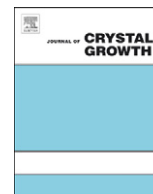




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Dynamic and topographic observation of calcite dissolution using enhanced in-situ phase-shift interferometry

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ABSTRACT

The dissolution rate of calcite in water with and without flow was measured using enhanced phase-shift interferometry (PSI). This technique uses a white light source instead of laser light to shorten the coherent wave-length providing quick and precise measurements of mineral dissolution and growth over relatively short time scales (several tens of minutes). Phase shift interferometry is non-invasive technique that allows surface observation at the molecular level in water as well as direct, simultaneous measurement of step velocity and the behavior of crystal surfaces during dissolution. The theoretical PSI resolution in the vertical direction in water is 0.78 nm; however the practical detection limit of the calcite dissolution experiments was 4.2 nm due to the effects of external and internal inferences such as apparatus drift, air drag, etc.

The calcite dissolution rate at zero water flow was estimated from the retreat velocity as 0.0494 nm/s, which corresponds to flux rate of 1.33E-10 mol/cm²/s. This is around the lower limit of previously published data obtained mainly by powder experiments. The dissolution rates for different vicinal slopes of the surface were also measured. These rates were well-correlated with the vicinal slopes in accordance with BCF theory indicating that there is a mutual interaction between neighboring growth/dissolution steps via diffusion, consistent with previously published AFM measurements.

The effect of topographical features on the microscopic dissolution behavior was clearly observed during the PSI measurements. The dissolution velocity at the isolated step in pure water was obtained as 2.8 nm/s by fitting the experimental data. Thus, it is possible to examine and determine global calcite dissolution rates using the topographical measurements determined from PSI experiments.

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1. Introduction

Carbonate minerals play an important role in the CO₂ budget, where growth fixes CO₂ into a solid mineral form and dissolution releases it. Thus in order to examine many different environmental issues a multitude of fundamental studies of calcite crystal growth and dissolution have been conducted in the past few decades [1–5]. These studies have used the effects associated with impurity chemistry and molecular and atomic mechanisms at the interface to describe the various behaviors observed at the growing or dissolving calcite surface. However, growth and dissolution seem to be discontinuous and need to be explained by a combination of surface and volume diffusion-limited theory [6] as well as nucleation theory [7]. The dissolution of carbonate minerals is still poorly understood as a dynamic process on the

molecular scale and information is missing in the literature for conditions such as zero flow, which is critical in simple static systems like those found in natural underground systems that are comprised of fine-grained and porous media.

Classically the global dissolution rate of mineral surfaces has been calculated using concentration measurements of components dissolved from a powdered sample. However, there is a large discrepancy between the reported dissolution rates obtained using these conventional techniques of up to an order of magnitude at pH 6 and above [8]. In an attempt to unite these findings with processes occurring at the dissolving mineral surfaces during dissolution, a large number of nanoscale dissolution measurements have now been added to the literature from atomic force microscopy (AFM) experiments [9–11] which provide excellent resolution in vertical as well as in lateral directions. Recent advancement in non-invasive interferometry methods used to examine the dissolving mineral surface by 2-D area [8] and time-space analysis [12] from sequentially obtained data can also provide information about the nanoscale processes occurring

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at the mineral surfaces. Interferometry techniques have the advantage of not only measuring dissolution rate as retreat velocity (e.g., nm/s) directly and precisely but also evaluating dissolution at specific surface features (topographies and mechanisms) in a large field of view. Similar to the AFM measurements, calcite dissolution rates measured by vertical scanning interferometry (VSI) show 5–100 times slower dissolution rates than the rates measured from powder experiments [8]. However, discrepancies between AFM and optical measurements such as interferometry have also been documented, for example, during lysozyme growth [13]. Use of AFM is known to cause two major problems during dissolution and growth analysis. Firstly, it is an invasive technique because the cantilever is inside the solution, thus movements of the cantilever within the solution easily changes the fluid dynamics inside the reaction cell including the solution flow and the concentration field above the dissolving surface [14]. Secondly the time-resolution during AFM measurements is low due to the time required to scan the surface for each image. Thus understanding the impact of the discrepancies between interferometry, AFM and powder dissolution measured rates remains an open problem when attempting to determine global dissolution rates applicable to natural systems.

To observe the dissolution behavior of calcite crystals in solution, in-situ measurements of calcite dissolution were carried out in a fluid-reaction cell using interferometry. Our enhanced PSI [12,15,16] is specially designed to improve the observation capability of mineral surfaces enabling non-invasive investigations that cover a large observation area ($200 \times 150 \mu\text{m}^2$), has a high time-resolution for the observation of dynamic processes, and results in absolute height information on a molecular level. Previously, our enhanced PSI was successfully used to examine anorthite dissolution in alkaline solution [12]. That study examined pre-existing steps on a cleaved surface of anorthite {110}. However, here we apply this PSI technique to examine calcite dissolution, particularly to provide a detailed investigation of the step behavior that accompanies etch-pit formation at different flow rates including almost zero flow and at different surfaces with various topographical features.

2. Experimental

2.1. Phase-shift interferometry

Interferometry techniques utilize the interference between a beam reflected from a sample surface and a reference beam reflected from a reference mirror to provide information about sample retreat or advancement [12,15,16]. Specifically a phase-shift interferometer takes three conventional interferograms at phase positions 0, $2/3\pi$ and $4/3\pi$ by shifting the reference mirror using a piezo actuator to generate a phase-shift interferogram. This phase-shifting technique is able to achieve topographic measurement with molecular-scale height resolution. Our enhanced PSI is based on an Olympus Fabulous interferometer, which adopts the Maki-prism modified from the Linnik-type interference optics [12], so that very precise and stable measurement can be achieved for long period. The schematic diagram of the setup of the PSI is described in Fig. 1. The sample and reference mirror are mounted on two independent focusing stages (Linnik configuration) and a Xe-lamp is used as a non-coherent white light source. The measurements were performed at a wavelength of $\lambda=532 \text{ nm}$, green light, by filtering the white light. The intensity distribution within each interference fringe is expressed by:

$$I(i)_{x,y} = a_{x,y} + b_{x,y} \cos(\phi_{x,y} + \delta(i)) \quad (1)$$

where $I(i)$ is the intensity of the conventional interferogram at each phase shifting position i , a is the background and b is the amplitude

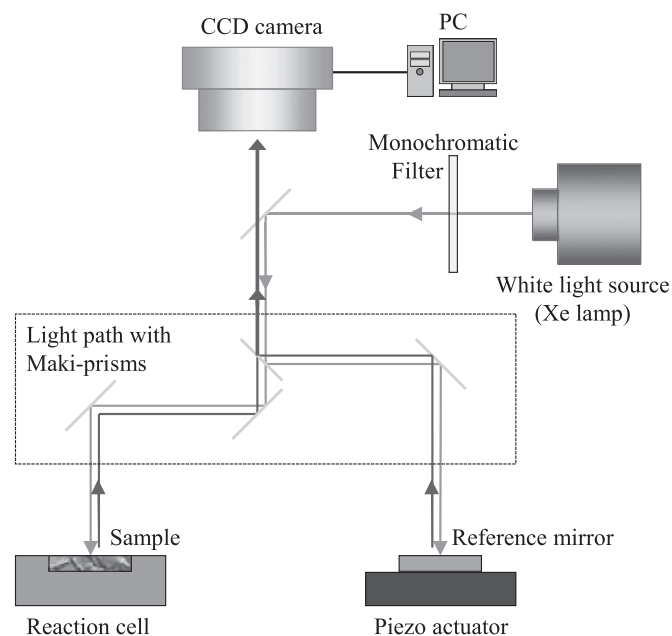


Fig. 1. Schematic diagram of the enhanced phase-shift interferometry developed for in-situ observation of crystal dissolution processes.

of the fringe wavelet, ϕ is the phase and $\delta(i)$ is the phase-shift, which is exactly known for each position i . When we measure $I(i)$ at positions $\delta(i)=0, 2/3\pi$ and $4/3\pi$ (i.e. $i=3$), ϕ can be obtained as a linearized interferogram from each $I(i)$ by canceling the other independent variables

$$\phi_{x,y} = \arctan \left(\frac{\sqrt{3}(I(3)_{x,y} - I(2)_{x,y})}{2I(1)_{x,y} - I(2)_{x,y} - I(3)_{x,y}} \right) \quad (2)$$

The conversion by Eq. (2) is called the three packet method. Finally the conversion from the contrast of the phase-shift interferogram $\phi_{x,y}$ (2π as full scale) to a height profile can be done according to

$$h_{x,y} = \frac{\lambda_{532} \phi_{x,y}}{2n \text{ GS}} \quad (3)$$

where $h_{x,y}$ is height in nanometer (nm) at position x,y and λ is wavelength in nanometer, n is refractive index of solution, $\phi_{x,y}$ is the phase intensity at position x,y , and GS is the grayscale information. With refractive indexes of $n=1$ for air and $n=1.33$ for pure water, and with 256 levels of grayscale information in an 8 bit per pixel image, the theoretical resolution limit in the vertical direction is ideally calculated as 1.04 nm in air and 0.78 nm in pure water. The real detection limit, however, is controlled by (i) the reflectivity of the crystal surface, (ii) disturbances in the optical paths, and (iii) the overall stability of the optical parts during measurement. To minimize any kind of displacement during the measurement the ambient air temperature has to be stabilized and the system has to be protected against air drag. Furthermore, an adequate anti-vibration system is necessary to isolate the apparatus from external disturbances.

The white light illumination used in our PSI has the advantage that it shortens the coherency, resulting in improved interference fringe quality if the optical condition in both sample and reference paths can be precisely balanced by adjusting the compensator (cover-glass) and gray filter. The working distance of approximately 30 mm provides enough space to easily arrange the specimen as well as sufficient solution space above the crystal surface in the reaction cell, both of which ensures stable growth or dissolution conditions even over long time periods.

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