Observation of atomic steps on $CaCO_3$ crystal surface*

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Abstract By using scanning polarization force microscopy, the deliquescence process and the atomic steps on the cleavage surface of $CaCO_3$ in air were studied in situ. Under an exposure to medium humidity (~57%), the slow step movement has been observed.

Keywords $CaCO_3$ crystal, Scanning polarization force microscopy, Atomic Steps, Deliquescence

1 Introduction

As adsorption of water on salt crystal surfaces, the deliquescence phenomenon can be observed usually. Deliquescence is an important scientific issue and has been studied for a long time. However, the micro-dynamic mechanism is not known very clearly. By using scanning polarization force microscopy (SPFM)[1,2,3], it is possible to observe in situ the deliquescence process in nanometer-scale. We have reported some results of deliquescence on NaCl surface, the atomic steps at a serious of humidity were observed.[4,5]

$CaCO_3$ is an ordinary salt in the world; and macroscopically, it's difficultly dissolved in water solution. We know that $CaCO_3$ is main constituent of many cultural relics and its efflorescence phenomenon is, therefore, concerned usually. The reasonable interpretation of this kind of erosion is confused so far, especially in microscopic, which is partly caused by the lack of suitable microscope techniques applied for real-time investigations under ambient conditions. In this paper, an observation of water adsorption on $CaCO_3$ crystal surface by SPFM and changes of its atomic steps in air at a medium humidity are described.

2 Materials and method

Nanoscope Ⅲa System of Digital Instruments (DI) used in our experiments was improved. The cantilevers, which are commercially available and also provided by DI, were made of Si_3N_4, their spring constant is 0.58 N/m. They became conductive by evaporating a layer of Pt (~30 nm thick) in vacuum. In this experiment, 5 V bias was applied to cantilever. The lever was allowed vibration with a resonant frequency. The amplitude of vibration is reduced when there is an attractive force between tip and sample, so we can use the software package of Nano Ⅲa with tapping mode. But in our case the tip does not contact with sample in whole process unlike in usual tapping mode. In scanning process, the attractive force keeps constant.

$CaCO_3$ crystal surface is obtained by cleavage in the ambient laboratory environment. The head of Nano Ⅲa is set in a sealed polymethyl methacrylate casing. Humidity adjustment is accomplished by ventilating dry N_2. Relative humidity(RH) are measured by a hydrometer (Vwr Scientific), the values noted for the RH should be considered to have an error within ±4%.

SPFM images are obtained by using electrical polarization forces between a conductive AFM tip and sample surface. The distance between tip and sample is larger than 20 nm. The long range of the electric forces is key to the SPFM applied in liquids. However it is necessary to minimize perturbation of its mobile surface in order that SPFM can image the water adsorbed on solid surface in stableness. The lateral resolution of SPFM is about 20 nm, and the vertical resolution is about 0.05 nm.

3 Results and discussion

Using SPFM, we have observed the atomic

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steps on $CaCO_3$ crystal surface, and found that, at a medium humidity(RH~57%), the very slow steps flow was observed on CaCO3 surface, as shown in images in Fig.1(a-c), taken in a period of more than 4 h. This interesting phenomenon is due to diffusion of the solvated ions according to the imaging principle of SPFM. A distinct bright strip, in middle part of all three images, can be taken as a reference to indicate the evolution of steps. On the upper side of the strip in Fig.1(a), there is an area like a leaf, however, edges of the same area have become to be analogous petal shape as shown in Fig.1 (b) and (c). The evolution around this area can be seen clearly. On the other side of the strip, changes in some steps can be observed. As a typical case, there is a step in lower-left corner of Fig.1(a), a period of time later, the step disappeared on the same location as shown in Fig.1(b) and (c). The mobility of the steps is most likely due to the diffusion of hydrated ions.[4,5] Hydration of surface ions weakens ionic bond strength, therefore, mobility of steps can be observed. Some steps disappeared due to dissolution of $CaCO_3$. On the other hand, some new steps are formed because of crystallization. So the moving of steps is not a singular process of salt molecules dissolution, there is a dynamic equilibrium between dissolution and crystallization. In addition, the process of salt separation out is accompanied.

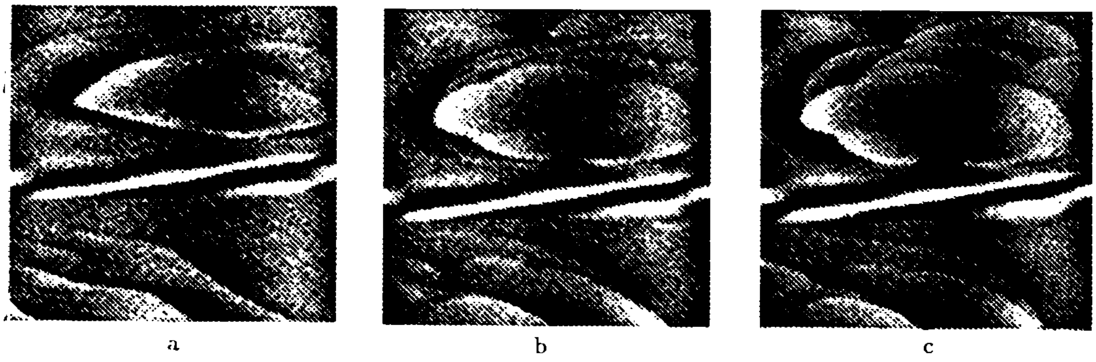

Fig.1(a-c) SPFM images(8μm×8μm) obtained at ambient RH ~57%, showing the change of the step's structure for a period of more than 4 h.

Another noticeable phenomenon is that there is no change in smooth area. It demonstrates that dissolution and crystallization mainly occurred at step edges as we suggested before.[4,5] In other words, the lattice of flat area may not be changed, and $CaCO_3$ molecules of crystal surface are preserved from dissolution since presence of steps.

4 Conclusion

Exposure to ambient condition, $CaCO_3$ will be dissolved by the adsorbed water layer, resulting in the change of surface lattice. At medium humidity, very slow step flowing can be observed.

References

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