In situ nanoscale observations of gypsum dissolution by digital holographic microscopy

Pan Feng[a,b,*], Alexander S. Brand[b], Lei Chen[c], Jeffrey W. Bullard[b]

[a] *Jiangsu Key Laboratory of Construction Materials, School of Materials Science and Engineering, Southeast University, Nanjing 211189, China*
[b] *Materials and Structural Systems Division, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*
[c] *Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

ARTICLE INFO

ABSTRACT

Recent topography measurements of gypsum dissolution have not reported the absolute dissolution rates, but instead focus on the rates of formation and growth of etch pits. In this study, the *in situ* absolute retreat rates of gypsum (010) cleavage surfaces at etch pits, at cleavage steps, and at apparently defect-free portions of the surface are measured in flowing water by reflection digital holographic microscopy. Observations made on randomly sampled fields of view on seven different cleavage surfaces reveal a range of local dissolution rates, the local rate being determined by the topographical features at which material is removed. Four characteristic types of topographical activity are observed: 1) smooth regions, free of etch pits or other noticeable defects, where dissolution rates are relatively low; 2) shallow, wide etch pits bounded by faceted walls which grow gradually at rates somewhat greater than in smooth regions; 3) narrow, deep etch pits which form and grow throughout the observation period at rates that exceed those at the shallow etch pits; and 4) relatively few, submicrometer cleavage steps which move in a wave-like manner and yield local dissolution fluxes that are about five times greater than at etch pits. Molar dissolution rates at all topographical features except submicrometer steps can be aggregated into a continuous, mildly bimodal distribution with a mean of 3.0 μmol m^{-2} s^{-1} and a standard deviation of 0.7 μmol m^{-2} s^{-1}.

1. Introduction

Mineral dissolution governs many geochemically- and environmentally-relevant processes, both in natural and man-made systems (Lüttge, 2006). Among the rock forming minerals, gypsum ($CaSO_4 \cdot 2H_2O$) and related calcium sulfate minerals, such as bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$) and anhydrite ($CaSO_4$), are abundant in nature, with extensive deposits underlying an estimated 25% of Earth's surface (Ford and William, 2007). Therefore, knowledge of water-gypsum interactions is important in many fields of inquiry, including geochemistry, materials science, soil science, and environmental science. A quantitative, mechanistic understanding of gypsum behavior in contact with aqueous solutions is also relevant for predicting the evolution of the wide areas of gypsum karsts, their instability, and their potential for collapse (Jeschke et al., 2001). In addition, the presence of calcium and sulfate ions in water influences the dissolution of other minerals that contain toxic metals (Kuechler et al., 2004), thereby potentially affecting the quality of drinking water (Raines and Dewers, 1997).

Traditional methods for measuring mineral dissolution rates focus on average bulk dissolution behavior, using batch and column experiments on particulate suspensions (Zhang and Nancollas, 1990; Singh and Bajwa, 1990), as well as techniques with controlled mass transport conditions, such as the rotating disk method and channel flow cells (MacInnis and Brantley, 1993; Burns et al., 2003; Brown et al., 1993; Compton and Daly, 1987; Svensson and Dreybrodt, 1992; Liu and Nancollas, 1971). More recent techniques focus on characterizing microscopic kinetic processes at surfaces. Among these are atomic force microscopy (AFM) (e.g., Cama et al., 2010; Chow et al., 2012; Jordan and Rammensee, 1998; Ruiz-Agudo et al., 2011) scanning force microscopy (SFM) (e.g., Bosbach et al., 1995; Bosbach and Rammensee, 1994; Hall and Cullen, 1996) scanning electrochemical microscopy (SECM) (e.g., Macpherson and Unwin, 1995; McGeouch et al., 2012) vertical scanning interferometry (VSI) (e.g., Arvidson et al., 2003; Asta et al., 2008; Kumar et al., 2013; Lasaga and Lüttge, 2001; Lüttge, 2006; Lüttge et al., 1999) and, more recently, digital holographic microscopy (DHM) (Brand et al., 2017; Abbott et al., 2013).

All of these more recent techniques are able to resolve nanoscale differences in surface elevation from one image pixel to another, and can provide insights about dissolution mechanisms that would be inaccessible using traditional bulk techniques (Lüttge and Arvidson,

2010). Recent investigations with such techniques have revealed how intrinsic heterogeneity within a crystalline solid manifests itself as a distribution or spectrum of dissolution rates (Fischer et al., 2012; 2014, 2015; Lüttge et al., 2013; Emmanuel, 2014; Fischer and Lüttge, 2017; Brand et al., 2017; Saldi, 2017), thereby demonstrating that rate kinetics are poorly described by a single or average value.

Although microscopic methods have been used to observe topography changes at gypsum surfaces, absolute dissolution fluxes at gypsum surfaces by *in situ* topographic measurements have not been reported previously. Instead, the dissolution process has been characterized in terms of the formation of etch pits or the movement of stepwaves. Nearly all topographic studies of gypsum dissolution, including this one, are made on the (010) cleavage plane because it is easy to produce as a flat surface with relatively few visible surface features. Bosbach and Rammensee (1994) and Hall and Cullen (1996) observed by SFM that growth and dissolution on (010) gypsum surfaces is a layer-by-layer process. Later, Bosbach et al. (1995) used SFM observations to conclude that gypsum (010) dissolves primarily by movement of molecular-scale steps parallel to the cleaved surface (Process I) and formation of terrace vacancies (Process II). That study rarely observed deep etch pits (Process III), which the authors attributed to screw dislocations intersecting the surface. Shindo et al. (1996) reported AFM observations of layer-by-layer dissolution of (010) anhydrite by the nucleation, growth, and coalescence of rectangular terraces. Peruffo et al. (2013) used AFM to link direction-specific microscopic fluxes, local mass transport effects and global macroscopic rates from analysis of etch pits formed in gypsum surfaces within the first 100 s of contact with water. Fan and Teng (2007) reported *in situ* AFM observations, using a fluid cell, of anisotropy in step velocity and an absence of deep etch pits. A complementary *in situ* AFM study by Burgos-Cara et al. (2016) evaluated the effects of ions in solution on the dissolution of gypsum.

In contrast to VSI and AFM, DHM offers a unique opportunity to measure *in situ* changes in nanoscale surface topography in real time as a solid dissolves in an aqueous solution (Brand et al., 2017). Holographic interferometry has been recognized as a valuable tool in solution chemistry since 1967 (Knox et al., 1967). In particular, in transmission mode it has been used to monitor the changes in concentration field within a solution near a dissolving solid surface to characterize the dissolution rate (Colombani et al., 1998; Colombani and Bert, 2007; Colombani, 2008; Pachon-Rodriguez and Combani, 2013). Reflection DHM in the present study is used to monitor the topography of the dissolving surface itself in real time. DHM is an optical interferometric method that splits a monochromatic coherent light source into a reference beam and an object beam, similar to scanning interferometry except that a digital CCD camera records the interference patterns as a full image hologram (Kim, 2010). The holograms are then numerically reconstructed to produce images of amplitude and phase, the latter of which can be converted to height data with potentially sub-nanometer vertical resolution (Kühn et al., 2008). The advantage of DHM for rate spectra measurement is that it can collect full-frame *in situ* measurements with a rapid acquisition rate that is limited only by the shutter speed of the CCD camera that collects the holograms.

This paper describes measurements by DHM of absolute dissolution rates at (010) gypsum cleavage surfaces submerged in pure flowing water. The real-time observations enable the spectrum of observed rates to be linked directly to the evolution of different topographical features on the surface, including deep or shallow etch pits, defect-free regions, and migrating steps with heights of about 100 nm.

2. Materials and methods

2.1. Materials

Freshly cleaved (010) surfaces of optically clear, single crystal gypsum (selenite from Washington County, Utah, USA) were used for
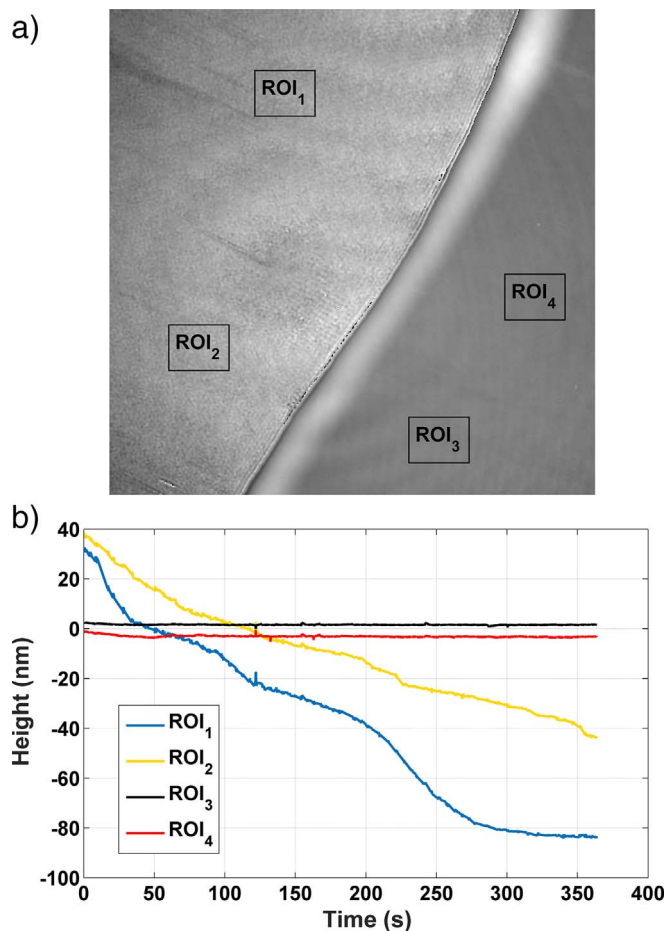

Fig. 1. (a) A phase map of a gypsum surface at the start of an experiment, showing the chromium mask on the right and the gypsum (010) surface on the left. (b) Time dependence of the height in two regions of interest (ROIs) marked on the gypsum surface as ROI_1 and ROI_2, and of two regions on the chromium mask marked as ROI_3 and ROI_4. Each of the ROIs has edge dimensions of 10 μm. Uncertainty in the individual height measurements along a profile is characterized by the temporal standard deviation of the measurement on a single pixel, 2 nm.

all the dissolution experiments. The dimensions of the specimens were on the order of several millimeters.

Measurements of absolute dissolution rate requires the availability of a reference plane that does not change in elevation during the experiment. This was accomplished by physical vapor deposition of 50 nm of chromium onto a portion of the surface. Chromium was used because it was observed to provide better adhesion to the gypsum surface than gold, platinum, Al_2O_3, SiO_2, or any of several thin polymer coatings that were tried. The chromium provides an inert, nominally flat (a few nanometers roughness), and reflective reference plane from which the relative phase (height) differences of the uncoated surface can be computed (see Fig. 1 (a)).

Deionized water with initial resistivity of 0.18 MΩ m was used in all experiments, and the water temperature was kept at a nominal temperature of 23 °C, which did not vary by more than 2 °C among all the experiments. A flow-through liquid cell was constructed for this study to provide a nearly constant solution flow rate across the gypsum surface. All components of the fluid cell are made of nonreactive polymer materials (e.g., polyether ether ketone and polytetrafluoroethylene). The fluid cell cavity has an approximate volume of 14.5 mL without the specimen and approximately 12.0 mL with a specimen loaded. Most experiments were conducted by flowing the water into the