Dissolution of the periclase (001) surface: A scanning force microscope study

GUNTRAM JORDAN,* STEVEN R. HIGGINS, AND CARRICK M. EGGLESTON

Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming 82071-3006, U.S.A.

ABSTRACT

In contrast to most ionic minerals studied by SFM, the periclase (001) surface dissolves not by retreat of monolayer steps parallel to (001), but by retreat of a rough surface perpendicular to (001). At pH < 2, dissolution has an additional contribution from retreating macro-steps at the edges of nearly square pits. The macro-steps have heights up to 120 nm. In general, step direction is parallel to [110] and equivalent directions. During dissolution at low pH, a soft near-surface region is formed. Other investigators have shown that the near-surface region is protonated. Protonation is supposed to stabilize the (111) surface of periclase. Due to the structural similarities between periclase (111) and brucite (001), and similar dissolution rates of periclase and brucite at pH < 5, we conclude that during dissolution the periclase (001) surface is restructured into “(111) nano-facets” representing brucite (001)-like layers and appearing as a rough and soft surface in SFM images. The most probable reasons that the slopes of these macro-steps (up to 50°) are lower than the slopes of perfect (111) facets are the likely poorly ordered structure of these layers, microtopography on these surface facets, and tip-surface convolution in SFM. By measuring the vertical position of the surface vs. time, we calculated the dissolution rate. At pH 1 and pH 2 we found the rates to be $17.1 \pm 5.8 \times 10^{-6}$ and $5.7 \pm 3.7 \times 10^{-6}$ mol/m²·s, respectively. These rates are in reasonable agreement with previously reported rates of periclase and brucite (001) dissolution, and are consistent with the idea that the MgO (001) surface consists of Mg(OH)₂ (001)-like layers.

INTRODUCTION

Dissolution of metal-oxides and aluminosilicates is among the most crucial reactions influencing the Earth’s surface by transforming rocks and soils into aqueous solutes (e.g., Sverdrup 1990; White and Brantley 1995). Such reactions can influence not only local water quality (e.g., Stumm 1985, 1987), but also global climate (Berner 1995). Recently, scanning force microscopy (SFM) has enhanced our ability to study dissolution mechanisms at a molecular level (e.g., Bosbach and Rammensee 1994; Gratz et al. 1990; Hillner et al. 1992a; Liang et al. 1996). Besides in-situ, real-time investigation of kinematics and microtopography of the solid-liquid interface with monolayer resolution, SFM also enables the acquisition of quantitative data such as the dissolution rate and the activation energy for dissolution (Jordan and Rammensee 1996, 1998). However, the dissolution rates of most oxides and silicates are too low for near-room temperature study by SFM.

One of the few oxides that allows SFM-investigation of dissolution rate and mechanism at room temperature is periclase (MgO). Due to its simple structure, MgO serves as a model oxide for studying the tendency of many oxides to transform into the more stable hydroxides under natural aqueous conditions. For MgO, this relationship is well known (e.g., Roy et al. 1953). Additionally, MgO is used as a substrate for high-temperature superconductor thin films; in this application, water can cause serious damage to both the film and the substrate (e.g., Watson et al. 1995).

This study aims to investigate the rate and mechanism of MgO dissolution, particularly the effect on dissolution of the tendency toward transformation to the hydroxide. The implications of this hydroxylation process for dissolution are poorly understood despite their importance for both MgO specifically and for many natural minerals generally. However, the effects of such transformation are different from most ionic crystals investigated by SFM so far, which show uniformly retreating monolayer steps during dissolution (e.g., calcite: Hillner et al. 1992b; Liang et al. 1996). In addition, this phenomenon has broad parallels to the formation of leached or altered layers on silicates (e.g., feldspars: Casey et al. 1989; Chou and Wollast 1985; Hellmann et al. 1990), and thus is a useful starting point for understanding how to deal with altered layer formation in SFM studies, especially as high-temperature SFM becomes available (Higgins et al. 1998).

EXPERIMENTAL METHODS

Periclase has the rock salt structure (space group: 4/m32/m) with a lattice constant of $a_0 = 0.42$ nm. There-