertical resolution, which is sub-angstrom.

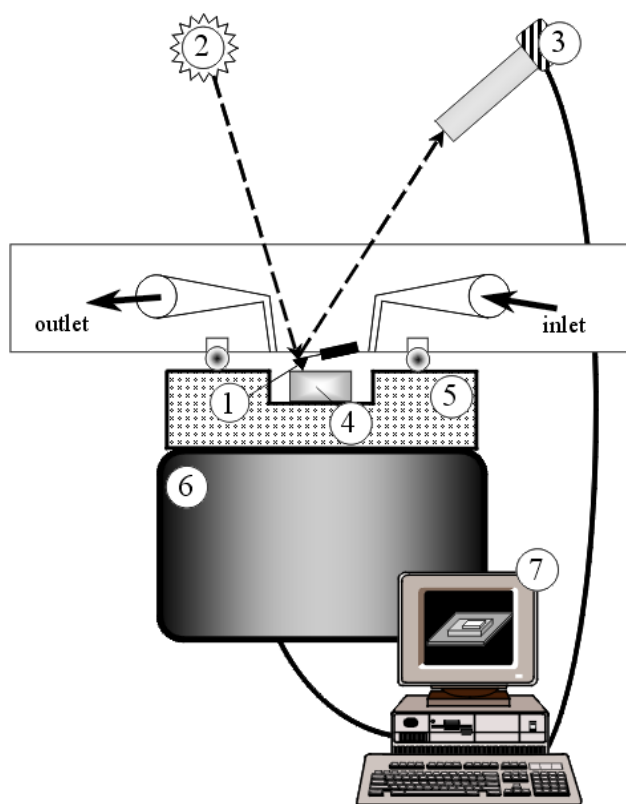


Fig. 1. Schematic drawing of an AFM equipped with a fluid cell for conducting crystal growth experiments. (1) Tip. (2) Laser. (3) Photodetector. (4) Sample. (5) Fluid cell. (6) Piezo for controlling the force between crystal and tip. (7) Computer.

The samples used in this work were natural crystals freshly cleaved on selected faces. Immediately after cleavage, samples were placed in the fluid cell of the AFM and different solutions were injected. The solutions were chosen so as to promote growth and they can be described by one basic parameter, the supersaturation, β , which expresses the excess of the solute above the equilibrium concentration (i.e., solubility).

3 RESULTS AND DISCUSSION

3.1 Crystal growth of simple solids: barite (BaSO_4) as a model substance

Barite crystallises in the orthorhombic system with lattice parameters $a = 8.88 \text{ \AA}$, $b = 5.46 \text{ \AA}$ and $c = 7.15 \text{ \AA}$ [10]. It has perfect cleavage on (001) and (210) faces. While barite (001) planes consist of two elementary growth layers half a unit cell in height (3.5 \AA) and related one to each other by a rotation of 180° (in crystallographic notation: 2_1 screw axis parallel to c), the elementary (210) growth layers are one unit cell in height [11]. At relatively high supersaturations both faces grow by two-dimensional growth mechanisms. Although our height and goniometric measurements of two-dimensional

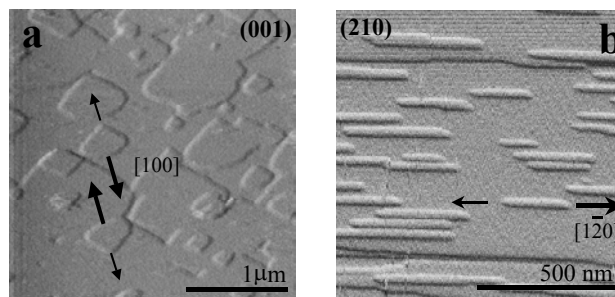


Fig. 2. AFM images of two-dimensional nucleation on barite. (a) Circular sector-shaped island on barite (001). The islands are 3.6 \AA in height (half a unit cell) and they have reversed orientations in successive layers. (b) Elongated islands 3.4 \AA in height (one unit cell) on a barite (210) face (image taken by P. Risthaus). Long and short arrows indicate fast and slow growth directions, respectively. Supersaturation, $\beta=19$.

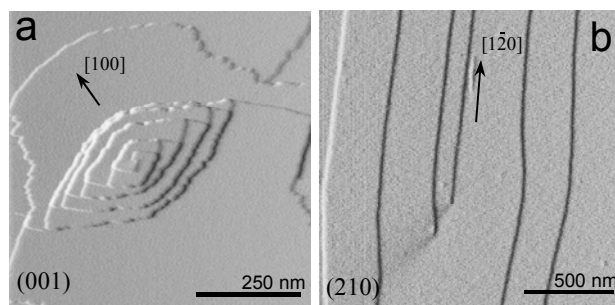


Fig. 3. (a) Growth spiral on barite (001) from a solution with supersaturation $\beta = 12$. Note that the lateral growth around the spiral is restricted. (b) Screw dislocation on a barite (210) face in a BaSO_4 supersaturated solution. Spiral growth was not observed at any supersaturation before the transition to a two-dimensional growth mechanism.

islands on AFM images are in agreement with theoretical predictions for elementary growth layers [12], an explanation for the shape and growth anisotropy of the two dimensional islands (Figs. 2a-b) requires the calculation of attachment energies of single ions at the surface using a molecular simulation model. Such calculations have allowed us to reproduce the shape of the two-dimensional islands and to justify their growth kinetics [13].

Below certain transitional supersaturation value, $\beta^* \approx 7$, the energy barrier for the formation of two-dimensional nuclei cannot be overcome and crystals grow according to a completely different mechanism, the so-called spiral growth at screw dislocations. Then, the combination of crystallographic restrictions and growth anisotropy has a dramatic effect on growth pattern. Fig. 3a shows a spiral on barite (001). The alternation of elementary growth layers with reversed fast and slow growth directions leads to a phenomenon of structure-induced self inhibition of the spiral growth not predicted by the Burton, Cabrera and Frank theory [13].

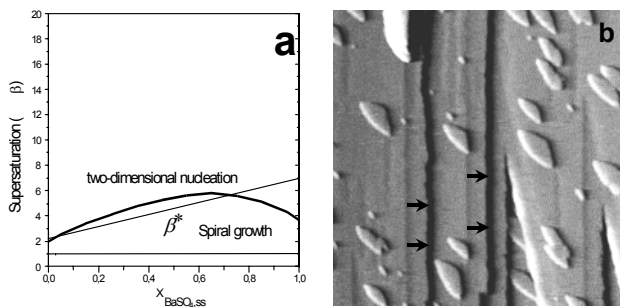


Fig. 4. (a) Relationship between the supersaturation distribution for a solution with composition $[\text{Ba}^{2+}] = 1 \mu\text{mol/l}$, $[\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 1100 \mu\text{mol/l}$ and growth mechanisms. The abscissa represents the molar fraction of BaSO_4 in the solid. The transitional line, $\beta^*(x)$ was determined from experimental data. (b) AFM image of barite (001) face growing from a solution with the same composition as in (a). The scan area is $10 \times 10 \mu\text{m}^2$. Two-dimensional nucleation and advancement of steps (arrowed) occur simultaneously. According to the model, steps and two-dimensional islands can have different compositions.

On the (210) face, growth inhibition is more extreme, and we never observed spiral growth at screw dislocations (Fig. 3b). This limitation of the spiral growth mechanism precludes it as a kinetically significant process, and also reveals that the surface structure (i.e., crystallography, attachment energies at specific surface sites, etc.) can have a strong effect on the crystal growth behaviour.

3.2 Crystal growth of solid solutions: $(\text{Ba},\text{Sr})\text{SO}_4$

In contrast to solids with fixed composition, the crystallisation of solid solutions implies the formation of solid with a range of compositions. Since each solid composition has, in principle, a different solubility, the supersaturation of a given aqueous solution with respect to the whole solid solution cannot be expressed by a single value, but it is given by a function, $\beta(x)$, where x is the molar fraction of one of the endmembers in the solid solution [8,9]. Similarly, the transitional supersaturation between two-dimensional nucleation and spiral growth mechanisms varies, in the case of the crystallisation of solid solution, with the solid composition: $\beta^*(x)$.

By representing the transitional supersaturation line, $\beta^*(x)$, and the supersaturation function for an aqueous solution, $\beta(x)$, together on a supersaturation-solid composition plot, we can make predictions about the growth behaviour of the $(\text{Ba},\text{Sr})\text{SO}_4$ solid solution. Figure 4a shows, as an example, the supersaturation distribution for an aqueous solution of composition $[\text{Ba}^{2+}] = 1 \mu\text{mol/l}$, $[\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 1100 \mu\text{mol/l}$ and the $\beta(x)^*$ line obtained from experimental data. This solution is supersaturated with respect to all compositions of the solid solution, but only the solid compositions with molar fractions X_{BaSO_4}

< 0.7 can grow by a two-dimensional nucleation growth mechanism. For molar fractions $X_{\text{BaSO}_4} > 0.7$, the only possible mechanism is spiral growth or advancement of steps. Figure 4b shows an AFM image taken a few minutes after the solution was passed over a barite (001) face. A number of two-dimensional islands nucleated on the surface and the cleavage steps advanced. Microprobe analyses of the islands showed that they are Sr-rich ($X_{\text{BaSO}_4} < 0.5$), in agreement with our predictions [14].

The application of similar approaches to a number of different systems permitted valuable interpretations and predictions to be made about the microtopographic surface features observed during the crystallisation of solid solutions from aqueous solutions [15,16,17]. All cases studied demonstrate the importance of considering the interplay between supersaturation, growth mechanisms and growth kinetics as functions of both the solid and the solution compositions.

3.3 Dissolution-crystallisation phenomena: replacement of phosgenite by cerussite

Under certain conditions, the dissolution of a crystal can occur simultaneously with the nucleation and growth of a new phase. In some cases, such a phenomenon results in a coupling between dissolution and growth rates and the whole process can be considered as autocatalytic. Since coupling between reactions is essentially a local process, crystal surfaces are highly suitable to observe the influence of the nucleation and growth of a secondary phase on the dissolution mechanism of the earlier phase.

The replacement of phosgenite ($\text{Pb}_2\text{Cl}_2\text{CO}_3$) by cerussite PbCO_3 provided us with an interesting model example of a dissolution-crystallisation reaction [18]. Phosgenite in contact with carbonated solutions begins to dissolve rapidly, and the formation of shallow and deep square-shaped etch pits on its (001) surfaces can be observed (Fig. 5a). Phosgenite dissolution leads to an increase in the Pb^{2+} and CO_3^{2-} in the surrounding solution which results in a sharp increase of the supersaturation with respect to cerussite (Fig. 5b). After a certain incubation time, cerussite crystals nucleate on phosgenite (001) surfaces, distorting the concentration field around them (Fig. 5c). As a consequence, phosgenite dissolution is accelerated. In turn, the increase in the phosgenite dissolution rate results in the increase of cerussite nucleation and growth rates leading to a positive feedback. Both the existence of an incubation time and the coupling between reaction rates are typical for autocatalysis, which is a feature of so-called complex behaviour [19].

Although we did not observe oscillatory reaction rates, self-organisation, pattern formation or other phenomena associated with complex behaviour, our observations demonstrate the strong effect that coupling reactions can have on surfaces at a molecular scale. This suggests that, for different experimental starting conditions, different

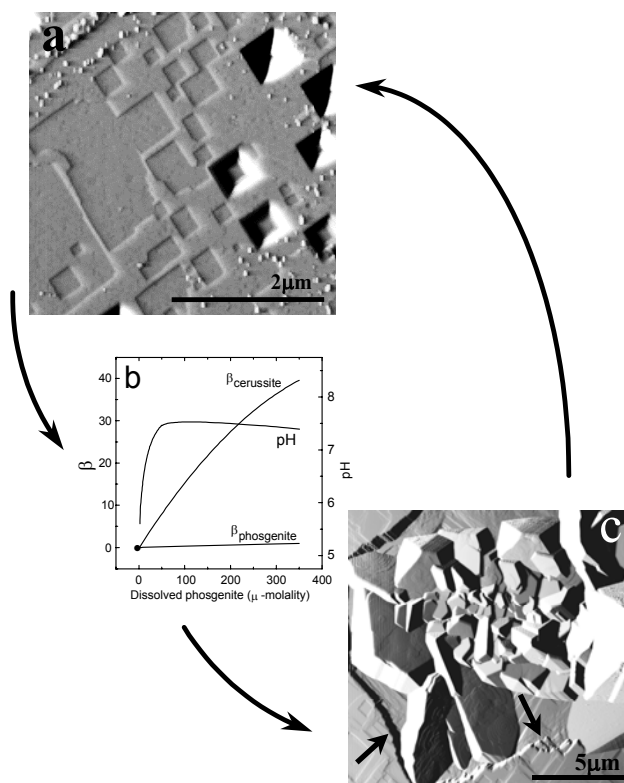


Fig. 5. Replacement of phosgenite by cerussite. (a) AFM image showing the initial dissolution of phosgenite when a carbonated solution is passed over the (001) face. The retreat of steps and the formation of shallow (one unit cell high) and deep etch pits are visible. (b) Evolution of the supersaturation with respect to phosgenite and cerussite during hypothetical dissolution of phosgenite. The evolution of pH is also shown. (c) AFM picture showing nucleation of cerussite crystals on a phosgenite (001) face. The influence of cerussite growth (spiral growth mechanism) on the dissolution of phosgenite can be recognised in the formation of irregular dissolution fronts (arrows).

dissolution-crystallisation behaviour patterns can be expected.

4 CONCLUSIONS

The three examples presented in this paper dealt with three different crystal growth processes, which were studied using Atomic Force Microscopy: growth of pure substances, solid solutions and dissolution-crystallisation reactions. While the study of surfaces of solids with fixed composition can provide information about the basic mechanisms of crystal growth from aqueous solution, the more complex cases of the solid solution formation and dissolution-crystallisation phenomena are of relevance in geosciences. Thus, the precise determination of the composition of minerals growing from multicomponent aqueous solutions, frequently used to infer physico-

chemical conditions in natural environments or to evaluate water and soil contamination, requires a good knowledge of the microscopic processes involved in the incorporation of ions or molecules on crystal surfaces. In addition, the microscopic rearrangement of surfaces by coupled dissolution-crystallisation is a widespread mechanism related to mineral replacement reactions which take place on the Earth's crust.

It is worth noting that, although AFM is a highly suitable for imaging *in situ* crystal growth phenomena at a molecular scale, the design and interpretation of experiments must be done on the basis of thermodynamic, kinetic and crystallographic calculations. Especially important is to conduct an adequate supersaturation evaluation for the crystallisation systems studied. This reference parameter always has to be considered in order to understand the behaviour of crystal surfaces during growth.

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