

FELDSPARS IN WEATHERING

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ABSTRACT. Feldspar weathering occurs via dissolution of all components into solution, with the subsequent precipitation of secondary minerals from solution, and it is the feldspars dissolution rate which controls the overall rate of feldspar weathering. The rate of feldspar dissolution is controlled by the kinetics of surface reactions at the mineral-water interface, not by mass transfer processes, either in solution or through a protective surface layer. At neutral to basic pH conditions, the entire range of feldspars compositions appears to dissolve nearly stoichiometrically, although a thin Al enriched surface layer ($<20\text{ \AA}$) may form, and cations, particularly Na^+ , may be exchanged with H^+ to depths of several 100 $\text{\AA}$. The exchange of cations with H^+ appears to be reversible, with cation occupancy favored in the basic pH region. It is not clear whether the observed Al enrichment on the surface is a consequence of slightly non-stoichiometric dissolution, or readsorption of Al from solution at charged surface sites. At acidic solution pH's, a silica-enriched surface layer 100's to 1000's of $\text{\AA}$ thick may form. This layer is highly hydrated and disordered, and analogous to an amorphous SiO_2 gel. The silica-enriched surface layer does not provide a diffusional barrier to the transport of Al and cations to solution, and does not appear to effect the destruction rate of the feldspar tetrahedral lattice.

Feldspars of all compositions have an experimental dissolution rate which increases with increasing H^+ activity at $\text{pH} < 6$, and increasing OH^- activity above $\text{pH} 8.5$, a pattern typical of many silicate minerals. In the acidic pH region ($<\text{pH} 6$) albite and K-feldspar have nearly identical experimental dissolution rates, with the dissolution rate (R) proportional to $[\text{H}^+]^{-0.5}$. This is in contrast to the observation in natural soils that albite weathers much more rapidly than K-feldspar. In the basic pH region, albite dissolution rates have a pH dependence of $R \propto [\text{OH}^-]^{-0.3}$, with K-feldspar dissolution rates having a stronger dependence on $[\text{OH}^-]$ than albite, and absolute dissolution rates approximately a factor of 10 slower than albite. The plagioclase series has a pH dependence of the dissolution rate of $R \propto [\text{H}^+]^{-0.5}$ in the acidic region in the compositional range An_{0-70} . However, at compositions of $\text{An}_{>70}$ there is a transition to increasing values in the exponent until $R \propto [\text{H}^+]^{-1.0}$ for $\text{An}_{>90}$. At a single solution pH, the dissolution rate of the plagioclase series increases gradually with increasing Ca content until $\sim\text{An}_{75}$, with a rapid increase in the dissolution rate of plagioclase between the compositions An_{75} and $\text{An}_{>90}$.

There is general agreement that feldspar dissolution in the acid region occurs by selective attack on the Al sites in the tetrahedral framework, and the rate limiting process must involve the hydrolysis of the Al-O-Si bond. It is therefore the increasing Al/Si ratio with increasing An content, and not the Na/Ca ratio, which causes the increasing dissolution rate with increasing An content. In the basic pH region, the relative importance of the Al/Si ratio and cation occupancy are more uncertain.

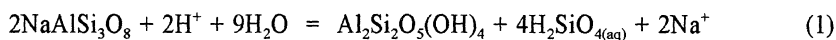
The most comprehensive models for the dissolution of feldspars employ surface speciation models, in which the dissolution rate is proportional to the equilibrium concentration of surface chemical complexes, which are preferential sites for dissolution reactions. Most commonly, the surface species involve the protonation and deprotonation of dangling tetrahedral oxygens to form positively and negatively charged surface sites in the acid and basic regions, respectively. The concentration of charged surface sites is controlled by adsorption isotherms of species in solution. The large effect of solution pH on feldspar dissolution rates is indirect, controlling the equilibrium concentration of surface species through an

adsorption process. The surface speciation model has major implications for the effects of temperature and adsorption of impurities on dissolution kinetics, which differ significantly from models based upon homogenous kinetic theory.

Field measurements of plagioclase dissolution rates from watershed mass-balance studies and from changes in the abundance of plagioclase in soils of different ages indicate that feldspar weathering is one to three orders of magnitude slower than predicted from laboratory studies. The leading explanation for this effect is the isolation of a large proportion of the feldspar surface area in isolated micropores. Alternative explanations include; (i) adsorption of inhibitors, of which Al and Fe are the most likely, (ii) the high saturation states of soil solutions, and (iii) experimental artifacts in the dissolution experiments. The reconciling of natural and experimental feldspar dissolution rates is a critical step before feldspar dissolution kinetics can be used reliably in predictive models.

1. Introduction

The weathering of feldspar is a major step in the geological cycling of crustal material, and it has a profound influence on many near surface processes. The overall feldspar weathering process can be simplified as the alteration of feldspar to common clay minerals, such as kaolinite. For example;



However, it is now widely recognized that this overall reaction for feldspar alteration involves two independent processes: (i) the initial dissolution of feldspar into solution, and (ii) the subsequent precipitation of kaolinite and other secondary phases from solution. These two reactions are linked by the effects of the solution composition on their relative rates, and in a closed system will reach steady-state. However, because the dissolution kinetics of feldspar are very slow, and most near-surface environments are open systems on this time scale, the feldspar dissolution rate should dominate the kinetics of the overall feldspar alteration process. Consequently, the dissolution of feldspar has been the focus of much of the research on mineral alteration and weathering.

Feldspar dissolution kinetics have been studied for many years, but have been the subject of increasing study over the last decade. Some of the motivations for this interest are: (i) understanding the effects of acid precipitation, and the long-term capacity of soils to neutralize anthropogenic acidic rainfall (e.g. Reuss and Johnson, 1986); (ii) the importance of silicate weathering in regulating atmospheric CO_2 concentration over geologic time, and consequently in controlling global climatic change (e.g. Walker et al., 1981; Berner, et al. 1983; Lasaga et al., 1985; Volk, 1987); (iii) the incorporation of chemical kinetics into reactive transport models, which require rate laws for the dissolution and precipitation of major minerals; and (iv) the tremendous advances in surface science and heterogeneous kinetics which have provided both new analytical and theoretical techniques, allowing progress on complex problems of heterogeneous kinetics such as feldspar dissolution.

A major advance in our understanding feldspar dissolution kinetics is recognition of the central importance of the mineral-solution interface. Neither the characteristics of the bulk solution nor the feldspar chemistry and structure control the rate of the dissolution reaction; rather, it is how the solution and mineral surface interact at the mineral/water interface which is the crucial chemical question. In this chapter will (i) summarize some of the experimental data for feldspar dissolution kinetics, (ii) present some of the theoretical approaches used to explain the observed experimental results, (iii) briefly summarize measurements of natural plagioclase weathering rates in soils, and (iv) compare these rates with the experimental results.

2. Experimental Determination of Feldspar Dissolution Rates

2.1. TRANSPORT VERSUS SURFACE REACTION CONTROL

There are three distinct phases observed during experimental feldspar dissolution experiments. There is a rapid exchange of H^+ for cations such as K^+ , Na^+ and Ca^{2+} , which occurs within minutes after feldspars are placed in solution, forming a hydrogen feldspar surface layer. This is followed by a period of rapid, sometimes non-stoichiometric dissolution. Finally, the dissolution rate approaches a nearly constant rate after several tens to many hundreds (or even thousands) of hours with a more or less stoichiometric release of elements.

The dissolution of feldspars (and all other materials) must involve two processes: (i) the *chemical reactions* which break bonds, allowing the removal of chemical species from the crystal lattice; and (ii) the *transport* of the reactants and products away from the surface (summaries by Berner, 1978; Lasaga, 1984). Transport control of the dissolution rate may itself occur in two ways: (i) Aqueous diffusion of solutes to and from the surface, and (ii) Solid-state diffusion of species through a protective (or armoring) layer on the surface. The former commonly limits the rate of rapid dissolution reactions, and may be recognized by the influence of stirring the solution on the reaction rate. This is the reason stirring your tea increases the dissolution rate of the sugar. The latter is a common phenomena in the corrosion of metals such as aluminum and iron. Feldspar dissolution rates are so slow that aqueous diffusion does not limit the dissolution rate. This leaves two major classes of theories for the rate control of feldspar dissolution: (i) surface-layer diffusion, and (ii) surface reaction kinetics.

Surface-layer diffusion theory suggests that the dissolution rate is limited by solid-state diffusion through a continuous surface layer with a different structure and composition than the original mineral. In this model, the freshly fractured feldspar surface has no protective layer, and consequently has a higher initial dissolution rate when first exposed to solution. As the dissolution reaction proceeds, a surface layer develops and thickens with time, providing a progressively greater diffusional barrier to both reactants and products of the dissolution reaction. The surface layer may form either by precipitation from solution, or by preferential removal of some components from the feldspar structure. A simple diffusional model predicts that the dissolution rate (R) should decrease as $R \propto t^{-1/2}$, a behavior often referred to as parabolic kinetics. The surface layer must be both tightly adhering and continuous in order to provide an effective diffusion barrier. As the reaction progresses, the surface layer will reach a thickness at which the rate of diffusion of feldspar components through the layer equals the dissolution rate of the layer itself. The overall feldspar dissolution rate will then reach a constant and stoichiometric steady-state value. This kinetic mechanism was proposed in much of the early work on feldspar dissolution (e.g. Wollast, 1967; Helgeson, 1971; Paces, 1973; Busenburg and Clemency, 1976) but is now considered very unlikely, although it cannot be totally discounted.

The surface reaction theories for feldspar dissolution center upon the rates of chemical reactions at the feldspar-solution interface. The important aspect of this approach is that it is the structure and chemistry of the feldspar surface in contact with the solution, and not necessarily the bulk chemistry of the feldspar, which controls the rate of the dissolution reaction. Therefore, surface properties such as the surface physical configuration of the surface, step density and surface roughness, and adsorption reactions effecting surface speciation become critical factors. The surface reaction theories include those based upon transition state theory (TST), surface speciation models, and surface configuration models such as surface nucleation and spiral growth/dissolution (i.e. Burton-Cabrera-Frank (BCF) theory). As we shall see, there is still much disagreement about the details, but most workers now agree it is the chemical and physical characteristics of the feldspar-solution interface which controls the rate of feldspar dissolution.

What we will now do is to look at the nature of the rapid, essentially equilibrium adsorption and exchange reactions on the feldspar surface, and then the period of rapid dissolution, finally finishing with a summary of the steady-state dissolution rates of feldspars and how they vary with solution chemistry and feldspar composition. However, we will first examine the issue of

surface area determinations. Because both dissolution rates and surface sorption reactions are expressed per unit surface area, surface area determinations are potentially a major source of error and/or misinterpretation encountered in feldspar surface chemistry and dissolution studies.

2.2. FELDSPAR SURFACE AREAS

Surface areas (SA) can be estimated geometrically, based on the size and shape of particles. However, this geometrical estimate will not include surface roughness or any internal surface area. Surface areas are most often determined by the BET (Brunauer-Emmett-Teller) method (Brunauer et al., 1938; Gregg and Sing, 1982) which measures the adsorption of a gas on the surface as a function of the partial pressure of the gas. The technique most commonly used adsorbs N_2 or Kr at 77°K, and measures the amount of gas released when the sample is warmed to room temperature. At a low and fixed N_2 or Kr partial pressure, the surface area is proportional to the amount of gas released. Because the diameter of the N_2 and Kr molecules is $\sim 4\text{\AA}$, surface roughness, porosity, and fractures with dimensions $>4\text{\AA}$ will be included in a BET surface area measurement. The $4\text{\AA}$ scale is very similar to the effective size of a water molecule ($\sim 3\text{\AA}$), and probably represents a reasonable estimate of the wetted surface area.

Table 1 shows both estimated geometrical surface areas and BET surface areas of freshly ground and washed feldspar particles used in dissolution experiments. The ratio of the BET to geometrical surface areas is called the surface roughness (SR) factor. This follows the surface science nomenclature, although this SR also includes any internal surface area such as etch pits, fractures or any other void and connected microstructures. The SR of freshly ground and unaltered feldspar generally fall in the range of 9 ± 6 , and can thus be estimated within a factor of ~ 3 from the grain size.

Weathered feldspars from soils typically have a SR of several hundreds (Table 1). The interpretation of the large discrepancy between the SA of freshly ground experimental and naturally weathered feldspar grains introduces a large uncertainty in the comparison of natural and experimental feldspar dissolution rates. Surface roughness of weathered feldspars measured by atomic force microscopy (AFM) can explain only a surface roughness of ~ 2 , suggesting that much of the observed increase in surface area results from internal surface area. This agrees with the extent of etching observed by SEM and TEM in weathered feldspars (e.g. Berner and Holdren, 1979; Banfield and Eggleton, 1990). Anbeek (1992a,b) suggested that even "pristine" mineral specimens used in dissolution experiments have extensive internal surface area. This is consistent with the high SR's of the experimental material reported in Table 1. In particular, the Grass Valley anorthite used by Holdren and Speyer (1987) has a surface roughness approaching that of highly weathered feldspar grains. Microporosity has been shown to commonly exist in many unweathered feldspars (Wordon et al.; 1990; Walker, 1990). The nature of microporosity in feldspars and its contribution to both natural weathering and experimental determination of feldspar dissolution kinetics has not been adequately addressed.

2.3. INITIAL ADSORPTION/EXCHANGE REACTIONS

2.3.1. Surface Titrations - Sorption and exchange reactions on mineral surfaces can be determined by surface titration. During surface titrations acid, base and other solutes are added to an aqueous suspension of the mineral, and the composition of the solution is monitored, often with specific-ion electrodes. The amount of a species adsorbed or desorbed from the surface can be determined by the difference between the amount of species added to the system, and the concentration of species in solution (e.g. Stumm and Morgan, 1981; Huang, 1981). Several cautions in the interpretation of surface titrations are warranted. Because we are implying surface chemistry from changes in solution chemistry, we have no direct information on the actual surface species involved in the reactions. We can only guess at the appropriate surface complexes based upon the observed stoichiometry. Furthermore, if the same aqueous species is involved in several different reactions, we may not be able to differentiate between reactions.

Table 1 - Surface areas of feldspar grains

mineral	Grain Size (μm)	Geometric Surface Area (m^2/g)	BET Surface Area (m^2/g)	Surface Roughness (SR)	mineral	Grain Size (μm)	Geometric Surface Area (m^2/g)	BET Surface Area (m^2/g)	Surface Rough. (SR)
Microcline ¹	300-600	0.005	0.067	14.0	Andesine ¹	300-600	0.005	0.119	24.8
Microcline ¹	150-300	0.010	0.073	7.6	Andesine ¹	150-300	0.010	0.134	14.0
Microcline ¹	75-150	0.019	0.114	5.9	Andesine ¹	75-150	0.019	0.210	11.0
Microcline ¹	37-75	0.038	0.327	8.5	Andesine ¹	37-75	0.038	0.386	10.0
Microcline ¹	300-600	0.005	0.067	14.0	Andesine ⁵	25-75	0.041	0.405	10.0
Microcline ¹	150-300	0.010	0.073	7.6	Andesine ⁵	25-75	0.041	0.350	8.6
Microcline ¹	75-150	0.019	0.114	5.9	Bytownite ¹	300-600	0.005	0.130	27.1
Microcline ¹	37-75	0.038	0.327	8.5	Bytownite ¹	150-300	0.010	0.127	13.3
Microcline ¹	300-600	0.005	0.056	11.7	Bytownite ¹	75-150	0.019	0.214	11.2
Microcline ¹	150-300	0.010	0.072	7.5	Bytownite ¹	37-75	0.038	0.473	12.3
Microcline ¹	75-150	0.019	0.107	5.6	Bytownite ⁵	25-75	0.041	0.200	4.9
Microcline ¹	37-75	0.038	0.179	4.7	Bytownite ⁵	25-75	0.041	0.270	6.6
Alkali feldspar ¹	300-600	0.005	0.039	8.1	Anorthite ¹	300-600	0.005	0.619	129.2
Alkali feldspar ¹	150-300	0.010	0.060	6.3	Anorthite ¹	150-300	0.010	0.700	73.0
Alkali feldspar ¹	75-150	0.019	0.089	4.6	Anorthite ¹	75-150	0.019	0.757	39.5
Alkali feldspar ¹	37-75	0.038	0.277	7.2	Anorthite ¹	37-75	0.038	1.020	26.5
Alkali feldspar ¹	300-600	0.005	0.050	10.4	Anorthite ⁵	25-75	0.041	0.520	12.8
Alkali feldspar ¹	150-300	0.010	0.072	7.5	Anorthite ⁸	20-50	0.060	0.500	8.4
Alkali feldspar ¹	75-150	0.019	0.108	5.6	Anorthite ⁸	50-100	0.029	0.300	10.4
Alkali feldspar ¹	37-75	0.038	0.176	4.6	Anorthite ⁸	100-250	0.012	0.110	9.2
Ab ₈₀ K ₂₀ ²	150-300	0.010	0.053	5.5					
Ab ₈₀ K ₂₀ ²	75-50	0.036	0.108	3.0					
Albite ¹	300-600	0.005	0.036	7.5	Average				8.5
Albite ¹	150-300	0.010	0.049	5.1	Standard Deviation				4.9
Albite ¹	75-150	0.019	0.066	3.4					
Albite ¹	37-75	0.038	0.154	4.0					
Albite ³	104-250	0.012	0.083	7.0					
Albite ³	53-104	0.028	0.106	3.8					
Albite ⁴	75-125	0.022	0.086	3.9					
Albite ⁴	75-125	0.022	0.092	4.2					
Albite ⁵	25-75	0.041	0.405	10.0					
Albite ⁵	25-75	0.041	0.490	12.1					
Albite ⁶	100-200	0.014	0.046	3.2					
Albite ⁶	50-100	0.029	0.075	2.6					
Oligoclase ¹	300-600	0.005	0.079	16.5					
Oligoclase ¹	150-300	0.010	0.090	9.4					
Oligoclase ¹	75-150	0.019	0.128	6.7					
Oligoclase ¹	37-75	0.038	0.334	8.7					
Oligoclase ⁵	25-75	0.041	0.180	4.4					
Oligoclase ⁵	25-75	0.041	0.645	15.9					
Oligoclase ⁷	75-150	0.019	0.116	6.1					

¹ Holdren and Speyer (1987)² Holdren and Speyer (1985)³ Rose (1991)⁴ Knauss and Wolery (1986)⁵ Casey et al. (1991)⁶ Chou and Wollast (1984)⁷ Mast and Drever (1987)⁸ Amrhein and Suarez (1992)⁹ J. Schulz (*per. comm.*)

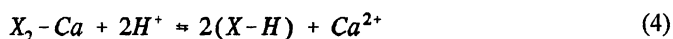
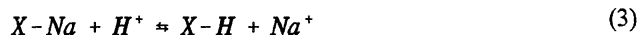
Feldspar grains from soils near Merced, Calif.

Mineral	Age (Kyr)	geometric	BET	SR
oligoclase ⁹	500-1000	.0014	0.39	271
oligoclase ⁹	500-1000	.0014	0.26	180
oligoclase ⁹	500-1000	.0014	0.46	320
oligoclase ⁹	500-1000	.0014	1.48	1029
Alkali fspr ⁹	500-1000	.0014	0.12	83
Alkali fspr ⁹	500-1000	.0014	0.26	180
Alkali fspr ⁹	500-1000	.0014	0.94	653
Alkali fspr ⁹	500-1000	.0014	0.81	563
Alkali fspr ⁹	250-500	.0029	0.32	111

Surface titrations also give no information on heterogeneity. They average the behavior of all exposed faces, yet we know that different crystallographic faces may have dramatically different chemical behaviors. For example, the (001) face of quartz dissolves 10^3 times faster than the prismatic faces in HF solution (Ernsberger, 1960), so that a surface titration would be heavily biased toward "unreactive" surface area. We currently have no information on the relative dissolution rates of feldspar surfaces, but the (001) faces of feldspar grains tend to be more heavily corroded. It has also been proposed that a large proportion of dissolution may occur at high energy "reactive" sites such as dislocations and impurities which are only a small fraction of the surface. These features would also not be reflected in surface titrations. Finally, surface titrations are very subject to experimental errors, especially precipitation of secondary phases, errors in electrode measurements, and inaccurate compensation for mineral dissolution and aqueous speciation of solutes.

2.3.2. Surface Complexes on Feldspars - When unaltered feldspar surfaces are first placed in solution, there are three fundamentally different types of rapid surface reactions which may occur. All are thought to reach equilibrium within minutes, and to be governed by classical exchange and partitioning relationships.

1) Exchange and/or sorption reactions involving non-framework cations such as K^+ , Na^+ , and Ca^{2+} . The proximity of a free surface allows these cations access to the solution to react or exchange. Examples of these reactions include:



where X represents a cation exchange site, and X^- is an empty exchange site which gives the surface a net negative charge. These exchange reactions result in an immediate decrease in solution $[H^+]$ concentration and release of cations when feldspar are first placed in solution. This exchange reaction was recognized early in the study of feldspar dissolution (Tamm, 1930; Nash and Marshall, 1956a,b; Garrels and Howard, 1959). Table 2 shows the depth of the exchange layer measured on albite, anorthite, and potassium feldspar, calculated from BET surface area

Table 2 - Depth of the Cation Exchange Layer

Reference	Mineral (cation)	sites/nm ²	depth (Å)
Wollast and Chou (1992) ¹	albite (Na)	11.8	21
Blum and Lasaga (1991) ¹	albite (Na)	8.4	15
Amrhein and Suarez (1988) ¹	anorthite (Ca)	14-17	25-30
Schweda (1989) ²	microcline (K)	21	37
Schweda (1989) ²	sanidine (K)	48	85

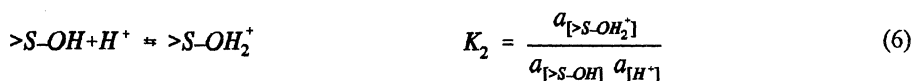
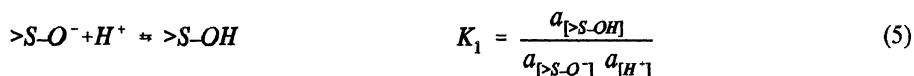
¹ determined by surface titration: total number of exchange sites.

² determined from non-stoichiometry of initial dissolution at ~30 min at pH 3. Assumed to represent total exchange.

and assuming a uniform exchange depth. The depth of the exchange layer is a several unit cells in albite, and slightly deeper in anorthite and the K-feldspars. The observed cation exchange depths of several unit cells is greater than can be explained by direct cation exposure at a surface terminating the bulk structure, and suggests higher H^+ and cation mobility near the feldspar surface. Possible explanations include surface relaxation, which may broadly enhance cation mobility in the near surface region, and defects intersecting the surface which may create localized regions of enhanced cation mobility. However, both the cause and distribution of the high cation exchange site densities in feldspars are not well understood.

At pH's <8 and low Na concentrations, albite exchanges essentially all the Na^+ for H^+ in the outermost few unit cells (i.e. eq. 2.3 goes completely to the right). There has been some controversy about the reversibility of the H^+/Na^+ exchange reactions for albite (Chou and Wollast, 1989; Murphy and Helgeson, 1989). Blum and Lasaga (1987, 1991) did not detect any Na^+ uptake during surface titrations of albite at low Na^+ concentrations. However, Wollast and Chou (1992) presented convincing evidence that the exchange of H^+ for Na^+ in albite is reversible, with significant Na^+ occupancy of the exchange sites at pH's >8, and moderate Na^+ concentrations. Thus, in saline environments, the exchange sites on the albite surface may have significant occupancy. This seems consistent with the common observation of secondary albite precipitation in saline diagenetic environments. The exchange of cations on the surfaces of feldspars of other compositions have not been studied in detail, but the common occurrence of diagenetic K-feldspars suggests that K^+ exchange may also be reversible.

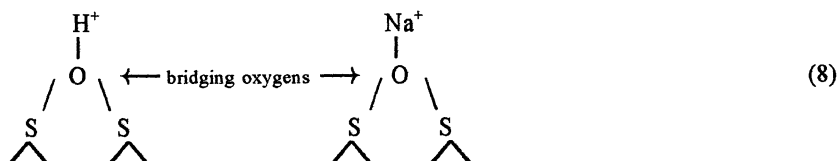
2) Adsorption and desorption reactions involving dangling oxygens are created by the termination of the tetrahedral lattice at the surface. These dangling oxygens are rapidly hydrated by atmospheric or aqueous water (Iler, 1979) to form hydroxyl groups. Sorption reactions at these sites result in charged surface species, for which equations and equilibrium expressions can be written. Examples of these reactions include:



where $>S$ is a tetrahedral Al or Si on the surface, $>S-O$ is a dangling oxygen on the surface, and M is any other adsorbing ligand. Blum and Lasaga (1991) performed surface titrations of albite and found they could describe eqns. 5 and 6 by a Langmuir adsorption isotherm, with $K = 2.7 \times 10^4$ and $K_2 = 9.4 \times 10^4$. In the acid region, they found a site density of $35 \mu\text{mol/m}^2$, and in the basic region of $27 \mu\text{mol/m}^2$. Blum and Lasaga (1991) interpreted the charged surface species as protonation and deprotonation of dangling Al-OH surface groups to $>Al-OH_2^+$ and $>Al-O^-$, respectively. Wollast and Chou (1992) examined only the basic region, but found a negative site density of $21.3 \mu\text{mol/m}^2$, in good agreement with Blum and Lasaga (1992). However, Wollast and Chou (1992) attribute the negative charge density to the removal of H^+

from cation exchange sites via eqn. 2. Amrhein and Suarez (1988) performed a surface titration of anorthite and found a total site density of $120 \mu\text{mol/m}^2$.

3) Adsorption may also occur at bridging oxygens exposed at the surface. Examples include the adsorption of H^+ or Na^+ :



Blum and Lasaga (1991) suggested that bridging oxygens on feldspar surfaces tend to be hydrophobic, based primarily on an analogy with quartz and silica surfaces (Iler, 1979). This implies that adsorption of cations at bridging oxygens should be very weak, and only a very small proportion of the sites will be occupied at any specific time. Such low surface coverage would not be detectable by surface titration or any other analytical technique. However, adsorption at bridging oxygens could still have a potentially large effect on the activation energy of breaking the bridging tetrahedral bonds (Lasaga and Gibbs, 1990; Dove and Crerar, 1990), and therefore, could still be important in controlling the kinetics of the overall dissolution rate. In contrast to Blum and Lasaga (1991), Wieland et al. (1988) and Stumm and Wollast (1990) have suggested a dissolution model for feldspars and other oxides, based upon the oxide dissolution kinetics of Furrer and Stumm (1986), which suggests that bridging oxygens behave identically to dangling oxygens during adsorption reactions, and are active adsorption sites.

2.4. RAPID INITIAL DISSOLUTION RATES

During feldspar dissolution experiments, the rapid surface sorption reactions are followed by a period of rapid dissolution, which decreases with time. Finally, the dissolution rate will approach a nearly constant dissolution rate after several tens to many hundreds (or even thousands) of hours. It is this long term steady-state dissolution rate which is most relevant to most geological systems. The cause of the rapid initial dissolution is generally unknown. Holdren and Berner (1979) suggested two possible explanations, (i) small particles adhering to the surface after sample grinding have a higher surface free energy, and would dissolve more rapidly than large grains, and (ii) disruption of the surface during grinding produces a disordered layer which dissolves more rapidly. Subsequent experiments in which most fine particles were removed prior to dissolution did not completely reduce the high initial rates. Petrovic (1981a,b) supported the idea of a disturbed surface layer produced during grinding, and this is still probably the most widely cited explanation. However, Chou and Wollast (1984, 1985) and many subsequent investigators have also observed a more rapid period of dissolution immediately after changing the solution pH during a continuous experiment. Mast and Drever (1987) also observed a high transient Al release after introducing oxalic acid into oligoclase dissolution experiments. They have suggested that the rapid release of elements may be a consequence of the presence of a thin steady-state surface layer with a non-stoichiometric composition. Changing the solution composition may require establishing a new steady-state surface composition. As the surface reequilibrates, there may be a transient release of those elements which have a lower concentration in the new surface layer. With this interpretation, the rapid dissolution rates observed at the start of the experiments may result from more rapid dissolution before a non-stoichiometric, steady-state, surface composition can evolve.

2.5. STEADY-STATE FELDSPAR DISSOLUTION RATES

2.5.1. Experimental techniques - The experimental techniques used to determine feldspar dissolution rates can be crudely divided into two groups, batch systems and flow through systems. Batch experiments are closed systems, in which the feldspar sample and starting solution are sealed in a closed vessel, usually a polyethylene or teflon bottle. Solutes released or consumed by reaction of the feldspar are allowed to accumulate in solution (free drift), resulting in a changing solution composition with time. Buffers may be used to minimize fluctuations in some solution properties, usually pH and/or ionic strength, and solutions may be changed periodically to prevent the solution from drifting over too large a compositional range. Precipitation of secondary phases can be a serious problem in batch systems, particularly at moderate pH, where the system almost always oversaturates with respect to gibbsite and/or kaolinite, rendering the results a minimum rate only.

Flow-through systems continuously add and remove solution from a well mixed reactor (e.g. Chou and Wollast, 1984). The dissolution rate is calculated from the difference in solute concentrations of the input and output solutions. The continuous changing of solution allows the experiment to be designed so that it is never saturated with respect to secondary phases, or to manipulate the concentration of solutes in a systematic fashion (e.g. Burch et al., 1993). Because the reactor is well mixed, the composition of the output solution is identical to the solution in contact with the mineral. After an initial transitory period, the flow-through system should reach a steady-state at which the output solution reaches a constant composition, allowing the feldspar dissolution rate to be determined under constant chemical conditions.

There are many factors which must be considered in determining and evaluating feldspar dissolution rates. Most emphasis in experimental studies has been on the effects of solution pH, temperature, and feldspar composition on the dissolution rate. Other factors considered include; (i) the catalytic or inhibiting effect of dissolved inorganic and organic solutes (including pH buffers), (ii) the effect of the saturation state of the solution, (iii) the type and concentration of both point and line defects within the feldspar, and (iv) compositional variations within the feldspar crystals. In addition, different studies have treated starting material differently, determined mineral surface areas differently, used mineral names inconsistent with the actual composition, and not always evaluated the possibility of precipitation of secondary phases. Variations in many of these factors between different studies mean that the comparison of results from different studies must be done carefully and critically.

2.5.2. Albite dissolution kinetics - The feldspar with the most intensively studied dissolution kinetics is albite, and its dissolution behavior is typical in most respects of feldspars of all compositions. Solution pH appears to be the most important single solution variable controlling the dissolution rate. This is because both H^+ and OH^- are important participants in feldspar dissolution mechanisms, and because H^+ and OH^- have wider fluctuations in commonly occurring natural concentrations than any other solute. Figure 1 shows a compilation of measured dissolution rates for albite as a function of pH at temperatures near 25°C. The first thing to note in Fig. 1 is that the dissolution rate has a minimum at pH 6 to 8, and increases in both the acid and basic regions. This pattern is common to all feldspars, as well as many other silicates (e.g. Helgeson et al., 1984; Lasaga, 1984; Murphy and Helgeson, 1987), and it strongly suggests at least two different dissolution mechanisms for feldspars; a proton promoted mechanism in the acid region, and a hydroxyl promoted mechanism in the basic region. Many workers (e.g. Murphy and Helgeson, 1987; Chou and Wollast, 1985; Knauss and Wolery, 1986; Mast and Drever, 1987) have suggested that the feldspar dissolution rates are independent of pH in the neutral pH region from ~5 to 8. They have interpreted this as a third dissolution mechanism for feldspars which dominates in the neutral pH region and is pH independent. Other workers (e.g. Blum and Lasaga, 1991; Brady and Walther, 1989) have proposed only two pH dependent mechanisms. However, the determination of the very slow feldspar dissolution rates at near neutral pH's is often problematic. Analytical detection limits of solutes in solution often

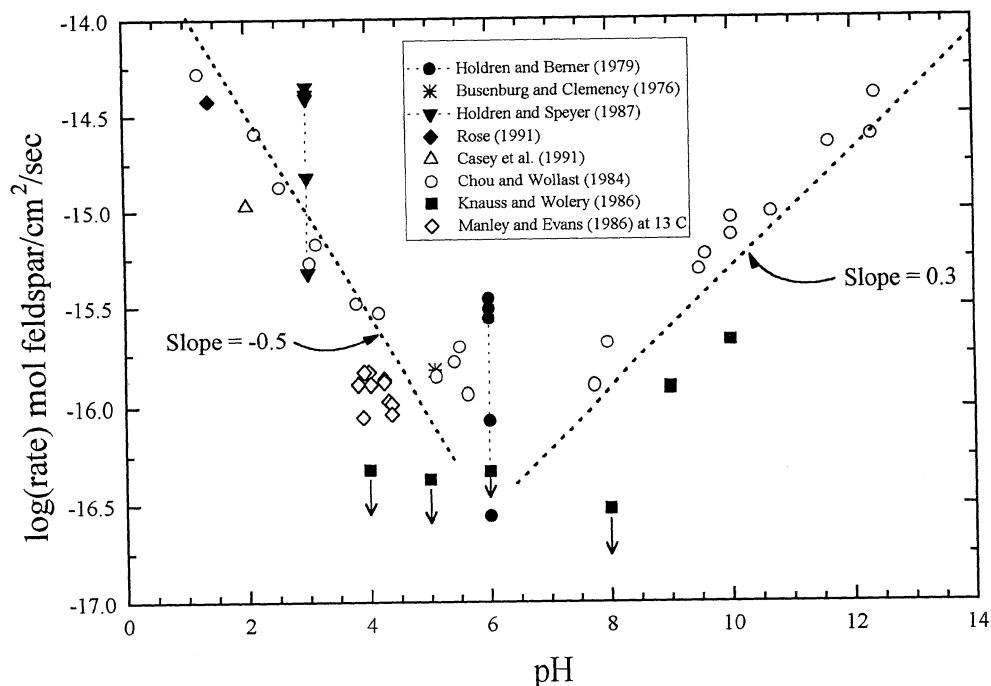


Figure 1 - Compilation of albite dissolution rates as a function of solution pH.

limit the sensitivity of the experiments. Very long reaction times are necessary to dissolve a significant volume of material and, therefore, definitively remove any anomalously high dissolution rate material on the surface. It is still not unambiguously resolved whether the feldspar dissolution kinetics are controlled by only a proton promoted mechanism in the acid region and a hydroxyl promoted mechanism in the basic region, or if a third pH independent mechanism operates in the neutral pH region. The neutral region includes many natural environments including most soils, surface and ground waters, and pH independence in the neutral region would greatly simplify the practical application of feldspar kinetics.

2.5.3. Potassium Feldspar Dissolution Kinetics - Figure 2 compiles K-feldspar dissolution rates as a function of solution pH at ~25°C. Fig. 3 compares the K-feldspar rates reported in fig. 2 with albite rates from fig. 1. At pH < 6, the dissolution rates of K-feldspars are indistinguishable from albite, both in their pH dependence ($R \propto [H^+]^{-0.5}$) and in their absolute rate. The major difference between the structures of albite and K-feldspar is the substitution of K^+ for Na^+ and the slight distortion of the tetrahedral lattice which accommodates the cation substitution. In acidic solutions both the albite and K-feldspar surfaces undergo rapid exchange of cations with H^+ to form a hydrogen-feldspar surface layer several unit cells thick. This implies that the structure and composition of the albite and K-feldspar surfaces at the mineral-solution interface are nearly identical, which is consistent with the similar dissolution kinetics of albite and K-feldspar in the acid region. The presence of a hydrogen feldspar surface layer also implies that it is the nature of the tetrahedral framework, and hydrolysis of the bridging oxygen bonds at tetrahedral sites which is controlling the dissolution rate of feldspars under acidic conditions, whereas the nature of the cation is of secondary importance. Calcic-plagioclase also forms a hydrogen-feldspar surface layer in the acidic solutions. By analogy, the differences between alkali feldspar and

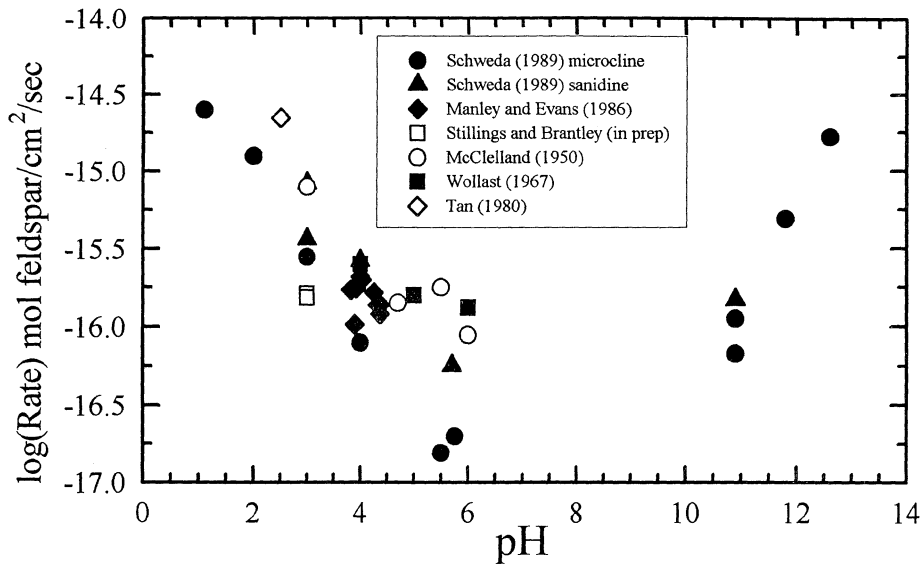


Figure 2 - Compilation of K-feldspar dissolution rates as a function of solution pH.

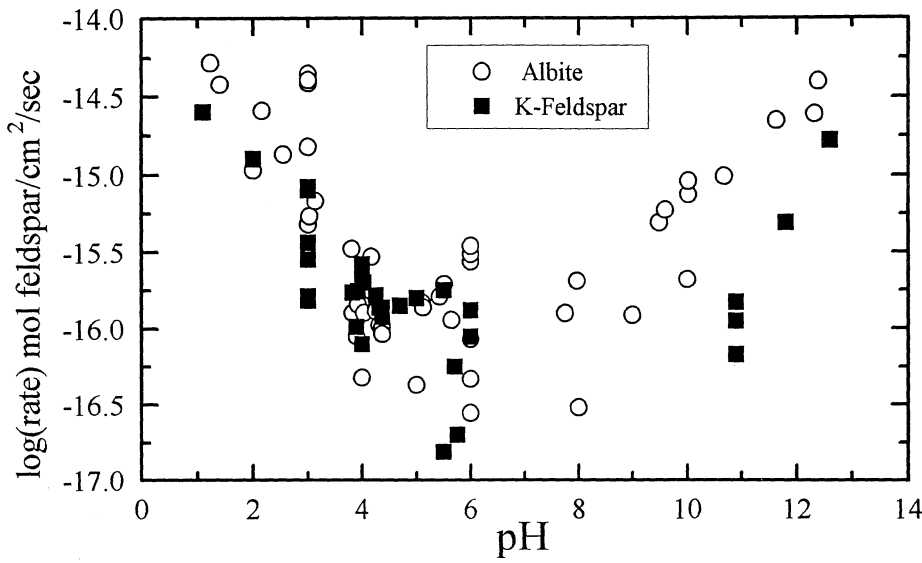


Figure 3 - Comparison of albite and K-feldspar dissolution rates as a function of pH (data from figs. 2 and 3).

plagioclase dissolution kinetics in the acid region are probably a result of the higher Al/Si ratio in the tetrahedral framework, and not the nature of the cation in the original mineral.

In the basic pH region the dissolution rate data for K-feldspar are sparse. However, it appears that K-feldspar has a slower absolute dissolution rate than albite by a factor of ~ 10 , and possibly a greater pH dependence than albite, although the slope is poorly defined. The slower dissolution rate of K-feldspar implies that cations may have an important influence on feldspar dissolution kinetics in basic solutions, presumably due to K^+ readsorption at cation sites stabilizing the surface more strongly than Na^+ . This is consistent with the observation of Wollast and Chou (1992) that Na^+ reversibly adsorbs on the albite surface. Since both the exchange constant and the stability of the resulting feldspar surface would be expected to increase with ΔG of adsorption, presumably K^+ exchanges on to the surface more strongly than Na^+ . This also implies that dissolution rates of feldspars in the basic region may be strongly influenced by the concentrations of any cations which can effectively compete for cation exchange sites on the feldspar surface.

In most soils, including acidic soils, it is commonly observed that K-feldspars weathering rates are much slower than sodic plagioclase. This is in contrast to the experimental results in fig. 3, which indicates approximately similar experimental dissolution rates for albite and K-feldspar. One possible explanation is that soil solutions, especially those in isolated pores, may reach higher solute concentrations than are achieved in most dissolution experiments. If K-feldspar is more prone to cation occupancy in the exchange sites, high solute concentrations may preferentially retard K-feldspar dissolution relative to albite. However, this is quite speculative, and the cause of the discrepancy between the experimental results and field observations is quite uncertain.

5.2.4. Plagioclase Dissolution Kinetics - It has been recognized for quite some time (e.g. Goldich, 1938) that the feldspar weathering rates in soils vary as calcic plagioclase > sodic plagioclase. There is abundant morphologic evidence for this relationship. A common example is the preferential weathering of the calcic cores of zoned plagioclase crystals before the weathering of the more sodic rims. Figure 4 compiles recent dissolution rate data for plagioclase as a function of feldspar composition (%An) at pH 2, 3, and 5. Casey et al. (1991) compiled similar plots for pH 2 and 3, and Stillings and Brantley (in press) at pH 3. At all three pH values, we observe a near-exponential increase in the feldspar dissolution rate with increasing anorthite content from An_0 to An_{80} . The total increase in dissolution rate from albite to anorthite ranges from a factor of $10^{2.5}$ to 10^4 , and %An is a strong control on plagioclase dissolution rates. There appears to be a discontinuity in the dependence of plagioclase dissolution rate on composition at $\sim An_{80}$, with anorthite dissolution rates increasing considerably faster than the trend predicted from the less calcic plagioclase data.

The anorthite measurements at pH 5 demonstrate wide disagreements, with differences of almost 10^6 in the measured dissolution rates. The higher values are from Fleer (1982) and Sverdrup (1990). Fleer (1982) used the geometric surface area of a single large crystal, and may have severely underestimated the BET surface area. The data from Busenburg and Clemency (1976) was collected using batch experiments at 1 atm CO_2 , and Busenburg (1978) reported that these experiments precipitated secondary phases. The data point is based on the linear release rate of Ca, but still represents only a minimum rate. The data from Amrhein and Suarez (1988, 1992) are also batch experiments which were run for up to 4.5 years, and in which significant secondary precipitates were reported. Thus, these low anorthite dissolution rates are probably the result of either the removal of material by secondary precipitates, or the high solute concentrations allowed to accumulate during the experiment which reduced the reaction rate. In either case, these experiments are not comparable with the other rate data in fig. 4c collected in dilute solutions far from equilibrium, and they have not been included in the indicated trends or in the interpretation. However, these discrepancies of a factor of 10^6 illustrate the difficulties in the comparison and interpretation of feldspar dissolution experiments.

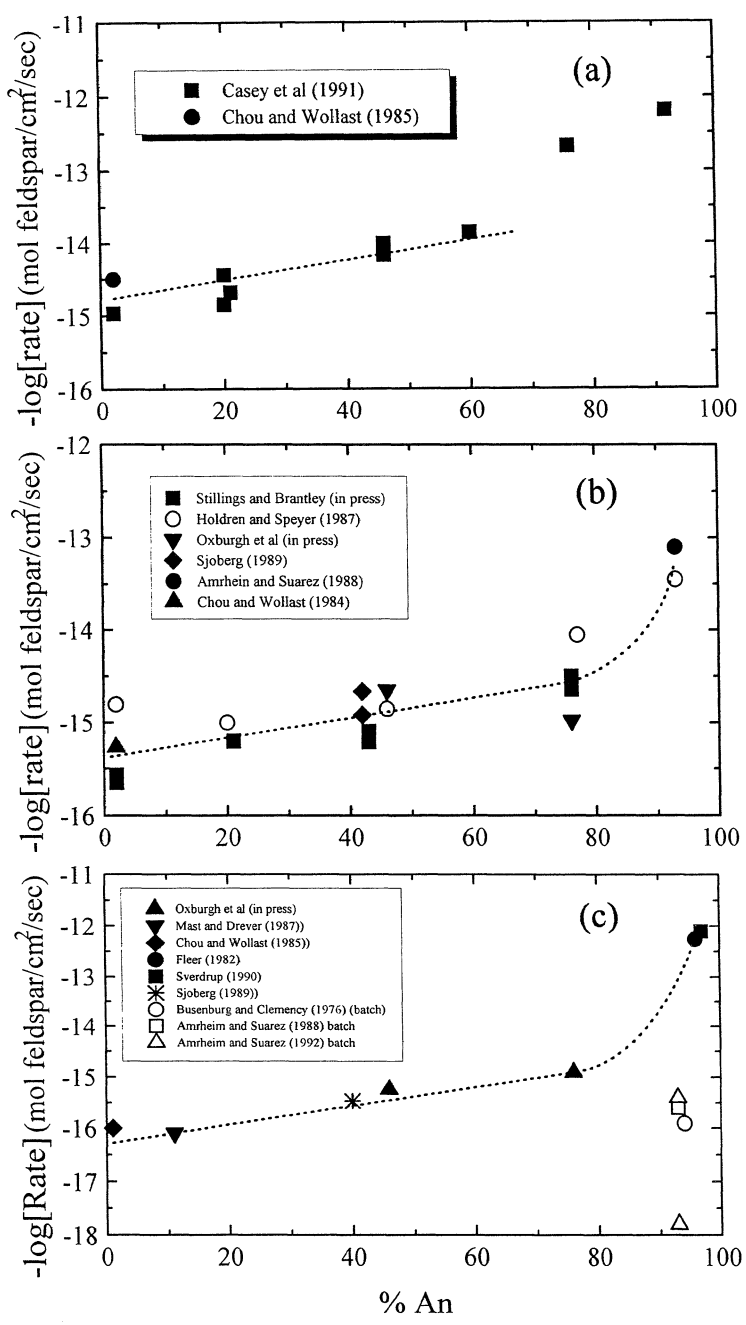


Figure 4 - Plagioclase dissolution rates as a function of anorthite content (%An) at (a) pH 2, (b) pH3, and (c) pH 5.

Fig. 5 shows the dissolution rate for a series of plagioclase compositions as a function of solution pH in the acid region. The plagioclase series from albite to $\sim\text{An}_{70}$ (as well as K-feldspar) have a dependence of $R \propto [\text{H}^+]^{-0.5}$, but the exponent increases to 0.76 for An_{76} (Oxburgh et al., *in press*), and 1.0 for anorthite (Sverdrup, 1990). This transition appears to occur at $\sim\text{An}_{70}$, and corresponds to the observed change in dissolution behavior with %An observed at pH 2, 3 and 5 (fig. 4). There appears to be a critical Al/Si ratio at An_{70-80} which dramatically effects plagioclase dissolution kinetics. This may be related to a decrease in the average size of linked clusters of Si tetrahedra after preferential attack and removal of tetrahedral Al. In albite with an Al/Si ratio of 3, preferential attack and removal of Al will still leave a fragmented but partially linked framework of tetrahedral Si. Removal of the Si will still require the hydrolysis of Si-O-Si bonds, although the Si centers will probably have several hydroxyl groups. In anorthite (An_{100}) the Al/Si ratio equals 1, and the ordering imposed by the aluminum avoidance principle means that removal of Al will leave completely detached Si tetrahedra, with the result that hydrolysis of Si-O-Si bonds are never required to decompose the anorthite tetrahedral lattice. There may be a critical Al/Si ratio at which the hydrolysis of Si-O-Si is no longer a control on the plagioclase dissolution rate, corresponding to a change in the overall dissolution mechanism.

2.5.5. Reproducibility of feldspar dissolution rates - The reproducibility of feldspar rate determinations by the same laboratory are generally $<\pm 50\%$ and almost always within a factor of 2. For example, Holdren and Speyer (1987) found a reproducibility of individual experiments of $<\pm 15\%$. The agreement between feldspar rate determinations conducted in different laboratories under similar conditions, such as in dilute solutions with no secondary precipitates, is generally within $\sim 10^{0.7}$, maybe a little better at low pH. The differences may reflect subtle differences in composition and microstructure of the mineral specimens, grain size used, solution saturation state, cation concentrations, surface area determinations, and the concentrations of other possible catalysts and inhibitors such as organic buffers and Al^{3+} , respectively.

Holdren and Speyer (1987) measured the dissolution rates of different grain size fractions

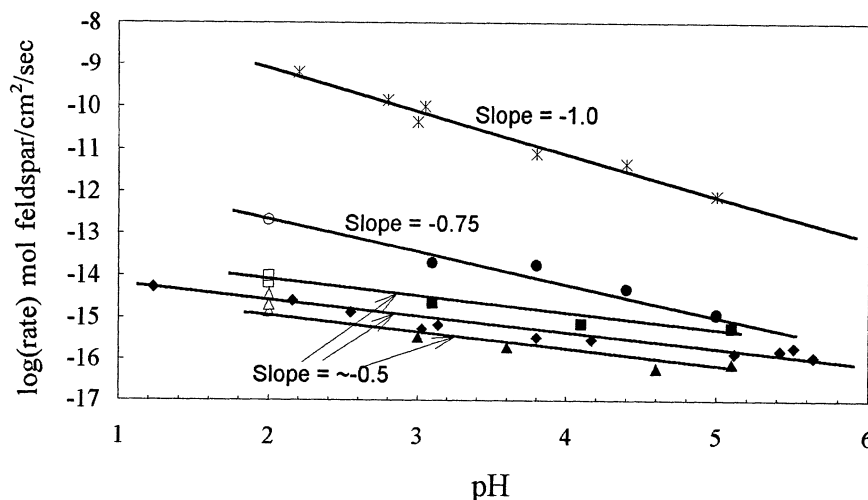


Figure 5 - Dissolution rate as a function of solution pH for plagioclase feldspars of different compositions. * anorthite, Sverdrup (1990); ● bytownite, Oxburgh and et al. (*in press*); ○ bytownite, Casey et al. (1991); ■ andesine, Oxburgh and et al. (*in press*); □ andesine, Casey et al. (1991); ▲ oligoclase, Oxburgh and et al. (*in press*); ▲ oligoclase, Casey et al. (1991); ◆ albite, Chou and Wollast (1985). (*after* Oxburgh and et al., *in press*)

from nine different feldspar compositions at pH 3, and one sample each at pH 2 and 6. They found a systematic decrease in dissolution rate with decreasing grain size from $>600\mu\text{m}$ to $<37\mu\text{m}$, with the rates decreasing by a factor from 2.8 to 28.5. Their data for albite is shown on Fig. 1 at pH 3 and 6, and their observed change in rate with grain size is greater than the variability between the rates of most other workers. A similar decrease in dissolution rate with decreasing grain size is reported by Amrhein and Suarez (1992) for anorthite. Holdren and Speyer (1987) proposed that the defect structures at twin boundaries and between exsolution domains are preferential sites for the dissolution of feldspars. Additionally, grinding of feldspar starting material preferentially cleaves the crystals along twin and exsolution boundaries effectively destroying them. Thus, the density of these high energy boundaries exposed on the grain surfaces decreases with decreasing grain size. This continues until the grain size drops below the average spacing of the defect. However, in contrast to the data of Holdren and Speyer (1985, 1987), Mast and Drever (1993) measured the dissolution rates of seven albite fractions from $0.5\mu\text{m}$ to $150\mu\text{m}$ at pH 4 and found the dissolution rate did *not* vary with grain size. Inskeep et al. (1991) observed differential weathering of the more calcic exsolution lamellae in experimentally dissolved labradorite using TEM, but they did not observe preferential dissolution along the lamellae boundaries.

2.5.6. Evidence for a Leached Layer on the Surface - There is considerable evidence for development of a Si-rich layer on the feldspar surface after dissolution in the acid region (≤ 3), both from direct measurement by surface analytical techniques (Petrovic et al., 1976; Berner and Holdren, 1979; Casey et al., 1988, 1989; Sjöberg, 1989; Hellmann et al., 1989, 1990; Goossens et al., 1989; Nesbitt and Muir, 1988; Nesbitt, 1990; Muir et al., 1989; Muir and Nesbitt, 1991, 1992) and from non-stoichiometric dissolution (Chou and Wollast, 1984; Holdren and Speyer, 1985; Schweda, 1989; and others). The thickness of the Si-rich layer is typically several thousand angstroms thick at a pH of 1-3, and the layers seem to be thicker and develop at higher pH's the more calcic, and therefore, the more rapid the dissolution rate of the feldspar. When the feldspar is removed from solution, the Si-rich layer has been reported to crack and spall (Casey et al., 1989). The silica-rich layer is highly porous as indicated by TEM imaging and nitrogen porosimetry measurements on labradorite (Casey et al., 1989), and ion beam measurements on albite (Petit et al., 1990), alkali feldspar (Petit et al., 1989), labradorite (Casey et al., 1989) and diopside (Petit et al., 1987; Schott and Petit, 1987). All indications are that the silica-rich layer has a structure similar to that of an amorphous hydrated silica gel, and TEM imaging indicates there is an atomically discrete interface between the silica layer and the feldspar surface (Casey et al., 1989). Diffusion rates though similar porous silica layers on glass and zeolites are very similar to aqueous diffusion rates (Bunker et al., 1984, 1986, 1988), and Westrich et al (1989) demonstrated O^{18} will diffuse into a $1000\text{ \AA}$ leached layer on labradorite within hours. Casey et al (1988), Westrich et al (1989), Hellmann et al (1990), Rose (1991) and Amrhein and Suarez (1992) all conclude that the dissolution rate of feldspars in acid solutions is not limited by diffusion through the Si-rich leached layer, and formation of the leached layer does not necessarily indicate any change in the rate controlling mechanism of the dissolution reaction which decomposes the feldspar structure.

A conceptual model for the formation of the leached layer is that during the dissolution process Al is preferentially removed from the tetrahedral lattice, leaving small fragments of Si tetrahedra with a few remaining bridging oxygen bonds. If the rate of feldspar dissolution is slower than the rate at which the silica fragments can be dissolved, then no silica layer will form. This is the case above pH ~ 3 to 5, where feldspar dissolution rates are slow. As feldspar dissolution rates increase below pH 3, the silica fragments start to accumulate near the surface where they can repolymerize to form a continuous, but porous and hydrous silica layer. There is evidence for the repolymerization of silinol groups within the silica layer, based upon hydrogen inventories measured by elastic recoil detection (ERD) by Casey et al, (1988), hydrogen inventories determined by ion beam analysis (Petit and others), and irreversible and rapid incorporation of O^{18} into the silica-rich layer by Westrich et al, (1989).

There is less agreement about the presence and nature of the leached layer above pH 3. Most studies agree that the cation and Al depleted layer reaches thicknesses $<20 \text{ \AA}$ between pH 5 and 8 for all the feldspars. This is comparable to the depth of rapid cation exchange measured by Chou and Wollast (1984) and Blum and Lasaga (1991) for albite and Amrhein and Suarez (1988) for anorthite, and there is a general consensus that no depleted layer forms during feldspar dissolution in the neutral pH region. There is some evidence that the leached layer persists but grows rapidly thinner between pH 3 and 5 (Nesbitt et al, 1991; Hellmann et al 1990; Sjöberg, 1989). However, Inskeep et al (1991) observed with TEM the preferential dissolution of Ca-rich exsolution lamellae in labradorite with a width of $700 \text{ \AA}$ to a depth of $1350 \text{ \AA}$. They have suggested that much of the evidence for non-stoichiometric dissolution of plagioclase based upon surface analytical techniques and dissolution stoichiometries in the pH 3-5 region can be explained by the preferential dissolution of calcium rich exsolution phases.

There is less information at basic pH. Casey et al. (1988) using Rutherford backscattering (RBS) analysis found no detectable leached layer and very low hydrogen inventories with ERD after labradorite reaction at pH 12, indicating no leached layer. Hellmann et al. (1990) observed a Si enriched layer $\sim 500 \text{ \AA}$ thick on albite at pH 10.8, but at an elevated temperatures of 200°C . Holdren and Speyer (1985) concluded that K-feldspar dissolution remained stoichiometric up to at least pH 9.

Dissolution experiments have a duration of from several hundred to several thousand hours, whereas natural weathering of feldspars may occur over 100,000's of years. With the slow feldspar dissolution rates at neutral pH, there is still some doubt if thick leached layer might form on feldspar surfaces given sufficient time. However, Berner and Holdren (1979) found no evidence of a leached layer $>20 \text{ \AA}$ thick on naturally weathered plagioclase with XPS. Blum et al. (1990) observed no cation depletion of $>50 \text{ \AA}$ for Na and Ca, and $>30 \text{ \AA}$ for K on the (001) faces of naturally weathered alkali and oligoclase feldspars using XPS. There was no indication of a non-stoichiometric Al/Si ratio greater than a few angstroms, with a slight Al enrichment which appears to be on the very near surface. The soils ranged in age from 10K to 800K years old, with soil pH's of 5-7. These results agree with experimental observations in near neutral pH solutions; cations are removed by exchange to depths of several 10's of $\text{\AA}$, and silica and aluminum dissolve essentially stoichiometrically. This indicates that the experimental results may reflect the natural weathering processes. However, Nesbitt and Muir (1988) used SIMS to measure surface compositions of 9 oligoclase grains from a 10K year old till in an acidic watershed in Ontario. They observed consistent Al enrichment of the surface to depths of $\sim 500 \text{ \AA}$, which contrasts with the dissolution experimental results. The reasons for the disagreement are unclear, but explanations such as the high Al^{3+} and other solute concentrations in acidified soil solutions (Muir and Nesbitt, 1991; Nesbitt et al., 1991), failure to remove secondary precipitates, or errors in the SIMS data interpretation have been suggested.

3. Theoretical Approaches to Surface Reaction Controlled Dissolution Kinetics

There are several different theoretical approaches to dissolution and precipitation kinetics in the fields of chemistry and materials science. These models approach the problem on very different scales and are often appropriate for very different applications. Geochemists are still in the process of selecting the most appropriate conceptual models to describe feldspar dissolution kinetics. There is still some ambiguity in how to relate the different types of approaches, and the description of geological systems may require the development of more comprehensive models. I have somewhat arbitrarily divided the models into three categories, based upon the conceptual scale.

3.1. ATOMISTIC MODELS

In atomic models of dissolution, we are looking at the detailed configuration and energetics of interactions between the mineral surface and the solvent atoms. The most widely applied atomistic approach to kinetics is transition state theory (TST) which has been applied to many studies of mineral dissolution kinetics (e.g. Lasaga, 1981b; Aagaard and Helgeson, 1982; Helgeson et al., 1984; Chou and Wollast, 1985; Hellmann et al., 1990). Geochemists usually write overall reactions, such as eq. 1, which reflect the overall stoichiometry of a chemical process. In contrast, an elementary reaction reflects the exact molecular species actually involved in the reaction at the atomic level, and there may be a large system of elementary reactions involved in a single overall reaction. An elementary reaction involves a collision between reactant molecules (e.g. $A+BC$), which initially are confined to a well defined potential energy well (fig. 6). As the reactants approach each other they must overcome an energy barrier, which is at a saddle point in the potential energy surface. The molecular configuration in the vicinity of the saddle point is the activated complex (ABC), which will then decompose to either the reaction products ($AB+C$) or back to the initial reactants. TST calculates the reaction rate by assuming equilibrium between the reactants and the activated complex, and calculating the concentration of the activated complex, and its decomposition rate. Both of these quantities are a function of the energetics of the molecular species, and can be calculated from their partition functions. Lasaga (1981b) gives a simple and concise summary of TST and its application to geochemistry.

Several aspects of transition state theory need to be considered in the application to feldspar dissolution kinetics: (i) The activated complex is a well defined molecular configuration. However, there is no energy barrier for the decomposition of the activated complex along the reaction coordinate, so that the decomposition rate will be on the order of the vibrational

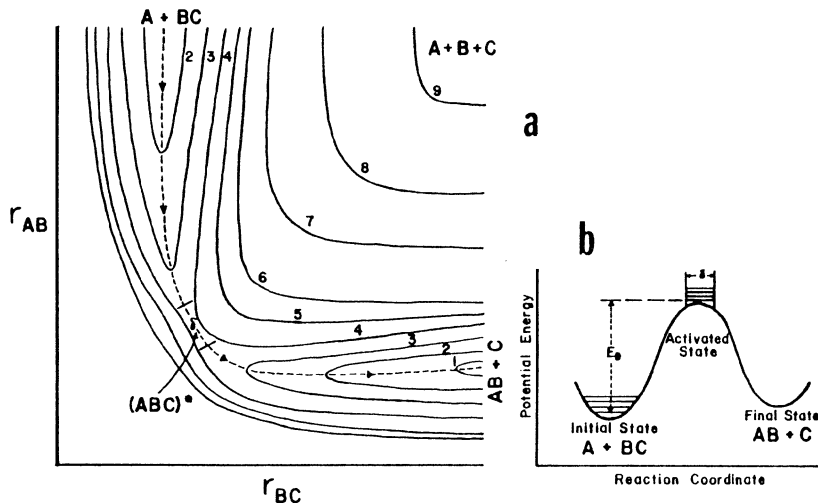


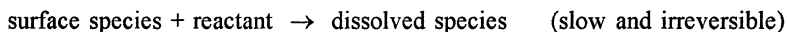
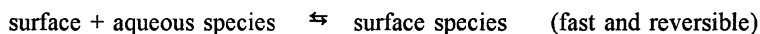
Figure 6 - Transition state theory. a) Schematic diagram of the potential energy as a function of the bond distance for a three atom system. The contours are labeled with arbitrary energy units. The reaction coordinate follows the trough in the energy surface, shown by a dotted line. The transition state is at the saddle point in the trough. This treatment can be extended mathematically into many dimensions for complex systems. b) Typical one dimensional representation of the reaction coordinate, which shows the total system energy as a function of linear distance along the reaction coordinate. (from Lasaga, 1981b)

frequency of the molecules ($\sim 10^{14}$ sec). Thus, the concentration of the activated complex at any specific time is extremely low; (ii) Application of TST to a specific reaction requires, as a minimum, knowledge of the elementary reaction of interest; (iii) Rigorous application of TST requires knowing such quantities as activity coefficient of the activated complex, which can generally be determined only by calculation; and (iv) TST is most successful when applied to homogenous systems with well defined chemistry and structure. It is difficult to apply TST to reactions where larger scale characteristics of the system, such as defect structures, have a large influence on the energetics of the reaction. In these cases, there may be a whole range of subtly different activation complexes at different sites, with a range of geometries and energetics. In this case, the overall reaction kinetics will then be the summation of all these subtly different pathways, and will be very difficult to quantify on an atomic scale. Our understanding of feldspar dissolution kinetics is not yet refined to the point where we can conclusively point to any specific elementary reaction or activated complex in the rate limiting step of the dissolution process. Despite these difficulties, TST is still a powerful conceptual framework which shapes much of our thinking about chemical kinetics.

The rapid advances in ab-initio quantum mechanical calculations hold the prospect of calculating proposed activated complexes, and testing the energetics of the proposed reaction mechanisms. Lasaga and Gibbs (1990a, 1990b) have used ab-initio calculations to investigate the hydrolysis of Si-O-Si bonds. They calculated the reaction trajectory and energetics of the transition state for a proposed mechanism, and applied the results to quartz dissolution kinetics. This computational approach has tremendous potential for testing proposed dissolution mechanisms for feldspar dissolution, and facilitating the quantitative application of TST. However, the application of quantum mechanical modeling to feldspar dissolution still requires making the correct choice of molecules interacting during the rate limiting elementary reaction. This requires insight which can only be obtained from detailed and well designed experiments.

3.2. SURFACE SPECIATION MODELS

Surface speciation models take a large step back in both rigor and scale from TST. Surface speciation models attempt to relate an observed dissolution rate to the surface concentration of specific chemical complexes on the surface. In this model, the dissolution rate is a consequence of a series of elementary reactions.



One of the early steps in that reaction sequence is a rapid and reversible adsorption reaction (such as described in section 2.3). The configuration of this surface complex then facilitates the next step in the reaction sequence which is a slow and irreversible reaction. In the case of feldspars, the slow step is probably the hydrolysis of bridging tetrahedral oxygen bonds. If the rate limiting reaction occurs with equal probability at each occurrence of a surface complex and only at sites with this specific surface complex, then

$$\text{dissolution rate (R)} = k_{\text{dis}} [\# \text{ surface complexes } (S_c)] \quad (9)$$

so that the dissolution rate (R, mol/m²/s) is directly proportional to the number of surface complexes (S_c , mol/m²), where k_{dis} is the rate constant in s⁻¹. In terms of TST, the presence of the surface complex provides a reaction path with a lower activation energy, and is essentially a stable intermediate in the dissolution reaction mechanism. Several points should be clarified. The actual "activated complex" for the rate limiting step is some unknown configuration in a subsequent slow reaction. Identification of the surface species gives only general insight into the rate limiting step, in that we are one step closer in the reaction mechanism, and *perhaps* the

surface species is one of the reactants. However, there may also be additional fast intermediate steps.

Nevertheless, surface complexation models may be extremely powerful. If we can identify the surface complex involved in the dissolution reaction: (i) We can predict dissolution rate using eq. 9 from only a knowledge of the rate constant (k) and the adsorption isotherms for the solutes involved in the surface complex. Determining the adsorption isotherm is in principle a much simpler matter than explicitly measuring the kinetics of slow reactions like feldspar dissolution over a full range of solution compositions; (ii) The activity of both poisons and inhibitors will probably result from competition for the adsorption sites, which are then either blocked or enhanced by the adsorbed species. These effects may also be quantified by surface adsorption measurements, and intelligent guesses as to the effects of solutes may be made even without measurements; and (iii) We are one step closer to the true "activated complex", and may be in a position to propose reasonable molecular clusters for testing using ab-initio quantum mechanical calculations.

3.2.1. Applications of Surface Speciation Models to Feldspar Dissolution Kinetics - The adsorption characteristics of simple oxides have been studied extensively, and surface complexation models have been developed to estimate the protonation reactions of hydroxyls at oxide surfaces, as well as the adsorption of other ligands (see Davis and Kent (1990), Wehrli et al. (1990) and Stumm and Wieland (1990) for summaries).

Furrer and Stumm (1986) and Guy and Schott (1989) found a correlation between the dissolution rate of simple oxides and their surface charge with a reaction order equal to the formal charge of the metal center.

$$\text{Dissolution rate} \propto c^n \quad (10)$$

where c is the surface charge and n is the formal charge of the metal center (i.e. $n = 2$ for Be, 3 for Al and Fe(III) and 4 for Si). This suggests that dissolution is occurring at metal centers at which n of the oxygens coordinated around that metal center are simultaneously protonated. Wieland et al. (1988) presents a model for this dependence. They have shown statistically that if each metal center has n possible adsorption sites, which are filled in completely random fashion, then the concentration of metal centers with all n sites filled (F) will vary as $F \propto (X_c)^n$ where X_c is the fraction of total number of surface sites which are filled. Blum (unpublished) has numerically verified the validity of this statistical result.

Blum and Lasaga (1988, 1991) measured the change in surface charge of albite as a function of pH by surface titration (fig 7). They did not observe Na^+ uptake during the titrations, and assumed that the protonation and deprotonation of surface hydroxyls (eqns. 5 and 6) were the major reactions controlling the change in surface charge. The inflection point in the surface charge is at pH 6.8, which Parks (1967) estimated to be the zero point of charge for tetrahedral Al. From this, and the depth of the adsorption layer, they concluded that it is protonation of Al sites which is controlling the surface charge of albite as a function of pH. Blum and Lasaga (1991) also observed a strong correlation between the surface charge of albite and the dissolution rate of albite measured by Chou and Wollast (1985) (fig. 8). They conclude that in the acid region (pH < 6.8) the albite dissolution rate is directly proportional to the positive surface charge, and in the basic region, to the negative surface charge, with both charged species occurring on Al sites. The rate laws are then:

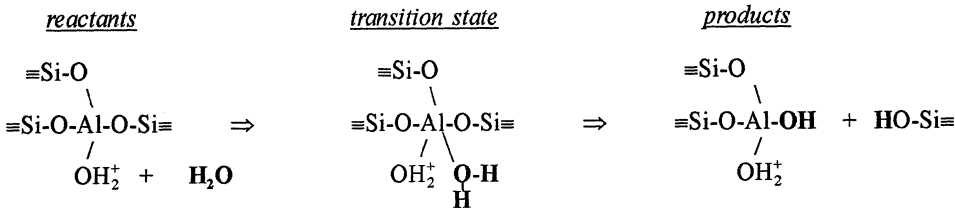
$$\text{Dissolution rate} = k_a c_{>\text{Al}-\text{OH}_2^+}^{-1.0} \quad (\text{pH} < 6) \quad (11)$$

where the reaction constants for the dissolution mechanisms in acid and basic regions are $k_a \approx 10^{-6.5} \text{ s}^{-1}$ and $k_b \approx 10^{-6.1} \text{ s}^{-1}$, respectively. They concluded that the hydrolysis rate of bridging

$$\text{Dissolution rate} = k_b c_{>\text{Al-O}^-}^{-1.0} \qquad (\text{pH} > 7.5) \qquad (12)$$

Al-O-Si bonds adjacent to the charged aluminum species is the rate limiting step in the feldspar dissolution process. Wollast and Chou (1992) found a similar linear relation between negative surface charge and the dissolution rate of albite in the basic region ($R \propto c^{-1.0}$). Schott (1990) conducted similar surface titrations of albite and found a good correlation between the dissolution rate and surface charge of albite in the basic region, but with a reaction order of 3.3 ($R \propto c^{-3.3}$). Amrhein and Suarez (1988) found a correlation between the dissolution rate and the surface charge of anorthite with a reaction order of 4 ($R \propto c^{-4.0}$). Reaction orders of 3 to 4 are consistent with the theory of Wieland et al. (1988) (eq. 10) for control of feldspar dissolution by surface species at Al centers. This is in contrast to the reaction order of 1 found by Blum and Lasaga (1991) and Wollast and Chou (1992).

The hydration reaction in which water reacts with the Al-O-Si bridging bonds of the feldspar lattice in the acid region can be schematically represented as:



The reaction above has been presented to represent my biases. The Al on the surface is shown with an OH₂⁺ surface complex adjacent to a bridging Al-O-Si bond which will be hydrolyzed, as proposed by Blum and Lasaga (1991). The approach trajectory of the water and

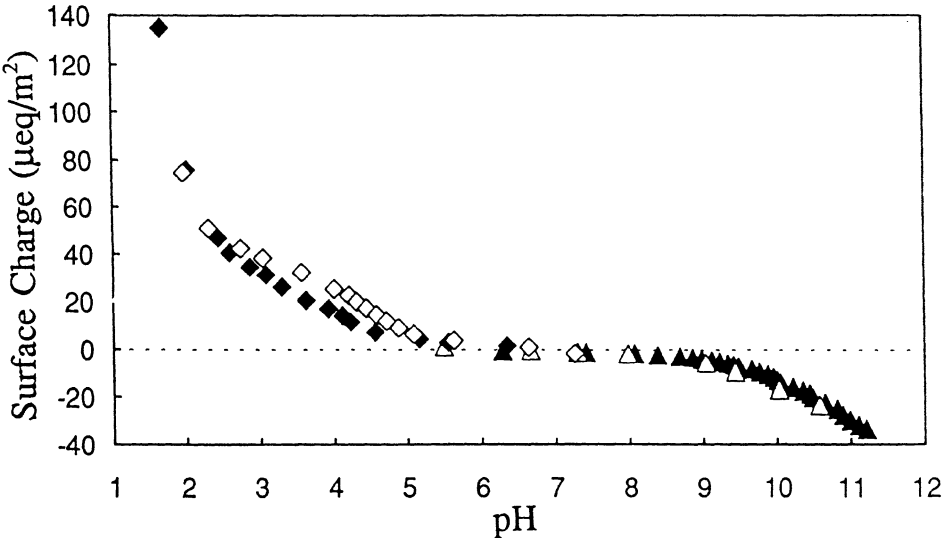


Figure 7 - Change in albite surface charge as a function of solution pH from surface titrations. Open symbols are the initial titrations, and open symbols are the back titration. (from Blum and Lasaga, 1991)

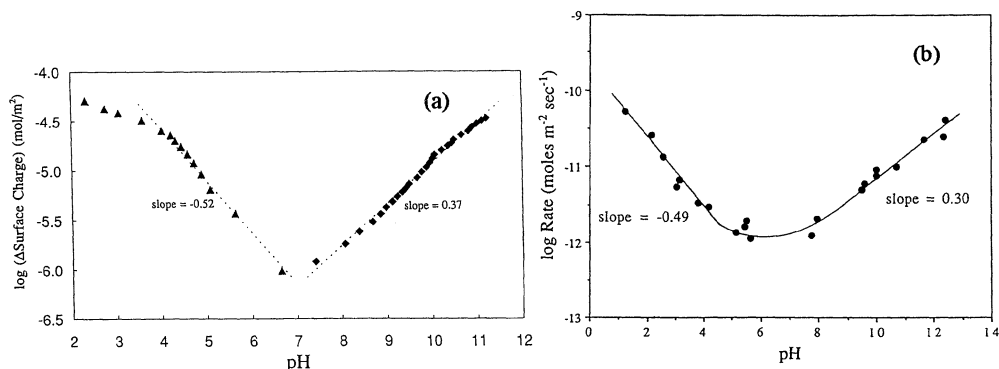


Figure 8 - Correlation between pH dependence of the albite surface charge and dissolution rate. a) Log of the change in positive surface charge in the acid region and of negative surface charge in the basic region as a function of solution pH. b) Data of Chou and Wollast (1985) for albite dissolution rate as a function of pH. (from Blum and Lasaga, 1991)

the configuration of the activated complex are analogous to those proposed by Lasaga and Gibbs (1990), based upon quantum mechanical modeling, for the hydrolysis of quartz Si-O-Si bonds. The presence of the positively charged surface species at the Al dangling oxygens may reduce the energy barrier for the approach of the negative oxygen dipole of the water toward the Al (i.e. reducing the activation energy). Wieland et al. (1988) and Schott (1990) suggest that the Al should have three charged groups. This may present a problem. If we envision the protonation of only dangling hydroxyls on the Al, then the mechanism can only apply to Al with only one remaining bridging tetrahedral bond. Those Al with only a single bridging bond should be the easiest to remove from the lattice, and it is unlikely that this is a rate limiting reaction. Alternatively, protonation may occur on bridging oxygens themselves. The model of Wieland et al. (1988) requires equivalent adsorption behavior at all sites in order for the relation $R=kc^n$ to be valid. Si-O-Si bonds have been shown to be highly hydrophobic on quartz and silica, and adsorption site densities on quartz are consistent with protonation of only dangling hydroxyls (Iler, 1979). The behavior of Si-O-Al should be at least crudely similar to Si-O-Si bonds. This does not appear consistent with the requirement of Wieland et al. (1988) that the adsorption characteristics of bridging oxygens and dangling oxygens must be nearly identical.

Brady and Walther (1989) examined the dissolution versus surface charge behavior of a range of oxides and silicates. They concluded that Si hydroxyls become highly deprotonated at basic pH, and it is the detachment of Si, and not Al, which controls the dissolution kinetics of feldspars in the basic region. Obviously, there is still considerable uncertainty concerning the feldspar dissolution mechanism in the basic pH region, with both inconsistent data and different proposed models. Nevertheless, the surface speciation approach holds great promise for a robust model of feldspar dissolution kinetics.

3.2.2. Implications of Surface Speciation on Temperature Effects - If the dissolution rate of feldspars is directly proportional to the surface concentration of surface species, then the traditional application of an Arrhenius plot to determine the activation energy is invalid, even if the reaction mechanism remains unchanged. The simple equation; where E_a is the apparent activation energy, and A is the pre-exponential frequency factor, assumes that the concentration of the reactants remains approximately constant. Eq. 13 should be valid for surface speciation controlled dissolution so long as the rate is expressed as [(mol reaction) (mol surface complex)⁻¹ sec⁻¹]. However, the determination of dissolution rates from

$$\text{rate} = A \exp\left(\frac{E_a}{RT}\right) \quad (13)$$

the appearance of solutes in solution typically yields a dissolution rate in $[\text{mol cm}^{-2} \text{ sec}^{-1}]$. Eq. 13 can be recast as;

$$\text{rate} = X_c(T, \text{pH}, \text{adsorb}) A \exp\left(\frac{E_a}{RT}\right) \quad (14)$$

where X_c is the mole fraction of potential sites for surface complex which are actually occupied by the surface complex, and the rate is expressed in $[\text{mol cm}^{-2} \text{ sec}^{-1}]$. As discussed earlier, the equilibrium concentration of surface complexes may be very sensitive to solution pH and competitive adsorption of other species at potential adsorption sites (*adsorb* in eq. 14). In addition, the equilibrium constant for surface complex formation quite likely temperature dependent, and therefore, X_c is temperature dependent. Consequently, both the linear and exponential terms in eq. 14 have a temperature dependence, and are not independent. Therefore, an Arrhenius plot will not yield a reliable activation energy, even at a constant pH, and even though the elementary reaction mechanism may remain unchanged.

3.3. MACROSCOPIC MODELS

Macroscopic models are those models based upon the surface configuration of the surface on the molecular scale. These approaches are most useful for dealing with features of the system which are defined only at scales larger than molecular clusters, such as the saturation state of the solution, and the effects of dislocations, impurities and other heterogeneities in the solid.

3.3.1. Surface nucleation models - Surface nucleation models were first proposed for growth (Nielsen, 1964; Ohara and Reed, 1973), but apply equally well to dissolution (Blum and Lasaga, 1987). In this discussion we will frame the problem in terms of dissolution kinetics. Figure 9 shows a schematic diagram of a crystal surface. The surface nucleation model takes a basic thermodynamic approach in which there are two competing energy terms to consider; (i) When a unit is removed from the crystal into an undersaturated solution, the energy released is $\Delta\mu = \mu_{\text{liquid}} - \mu_{\text{solid}}$ where $\Delta\mu$ is the change in chemical potential, which is related to the solution composition by $\Delta\mu = kT \ln(Q/K)$ where k is Boltzmann's constant, Q is the activity product and K is the equilibrium constant; and (ii) Silicate surfaces in aqueous solution have a positive surface free energy (σ), indicating the creation of surface area is thermodynamically unfavorable, and the energy required to increase the surface area by A equals $A\sigma$. For quartz, Parks (1984) suggested a value for σ of 350 ergs/cm^2 , and Lasaga and Blum (1986) estimated σ at 500 ergs/cm^2 for feldspars.

The free energy change for the formation of either a cluster on the surface by the precipitation of n atoms or a pit formed by the dissolution of n atoms is then:

$$\Delta G_n = -n\Delta\mu + A_n\sigma \quad (15)$$

For a cluster or pit with a height of h units, a radius of r units, and an atomic volume v ,

$$nv = \pi r^2 h \quad (16)$$

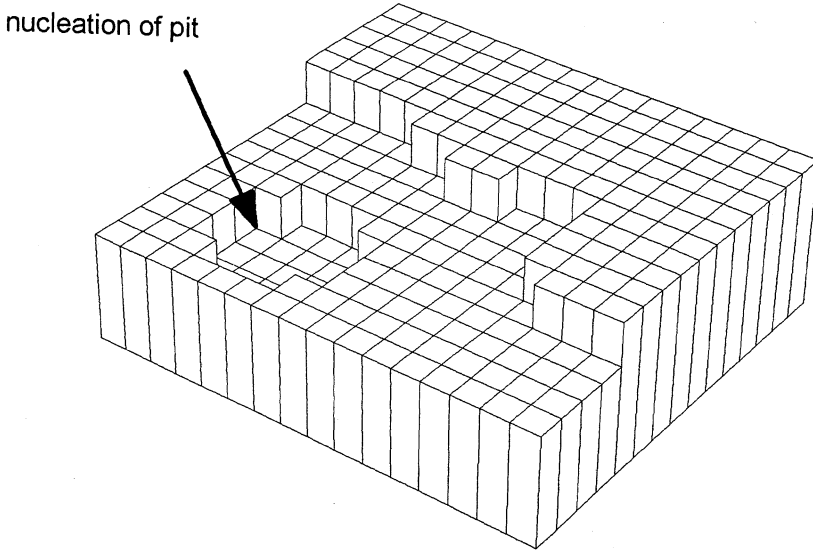


Figure 9 - Schematic diagram of a nucleation pit on the surface.

The *new* surface area created by the formation of the pit (i.e. along the edges) is then:

$$A_n = 2\pi rh \quad (17)$$

Substituting eq. 16 into eq. 17 to solve for r and inserting this into eq. 15, we find that ΔG_n initially increases with increasing n , and reaches a maximum when

$$n_c = \frac{\pi v h}{\Delta \mu^2} \sigma^2 \quad \text{or} \quad r_c = \frac{\sigma v}{\Delta \mu} \quad (18)$$

Thus, there is an energy barrier (ΔG_c) which must be overcome in order to form a dissolution pit of radius r_c . At pit sizes above r_c , continued enlargement of the pit is thermodynamically favorable, and it will continue to expand outward until the entire layer is dissolved. The hardest part in dissolution is getting those first few atoms out of a flat surface. The creation of an incipient dissolution pit creates a lot of new surface area relative to the small amount of material which has been dissolved. At solution compositions common in near-surface environments, r_c for feldspars and other silicates is on the order of several nanometers (Lasaga and Blum, 1986).

The nucleation rate of pits on the surface, R , depends exponentially on the energy barrier (ΔG_c) necessary to form a pit with the critical radius:

$$R \propto \exp \left[\frac{-\Delta G_c}{RT} \right] \quad \text{where} \quad \Delta G_c = \frac{\pi h v \sigma^2}{\Delta \mu} \quad (19)$$

The nucleation rate (R) calculated using eq. 19 predicts far too strong a dependence of the dissolution rate on the solution saturation state, and greatly underestimates dissolution and

growth rates close to equilibrium. However, the concept of the critical radius is commonly used in dissolution theory.

3.3.2 Dissolution at dislocations - Extensive crystallographically controlled etch pits are a ubiquitous feature in both naturally weathered (e.g. Berner and Holdren, 1979; Velbel, 1986; Banfield and Eggleton, 1990) and experimentally dissolved (e.g. Wilson and McHardy, 1980; Holdren and Speyer, 1985; Knauss and Wolery, 1986) feldspars. The morphology of the etch pits is similar to etch pits shown to form at the intersection of dislocations with the surface. There are several ways in which dislocations may potentially affect feldspar dissolution rates. The intersection of screw dislocations with the surface provides a continuous source of steps on the surface (fig. 10) which circumvents the need to nucleate pits on the surface (eq 19). This is the basis for the Burton-Cabrera-Frank (BCF) theory for spiral dissolution and growth (Burton et al., 1951; see also Ohara and Reed, 1973; Christian, 1975; Bennema, 1984). BCF theory is also completely equivalent for dissolution and growth, with the only difference a change in sign of $\Delta\mu$. In BCF theory, the step produced at a screw dislocation is a preferential site for dissolution and growth. The geometry imposed by the step being fixed at one end causes the propagating step to wind into a large spiral, either as an etch pit during dissolution or a growth hillock during precipitation. The distance between the steps (r_{step}) of the spiral are predicted to be $r_{\text{step}} \approx 19r_c$, where r_c is the critical radius given by eq 18. The step velocity is found to be proportional to the saturation state at small values of $\Delta\mu$ and independent of saturation state and at large values of $\Delta\mu$. This yields the relationship that at small values of $\Delta\mu$ (i.e. near equilibrium):

$$R \propto \Delta\mu^2$$

At large values of $\Delta\mu$ (far from equilibrium)

$$R \propto \Delta\mu$$

These relationships are often cited in the literature, and BCF theory has been very successful in describing the behavior of many synthetic systems in the materials literature, although predominately for precipitation. Growth spirals have also been observed in natural kaolinite, beryl, quartz and other minerals.

Dislocations may effect dissolution in a second way. In the vicinity of dislocations, the

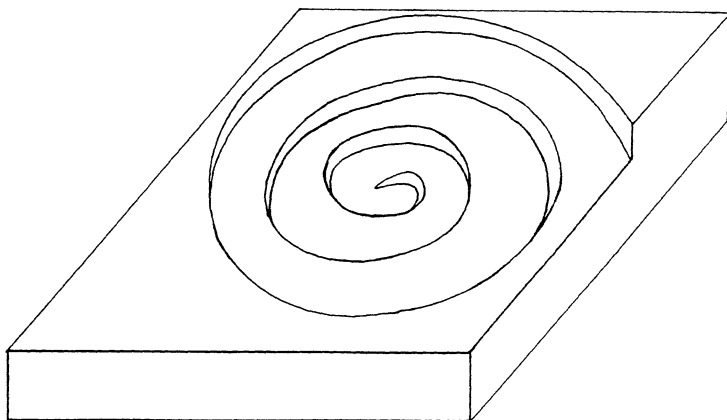


Figure 10 - Schematic diagram of a growth spiral on the surface.

crystal lattice is distorted, introducing strain energy into the lattice. The magnitude of this strain energy is too small to effect the overall thermodynamic properties of the mineral (Helgeson et al., 1984; Wintsch and Dunning, 1985). However, the concentration of strain energy in the vicinity of the dislocation provides a localized area of increased solubility. This provides an additional mechanism for forming etch pits which exceed r_c , and are thermodynamically favored to continue dissolution. Thus, strain energy around dislocations provides an alternative mechanism to surface nucleation or BCF for mineral dissolution (Cabrera and Levine, 1956; Van der Hoek et al., 1982; Lasaga, 1983). Note that strain energy accelerates dissolution, but will marginally inhibit growth. Blum and Lasaga (1987) used Monte Carlo simulations to demonstrate that strain energy is probably the dominant mechanism of etch pit formation at dislocations in quartz and feldspars (fig. 11). They found that far from equilibrium, the strain energy mechanism was ~8 fold faster than the BCF mechanism, with the ratio increasing toward equilibrium. An important prediction of this theory is that there is a critical solution saturation state (ΔG_{bulk}^{crit}) below which macroscopic etch pits will not form and above which the dislocation cores will "open" to form etch pits.

$$\Delta G_{bulk}^{crit} = - \frac{2\pi^2 \sigma^2 K_{orient}}{\mu_s b^2} \bar{V} \quad (20)$$

where

$$\Delta G_{bulk} = RT \ln \left[\frac{Q}{K} \right] \quad (21)$$

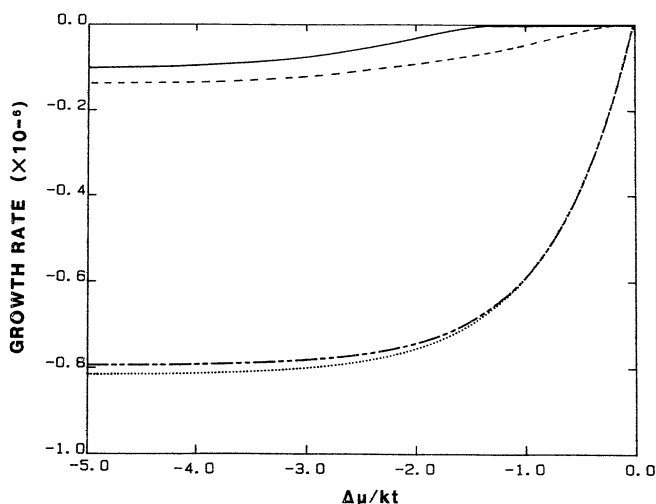


Figure 11 - Dependence of the dissolution rate on the dissolution mechanism as determined by Monte Carlo simulations. The X-axis is the saturation state, with 0 at equilibrium and becoming more undersaturated with more negative values of $\Delta\mu/kT$, and more rapid dissolution rates along the Y axis from 0 to -1. Defect free surface;

----- step at screw dislocation only; strain field around dislocation only; - . - . - . step and strain field around dislocation. (from Blum and Lasaga, 1987)

and μ_s is the shear modulus, b is the magnitude of the dislocation Burger vector, $\bar{V}$ is the molar volume, and K_{orient} is a constant related to the orientation of the dislocation. Lasaga and Blum (1986) suggest that the presence or absence of etch pits may be used as an indicator of solution saturation state in soils and ground water. This effect has been observed experimentally by Burch et al. (1993) for albite and by Brantley et al. (1986) for quartz in soils.

The observation of extreme etch pitting in virtually all feldspars which have undergone extensive dissolution suggests that a large amount of the total dissolution is occurring at etch pits. However, Blum and Lasaga (1987) suggested that dislocation density would have a minimal effect on the overall dissolution rate of quartz and other silicates based upon Monte Carlo model results. Murphy (1989) studied the dissolution rate of sanidine with low and high dislocation densities, and found no difference in the dissolution rates. Similar experimental results were found for quartz (Blum et al., 1990), rutile (Casey et al., 1988) and calcite (Schott et al., 1989). All of these experiments were conducted far from equilibrium. Blum et al. (1990) predicted on theoretical grounds that dislocations should have a larger effect on the overall dissolution rate close to equilibrium.

Burch et al. (1993) conducted albite dissolution experiments at pH 8 and 80°C varying the solution composition over a wide range of saturation states (fig. 12). They observed a dramatic decrease in the dissolution rate of albite as they approach equilibrium, with an abrupt decrease in the dissolution rate at $\Delta G_r = -6$ kcal/mol, which corresponds to a Q/K of $10^{-4.4}$. Thus, the solution saturation state can significantly depress the dissolution kinetics of albite, even in very dilute solutions. They point out that the shape of this curve is inconsistent with the classical TST formulation of the rate law. However, the abrupt transition in dissolution rate occurs approximately at the ΔG_{crit} predicted for the opening of etch pits, and examination of the experimental material with SEM reveals etch pits only in the most undersaturated experiments. A similar dependence of the gibbsite dissolution rate on solution saturation state was observed by Nagy and Lasaga (1992), and also attributed to the opening of dislocations.

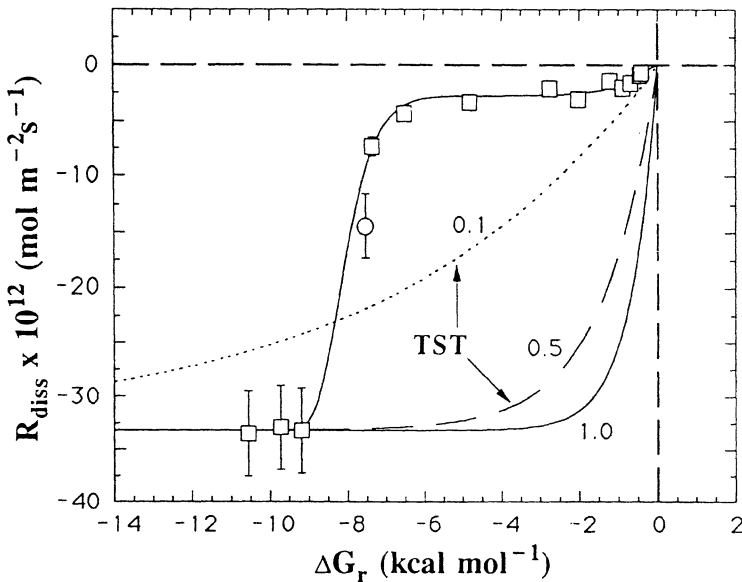


Figure 12 - Experimentally determined dissolution rate of albite as a function of solution saturation state. $\Delta G_r = 0$ at equilibrium and grows more negative at greater undersaturation. More negative values of R_{diss} indicate increasing dissolution rates (from Burch et al., 1993).

3.3.3. Numerical Models of Dissolution Kinetics - There is currently a difficulty in relating macroscopic effects, such as dislocations, impurities, and solution saturation state to molecular scale models such as those described by surface speciation and TST models. The most promising approach to including effects at both the molecular and macroscopic scale are numerical simulations. Two approaches have been proposed; Monte Carlo simulations (e.g. Gilmer, 1980; Blum and Lasaga, 1986; Wehrli, 1989) and molecular dynamics simulations (e.g. Lasaga, 1990). The Monte Carlo approach assigns relative probabilities to each molecular reaction which can occur on the surface. The relative reaction probabilities can be estimated from ΔH of reaction (not the activation energy), and can therefore be easily adjusted for small change in the energetics of different types of sites. The simulation progresses by taking small time steps and allowing reactions to occur randomly at each site on the surface, scaled by the relative probability of each particular type of site reacting. The use of relative probabilities allows the description of a large number of different types of sites on the surface without needing detailed knowledge of the mechanism or activation energy for the elementary reactions. This may include a wide range of subtle differences in the energy, such as in the strain field around a dislocation (Blum and Lasaga, 1986) or small variations in composition. Use of the Monte Carlo method using random probabilities avoids having to solve large systems of simultaneous equations.

Molecular dynamics (MD) simulations model a chemical system by calculating the time averaged motions of atoms to predict the behavior of a macroscopic system. The general MD scheme places several hundred to thousand atoms (limited by computer capacity) with arbitrary initial velocities in a box of finite size but with periodic boundary conditions. All of the interatomic forces between the atoms are calculated, and new velocities and positions are predicted for some small time step in the future. The atoms are then moved to the new positions and the calculation of interatomic forces is repeated. In this manner, the motions of the molecules can be accurately modeled. Reactions occur when the random fluctuations in the localized energy of a molecular cluster exceeds the activation energy of reaction. This often occurs when the translational energy of one cluster is effectively transferred to a vibrational mode of another cluster, providing enough energy to break the bond. In order for MD simulations to accurately reflect these types of atomic interactions, the time step used during the simulations must be less than 1/5 to 1/10 of the vibrational period. For silicates, the time step is typically 10^{-15} sec. Typical simulations utilize several thousand time steps, and therefore simulate a total time of 10^{-11} to 10^{-12} sec. For a dissolution rate of 10^{-15} mol/cm²/sec (e.g. albite at ~pH 3), the surface retreat rate is $\sim 4 \times 10^{-13}$ cm/sec. Treating the top 1 Å of the bulk crystal as the surface, the average residence time for any individual Al or Si atom on the surface before dissolving into solution is $\sim 10^5$ sec. Thus, the odds of observing even one dissolution event during a MD simulation is minuscule (~ 1 in 10^{15}), and I don't believe MD will be a useful technique for the direct modeling of feldspar dissolution kinetics. However, MD may be extremely useful in quantifying the structure of the hydrated feldspar surface, and perhaps the configuration and kinetics of the rapid exchange and adsorption reactions on the feldspar surface which may proceed the dissolution reaction.

4. Field Measurements of Feldspar Weathering Rates

The motivation for much of the work on feldspar dissolution and weathering rates is to develop the ability to predict feldspar dissolution rates in natural environments, and how variables such as acid rain and climatic change will effect those rates. A critical step in this endeavor is the comparison of field estimates of feldspar weathering rates with laboratory measured dissolution rates. There are two approaches which have been used to quantify natural plagioclase weathering rates in soils. Paces (1973), Velbel (1985,1992), Schnoor (1990) and Swoboda-Colberg and Drever (1993) estimated feldspar weathering rates from mass balance calculations of natural systems. White et al. (1992, in prep) estimated oligoclase weathering rates

from the change in abundance of plagioclase in a series of soils of different ages. All the studies agree that natural weathering rates are 10-3000 times slower than predicted from experimentally determined dissolution rates. Reproducibility of experimentally determined rates between studies is generally less than one order of magnitude, suggesting these differences are real.

A major uncertainty in the earlier studies of Paces (1973) and Velbel (1985) was the estimation of feldspar surface areas. White et al. (in prep.) directly determined the BET surface areas of weathered plagioclase. Schnoor (1990) and Swoboda-Colberg and Drever (1993) conducted dissolution measurement on material from the soils, and normalized the results per unit mass, eliminating the uncertainty introduced by surface area determination. In all these cases, significant differences between field and experimental feldspar dissolution rates were observed.

Many explanations have been advanced to explain the discrepancy between field and experimental feldspar dissolution rates. Several of the stronger arguments are:

- 1) Soil temperatures are typically less than experimental temperatures of 25°C, and lower soil temperatures should depress natural weathering rates. However, the effect of temperature is estimated to be about a factor of 5, and is not sufficient to explain all of the discrepancy natural and field rates.

- 2) Dissolution experiments are typically run for only a few thousand hours. A small volume of more rapidly solubilized material at high energy sites such as dislocations or impurities may elevate laboratory rates, perhaps for years. In the field, more reactive material has already been removed, usually by thousands of years of weathering, resulting in lower net dissolution rates. In addition, experiments commonly use unusually pure and defect free feldspar samples, which may not accurately represent common feldspars in igneous and metamorphic rocks. However, the data of Schnoor (1990) and Swoboda-Colberg and Drever (1993) in which they used the field material in their dissolution experiments strongly argue against these explanations.

- 3) The presence of higher solution concentrations of Fe and Al in natural systems may poison the feldspar surface, decreasing field weathering rates. Chou and Wollast (1985) and Amrhein and Suarez (1992) report that increasing Al concentration depresses the dissolution rate of albite and anorthite, respectively. Blum and White (1992, in prep) analyzed weathered feldspar grain surfaces with XPS, and found trace amounts of Fe³⁺ on the surface of all weathered grains as a widely dispersed coating <5Å in thickness. This is consistent with Fe adsorption at charged sites on the surface, which may poison surface sites. There is currently no quantitative evaluation of the effects of Al and Fe adsorption in natural systems on feldspar dissolution rates.

- 4) Soil solution compositions may be thermodynamically close enough to saturation with respect to feldspars as to reduce the dissolution rate. Velbel (1989) evaluated this effect in terms of a linear dependence between the dissolution rate and $\exp(1-\Delta G_{\text{rxn}}/RT)$ (see Nagy et al., 1991 for derivation), and concluded that this effect was negligible. However, Burch et al. (1993) experimentally found a much higher dependence of the albite dissolution rate on saturation state than the thermodynamic effect used by Velbel (1989). Burch et al. (1993) argue that their measured depression of the dissolution rate of albite by a saturation state effect can explain the discrepancy between field and experimental feldspar dissolution rates.

- 5) Fluid flow in the vadose zone of soils may be extremely heterogeneous (e.g. Glass et al., 1988; Hornberger et al., 1990, 1991; Booltink and Bouma 1991; Gee et al., 1991). The overwhelming proportion of fluid flow in soils may occur along very restricted preferential flow paths (often called macropores). This may leave most of the mineral surface area located in hydrologically isolated micropores, which may not contribute significantly to the mineral dissolution rate. Solutions moving downward through a soil profile and eventually out of the watershed may actually contact only a small proportion of the mineral surface area present in the soil profile, resulting in a much lower weathering flux than predicted based upon the total mineral surface area in the soil profile. This explanation is proposed by Schnoor (1990), Velbel (1993) and Swoboda-Colberg and Drever (1993), and is probably the most widely favored explanation. Velbel (1993) argues that typically 90-99.9% of the mineral surface area is located

in isolated micropores, and are not participating in weathering reactions which contribute solutes to solutions flowing out of the watersheds.

The concept of preferential fluid flow and isolated microporosity in soils may be the dominant process controlling the observed low natural weathering rates, but is not in itself sufficient. Hysteresis in the permeability of unsaturated media may result in transient preferential flow regions (fingering), even in uniform porous media (Hill and Parlange, 1972; Glass et al., 1989a,b,c, 1990). However, this is a thermodynamically unstable situation. In long lived systems such as soils, differential matrix (or capillary) pressure will eventually fill all the micropores, and these micropores will be the last areas to empty of solution during drying of the soil. Micropores, therefore, will almost always remain filled with solutions, although they may be isolated solutions, both hydrologically and chemically. Weathering (i.e. feldspar dissolution and clay precipitation) will progress in these micropores until some mechanism, probably related to either the proton balance or the accumulation of solutes within the micropore, retards feldspar dissolution to a very low rate. The weathering reactions may not proceed again until the solution in that micropore becomes hydrologically connected, and the solution is flushed. However, there must be a chemical mechanism which is retarding the feldspar dissolution rate. The cause of the retardation in feldspar dissolution rate, however, may not be reflected in the chemistry of sampled soil solutions or in the fluxes out of the watershed.

5. Summary

5.1. EXPERIMENTAL DATA

The dissolution of feldspar is controlled by rate of reactions at the mineral-surface interface, not by diffusion through a protective surface layer. A thick Si-rich surface layer does form in strongly acidic solutions, but this layer is too porous and loosely bound to impede the dissolution reaction kinetics. Albite and K-feldspar have similar dissolution kinetics at $\text{pH} < 6$, with the dissolution rate $R \propto [\text{H}^+]^{-0.5}$. In the basic pH region albite has a pH dependence of $R \propto [\text{OH}^-]^{-0.3}$, with K-feldspar dissolution rates having a stronger dependence on $[\text{OH}^-]$ and absolute rates approximately 10 fold slower than albite. In the acidic region the plagioclase series has a pH dependence of $R \propto [\text{H}^+]^{-0.5}$ for An_{0-70} , but there is then a transition of increasing values in the exponent until $R \propto [\text{H}^+]^{-1.0}$ for anorthite. This trend is reflected in the dissolution rates of plagioclase of different An content at the same pH. The dissolution rate increases gradually with increasing Ca content until $\sim \text{An}_{75}$, with a large increase in the dissolution rate of plagioclase between the compositions An_{75} and An_{90} . The reproducibility of feldspar dissolution rates is generally within $10^{0.7}$ between investigations and within a factor of < 2 within the same laboratory.

5.2. FELDSPAR DISSOLUTION MECHANISMS

All the feldspars appear to have two different dissolution rate mechanisms, a proton promoted mechanism in the acid region ($\text{pH} < 5$) and a hydroxyl promoted mechanism in the basic region ($\text{pH} > 7.5$). It is possible there is a separate pH independent mechanism in the neutral pH region.

5.2.1. Feldspar Dissolution in the Acid Region - There is general agreement that feldspar dissolution in the acid region occurs by selective attack on the Al sites in the tetrahedral framework, and the rate limiting process must involve the hydrolysis of the Al-O-Si bond. There are several observations supporting this conclusion: (i) The presence of a Si-rich layer at low pH indicates the strong preferential removal of Al; (ii) Feldspars of all compositions form cation depleted layers on the surface in acidic solutions, so that the feldspar surface in contact with solution is always hydrogen-feldspar. Albite and K-feldspar have similar Al/Si ratios and have similar dissolution behaviors. The plagioclase dissolution rate increases with increasing anorthite

content. The major change in the structure of the plagioclase surface layer in contact with solution with increasing An content is the increasing Al/Si ratio, implying it is Al which is destabilizing the structure; (iii) There is clearly an increase in the positive surface charge of feldspars with increasing $[H^+]$. The zero point of charge for SiO_2 is $\sim pH\ 2$, implying that very little Si on the feldspar surface should be protonated in the acid region. Al(IV) has a zero point of charge of 6.8, and is the more probable site of adsorption. The change in the surface speciation of Al with pH also points to Al as the critical species in the dissolution mechanism.

5.2.2. Feldspar Dissolution in the Basic Region - Feldspar dissolution in the basic region is less well understood than the acidic region. Blum and Lasaga (1991) proposed a mechanism very similar to the acid region (eq. 12), but with a negatively charged $>Al-O^-$ surface species rather than a positive charged surface species. However, the difference in dissolution rates between albite and K-feldspar and the evidence of Wollast and Chou (1992) for Na readsorption by albite suggest that cation occupancy in the lattice sites may influence feldspar dissolution kinetics in the basic pH region. Finally, the argument of Brady and Walther (1989) for deprotonation of Si in the basic region controlling the dissolution rate cannot be conclusively refuted. While soils in many of the acid-rain impacted regions of the world happen to be acidic, most surface and ground waters and many soil solutions have a neutral to basic pH, and resolving feldspar dissolution in the neutral and basic pH regions is of considerable practical interest.

5.2.3. Weathering Rates of Feldspars - Field measurements of plagioclase dissolution rates from watershed mass-balance studies and from changes in the abundance of plagioclase in soils of different ages indicate that feldspar weathering is one to three orders of magnitude slower than predicted from laboratory studies. The leading explanation for this effect is the isolation of a large proportion of the feldspar surface area in isolated micropores. Alternative explanations include; (i) adsorption of inhibitors, of which Al and Fe are the most likely, (ii) the high saturation states of soil solutions, and (iii) experimental artifacts in the dissolution experiments, particularly the short duration of the experiments relative to geologic time scales. The reconciling of natural and experimental feldspar dissolution rates is a critical step before feldspar dissolution kinetics can be used reliably in predictive models. Addressing this problem is currently the focus of much of the work in mineral dissolution kinetics, both in field and laboratory studies.

6. References

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