A leached layer hydrolysis model: a better way to understanding feldspar dissolution at elevated temperatures and pressures?

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Introduction

The dissolution behavior of complex multi-oxide silicate minerals, such as feldspars, has been the subject of experimental and theoretical studies over several decades now. To date, most of the theories on the mechanisms of feldspar dissolution have been based on work carried out at low temperatures, which in the majority of cases has been at 25°C. However, with the exception of chemical weathering reactions at the Earth/Es surface, most mineral-water reactions take place in sub-surface crustal environments, where temperatures can range into the hundreds of degrees (see review in Hellmann, 1994). It has thus become necessary to question whether our present assumptions on the mechanisms of feldspar hydrolysis are also valid at elevated temperatures.

When specifically considering feldspar dissolution, two general models for hydrolysis have been proposed in the literature. The first proposes that the overall dissolution rate is limited by diffusion, the second is based on the rate being limited by surface chemical reactions. The diffusion model is based on the hypothesis that the initially observed incongruent release of certain elements must inherently lead to the development of leached layers with a composition different from that of the bulk. The inward diffusion of reactants and/or the outward diffusion of hydrolysis products through this layer is thought to control the overall rate of dissolution (see, for example, Chou and Wollast, 1984, 1985). On the other hand, the surface reaction model postulates that detachment reactions at the solution/surface interface control the overall rate of reaction. This theory is supported primarily by linear reaction kinetics at steady state conditions and by SEM images of reacted surfaces, which show etch pits that formed at surface sites with excess energy (dislocations, twin boundaries, etc.) (see Lagache, 1965; Berner and Holdren, 1979).

Despite evidence for surface reaction-controlled dissolution, definitive proof for the existence of leached layers, up to several thousand Å in thickness, has been revealed over the last decade by the application of several spectroscopic (XPS, Auger) and ion beam techniques (RNRA, RBS, ERDA, SIMS) to the study of surface and near surface regions of hydrolyzed feldspars and other silicates (Petit *et al.*, 1987, 1990; Casey *et al.*, 1988, 1989; Hochella *et al.*, 1988; Muir *et al.*, 1989, 1990; Hellmann *et al.*, 1990).

It appears that both the diffusion and surface reaction models, taken by themselves, do not describe the dissolution process with complete accuracy, especially at elevated temperatures and pressures. Recent experimental evidence (Hellmann, 1994b- submitted) suggests that the overall dissolution rate is not only a function of reactions occurring at the solid/liquid interface, but it is also dependent on reactions taking place at significant depths within the structure. Reactions occurring at depth within the structure are due to the creation of leached layers. The proposed 'leached layer hydrolysis' model specifically considers the formation of leached layers and their influence on the overall reaction kinetics of dissolution.

In order to study the formation of leached layers in feldspars, albite was hydrolyzed over a wide-range of pH conditions at 100, 200 and 300°C in a flow through reactor. The release rates of Na, Al and Si were measured as a function of time from the initial, pre-steady state phase to the attainment of steady state, congruent dissolution conditions. The reactions which occur within the structure are elementally rate-specific; that is to say that each element within the structure reacts at a different rate with the reactant molecules which diffuse into the structure. The differential rates of detachment lead to the formation of leached layers which have a chemical composition and a physical structure different from that of the bulk mineral. The formation of leached layers is an important factor in providing hydrolyzing molecules (H^+, H_2O, OH^-) access to Si-O-Si and Al-O-Si bond sites deep within the structure. Thus, leached layers influence both the number of bonds available for hydrolysis as well as the rates of bond breakage and the subsequent release of both network modifying elements (alkalis) and network forming elements.

Results

Leached layers developed during the initial stages of dissolution due to the preferential release of Na with respect to Al and Si under all pH and temperature conditions. The preferential release of Na was due to the higher rate of ion exchange reactions vs. hydrolysis reactions associated with the release of Si and Al. The depths of Na preferential leaching showed a pH-dependence; maximum depths on the order of 1500 and 1200 Å were recorded at acid and basic pH conditions, respectively. Leached layers deficient in Al (with respect to Si) were recorded at acid and neutral pH conditions. At mildly basic pH conditions, either Al or Si was preferentially released, and at more extreme basic pH conditions, only Al was preferentially released. The depths of Al preferential leaching were not determinable under all conditions due to the precipitation of an Al surface phase; a maximum recorded depth of 250 Å was determined at basic pH conditions. The preferential release behaviour of Al and Si is ascribed to the pH-dependency of the speciation of Al-OH and Si-OH groups. However, at very basic pH conditions, the preferential release of Al was probably due to the intrinsically greater reactivity of Al-bridging oxygen bonds.

Calculations of diffusion coefficients for Na diffusion within the leached layers suggest that leached layers are structurally more 'open' and porous than unaltered, crystalline albite. In addition, the calculated diffusion coefficients showed a strong pH-dependence. This result implies that leached layers formed at acid and basic pH conditions underwent a greater degree of preferential leaching, thereby creating structures more 'open' than those formed at neutral pH.

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