

The hydration and dissolution of periclase

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The dissolution of powdered periclase, MgO, in near neutral to acidic solutions, proceeds *via* a brucite, Mg(OH)₂, intermediate. The hydration reaction is apparent from the similarity of the dissolution rates (Vermilyea, 1969) and X-ray diffraction of the reacting powder. There is evidence from both natural samples (Gorshkov *et al.*, 1992) and calculations (Refson *et al.*, 1995) that a topotactic relationship exists between the (111) planes of periclase and the (0001) planes of brucite. Calculations indicate that the dissociation of water on the (001) surface is endothermic. Chemisorption on surfaces comprising atoms of lower coordination is more favourable, with the hydroxylated (111) surface being of lowest energy (Refson *et al.*, 1995; de Leeuw *et al.*, 1995). A proposed reaction mechanism involves the replacement of magnesium by hydrogen along (111) periclase planes. This was studied for the periclase (001) surface. Elastic recoil detection analysis (ERDA) results have been reported which suggested the formation of a 1000 Å layer with composition Mg(OH)₂ for a sample reacted at pH 2 for 2 hours (Wogelius *et al.*, 1995). In this paper we present ERDA and SIMS results which contradict this finding.

Experimental

Periclase cleavage plates were obtained commercially. These were either freshly cleaved or chemomechanically polished before use. Samples were reacted at constant pH using a Mettler DL-77 auto-titrator. Deuteration experiments used D₂O (99.9%) acidified with HNO₃ (10 M).

ERDA used a 7.5 MeV ¹⁶O⁴⁺ beam. Recoiled protons were counted using a surface barrier detector covered with a kapton filter to reject scattered ¹⁶O. The sample was tilted 15°, and the detector 40°, relative to the incident beam. The detector energy

was calibrated using the α -particle decay of ²⁴¹Am. Spectra were normalised against the simultaneously recorded PIXE signal. SIMS spectra were recorded in both point and raster mode. Proton concentration was calibrated using hydrous minerals and hydrogen implanted silicon.

Results

The normalised ERDA spectra of brucite and a polished periclase (001) surface reacted at pH 4 for 14 hours, recorded under identical conditions, are shown in Fig. 1. SIMS was used to analyse samples reacted at pH 2 for 2 and 6 hours, pH 5.7 for 72 hours, a blank handled in air, and a blank heated at 600°C and handled under nitrogen. No significant differences in any of the hydrogen profiles could be determined. A mass scan of a brucite standard indicated that ¹H₂ and ²D could be easily resolved. Point mode analysis of a (001) surface reacted at pH 2 for 2 hours in D₂O indicated only trace amounts of ²D. The ²D concentration was below the detection limit in depth profile mode. SIMS was able to clearly resolve 0.035 wt.% implanted hydrogen at a depth of ~1700 Å in silicon.

SEM and atomic force microscopy (AFM) images reveal dissolution in the form of etch pits. The pits are square based pyramids with sides parallel to [100], and are aligned along either [110] or [100] type directions. For the [100] aligned pits, the apex of the pyramid is shifted from the geometrical centre. The resulting asymmetry is present in both the [100] and [010] directions, with the faces making angles of typically either 13° or 26° with (001).

Discussion

ERDA profiles hydrogen concentration from the energy of protons recoiled by a beam of heavy

ions. Recoil energy decreases with increasing depth due to energy loss in the solid of both the incident beam and the exiting protons. The constant recoil intensity with decreasing energy of the brucite spectrum (Fig. 1(b)) is indicative of a uniform proton distribution. The spectrum can be thought of as the summation of successive layers of constant composition contributing an energy width ΔE , in the limit as $\Delta E \rightarrow 0$. A thin hydrated layer of $Mg(OH)_2$ composition on periclase would therefore contribute a peak with intensity comparable to the brucite spectrum, but with a width on the energy scale that is dependent upon the layer thickness. This is not observed for the reacted sample. The ERDA peak is instead attributed to surface adsorbed water. A similar peak was observed for periclase samples reacted at pH 2 for 2 hours, pH 5.7 for 72 hours, a variety of olivine crystals, and hydrogen implanted silicon. The anomalously large width of the peak, derived from presumably only several monolayers of water, is a result of the energy resolution. The resolution is limited by the ^{16}O beam intensity and subsequent acquisition time. High resolution requires detector slits, a small detector angle, and a large detector-sample distance, all at the expense of signal intensity.

The previously reported ERDA spectrum (Wogelius *et al.*, 1995), modelled to indicate a 1000 Å brucite-like layer, is similar to the peaks we ascribe to surface water. In this earlier work, the blank was heated to remove adsorbed water, and gave a flat baseline. We believe that poor energy resolution, an inappropriate blank, and absence of an intensity calibration, led to a misleading interpretation of this ERDA spectrum.

The hydrogen SIMS profile finds no evidence of a hydrated layer, however, a large surface water contribution obscures results for the first 300 Å. The presence of a deuterated layer should be easily distinguished from adsorbed water, since any 2D signal must derive from the sample. The inability to detect 2D by SIMS for these samples is compelling evidence against a zone of brucite composition.

Etch pits on the (001) surface of periclase have been shown to coincide with dislocations emerging at $\{110\}$ slip planes (Sangwal, 1987). Pits derived from edge dislocations are parallel to $[110]$, while those associated with screw dislocations will be parallel to $[100]$. Asymmetrical etch pits occur when the dislocation line is inclined to the surface. The angle of inclination was calculated for a number of pits and found to be close to 45° in both the $[100]$ and $[010]$ directions. Pit nucleation therefore appears to occur

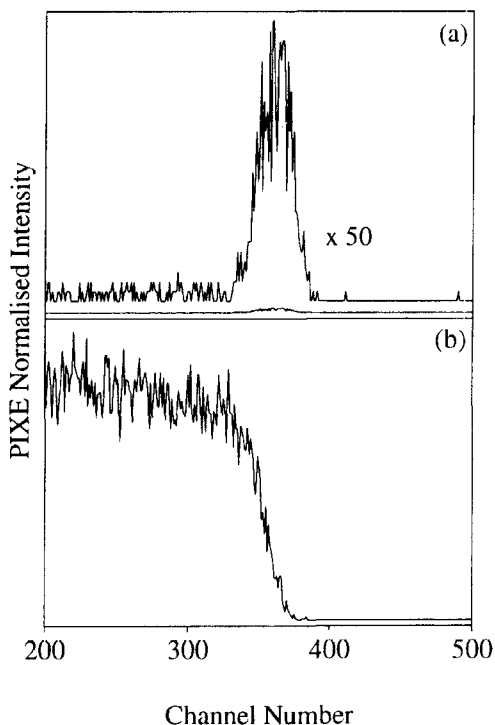


FIG. 1. ERDA spectra of (a) periclase (001) reacted at pH 4 for 14 hours, and (b) brucite.

at the intersection of slip planes on the (001) surface. This suggests that under the reaction conditions, dissolution occurs at discrete defect sites, rather than from a thick hydrated layer. The mechanism of the dissolution process, and a discussion of the thermodynamic stability of the etch pit surfaces, will be the subject of a future paper.

Summary

The previously reported conversion of the periclase (001) near surface region to a brucite-like layer could not be substantiated. The results on which this conclusion were based are believed to be in error. If a hydrated layer does exist, it is too thin to be detected. Defect sites on the (001) surface appear to promote dissolution, rather than form stable (111) hydroxylated surfaces that penetrate into the sample. In a powder, the high defect density will expose numerous (111) type planes, possibly allowing conversion to brucite according to the proposed mechanism.