

The dissolution behaviour of crystalline and amorphous albite in acidic and basic environments at 25°C

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The dissolution behaviour of crystalline feldspar in the laboratory has been studied extensively for many years (Blum and Stillings, 1995). From these studies, three well-known models evolved to describe the mechanisms of feldspar dissolution. The first model, which has generally been discredited, is based on diffusion-controlled kinetics in which the feldspar dissolution rate is controlled by the diffusion of reaction products through an altered layer on the mineral surface. The second model is based on surface-reaction controlled kinetics in which reactions at the solid/solution interface control the rate of feldspar dissolution. A third model, which combines ideas from the other two models, is based on reactions at the surface and within the leached layer that control the overall dissolution behaviour of the feldspar (Hellmann, *et al.*, 1990; Brantley and Stillings, 1996).

The resistance to dissolution of some sodium-aluminosilicate glasses (including the albite composition) make them excellent matrices for the immobilization of radioactive fission products. Because the dissolution of crystalline albite is controlled by a surface-reaction mechanism, whereas the dissolution of albite glass is controlled by diffusion through an altered surface layer (Zellmer and White, 1986), comparisons of the kinetics of these two phases should shed light on the mechanism of dissolution. Few studies compare the dissolution kinetics of crystalline albite with amorphous albite and none of these studies were conducted at room temperature. Zellmer's study indicates that the dissolution rate of albite glass is slightly faster than crystalline albite over a pH range of 2–10 at 70°C (Zellmer and White, 1986). In this study, the leaching and dissolution behaviour of crystalline and amorphous albite was investigated in acid and base at 25°C.

Experimental Procedures

High purity albite crystals from Amelia Courthouse, Virginia were used in this investigation. Albite glass

was prepared by melting crushed albite crystals in a platinum crucible at 1550°C for 15 hours and annealing at 700°C overnight. Albite crystals and glass were crushed to a 74–149 µm grain size (100–200 mesh) in an agate mortar and subsequently cleaned in high-purity acetone. Also, crystals and glasses about 2 cm in length were polished to 0.05 µm grit size, acetone cleaned, and etched in 1N NaOH solution at 80°C for 3 minutes.

Glass and crystal samples were reacted with solutions having initial pH values of 2 and 9 prepared with HCl and LiOH, respectively. Specimens were immersed in these solutions for up to 5000 hours at 25°C under static conditions. In a separate experiment, both polished and crushed specimens were reacted in flow-through cells. Input solutions of pH 2 (HCl), pH 5.6 (DI water), and pH 9 (LiOH) were flowed through the cells at a rate of ~2 ml/hr. Reactions were allowed to proceed until near attainment of steady state was achieved.

Results and discussion

The steady-state dissolution rates for both albite crystals and glasses in acid, water, and base were determined from the flow experiments (dissolution was undetectable in the batch reactors based upon solution chemistry). Dissolution rates based on flow experiments are generally reported with respect to the measured output solution pH. The dissolution rate of both crystalline and amorphous albite (normalized to initial glass or crystal surface area) decreased from pH 2.0 (log rate ~ -14.5 moles Si/cm²/s) to pH 5.6 (log rate ~ -15.3 moles Si/cm²/s), but increased slightly at pH 8.4 (log rate ~ -15.2 moles Si/cm²/s). These results corroborate data already available in the literature for crystalline albite (see Blum and Stillings, 1995 for a review), but represent the only published dissolution rates for albite glass (see, however, Zellmer and White, 1986; Tsuzuki, *et al.*, 1985). In addition, the experiments in this study were

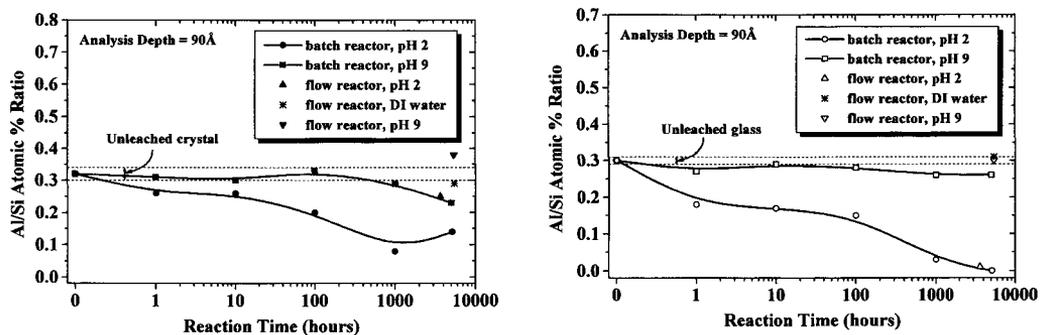


FIG. 1. (a) Al/Si ratios (atomic %) as measured with XPS, plotted as a function of reaction time for Amelia albite crystals in pH 2, DI water, and pH 9 solutions at 25°C. The dashed lines represent the highest surfaces. XPS analysis depth = 90 Å. (b) Al/Si ratios (atomic %) as measured with XPS, plotted as a function of reaction time for Amelia albite glasses in pH 2, DI water, and pH 9 solutions at 25°C. The dashed lines represent the highest and lowest Al/Si ratios measured on 10 surfaces.

maintained for longer reaction times than reported previously. As a result, the steady state dissolution rates are slower than previously reported rates, which may be attributed to closer attainment of steady state.

More importantly, however, these data indicate that the dissolution rate of albite glass is identical, within error, to that of albite crystal at each pH (e.g. at pH 2, albite crystal vs glass showed log dissolution rates of -14.5 ± 0.2 vs -14.4 ± 0.2 moles Si/cm²/s). Despite similarity in the dissolution rates of crystalline and amorphous albite, the formation of altered layers is more extensive on glass than on crystal surfaces at pH 2. The surface compositions of albite glass and crystal, as measured with XPS, are presented in Figs 1a and 1b; Al/Si atomic percent ratios (as measured for the outermost ~90 Å) are plotted as a function of reaction time at each pH for both batch and flow reactors. XPS indicates more Na and Al depletion from albite glass than crystal after 3400 hours in flowing pH 2 solution. Furthermore, depletion of Na and Al from glass is more severe than from crystal in the batch reactors at pH 2, especially in the early stages of dissolution. Albite glass has a density of ~2.38 g/cm³ and a structure consisting predominantly of 6-membered rings of tetrahedra (Taylor and Brown, 1978). Crystalline albite has a density of ~2.62 g/cm³ and a structure consisting predominantly of 4-membered rings (Taylor and Brown, 1978). Diffusion of molecular water and modifier ions is easier in the more open glass structure, resulting in the formation of more extensive surface layers. Similarity in the dissolution rates of crystalline and amorphous albite at low pH is

consistent with a surface-leached layer model for dissolution (Hellmann, *et al.*, 1990) in which a disordered glass-like surface layer controls the rate of release of Na, Al, and Si into solution.

The sodium, aluminum, and silicon depth profiles of the reacted glass and crystal surfaces, as measured with SIMS did not indicate the formation of extensive altered layers. However, the depth sensitivity of SIMS profiling under the experimental conditions, is limited to ~200–500 Å; therefore, changes in the outermost 200–500 Å may not be apparent in the SIMS profiles. XPS and SIMS indicate a minimum altered layer thickness of ~90 Å and a maximum thickness of ~200–500 Å on the albite glass and crystal surfaces at pH 2. FTIR reflectance spectra of the reacted glass surface was also identical to that of the unreacted glass surface. However, the analysis depth of this technique is much greater than the thickness of the altered surface layer. Therefore, structural changes of the altered layer on the albite glass surface with respect to the bulk glass structure may not be deduced from FTIRRS.

In contrast to extensive leaching at pH 2, XPS indicates less depletion of Na and Al from surfaces dissolved solutions at pH 5.6 and 9 with little or no surface layer formation. Therefore, at the higher pH, the rates of Na and Al leaching from the glass and crystal surfaces must be similar to their respective rates of Si hydrolysis. (Note: flow experiments generally exhibited extremely low, but measurable, concentrations of Na, Al, and Si in these solutions.)