

Hydration reactions at the mineral–fluid interface: experimental and computational studies

R.A. Wogelius
K. Refson
D.G. Fraser
J.P. Goff
G.W. Grime

University of Oxford, Department of Earth Sciences,
Parks Road, Oxford OX1 3PR.

Oxford Physics, Clarendon Laboratory, Oxford OX1 3PU.
University of Oxford, Scanning Proton Microprobe Unit,
Nuclear Physics Laboratory, Keble Road, Oxford, OX1 3RH.

Introduction

Reactions that occur at the mineral–fluid interface, such as mineral dissolution, trace element adsorption, and secondary phase precipitation, are of particular interest to geochemists. Several new surface-sensitive analytical techniques have recently been applied to the study of these reactions. In addition, recent advances in *ab initio* quantum mechanical calculations have made it much easier to translate experimental results into models of the actual atomic-scale reactions that occur at surfaces.

The penetration depth of protons into the feldspar near-surface environment during hydrolysis has been successfully measured using Elastic Recoil Detection Analysis (ERDA) (Casey *et al.*, 1989). Using this method, the penetration profile of H^+ in minerals as a function of reaction time, temperature, pH, and crystallographic orientation can be determined. The H^+ distribution in the mineral near-surface can be used to: [1] constrain the thicknesses of surface layers that have hydrated to form distinct new crystal structures, [2] define the depth to which cation-proton exchange reactions penetrate, and [3] construct a charge balance inventory.

Surface sensitive X-ray techniques, such as X-ray absorption spectroscopy (electron-yield geometry), X-ray reflectivity, and low-angle surface diffraction have also been applied to mineral surface experiments and can provide unique atomic-scale structural and physical data (Chiarello *et al.*, 1993). Detailed information about changes in surface morphology, the nature and growth dynamics of altered or recrystallized layers, and the atomic arrangements of adsorbates can all be produced by these types of measurements. Unambiguous results with simple oxides such as periclase will provide a foundation to our understanding of how more complicated Mg-bearing minerals react with aqueous fluids. X-ray results for periclase and ERDA results for olivine (F_{090}) are presented below.

Accurate periodic Hartree-Fock calculations (Scamehorn *et al.*, 1993) and experiments (Onishi *et al.*, 1987) show that water physisorbs onto clean (100) periclase surfaces but that there is no dissociation or chemisorption. However a reaction takes place on exposure to water over a period of several hours to produce an opaque layer at the surface (presumably brucite). A reconstructive mechanism is necessary to explain the slow reaction rate. We observe that the atomic structure at a periclase (111) surface is isomorphic to brucite (0001) with a 5% discrepancy in lattice parameter. This suggests that protonation acts to stabilize the otherwise unstable (111) surface by forming a brucite-like layer and allows the hydration reaction to proceed by growth of brucite at (111) etch pits. Theoretical calculations will demonstrate this stabilization.

Methods

Mineral standards were prepared by implanting polished wafers with known fluxes of deuterium (D) at 15 keV and then analyzed using a 7.5 MeV oxygen beam with a surface barrier detector placed at a scattering angle of 24 degrees. A thin Al window was inserted between sample and detector to filter out forward scattered oxygen and the sample was tilted 15 degrees. ERDA measurements on an olivine standard show that the near-surface D concentration is approximately 10^{17} atoms/cm², in good agreement with simulated profiles. ERDA mineral standards will be used to quantify measurements of proton penetration profiles produced under precisely controlled laboratory conditions for periclase, olivine, and other minerals.

X-ray reflectivity. Single-crystal periclase with a chemo-mechanically polished (100) surface was heated overnight to 600°C and then transferred under an inert atmosphere into an X-ray cell with Mzylar windows. During analysis the sample cell was kept at a positive pressure of ultra-pure

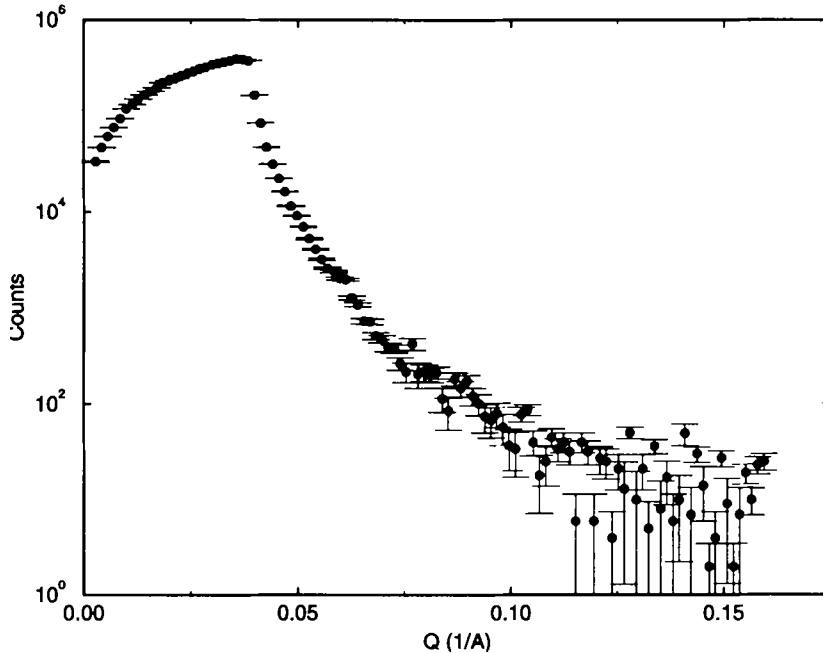


FIG. 1. X-ray reflectivity of a polished periclase (100) surface in ultra-pure nitrogen.

nitrogen to preclude reaction of the surface with atmospheric water vapour. The X-ray source was a Cu-target rotating anode fitted with a monochromator emitting X-rays with a wavelength of 1.54056 Å. Surface roughness as estimated by the manufacturer was 15 Å.

Calculations. *Ab initio* computations using density functional (Car-Parrinello) methods allow sensitive and reliable prediction of surface structures and energies (Stich *et al.*, 1991). By comparing the calculated energetics of water physisorption and chemisorption we plan to identify the correct protonated surface structure and establish a likely reaction pathway for conversion of brucite to periclase.

Results

Fig. 1 presents the results of the low-angle X-ray scattering experiment completed with periclase. These are the raw data presented with counts as a function of the momentum transfer vector (Q). The decrease in reflectivity as a function of Q was compared with calculated reflectivity curves and is consistent with a surface rms roughness of 15 Å. Surface miscut is 0.372°. Reflectivity measure-

ments of changes in surface roughness during reaction with aqueous fluids under controlled conditions will be presented. Combined with measurements of the surface proton inventory and low-angle diffraction results, these data will give a detailed model of how the periclase (100) surface roughens during hydrolysis and how it hydrates. Preliminary computational results show that protonation in a brucite-like structure does indeed stabilize the (111) surface of periclase.

References

- Casey, W.H., Westrich, H.R., Arnold, G.W., and Banfield, J.F. (1989) *Geochim. Cosmochim. Acta*, **53**, 821–32.
- Chiarello, R.P., Wogelius, R.A., and Sturchio, N.C., (1993) *Geochim. Cosmochim. Acta*, **57**, 4103–10.
- Onishi, H., Egawa, C., Aruga, T., and Iwasawa, Y., (1987) *Surf. Sci.*, **191**, 479–91.
- Scamehorn, C.A., Hess, A.C., and McCarthy M.I., (1993) *J. Chem. Phys.*, **99**, 2786–95.
- Stich, I., Payne, M.C., King-Smith, R.D., Lin, J-S., and Clarke, L.J., (1992) *Phys. Rev. Lett.*, **68**, 1351–4.