

Application News

No. S51

High Resolution Scanning Probe Microscope HR-SPM /
Frequency Modulation Atomic Force Microscope FM-AFM

Atomic Resolution Observation of Calcite by SPM-8100FM

Introduction

Calcite is a calcium carbonate mineral which commonly found in the natural world and living organisms and has important functions in the ecosystem. For example, the phenomenon of biomineralization, by which living organisms precipitate inorganic minerals such as calcium carbonate, may possibly lead to synthesis of environment-friendly materials and has also attracted attention in the field of biomimetics. Observation of the crystal structure of calcite with atomic resolution provides clues for elucidation of the mechanism and process of biomineralization. Fig. 1 shows a calcite crystal sample collected from the natural world.

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Fig. 1 Crystal of Calcite

Analysis of Crystal Structure

In addition to scanning probe microscopes (SPM/AFM), it is also possible to analyze the structures of crystals by X-ray diffraction and transmission electron microscopy (TEM). However, direct visualization of periodic arrays of atoms is not possible by X-ray diffraction. Observation of atomic arrays is possible by TEM, but measurement is not simple, as sample preparation is difficult and measurements must be performed in a vacuum under high pressure.

With the Shimadzu SPM-8100FM high resolution scanning probe microscope, observation can be conducted with atomic resolution under normal temperature/normal pressure conditions without special sample treatment, and cross-sectional imaging enables observation of the structure of liquids at the interface between solid materials and liquids. Thus, 3-dimensional analysis of the effects of the structure of a crystal surface on liquids is possible by considering the atomic and molecular arrays obtained by observation of the crystal surface topography in combination with the features of the liquid structure obtained by cross-sectional imaging. Fig. 2 shows an image of crystal structure observation and liquid structure observation by the SPM-8100FM.

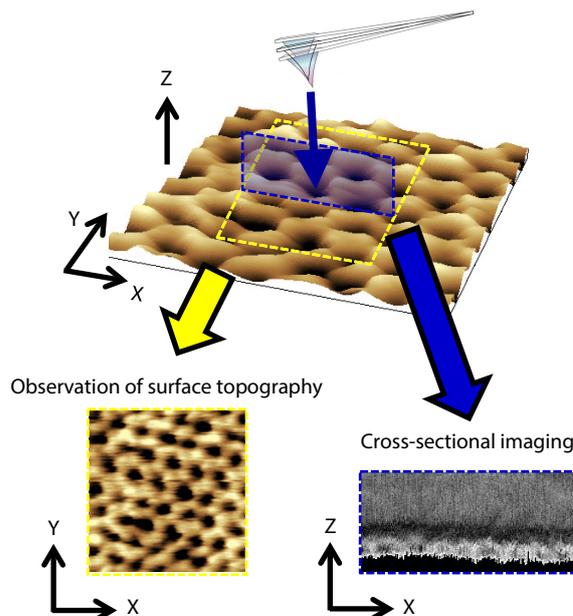


Fig. 2 Image of Crystal Structure Observation and Liquid Structure Observation by SPM-8100FM

Observation in Liquid by SPM-8100FM

The lattice structure of the calcite (104) crystal plane in water and the structure of the water at the interface were evaluated by using the SPM-8100FM.

In observation in a liquid by the SPM-8100FM, a Petri dish type solution cell (option) is filled with the liquid sample after solid sample is fixed at the bottom surface of dedicated solution cell, and the cantilever is brought near the solid-liquid interface and scanned. Fig. 3 shows the setting for observation in a liquid.

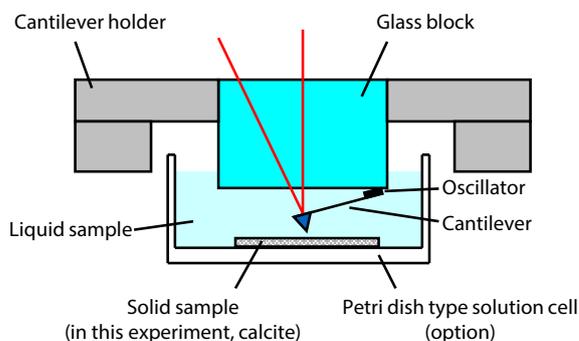


Fig. 3 Setting for Observation in Liquid

Atomic Image of (104) Cleavage Plane of Calcite

Fig. 4(a) shows an atomic image of the (104) cleavage plane of calcite measured using the SPM-8100FM. It can be understood that the atoms are arranged regularly. The lattice size was 0.82 nm × 0.42 nm, as indicated by the white broken lines in the figure.

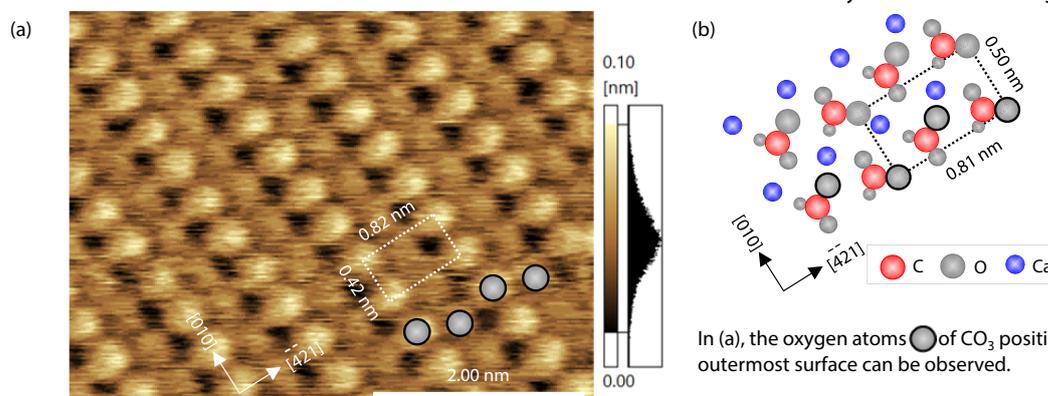


Fig. 4 (a) Atomic Image of Calcite Measured by SPM-8100FM and (b) Diagram of Crystal Structure of (104) Cleavage Plane of Calcite

Liquid Structure at Interface of (104) Cleavage Plane of Calcite and Water

Fig. 5 shows an image obtained by cross-sectional imaging of the interface between the (104) cleavage plane of calcite and water. The black region at the bottom of the image is calcite, and the gray region at the top is the bulk water (region where Brownian motion of water molecules occurs). The white points visible in the area between the upper and lower regions (e.g., areas surrounded by circles) are water molecules whose arrangement is influenced by the calcite surface.

Fig. 4(b) shows a crystal structure diagram of the (104) cleavage plane of calcite⁽¹⁾. If the crystal structure is compared with the atomic image obtained by measurement, the oxygen atoms of the CO₃ positioned at the outermost surface can be observed in the atomic image, and it can be understood that the crystal orientation is as shown by the arrows in the figure.

In (a), the oxygen atoms of CO₃ positioned at outermost surface can be observed.

The curves shown at the right of the image are the profiles at the locations indicated by light blue (broken lines) and yellow (solid lines) in the figure, respectively. In the 1st layer, which is closest to the calcite surface, water molecules were observed 0.15 nm above the calcite surface, and in the 2nd layer, the water molecules were observed 0.34 nm above the surface. These values are in good agreement with the results of a theoretical calculation (in which the water molecules of the 1st layer are positioned 0.12 to 0.23 nm from a solid surface, while those of the 2nd layer are positioned 0.3 to 0.35 nm from the surface⁽²⁾).

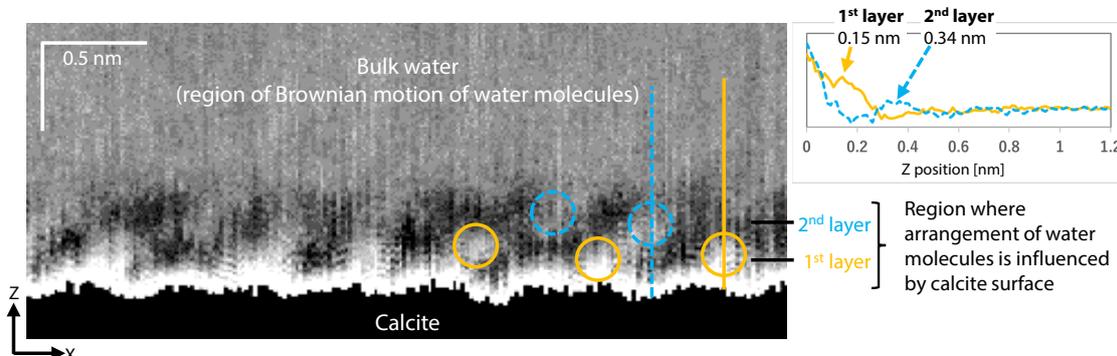


Fig. 5 Liquid Structure at Interface of (104) Cleavage Plane of Calcite and Water Measured by SPM-8100FM

Conclusion

The crystal lattice structure of the (104) crystal plane of calcite was observed using the high resolution function of the SPM-8100FM. The liquid structure at the interface between the calcite crystal plane and water was also observed by cross-sectional imaging utilizing the high force sensitivity of the SPM-8100FM. These results elucidated the interaction between the calcite crystal surface and water at the molecular level, and will be helpful in clarifying the mechanisms of the actions of calcite in the natural world, such as the mechanism of biomineralization.

<References>

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- (2) Paolo Raiteri, Julian D. Gale, David Quigley and P. Mark Rodger.: Derivation of an Accurate Force-Field for Simulating the Growth of Calcium Carbonate from Aqueous Solution: A New Model for the Calcite-Water Interface, *J. Phys. Chem., C*, 114, 5997–6010, (2010)