RELATION BETWEEN RATES OF ALUMINOSILICATE MINERAL DISSOLUTION, pH, TEMPERATURE, AND SURFACE CHARGE

JOHN V. WALThER
Department of Geological Sciences, Southern Methodist University, Dallas, Texas 75275

ABSTRACT. At 25°C surface charge on Al₂O₃ and SiO₂ is directly proportional to the rates at which these oxides dissolve with the minimum dissolution rate per unit surface area occurring at their pH of zero point of charge, 8.4 and 2.5, respectively. As charged surface complexes polarize and therefore weaken the Al-O and Si-O surface bonds, the first order relation between surface charge and dissolution rate for aluminosilicates can be predicted by combining the effects on Al₂O₃ and SiO₂. This analysis explains the pH dependence of the initial non-stoichiometric dissolution of aluminosilicates such as that documented for kaolinite and albite as well as the dynamics of stoichiometric and steady-state Al and Si detachment at both low and high pH where rates increase relative to near neutral pH solutions. Aluminosilicates do not dissolve with a minimum rate at their pH of zero point of charge but where the sum of the absolute value of charge from Al surface sites plus the absolute value of charge at Si surface sites is a minimum. It is argued that the ratio of Al and Si surface charge sites changes during the initial nonstoichiometric period of detachment converging to the ratio needed for stoichiometric dissolution of the aluminosilicate.

The temperature dependence of dissolution rate appears to be directly correlated with the increase in surface charge with temperature at constant pH. In alkaline solutions the log of the concentration of negative Si surface complexes on silicates, and, therefore, log dissolution rate is a linear function of pH whose slope increases with increasing temperature from 0.3° at 25° to 0.6° at 80°C. These slopes display Arrhenius behavior; decreasing linearly with the inverse of temperature. However, it is postulated that at supercritical temperatures the neutral surface complexes of Al and Si become dominant over an increasing range of pH at near neutral pH with increasing temperature. Under these conditions the rates of mineral dissolution become nearly independent of pH except at extreme pH.

INTRODUCTION

Because reaction rates between silicate minerals and aqueous solutions are generally controlled by processes at the mineral surface, one needs to understand surface reactions in order to understand the rate
limiting steps in silicate dissolution. Therefore, numerous studies have documented the rates of surface reactions in various solutions with most investigating the pH dependence (Lagache, 1965; Busenberg, 1978; Holdren and Berner, 1979; Schott, Berner, and Sjöberg, 1981; Furrer and Stumm, 1986; Knauss and Wolery, 1986, 1988; Amrhein and Suarez, 1988; Carroll-Webb and Walther, 1988; Dove and Crerar, 1990; Brady and Walther, 1990; Carroll and Walther, 1990; Casey, Westrich, and Holdren, 1991; Rose, 1991; Vogelius and Walther, 1991; Wieland and Stumm, 1992; Burch, Nagy, and Lasaga, 1993; Hellmann, 1994; Oxbergh, Drever, and Sun, 1994; Ganor, Mogollón, and Lasaga, 1995; to name some of the experimental studies). From the concept of local charge neutralization the positive cation valence in a mineral can be considered to be equally distributed over the coordinating oxygens while the negative oxygen valence is equally distributed over the coordinate cations. For a mineral surface with oxygen in contact with an aqueous solution the negative charge is balanced by an adsorbed layer of protons and other charged aqueous species at the surface (Davis and Leckie, 1978; Westall and Hohl, 1980; Schindler, 1981; Stumm and Morgan, 1981; Sposito, 1983, 1984). This adsorbed layer causes the development of a diffuse layer of ions of opposite charge in the solution adjacent to the surface. A region of charge separation that can be modeled as an electrostatic double layer is produced (Stumm, 1992). The development of this charge gradient and adsorbed complexes at the mineral surface alter the bonding structure of the cation to the oxygen atoms at the surface (Zinder, Furrer, and Stumm, 1986). Depending on the nature of the adsorbed layer, differences in bond energy can lead to differences in rates of dissolution and influence the nature of the initial non-stoichiometric dissolution rates of aluminosilicates. One of the implications of the initial non-stoichiometric dissolution behavior of aluminosilicates is that Si, Al, and other cations at the surface react, to a first approximation, independently with the aqueous solution and should not be strongly influenced by the nature of neighboring cations, except for their contribution to changes in the electrostatic energy in the double layer environment.

The initial non-stoichiometric dissolution of an aluminosilicate continues until its surface molecular structure evolves to where the cation that is initially released at greater than stoichiometric rates decreases its surface concentration so that its rate of release to the aqueous solution per unit surface area decreases to equal the rate of the cation released initially at the lowest rate, and the rates become stoichiometric. For instance, in acid solutions the preferential loss of the non-silicon cations can cause the dangling silanol groups to condense to siloxane bridges at the surface (Casey and others, 1993) producing a Si rich surface layer. Surface layers depleted in alkalis and Al or Si develop whose composition is pH dependent (Chou and Wollast, 1984). Apparently these layers do not inhibit the long-term rate of reaction as reactants are released to solution at a constant rate with respect to time rather than the square root
of time signifying a diffusional rate limiting process. Also the constant release rate implies there is no significant change in surface area as a function of time. It would appear that BET gas adsorption measurements that have been interpreted as indicating increased surface area as a function of time during dissolution of feldspars (Stillings and Brantley, 1995) need to be re-assessed. The interpretation of BET surface area measurements is a complex topic (Anbeek, 1992). Perhaps the N\textsubscript{2} gas used in the BET measurements is also adsorbing to the atoms in the surface layer as well as on the feldspar, or it may be that the leached surfaces partly separate from the reacted feldspar during drying, exposing new surface area (see Casey and others, 1990). Presumably, the surface layer reaches a steady-state thickness and composition given sufficient time. Surface controlled dissolution then becomes steady-state and stoichiometric. That is, the ratio of surface cations in the double layer changes so that for each cation its surface concentration times its rate of detachment converges with time to the stoichiometric ratio in the mineral if the composition of the aqueous solution with which it reacts remains constant (Schnoor, 1990; Xie and Walther, 1992).

Rates of dissolution increase in acidic and basic solutions relative to near-neutral solutions because multi-cation silicates form increasing concentrations of charged surface complexes as pH is lowered or raised relative to near neutral pH conditions. These charged surface complexes focus the bonding electron cloud, polarizing the surface cation-oxygen bonds (Zinder and others, 1986). Therefore, the surface cation-oxygen bond is weakened leading to a greater probability of surface detachment, that is rate of dissolution (Stumm, Furrer, and Kunz, 1983). Brady and Walther (1989, 1992) have argued that for silicates, the negatively charged surface complex at the Si surface site determines the dissolution rate at high pH, whereas the positively charged surface complex at the non-Si cation site establishes the dissolution rate at low pH. I will consider these observations in more detail below.

**Proton Adsorption and Desorption**

Surface complexes can be related to protons in the aqueous solution in the diffuse layer through the following reactions and their equilibrium constant expressions (Schindler and Stumm, 1987):

\[
>M-\text{OH}_2^+ = >M-\text{OH} + H^+ \quad K_{(1)} = \frac{\gamma_0 [>M-\text{OH}] a_{H^+}}{\gamma_+ [>M-\text{OH}_2^+]}
\]

\[
>M-\text{OH} = >M-\text{O}^- + H^+ \quad K_{(2)} = \frac{\gamma_- [>M-\text{O}^-] a_{H^+}}{\gamma_0 [>M-\text{OH}]}
\]

where \(>M-\text{OH}_2^+, >M-\text{OH}, \) and \(>M-\text{O}^-\) stand for the positively, neutral, and negatively charged surface site complexes at the M cation site on the mineral surface. Their activity coefficients relative to standard state conditions are given by \(\gamma_+\), \(\gamma_0\), and \(\gamma_-\) respectively. The brackets are used
to denote the concentration of these surface sites using moles per cm$^2$ of surface. $a$ stands for the activity of the subscripted aqueous species. The subscript dl is used to indicate it is the concentration and Gibbs free energy of H$^+$ per mole in solution in the diffuse layer at the surface that is required. This will be different from the concentration and energetics of H$^+$ in the bulk solution.

The standard state for surface species is a hypothetical state of one mole of surface sites per cm$^2$ behaving as though they are neutral with no electrostatic interactions with other charged species on the surface or in solution. This solution is a one molal singly charged electrolyte solution referenced to infinite dilution at the pressure and temperature of interest. Thus the activity of the surface species contains effects of both concentration and its residence in an electrical potential field. As a first approximation one can take the difference in the energies of the uncharged hydroxyl and the protonated or deprotonated hydroxyl sites at the surface as the electrostatic energy needed to add or remove an H$^+$ from the surface, respectively. This assumes energetic effects of concentration differences in solution and dispersive interaction between sites are similar for the three sites so the ratios, $\gamma_0/\gamma_+$ and $\gamma_-/\gamma_0$, are equal to $\exp (-\psi^0/RT)$. $F$ stands for Faraday's constant, $T$ is temperature in K, $R$ denotes the gas constant, and $\psi^0$ represents the electrostatic potential at the surface relative to the bulk solution (Chan, Perram, and White, 1975). Because the charging is non-Nernstian and $\psi^0$ is not directly measurable and depends on the aqueous solution's ionic strength, a model must be used to determine the activity coefficient ratios. When considering the effects of $\gamma_0/\gamma_+$ and $\gamma_-/\gamma_0$ on the energetics between neutrally and singly charged surface sites I will use the notation:

$$\Delta \gamma = \gamma_0/\gamma_+ = \gamma_-/\gamma_0 = \exp (-\psi^0/RT)$$

for the development below.

The standard state for protons in solution in the double layer surface phase, $H^+_{dl}$, is taken as a hypothetical one molal solution of H$^+$ at infinite dilution in bulk H$_2$O. This standard state is chosen because the activity of H$^+$ can be measured and the energetic difference of H$^+$ between the bulk solution and infinite dilution can be readily calculated so that the conventional standard state Gibbs energy difference between H$^+$ and other charged solution species can be determined. Because of the equilibrium between H$^+$ at the surface and in the bulk solution, the chemical potential and therefore the activity of H$^+$ in the surface environment is the same as in the bulk solution. That is, $a_{H^+}$ is equal to $a_{H^+}$, the activity of H$^+$ in the bulk solution, when referenced to the same standard state. For the remainder of the analysis I will use the notation $a_{H^+}$ to indicate the activity of H$^+$ no matter which environment it is in. This does not mean H$^+$ concentrations are the same in the two environments. The surface
excess concentration in the double layer over the value in the bulk solution per unit surface area, $\Gamma_{H^+}$, can be calculated from:

$$\Gamma_{H^+} = \int_0^\infty C_{H^+}(x) \, dx$$

(4)

where $x$ is the distance from the surface and $C_{H^+}(x)$ is the molar concentration gradient of $H^+$ as a function of $x$. $H^+$ will have a Gibbs energy per mole dependent on its distance from the surface because of the gradient in electrical potential. This leads to a difference in the concentration of $H^+$ between the surface and bulk solution so that the activity remains constant. That is:

$$a_{H^+} = \gamma_{H_{bs}^+}[H_{bs}^+] = \gamma_{H_{dl}^+}[H_{dl}^+]$$

(5)

where $\gamma_{H_{bs}^+}$ and $[H_{bs}^+]$ are the activity coefficient and molality of $H^+$ in the bulk solution whereas $\gamma_{H_{dl}^+}$ and $[H_{dl}^+]$ are the activity coefficient and molality of $H^+$ in the double layer, respectively. Note that the values of $\gamma_{H_{dl}^+}$ and $[H_{dl}^+]$ are a function of $x$.

It is not universally accepted that the stoichiometry of surface charging as a function of pH is appropriately represented by eqs (1) and (2). The experimental observations have been described by assuming only one acidity equilibrium with no neutrally charged complexes (Parks, 1965) as well as modeled with a fractional complex charge (Heimstra, van Reimsdijk, and Bolt, 1989). I will use the formalism of three types of surface sites and unit charge on complexes. In the model presented, one can change the concentration of sites on the surface to obtain the effects of a unit of charge if sites are best described with fractional electrostatic charge. Because the metal centers are typically bonded to more than one surface oxygen, a more chemically explicit representation of reactions (1) and (2) would be to model them as diprotic acid groups. Reaction (1) and (2) could then be written as:

$$>M < \text{OH}_2^{+1} \text{OH} = >M < \text{OH}_0^{0} \text{OH} + H_{dl}^+$$

(6)

and

$$>M < \text{OH}_0^{0} \text{OH} = >M < \text{O}_0^{-1} \text{OH} + H_{dl}^+$$

(7)

respectively (for example: House and Hickinbotham, 1992).

There are many assumptions and, therefore, many different surface complex models to account for the charge separation and the nature of the electrostatic double layer. Two of the most widely used are the constant capacitance (Schindler and Kamber, 1968; Schindler and Stumm, 1987) and the triple layer (Davis and Leckie, 1978; Hayes, ms) models.
These models of charge separation dictate the form of $C_{H^+(x)}$ in eq (4) and therefore specify the energy difference per mole of $H^+$ as a function of distance from the surface.

Given the discussion above, the equilibrium constant for reaction (1) can be rewritten as:

$$K_{(1)} = \frac{[>\text{M-OH}]_Y H^+ [H^+_{bs}]_Y \Delta \gamma}{[>\text{M-OH}^+]} = K_{(1)}^\text{app} Y H^+_{bs} \Delta \gamma$$  \hspace{1cm} (8)

and the equilibrium constant for reaction (2) rewritten as:

$$K_{(2)} = \frac{[>\text{M-O}^-]_Y H^+ [H^+_{bs}]_Y \Delta \gamma}{[>\text{M-OH}]} = K_{(2)}^\text{app} Y H^+_{bs} \Delta \gamma$$  \hspace{1cm} (9)

where $K_{(1)}^\text{app}$ and $K_{(2)}^\text{app}$ stand for the surface equilibrium concentration ratios (the “apparent” equilibrium constants):

$$K_{(1)}^\text{app} = \frac{[>\text{M-OH}]_Y [H^+_{bs}]}{[>\text{M-OH}^+]}$$  \hspace{1cm} (10)

and

$$K_{(2)}^\text{app} = \frac{[>\text{M-O}^-]_Y [H^+_{bs}]}{[>\text{M-OH}]}$$

Note that the values of $K_{(1)}^\text{app}$ and $K_{(2)}^\text{app}$ change with changes in the solution composition, and therefore, they are not thermodynamic constants (Schindler and Stumm, 1987).

The solution pH where the surface has zero net charge in the absence of adsorbed ions other than $H^+$ and $OH^-$, $pH_{zpc}$, the pH of the zero proton condition (Sposito, 1984) is given by:

$$pH_{zpc} = 0.5(pK_{(1)} + pK_{(2)})$$  \hspace{1cm} (12)

At the $pH_{zpc}$ $\Delta \gamma = 1$ so $K_{(1)}^\text{app}$ will equal $K_{(1)}$, and $K_{(2)}^\text{app}$ will equal $K_{(2)}$ if $Y H^+_{bs} = 1$. If $Y H^+_{bs}$ cannot be taken as one then its value must be combined with the experimentally derived values of $K_{(1)}^\text{app}$ and $K_{(2)}^\text{app}$ to determine $K_{(1)}$ and $K_{(2)}$. Any departure of $\gamma H^+_{bs}$ from unity can generally be determined with the aid of Debye-Hückel charging theory from the infinitely dilute standard state. Values of $K_{(1)}^\text{app}$ and $K_{(2)}^\text{app}$ extrapolated to the $pH_{zpc}$ are often referred to as “intrinsic constants.” In this communication, with the standard state chosen for surface species, these intrinsic constants are equivalent to the values for the equilibrium constants, $K_{(1)}$ and $K_{(2)}$.

To determine surface charging on multi-cation silicates requires knowledge of changes in $K_{(1)}^\text{app}$ and $K_{(2)}^\text{app}$ as a function of pH for each cation type, $M$, exposed on the mineral surface. In fact, the variety of different types of cation-oxygen bonds in aluminosilicates can cause differences in
the protonation and deprotonation of the various types of surface sites of the same cation on the mineral. One would need to determine [\(>\text{M-OH}^+\)] and [\(>\text{M-O}^-\)] for each type of oxygen coordination that exists for each cation bond type exposed on the surface. For example in sheet silicates, surface cations on a basal sheet may protonate and deprotonate differently from the same cation sites on the mineral edges because of local differences in cation-oxygen bonding (Wieland and Stumm, 1992). However, in the present state of knowledge for multi-cation silicates, it is reasonable to assume that surface species act independently and that all the different types of sites of a particular cation behave similarly (Carré, Roger, and Varinot, 1992). With this assumption one can describe the charging behavior of complex silicates by averaging the values for charging of sites at cations on simple oxides (Parks, 1967).

**CATION SURFACE SITES**

For the analysis below, I will approximate the behavior of Si surface sites on multi-cation silicates by considering Si sites on quartz and silica gels. These Si surface sites at 25°C have a \(\text{pH}_{zpc}\) of 2.5 ± 0.6 (Parks, 1967) and \(\text{pK}_{(2)}\) near 6.8 (Schindler and Kamber, 1968). Using these values with eq (12) gives \(\text{pK}_{(1)} = -1.8\). Using \(\text{pK}_{(1)} = -1.8\) and \(\text{pK}_{(2)} = 6.8\) with eqs (8) and (9) indicate that the Si surface sites will carry little charge at low pH but become increasingly negatively charged as pH increases to 6.8 and above. Therefore, Si sites should not significantly contribute to aluminosilicate surface charge at acid conditions (above a pH = -1.8) but become increasingly important as negative charge centers with pH increases in alkaline solutions.

The cation sites on non-silicate oxides at 25°C have a \(\text{pH}_{zpc}\) at significantly higher pH than the Si sites. For instance, Al surface sites on \(\text{Al}_2\text{O}_3\) have a \(\text{pH}_{zpc}\) of about 8.4, with \(\text{pK}_{(1)} = 8.0\) and \(\text{pK}_{(2)} = 9.0\) (Huang and Stumm, 1973; Carroll-Webb and Walther, 1988). In general, values determined for the \(\text{pH}_{zpc}\) of Al surface sites on Al oxides and hydroxides are reported to be between 7.0 and 8.7 (Schindler and Stumm, 1987). The 25°C \(\text{pH}_{zpc}\) of the Mg site on \(\text{Mg}_8\text{O}\) is about 12 (Parks, 1965), and the difference between \(\text{pK}_{(1)}\) and \(\text{pK}_{(2)}\) is also about one. In general for the major rock-forming non-silica oxides and hydroxides, surface sites have a \(\text{pH}_{zpc}\) greater than 7 with \(\text{pK}_{(2)} - \text{pK}_{(1)}\) less than 3. Therefore, the non-Si surface sites on a multi-cation silicate tend to have little charge at high pH near their \(\text{pH}_{zpc}\) but will have significant positive charge at low pH. As pointed out by Brady and Walther (1989) as a first approximation to understanding surface charging as a function of pH for multi-cation silicates one can separately determine the concentration of the positively charged non-Si surface sites at low pH and the negatively charged Si sites at high pH.

Because of the great abundance of aluminosilicates in the Earth’s crust and the observation that alkalis (Garrels and Howard, 1959; Wollast and Chou, 1992) and alkaline earth cations (Rimstidt and Dove, 1986; Xie and Walther, 1994) are rapidly leached from the silicate surface and
replaced by protons, I will construct a simple model for aluminosilicate surface charging by regarding Al as the non-silica cation on the mineral surface. Therefore at low pH, the charge on an aluminosilicate will be largely due to \( >\text{Al-OH}\_2^+ \) whereas the Si sites will carry the charge as \( >\text{Si-O}^- \) in alkaline solutions.

**DEPENDENCE OF SURFACE CHARGE ON pH**

In order to examine the behavior of aluminosilicate surface charging in detail one can assume \( \gamma_{\text{H}_2\text{O}^+} = 1 \) and make the substitution given by eq (3) into eqs (8) and (9). The logarithm of \( K_{(1)} \) and \( K_{(2)} \) then become

\[
\log K_{(1)} = \log K_{(1)}^{\text{app}} - \frac{F\psi^0}{2.303RT}
\]

and

\[
\log K_{(2)} = \log K_{(2)}^{\text{app}} - \frac{F\psi^0}{2.303RT}
\]

To continue the analysis of surface charging, a model of the electrical double layer needs to be stipulated. For present purposes a simple constant capacitance model can be used (Schindler and Kammer, 1968; Hohl and Stumm, 1976). This model assumes the electrical double layer is a parallel plate capacitor with a constant capacitance across the layer. For this case \( \Psi^0 = \sigma/C_i \) where \( \sigma \) is the surface charge and \( C_i \) is the integral capacitance in farads cm\(^{-2} \) of the surface layer charged by the ith surface species. At a pH below the \( \text{pH}_{zpc} \) where the only significant charged species is \( >\text{M-OH}\_2^+ \) the substitution of \( F[>\text{M-OH}\_2^+] \) for \( \sigma \) can be made yielding:

\[
\log K_{(1)}^{\text{app}} = \frac{F^2}{2.303RTC_+} [>\text{M-OH}\_2^+] + \log K_{(1)}
\]

Therefore assuming a constant capacitance, \( C_+ \), a plot of \( pK_{(1)}^{\text{app}} \) as a function of \( [>\text{M-OH}\_2^+] \) will be a straight line with a slope of \( -F^2/2.303RTC_+ \) and an intercept of \( pK_{(1)} \). Similarly, at a pH above the \( \text{pH}_{zpc} \) where \( >\text{M-O}^- \) is the only significant charged surface species, \( \sigma = -F[>\text{M-O}^-] \) and one has:

\[
\log K_{(2)}^{\text{app}} = -\frac{F^2}{2.303RTC_-} [>\text{M-O}^-] + \log K_{(2)}
\]

At constant temperature and integral capacitance a plot of \( pK_{(2)}^{\text{app}} \) as a function of \( [>\text{M-O}^-] \) will be a straight line. Thus the equilibrium constants, \( K_{(1)} \) and \( K_{(2)} \), can be derived from the linear extrapolation of \( K_{(1)}^{\text{app}} \) and \( K_{(2)}^{\text{app}} \) to the \( \text{pH}_{zpc} \) (Schindler and Gamsjäger, 1972), and the integral capacitance determined from the slope. For the analysis given below I let
\( \alpha_i \) stand for this slope defined for the ith charged species and integral capacitance as

\[
\alpha_i = \frac{Z_i F^2}{2.303 R T C_i}
\]

(17)

where \( Z_i \) is the charge valence of the ith charged surface species.

To continue the analysis the numerator and denominator of the right side of the expression given for \( K_{(1)}^{\text{app}} \) in eq (10) can be divided by the total number of surface sites per \( \text{cm}^2 \), \( S_T \). For a solution with a pH below the pH_{zpc} where only \( \text{M-OH}^+ \) and \( \text{M-OH} \) are significant, the logarithm of eq (10) is then:

\[
\log K_{(1)}^{\text{app}} = \log \left( \frac{1 - X_{\text{M-OH}^+}}{X_{\text{M-OH}^2}} \right) - \text{pH}
\]

(18)

where \( X_i \) is the mole fraction of the ith site on the surface. At a pH above the pH_{zpc} where \( \text{M-O}^- \) and \( \text{M-OH} \) are the dominate species the logarithm of eq (11) becomes

\[
\log K_{(2)}^{\text{app}} = -\log \left( \frac{1 - X_{\text{M-O}^-}}{X_{\text{M-O}^-}} \right) - \text{pH}
\]

(19)

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**Fig. 1.** A graph of the function \( \log \left(1 - \frac{X}{X} \right) \) indicating the near linearity of the function when \( X \) is between 0.2 and 0.8.
As shown in figure 1 the function \[ \log \left( \frac{1 - X}{X} \right) \] equals zero at \( X = 0.5 \) and varies nearly linearly with a slope of \(-2\) as a function of \( X \) between 0.2 and 0.8. As a first approximation one can assume that:

\[
\log \left( \frac{1 - X}{X} \right) = 1 - 2X \quad (0.2 < X < 0.8) \tag{20}
\]

Therefore, between a mole fraction of positively charged surface species of 0.2 and 0.8, eq (18) can be rewritten as

\[
\log K_{(l)}^{\text{app}} = 1 - 2X_{>\text{M-OH}_2^+} - \text{pH} \tag{21}
\]

so that combining eqs (15), (17), and (21) one obtains

\[
[\text{>M-OH}_2^+] = -\frac{1}{2/S_T + \alpha_+} \text{pH} + \frac{1 - \log K_{(l)}}{2/S_T + \alpha_+} \tag{22}
\]

and by similar arguments for \( \text{>M-O}^- \) when \( X_{>\text{M-O}^-} \) is between 0.2 and 0.8 eq (19) can be transformed to

\[
\log K_{(2)}^{\text{app}} = 2X_{>\text{M-O}^-} - 1 - \text{pH} \tag{23}
\]

so that

\[
[\text{>M-O}^-] = \frac{1}{2/S_T - \alpha_-} \text{pH} + \frac{\log K_{(2)} + 1}{2/S_T - \alpha_-} \tag{24}
\]

Therefore, at a constant ionic strength a plot of the concentration of charged species, \([\text{>M-OH}_2^+]\) or \([\text{>M-O}^-]\), should linearly depend on pH between a mole fraction of charged species of 0.2 and 0.8. The extent of the linear relation of the concentration of charged surface sites to pH given by eqs (22) and (24) can be assessed by examining oxide surface protonation data.

**SURFACE PROTONATION ON CORUNDUM AND QUARTZ**

Figure 2 plots 25°C values of surface protonation as a function of pH in 0.1 molar \(\text{NaNO}_3\) of \(\gamma\)-\(\text{Al}_2\text{O}_3\) determined by Furrer and Stumm (1986) and of \(\alpha\)-\(\text{Al}_2\text{O}_3\) reported by Carroll-Webb and Walther (1988) as triangles as well as protonation of quartz from Bolt (1957) and Brady and Walther (1992) as circles. The dashed-dot line extends the negative surface charge on \(\text{Al}_2\text{O}_3\) to higher pH (see below). Note that the surface protonation of \(\text{Al}_2\text{O}_3\) is a good linear function of pH between pH = 3.5 and 10, that is for \([\text{>Al-O}^-]\) and \([\text{>Al-OH}_2^+]\), above and below the \(\text{Al}_2\text{O}_3\) pH\(_{zpc}\), respectively. At a pH below the pH\(_{zpc}\) the relation between surface charge and pH shown by the solid straight line is computed from:

\[
[\text{>Al-OH}_2^+] = -5.4 \times 10^{-11} \text{pH} + 4.32 \times 10^{-10} \quad (3.5 < \text{pH} < 8.0) \tag{25}
\]
Fig. 2. Surface charge on $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ in moles per cm$^2$ times $10^{10}$ as a function of pH given by triangles and circles, respectively. The dashed-dot line is the proposed behavior of surface charge on $\text{Al}_2\text{O}_3$ due to $>\text{Al-O}^-$ at high pH. Open triangles are from Furrer and Stumm (1986), filled triangles from Carroll-Webb and Walther (1988), open circles from Bolt (1957), and filled circles from Brady and Walther (1992).

The linearity of the measurements indicates the measurements are probably within the range where the mole fraction of charged surface sites is between 0.2 and 0.8, and the other assumptions of the model are reasonable. In fact the measurements of Brady and Walther (1992, fig. 1) indicate the linearity of $[>\text{Al-OH}_2^+]$ exists to a pH of about 2.5 before it begins to increase approximately exponentially with decreasing pH. It is possible that with the increased rates of dissolution at low pH this exponential dependence is an artifact of significant concentrations of dissolved Al during the measurements at low pH. In this case the linearity may exist to even lower pH. $S_T$ must be above the greatest concentration of charged species shown in figure 2, that is, above $2.5 \times 10^{-10}$ moles cm$^{-2}$ or 1.5 sites per nm$^2$. It seems reasonable to suggest $S_T$ is approximately equal to the linear extension of eq (25) to pH 2.5 divided by 0.8 or 2.2 sites per nm$^2$.

The crystallographically determined concentration of cations on an oxide surface is generally on the order of 5 sites per nm$^{-2}$. In order to make these determinations one must specify how close to the surface the cation must reside in order to produce a surface site that can undergo H$^+$ exchange. For Si, site concentrations are generally calculated to be between 2 and 10 sites per nm$^{-2}$ (Iler, 1979; Schindler and others, 1976).
These values of surface site densities seem to be consistent with the linearity of the measurements shown in figure 2 and therefore the approximations made to obtain eqs (22) and (24).

The surface adsorption data for amorphous silica in 0.1 M NaCl from Brady and Walther (1992) and Bolt (1957) at high pH where >Si-O− surface sites become important can also be assessed from figure 2. Because the pK_{a(2)} of silica sites is near 6.8, one could argue that the data are consistent with a linear relationship for about 2 pH units on either side of pK_{a(2)}. This would be equal to a value of [>Si-O−] of about 1.0 × 10^{-10} mole cm^{-2} or 0.6 sites per nm^{-2} at pH = 8.8. However, as pH increases to 9, [>Si-O−] increases to an increasing degree. Unlike the increase in >Al-O_2{^+} on corundum at pH below 2.5 this increasing concentration of >Si-O− occurs before the Si surface sites have saturated with >Si-O−. This increased de-protonation at high pH probably occurs because there are strong nearest neighbor site interactions at high mole fractions of >Si-O−. The greatest concentration of negatively charged Si sites shown in Figure 2 is 4.4 sites nm^{-2}, and this is probably below the saturation of the surface with >Si-O− (Iler, 1979).

The increased rate of deprotonation of the Si surface sites with increasing pH at high pH is likely energetically similar to what happens with Si species in aqueous solutions. In aqueous solutions at high pH one observes the reaction:

\[ \text{H}_3\text{SiO}_4^{−} = \text{H}_2\text{SiO}_4^{2−} + \text{H}^+ \]  

proceeds to the right with increasing pH. The analogous surface reaction considering the site stoichiometry given in eq (7) is:

\[ >\text{Si}< \text{O}^{-1}_{\text{OH}} = >\text{Si}< \text{O}^{-2}_\text{O} + \text{H}_d^+ \]  

For the purpose of determining the relationship between concentration of charged species and rate of surface dissolution one can, somewhat arbitrarily, fit the values of [>Si-O−] shown in figure 2 to a log function to get a reasonably accurate representation of total surface charge as a function of pH. This is shown by the solid curved line in figure 2 and is given by:

\[ \log [>\text{Si-O}^{-}] = 0.3 \ \text{pH} - 12.67 \ \ (5 < \text{pH} < 12) \]  

**25°C DISSOLUTION RATES**

The charged surface complexes are reactants in, or are in equilibrium with, the reactants in, the reaction to form the activated complex in the rate limiting molecular reaction for cation detachment at an oxide surface (Wieland, Wehrli, and Stumm, 1988). If this reaction requires one charged surface species to form each activated complex, the number of charged surface species and the rate the cation is detached from the oxide should be linearly dependent. That is, the rate should be a
minimum at the pH$_{zpc}$ and increase linearly at pH above and below the pH$_{zpc}$ similar to the pH dependence for the charged surface complexes.

Shown in figure 3 are the measurements of corundum ($\alpha$-Al$_2$O$_3$) dissolution rate at ionic strengths of 0.005M, 0.025M, and 0.05M represented by diamonds, filled circles, and open circles, respectively, from Carroll-Webb and Walther (1988) as a function of pH. The inset is an expansion of the figure for the lower pH region. Furrer and Stumm (1986) have measured $\gamma$-Al$_2$O$_3$ dissolution rates. Their rates are about an order of magnitude greater than those shown in figure 3. Furrer and Stumm's determinations were made using reaction times of 50 hrs or less. Carroll-Webb and Walther also obtained rates that were an order of magnitude greater than their reported long-term rates when rates were calculated from solution compositions of less than 200 hrs. Carroll-Webb and Walther's rates determined from the linear increase in solution compositions between 200 and 1000 hrs appear to reflect more closely the long-term steady-state rates of corundum dissolution. For these reasons the rates of $\gamma$-Al$_2$O$_3$ dissolution reported by Furrer and Stumm were not used in the analysis. Some of the significant scatter in Carroll-

![Graph](image)

**Fig. 3.** Long-term steady-state rate of corundum dissolution at 25°C as a function of pH. The inset is an expansion of the scale at low pH. Values from Carroll-Webb and Walther (1988) in moles of Al per cm$^2$ per sec times $10^{17}$ as a function of pH. Ionic strengths of 0.005, 0.025, and 0.05 are given by solid diamonds, filled circles, and open circles, respectively. The solid straight lines give fits to the data as discussed in the text.
Webb and Walther's rate determinations probably results from the difficulty of measuring low concentrations of Al in solution and therefore calculating the rates from the time derivative of these measurements. Given this scatter the data are most simply interpreted as being a linear function of pH both above (to pH = 10) and below (to pH = 2) the pH$_{zpc}$ of Al sites (~8.4) as shown by the straight lines, although a more complicated functional dependence is also consistent with the measurements. These rates are consistent with the similar behavior as a function of pH of the data on the extent of surface charge shown in figure 2. That is, there appears to be a linear relation between rate of dissolution and pH both below and above the pH$_{zpc}$ of Al sites to a pH of 10. As shown in figure 3 with pH increases above 10, the rates increase to an increasing extent. It seems reasonable to conclude that [>Al-O$^-$] is also increasing to an increasing degree similar to the behavior of Si surface sites at high pH. Carroll-Webb and Walther, however, didn't measure surface protonation on corundum at pH above 10.4 (see fig. 2), so this is not known for certain.

Because surface charge increases with increasing ionic strength (Dzombak and Morel, 1990), the rates should also increase somewhat with increasing ionic strength (Brady and Walther, 1990). However, given the scatter in the measurements shown, this dependence can not be determined. It does appear, however, that the rates measured at the highest ionic strength, 0.05 M, are on average greater than at the other two ionic strengths. Some of the scatter, as pointed out by Carroll-Webb and Walther, may also be due to the organic ligand buffers present in some of the experimental runs (Furrer and Stumm, 1986).

The straight line in figure 3 giving the rate of dissolution of corundum, R$_{Cor}$, at pH less than the pH$_{zpc}$ is constructed from:

$$R_{Cor} \text{ (mol cm}^{-2} \text{ s}^{-1}) = -4.7 \times 10^{-18} \text{ pH} + 3.95 \times 10^{-17}$$

$$2.0 \leq \text{pH} \leq 8.4 \quad (29)$$

Combining eqs (25) and (29) the relation between R$_{Cor}$ and the concentration of >Al-OH$_2^+$ can be expressed as:

$$R_{Cor} = 8.4 \times 10^{-8} [\text{>Al-OH}_2^+]$$

$$\text{ (mol cm}^{-2} \text{ s}^{-1}) \quad (s^{-1}) \quad (\text{mol cm}^{-2})$$

$$2.5 \leq \text{pH} \leq 8.4 \quad (30)$$

Eq (30) gives the one to one correspondence between the rate of corundum dissolution and the concentration of charged Al surface site species at low pH. A similar analysis can be made for corundum at pH between 8.4 and 10. This suggests the activated complex in the rate determining molecular reaction is dependent on the molecular concentration of >Al-OH$_2^+$ and >Al-O$^-$ both below and above the pH$_{zpc}$, respectively, to the first power. Furrer and Stumm (1986) have argued for a rate dependence of [>Al-OH$_2^+$] on γ-Al$_2$O$_3$ to the third power based on their
shorter term experiments. However, the results of Carroll-Webb and Walther for corundum as well as the analysis below for Si surface sites indicate that the activated complex for Al detachment is likely preceded by the formation of a single protonated or deprotonated cation surface complex.

The relation between surface charge and Si dissolution can also be determined. Plotted in figure 4 are the measurements of quartz dissolution in mol cm$^{-2}$ s$^{-1}$, $R_{	ext{Qtz}}$, reported by Wollast and Chou (1986) at 25°C as a function of pH. The inset in the figure is an expansion of the low pH region. A number of investigators have reported measurements of quartz dissolution rate as a function of pH (Bennett and others, 1988; Brady and Walther, 1990). Wollast and Chou's set of quartz dissolution measurements was used because it was done at a uniform ionic strength (0.2 M NaCl), whereas Bennett and others (1988) looked at the effects of organics, and Brady and Walther (1990) used a variety of buffer solutions. Note that below the pH$_{zpc}$ of quartz of 2.5, the data can be interpreted to indicate a slight linear dependence on pH to the pH$_{zpc}$ of Si sites while at pH above the pH$_{zpc}$ the data appear to indicate the rates increase linearly with pH to approx 7 as shown by the solid lines in the

Fig. 4. Long-term steady-state rate of quartz dissolution at 25°C as a function of pH. The inset is an expansion of the scales at low pH. Values from Wollast and Chou (1986) in moles of Si per cm$^2$ per sec times $10^{17}$. The solid straight lines give fits to the data as discussed in the text. The dashed line shows the 0.3 exponential increase of the rate of quartz dissolution with increasing pH.
figure inset. Above a pH of 7 there appears to be an exponential increase in $R_{Qtz}$ as a function of increasing pH as shown by the dashed line. This increase is similar to the increase of [{$\text{Si-O}^-$}] as a function of pH given in eq (28) and shown in figure 2. The dashed line shown in figure 4 is constructed from:

$$\log R_{Qtz} (\text{mol cm}^{-2} \text{s}^{-1}) = 0.3 \text{ pH } - 19.44 \quad 7 \leq \text{pH} \leq 12 \quad (31)$$

Combining eqs (28) and (31), the relation between dissolution rate and [{$\text{Si-O}^-$}] in a solution where I is near 0.2 M is given by:

$$R_{Qtz} = 1.7 \times 10^{-7} \left[\text{Si-O}^-=\right] \quad 7 \leq \text{pH} \leq 12 \quad (32)$$

Both oxides, $Al_2O_3$ and $SiO_2$, display a minimum in dissolution rate at their pH$_{zpc}$, have similar rate constants, and a one-to-one correspondence between the concentration of charged surface species and the rate of dissolution in the pH range where they could control surface adsorption and dissolution processes on an aluminosilicate mineral.

**Dissolution of aluminosilicate minerals.**—If the mechanisms outlined above for Al and Si detachment and the mixed oxide surface charge analogy are correct then combined they should help one elucidate the relation between rates of dissolution and solution pH for an aluminosilicate mineral. That is, one should be able to combine the effects for these simple oxides and extend the analysis to multi-oxide minerals.

Initially, aluminosilicates dissolve non-stoichiometrically with Al release rates greater than Si release rates at low pH while Si release rates are greater than Al release rates at mildly alkaline pH (compare Chou and Wollast, 1985; Carroll-Webb and Walther, 1988). Depending on the extent of non-stoichiometric release during this initial reaction period a hydrolyzed layer depleted in the more rapidly reacting cation can form. Once formed, this layer eventually builds to a steady-state configuration. At this point the dissolution becomes stoichiometric. Considering the analysis of quartz and corundum given above, one can argue that this depleted layer is developed because of the different surface charging characteristics that control the differences in detachment rate at Al and Si surface sites on an aluminosilicate mineral as a function of pH. In contradiction to the observations of Carroll-Webb and Walther, Wieland and Stumm (1992) observed that during the initial dissolution Si is preferentially lost over Al from the kaolinite surface at low pH. Based on their results, Stumm (1992) argues that the detachment of Al and Si from the kaolinite surface is stoichiometric from the beginning of dissolution, and Wieland and Stumm’s observations can be explained by the fact that some Al becomes bound to the siloxane layer during the dissolution process. There are problems with Wieland and Stumm’s analysis. As discussed by Xie and Walther (1992) it appears that the preferential release of Si over Al at low pH observed by Wieland and Stumm was due
to their pretreatment of the kaolinite in solutions of greater acidity (pH = 1.5 and 2.8) to dissolve amorphous material. This would also strip the surface of much of its surface Al. Reacting this surface at somewhat higher pH would then preferentially release Si from the surface because the ratio of [SiO$^{-}]/[>\text{Al-OH}_{2}^{+}]$ increases with increasing pH (see below). Other investigators as well as Carroll-Webb and Walther (1988) have also found preferential release of Al at low pH for aluminosilicates (Chou and Wollast, 1984, 1985; Holdren and Speyer, 1985a,b). These observations are consistent with the Si rich surface layers that develop on aluminosilicates when they are reacted at low pH. It seems reasonable to conclude that nearly all aluminosilicates dissolve non-stoichiometrically initially with Al preferentially released at low pH.

One can consider the relation between early non-stoichiometric Al and Si release and surface charge for aluminosilicates with the aid of figure 2. Figure 2 indicates that $>\text{Al-OH}_{2}^{+}$ will dominate surface charge on an aluminosilicate at pH below 7. With an increase in pH to mildly alkaline conditions (7 ≤ pH ≤ 10.5), the concentration of negatively charged Si surface sites increases and Al sites lose much of their charge, accounting for little of the total surface charge. Therefore Si-O$^{-}$ will account for most of the surface charge. Al-OH$_{2}^{+}$ will begin to dominate surface charge again above pH = 11 according to the extrapolation of negative surface charge to higher pH shown in figure 2. From these considerations, for a mineral with a 1 to 1 Al to Si ratio, the pH where the combined determinations of the absolute value of charge for both Al and Si sites is a minimum should be somewhat below the pH$_{zpc}$ of Al$_{2}$O$_{3}$ of 8.4, being in the range of pH 7 to 7.5 while a mineral with a 2 to 1 Al to Si ratio should be somewhat higher than this but below 8.4. There are major problems with many determinations of the pH$_{zpc}$ of aluminosilicates, as acid and base are often reacted with the mineral during sample preparation, and this can change the concentration of Al to Si surface sites on the sample. Even if this has not occurred, the ratio of Al to Si surface sites in the natural samples may be influenced by its history of interacting with ground waters before analysis. Also, as indicated in figure 2, the region where surface charge on an aluminosilicate sums to zero is very pH sensitive. For instance, pH$_{zpc}$ determined for kaolinite have been reported to be between 1.8 to 5 depending on the sample identity and preparations techniques. Some care must be taken with these numbers as they are dominated by sites along the sheets which can be a strong function of the sample identity and surface preparation. It is, however, generally agreed that kaolinite edges will retain a 1 to 1 Al to Si site ratio despite dissolution, and they appear to have a pH$_{zpc}$ between 7 and 8 (Wieland and Stumm, 1992). Reported values of the pH$_{zpc}$ of the 2 to 1 Al to Si site mineral, andalusite, are between 5.2 and 8.0 with the latest measurements with minimal surface preparation giving a pH$_{zpc}$ = 8.0 (Cruz and Walther, 1995). Also, recent initial immersion pH measurements of adularia (Stillings, Brantley, and Machesky, 1995), a 3 to 1 Al to
Si site feldspar, which was only prepared by washing in H$_2$O, are between 8 and 9.5. If one assumes that the H$_2$O had little effect on the surface composition then these measurements can be interpreted as the pH$_{zpc}$ of the unreacted adularia surface before H$^+$ for K$^+$ surface exchange has occurred. However, care must be taken because the rapid H$^+$ for K$^+$ surface exchange that takes place on alkali feldspars has probably biased surface titration and electrokinetic measurements, lowering the determined pH$_{zpc}$ to values of 2.0 to 2.4 (Parks, 1967). Surface preparation should have less of an effect on orthorhombic andalusite than the sheet silicate, kaolinite, or on an alkali feldspar. These observations suggest that aluminosilicate surface charge on a stoichiometric surface can be modeled by considering the charge on a stoichiometric combination of similar oxide or hydroxide components.

One, therefore, can argue that at low pH the positively charged Al surface sites weaken the Al-O bonds, and this leads to a greater rate of initial Al detachment from the surface than Si. At mildly alkaline pH the greater charge on Si sites weakens Si-O bonds leading to an increased initial Si detachment rate over Al$^+$ detachment, at least to a pH of 10. Whether in acid or alkaline solutions this non-stoichiometric dissolution should expose more of the slower dissolving cation sites to the solution at the surface. This non-stoichiometric dissolution continues until the number of Al sites per unit surface area times their rate of detachment equals the number of Si sites per unit surface area times their rate of detachment. This initial non-stoichiometric dissolution will develop a surface leached layer that depends on the pH of the solution and the atomic structure of the mineral. However, given enough time at constant composition of the aqueous phase, including constant pH and ionic strength, the dissolution becomes steady-state and stoichiometric.

Plotted in figure 5 are rates of release of Al from corundum and Si from quartz as a function of pH derived from figures 3 and 4. If the effect of charged complexes and energetics of bonding of Al and Si on dissolution for an aluminosilicate were similar to their effects on the oxides, corundum, and quartz, the initial rate of dissolution of Al and Si from a one Si to one Al aluminosilicate like kaolinite would be similar to the values shown. That is, the initial rate of dissolution would be non-stoichiometric with Al released more rapidly than Si from the surface at a pH below about 6 as shown by the fact that corundum dissolution is greater than quartz dissolution per unit surface area to pH = 6. At pH between 7 and 10, Si would detach more rapidly than Al while above pH = 10 Al would initially dissolve more rapidly than Si from the surface. This is similar to the pH dependence of the relative surface charge for corundum and quartz shown in figure 2.

Carroll-Webb and Walther (1988) have reported that kaolinite dissolves with a greater initial rate of Al than Si detachment at pH of 6 and less for the first 200 hrs. At pH between 6 and 9.3 initial Si release is greater than Al release, and above pH = 9.3 initial Al release is greater than Si release. These observations are consistent with the relationships
shown in figures 2 and 5 and suggest the decrease in the strength of bonding of Al and Si to the surface caused by charged complexes at the Al and Si surface sites on kaolinite is similar to the decrease occurring on the oxides, corundum, and quartz. It also supports the assumption that kaolinite dissolution can be modeled by considering reactions at Al and Si surface sites separately.

As argued above the ratio of Al surface sites to Si surface sites exposed during the initial non-stoichiometric dissolution will change as a function of reaction time but will converge to a constant value as stoichiometric aluminosilicate dissolution is achieved. However, the value of the ratio when stoichiometric dissolution is achieved will be a function of the pH in solution because the charging of Al and Si surface sites and therefore, their relative rates of dissolution change as a function of pH.

Long-term steady-state stoichiometric dissolution rates of aluminosilicates are greater at both low and high pH relative to rates at near neutral pH, because the total surface charge is greater at low and high pH (see fig. 2). Also the increased rate of the more rapidly dissolving cation exposes more of the slower dissolving cation to the solution, and its rate per unit surface area, therefore, also increases. This mechanism also helps explain why relatively large amounts of Al and Si are released to
solution when an aluminosilicate mineral is initially reacted in solution even after particle size and dissolution at high energy sites (for example, defects) are accounted for. For instance, when the pH of the input solution is changed in a fluidized bed reactor measuring the dissolution rate of an aluminosilicate, the rates of Al and Si release both rise rapidly (Chou and Wollast, 1984, 1985) before decreasing to a steady state rate when the surface reaches the Al to Si ratio necessary for stoichiometric dissolution. Presumably, the introduction of solutions with higher concentrations of H\(^+\) or OH\(^-\) increases the number of charged species per unit surface area at one of the cation surface sites which increases its dissolution rate dramatically. The detachment of this cation increases the exposure of the other cation with the lower concentration of charged species. Its rate will, therefore, also increase. The fact that the dissolution rates of both cations increase before decreasing to the steady state rate demonstrates the parallel nature of the molecular reaction mechanisms at the Al and Si surface sites.

Chou and Wollast (1984, 1985) have determined the extent of the initial non-stoichiometric dissolution of albite as a function of pH. Initial Al release is greater than stoichiometric at a pH of about 6 and below. Initial Si release is greater than stoichiometric between a pH of 6 and 10. Above a pH of 10, initial Al release becomes greater than stoichiometric. They have also calculated the thickness of the steady-state depleted layer formed on the albite surface as a function of pH after stoichiometric dissolution has been achieved. Na, on average, is completely depleted to a thickness of about two unit cells being replaced by H. The pH dependent relative depletion of Al to Si is on the order of a unit cell or less above a pH of 2.5 given the uncertainty in determining the surface area at the unit cell level for an H-enriched feldspar. These observations are consistent with a changing ratio of Al and Si charged surface sites on the component Al and Si oxides as a function of pH as shown in figure 2. In fact, the pH dependency of the non-stoichiometric dissolution is similar to that of kaolinite suggesting the mechanisms of Al and Si release are similar in the two minerals. This seems reasonable because they can both be related to dissolution mechanisms on corundum and quartz surfaces.

Steady-state kaolinite dissolution.—Shown in figure 6A and B are the long-term steady-state kaolinite dissolution rates in solutions with ionic strengths of 0.005M, 0.025M, and 0.05M as a function of pH measured by Carroll-Webb and Walther (1988) from the concentration of Al and Si released to solution. The inset in each figure is an expansion of the figure at low pH. Not plotted on the diagrams are the measurements reported for dissolution between pH 8 and 10.3. Carroll-Webb and Walther indicated that there are probably some problems with the measurements reported at these pH because of precipitation of an illite/smectite phase. Wieland and Stumm (1992) as well as Ganor, Mogollón, and Lasaga (1995), have also measured dissolution rates of kaolinite. Carroll-Webb and Walther’s results were considered most accurate because 1000 hrs were used to approach steady-state dissolution while the reaction times in
Fig. 6. Rate of kaolinite dissolution in moles per cm$^2$ per sec times $10^{17}$ at 25°C from Carroll-Webb and Walther (1988) plotted as a function of pH. Values for Al release (A) and Si release (B) are for ionic strengths of 0.005, 0.025, and 0.05 given by solid diamonds, filled circles, and open circles, respectively. The lines give fits to the data as discussed in the text.
the other two studies were considerably less. Both studies give rates of reaction greater than those of Carroll-Webb and Walther's, and apparently the reactions that were observed did not reach steady-state stoichiometric dissolution. Ganor, Mogollón, and Lasaga evaluated the degree of non-stoichiometry of rates by plotting log $S_R$, the logarithm of the rate of molar Al release minus the logarithm of molar Si release. They argued that a greater than $\pm 15$ percent departure of $S_R$ from unity, which was their stated analytical error, indicated non-stoichiometric rates. However, two-thirds of this error was uncertainty in BET surface area measurements. Since this will cancel in determining the degree of non-stoichiometry of rates, the analytical error on $S_R$ is on the order of $\pm 5$ percent. Inspection of Ganor, Mogollón, and Lasaga's figure 2 suggests that many of their values are non-stoichiometric to greater than 5 percent which is expected for these short time period experiments. To prepare the starting material Ganor, Mogollón, and Lasaga used a pH = 3 solution whereas Wieland and Stumm used solutions of pH = 1.5 and 2.8. Reaction with these solutions will change the relative concentration of Al to Si sites on the surface toward the stoichiometric dissolution ratio at these pH's. Using this surface at higher pH's (but below about pH = 8) will cause the initial degree of non-stoichiometry as reflected in log $S_R$ to be negative while at pH's lower than these solutions will give a positive log $S_R$. This is trend of log $S_R$ for both Ganor, Mogollón, and Lasaga's as well as Wieland and Stumm's results. That is, discernible in Ganor, Mogollón, and Lasaga's figure 2 is a trend in values of log $S_R$ as a function of pH of both studies that plot along a trend that goes through log $S_R = 0$ at the pH of the preparation solution. This suggests non-stoichiometric dissolution is still occurring in many of the experiments in both studies. In contrast Carroll-Webb and Walther's $S_R$'s do not show this trend. Also, in their analysis Ganor, Mogollón, and Lasaga used surface area determinations after their experiments were run. This was an increase of up to 44 percent from the initial surface area. As discussed above, this increase in surface area is inconsistent with the constant release rate found by Carroll-Webb and Walther and most other investigators for stoichiometric aluminosilicate dissolution after the development of a steady-state surface layer. It is likely that this increase represents adsorption of the N$_2$ gas onto the silica rich surface layer that forms during the experiments. As one wants the reactive surface area of Al and Si detachment at the mineral surface rather than the surface area exposed in the leach layer using these values will underestimate the rates obtained. This may help explain some of the large scatter of rates at pH near 3 found by Ganor, Mogollón, and Lasaga (1995). For these reasons the rate determinations of Carroll-Webb and Walther (1988) are considered to be the most accurate in reflecting the long-term steady state rates of kaolinite dissolution as a function of pH rather than the limited reaction time measurements of Ganor, Mogollón, and Lasaga (1995) and Wieland and Stumm (1992).

Even in the experiments of Carroll-Webb and Walther run for 1000 hrs there was still significant differences between the rates determined
from Al and Si release. This implies that at 25°C the dissolution reactions remain somewhat incongruent even after 1000 hrs. Presumably the ratio of Al to Si sites on the surface has not completely adjusted itself to the stoichiometric dissolution ratio for the pH of the experiment. This may be a problem particularly with sheet silicates as dissolution at the edges of kaolinite sheets can expose the same cation rather than a cation of the other type, and thus sheet silicate dissolution can remain non-stoichiometric for extended periods.

Figure 6A and B indicates that the long-term steady-state rates decrease with increasing pH from a pH of 1 to about 7 or 8 and then increase dramatically by pH = 11.5. The minimum dissolution rate is above the $\text{pH}_{zp}$ of kaolinite determined by Carroll-Webb and Walther (1988) of about 4 but in the pH region where the initial rate of dissolution was reported to be close to stoichiometric and combined Al and Si surface charge from the oxide components is a minimum (see fig. 2). Therefore, the minimum in dissolution rate appears to reflect the minimum in the sum of the absolute values of negative and positive surface charge at the two cation sites occurring near a pH of 7 or 8. Thus the pH where the sum of negative and positive charge is zero ($\text{pH}_{zp}$) may not be the pH where the absolute value of the Al surface charge plus the absolute value of the Si surface charge is a minimum. One needs to be careful in obtaining a $\text{pH}_{zp}$ because for purely arithmetic reasons one would not expect the $\text{pH}_{zp}$ of a complex silicate to be the average calculated from a stoichiometric sum of the $\text{pH}_{zp}$ of each oxide type. The problem is with averaging the logarithmic functions involved.

Similar to corundum dissolution, at pH below 8 but above 2.5 the dependence of the long-term steady state rate on pH can be characterized as a linear function of pH. For kaolinite this is:

$$R_{\text{Kaol}} = -2.5 \times 10^{-18} \text{pH} + 2.1 \times 10^{-17} \quad 2.5 \leq \text{pH} \leq 8 \quad (33)$$

and is shown by the solid straight lines in the insets in figure 6A and B. At pH below 2.5 the kaolinite dissolution rates increase exponentially as pH is lowered. The increase in dissolution rate with decreasing pH is possibly also occurring with corundum dissolution (see fig. 3), although the scatter in the data does not demonstrate this convincingly. Because of the nearly exponential increase in dissolution rate as a function of pH at low pH the data were fit to an exponential curve. The dashed lines shown in the insets in figure 6A and B are constructed from:

$$\log R_{\text{Kaol}} = -0.12 \text{pH} - 16.4 \quad 1 \leq \text{pH} \leq 8 \quad (34)$$

At a pH above 10 the rates appear to increase to an increasing degree with increasing pH. The approximately exponentially increasing rate with increasing pH is similar to rates of quartz dissolution. As shown by Brady and Walther (1989) the limited data for kaolinite as well as that for nearly all other silicates can be modeled as an exponential increase in rate
between a pH of 8 and 12 that has the same dependency on pH as quartz dissolution. For kaolinite this relation is:

$$\log R_{\text{kaol}} = 0.3 \, \text{pH} - 19.68 \quad 8 \leq \text{pH} \leq 13$$  \hspace{1cm} (35)

and is shown by the solid curved lines in figure 6A and B.

As indicated in eqs (30) and (32) there is a one-to-one relation between surface charge at >Al-OH$^+$ surface sites at low pH and >Si-O$^-$ surface sites at high pH. This is consistent with the dissolution rate of kaolinite given by eqs (33) and (35), respectively (see also Brady and Walther, 1989). Because of the exponential changes of >Si-O$^-$ as a function of pH at high pH, it makes sense to consider the log rates of dissolution when considering rates at high pH as given in eq (35). At low pH the dissolution rates appear to be a linear function of pH to about 2.5. At pH below 2.5 the concentration of >Al-OH$^+$ and the rates of dissolution increase exponentially with decreasing pH.

**Steady-state albite dissolution.**—Perhaps the most extensive investigations of the long-term dissolution rate of an aluminosilicate at 25°C are the studies of albite dissolution of Chou and Wollast (1984, 1985). A plot of the logarithms of their long-term steady-state rates, $R_{\text{Alb}}$, as a function of pH is shown in figure 7. If the rates are controlled by the formation of >Si-O$^-$ at high pH then the log rates should be a good linear function of

![Graph](image_url)

**Fig. 7.** Logarithm of the rate of long-term steady-state dissolution of albite at 25°C from Chou and Wollast (1994, 1985) as a function of pH. The solid straight line gives a fit to the alkaline pH data with a slope of 0.3 as discussed in the text.
pH with a slope of 0.3, similar to the increase in $>\text{Si-O}^-$ on quartz as given in eq (28). This relation is shown by the solid straight line at high pH given by:

$$\log R_{\text{Alb}} = 0.3 \, \text{pH} - 18.1 \quad 7.5 \leq \text{pH} \leq 12.5 \quad (36)$$

If, at low pH, the rates are controlled by the concentration of $>\text{Al-OH}_2^+$ then they should be a good linear function of the rate of dissolution of albite from pH of 7 to about a pH of 2.5 controlled by the increase in $>\text{Al-OH}_2^+$ given in eq (25). A plot of $R_{\text{Alb}}$ as a function of pH in acid solutions is shown in figure 8. The inset in figure 8 is an expansion of the diagram for data between a pH of 2.5 and 6. Note that $R_{\text{Alb}}$ can be interpreted as a linear function of pH between about 2.5 and 6 as shown by the solid line in the inset which is constructed from:

$$R_{\text{Alb}} = -1.6 \times 10^{-16} \, \text{pH} + 1.0 \times 10^{-15} \quad 2.5 \leq \text{pH} \leq 6 \quad (37)$$

As with the concentration of $>\text{Al-OH}_2^+$ and the behavior of kaolinite dissolution the rates rise exponentially with decreasing pH below a pH of about 2.5.

Extending the analysis of kaolinite and albite dissolution to rates reported for other aluminosilicates as done by Brady and Walther (1989),

![Graph](image_url)

Fig. 8. Long-term steady-state rate of albite dissolution at 25°C from Chou and Wollast (1994, 1985) as a function of pH at acid pH. The inset is an expansion of the scales between a pH of 2.5 and 6.0. The solid straight line gives a fit to the mildly acid pH data as discussed in the text.
it is apparent that at high pH the log of the rates of silicate dissolution at 25°C increase by 0.3 for each increase in pH as given in eqs (35) and (36), but the intercepts vary according to differences in the strength of the Si-O bonding and the extent of bond polarization by the charged surface complex for a particular mineral.

Therefore, the increased steady-state long-term dissolution of aluminosilicates in acid solutions as pH is lowered occurs because the surface concentration of >Al-OH$_2^+$ has increased (Brady and Walther, 1989; Blum and Lasaga, 1991). The increased concentration of >Al-OH$_2^+$ on the surface increases the detachment of Al. This increased detachment of Al exposures more Si sites on the surface creating, in many cases, a porous Si rich surface layer. This increases the total number of Si sites exposed in the surface layer leading to greater detachment of Si. Even though the ratio of charged Si surface sites to total Si surface sites decreases with decreasing pH, increased Si detachment occurs because of the increased number of Si sites in the surface layer. This increased detachment at both Al and Si surface sites establishes a greater stoichiometric dissolution rate with decreasing pH. At 25°C >Al-OH$_2^+$ increases as a linear function of pH with decreasing pH from about 6 to 2.5. However, below a pH of 2.5, >Al-OH$_2^+$ increases exponentially as pH is decreased. [>Al-OH$_2^+$] as a function of pH is similar to the pH dependence of the rate of dissolution of aluminosilicates at low pH. Note that in mildly acidic solutions, the rate of dissolution of each aluminosilicate has a different linear dependence on pH. This suggest that α$_+$ is different because of differences in coordination of Al surface sites on each mineral.

The effect of Al to Si ratio on dissolution rate of plagioclase at constant pH has been investigated by Casey, Westrich, and Holdren (1991) and Oxburgh, Drever, and Sun (1994). In Casey, Westrich, and Holdren’s (1991) investigation at pH = 2.0 and an analysis of published data at pH = 3, the rate of dissolution was shown to increase with increasing anorthite content. This apparently occurs because in these acid solutions, initially Al is preferentially released over Si from aluminosilicates. The rapid release of Al exposes more Si to the solution per unit surface area. With the development of more Si surface complexes, their rate of release should also increase. Therefore, the long-term steady-state rate should increase with increasing Al content. Casey, Westrich, and Holdren (1991) argue that one of the reasons that the rates increase to an increasing degree is that as the anorthite composition is approached the Si tetrahedra become more isolated from each other, weakening their bonding to the mineral surface. Also, as pointed out by Brady and Walther (1989) because of the changing Al to Si ratio the oxygen-cation bonding in albite is stronger than in anorthite, and therefore rates should tend to increase with increasing anorthite content. In Oxburgh, Drever, and Sun’s (1994) investigation oligioclase, andesine, and bytownite were reacted in near neutral to pH 3 solutions. Their results demonstrate a similar behavior to that of Casey, Westrich, and Holdren’s (1991) study in
that the rates increased with increasing anorthite content at all pH, consistent with the interpretation given in this contribution. Increased surface charge with increasing concentration of Al surface sites leads to increasing rate of dissolution when surface bonding is of similar magnitude.

**TEMPERATURE DEPENDENCE**

As temperature increases, the concentration and pH dependence of charged surface complexes will change. Figure 9 shows the proton adsorption measurements of Brady and Walther (1992) on Al₂O₃ in 0.1 M NaCl at 80°C as a function of pH as filled circles as well as those of Furrer and Stumm (1986) and Carroll-Webb and Walther (1988) at 25°C given by open symbols. Brady and Walther’s, values reported in moles per gram, were converted to moles per cm² by using a surface area of 3.7 m² per gm (Carroll-Webb and Walther, 1988). Note that the 80°C values indicate the concentration of >Al-OH⁺ increases nearly linearly with decreasing pH between a pH of 4.5 and 2.5. If these values are extrapolated to higher pH, [>Al-OH⁺] becomes quite small implying that as temperature increases the neutral surface complex, >Al-OH⁰, should dominate to an increasing extent in near neutral pH solutions. Below a

![Graph showing surface charge on Al₂O₃ in moles per cm² times 10¹⁰ as function of pH at 25°C (open circles from Carroll-Webb and Walther 1988 while open squares from Furrer and Stumm, 1986) and 80°C (filled circles from Brady and Walther, 1992).]
pH of 2.5, [\( >\text{Al-OH}_2^+ \)] apparently increases to an increasing extent as pH is lowered given the limited data reported by Brady and Walther. This behavior is similar to [\( >\text{Al-OH}_2^+ \)] at 25°C, however, the pH dependence of [\( >\text{Al-OH}_2^+ \)] has increased. Therefore, rate constants of aluminosilicate dissolution at elevated temperatures and low pH should have a greater pH dependence than at 25°C. This has been demonstrated by Brady and Walther from the rate determinations on kaolinite of Carroll and Walther (1990). More recently, Gnar, Mogollón, and Lasaga (1995) have questioned the validity of the determinations of Carroll and Walther (1990) arguing from their measurements for a constant dependence of kaolinite dissolution on pH as a function of temperature in acid solutions at 25° and 50°C. As mentioned above the short duration of their experiments and small number of reported values compared to Carroll and Walther’s determinations makes their measurements suspect. It should also be pointed out that dissolution of the aluminosilicate, albite, at acid pH becomes more pH dependent with increasing temperature from 100° to 300°C (Hellmann, 1994) in agreement with the analysis of Brady and Walther (1990, 1992) and the results of Carroll and Walther (1990).

If the rate of dissolution of silicates is controlled by the concentration of \( >\text{Si-O}^- \) at alkaline pH conditions, one can examine [\( >\text{Si-O}^- \)] as a function of pH at elevated temperatures. Shown as filled circles in figure 10 are values of log [\( >\text{Si-O}^- \)] as a function of pH at 60°C on silica from Brady and Walther (1992). Also plotted in figure 10 as open symbols are the [\( >\text{Si-O}^- \)] determinations at 25°C from Bolt (1957) and Brady and Walther (1990). The solid straight lines through the results at 25° and 60°C give the pH dependence of the surface charge with slopes of 0.3 and 0.5, respectively. Their increased pH dependence with increasing temperature is similar to the behavior of [\( >\text{Al-OH}_2^+ \)]. These changes in log [\( >\text{Si-O}^- \)] as a function of pH at elevated temperature should also be reflected in the dissolution rates of silicates.

To test the relation between log [\( >\text{Si-O}^- \)] and log rates in alkaline solutions with increasing temperature one can examine the pH dependence of the log rates of silicate dissolution at elevated temperature. They should be similar to the slopes of 0.3 and 0.5 obtained for the pH dependency of log [\( >\text{Si-O}^- \)] in alkaline solutions at 25° and 60°C, respectively. Figure 11 shows the release rates of Al and Si from kaolinite dissolution at 80°C from Carroll and Walther (1990). While rates determined at near neutral pH are still somewhat incongruent, the rates at low and high pH have become congruent during the \(~450\) hrs of reaction time. The solid line through the high pH determinations has a slope of 0.6. The measurements of Knauss and Wolery (1986, 1988) for quartz and albite dissolution under alkaline pH conditions at 70°C are shown in figure 12A and B, respectively. The straight lines fit through the plots of the logarithm of the rate of dissolution as a function of pH have slopes of 0.55.

The slopes determined from figures 10, 11, and 12A and B at alkaline pH are plotted in figure 13 as a function of the inverse of
temperature. The linearity of this measured parameter as a function of the inverse of temperature indicates a similar Arrhenius relation between the change in pH dependency of both log rates and log [Si-O⁻] exists. Therefore rates in alkaline solutions and [Si-O⁻] can be predicted as a function of pH between 25° and 80°C as well as extrapolated to higher temperatures. However, care needs to be taken. As the rates become more pH dependent at both low and high pH as a function of increasing temperature from 25° to 80°C, they are apparently much less pH dependent at supercritical pressure and temperature conditions. The results of Lagache (1976) and analysis of Wood and Walther (1983) indicate that pH and other solution variables are less important at temperatures of 300°C and above. Also, Hellman’s (1994) results for albite dissolution indicate that both the pH dependency of rates at low and high pH as well as the region of pH independence increases from 100° to 300°C. This is consistent with the nature of surface charging as a function of temperature. The absolute concentration of charged sites becomes very low at near neutral pH, and this region broadens with temperature implying the dominate dissolution mechanism involves the neutral sites. This may help explain the incongruent nature of kaolinite dissolution at 80°C and near neutral pH shown in figure 11. Although not known for certainty, a possible explanation for the decrease in the concentration of charged
surface complexes at near neutral pH could be that the dielectric constant of bulk H₂O decreases with increasing temperature, and this would translate to a lower dielectric constant in the double layer. Such a decrease would promote the neutrally charged complex over charged complexes at the surface (Davis and Leckie, 1978). Under these conditions changes in solution pH no longer have a strong effect on changes in surface charge and, therefore, on dissolution rates.

CONCLUDING REMARKS

For aluminosilicates, where other surface species are not important, the pH dependence of far from equilibrium surface controlled dissolution rates appears to be dominated by the combined effects of dissolution at charged Al and Si surface sites on the mineral surface. These charged complexes polarize and weaken the critical surface Al-O and Si-O bonds leading to a greater probability of detachment relative to uncharged surface sites (Zinder, Furrer, and Stumm, 1986). When an aluminosilicate is first reacted in solution the rates of the preferential release of Al or Si are directly related to the relative concentration of charged complexes at the surface at the pH of the reaction. At constant pH with increased time of reaction the surface concentration of Al and Si sites changes, until the relative concentration of charged complexes on the surface times
Fig. 12. Logarithm of the long-term steady-state rate of quartz and albite dissolution at 70°C as a function of pH. The solid straight lines give fits to the alkaline pH data with a slope of 0.55 as discussed in the text. (A) Quartz dissolution from Knauss and Wolery (1988); (B) albite dissolution from Knauss and Wolery (1986).
their rate of detachment converge to the value for stoichiometric dissolution. In extremely low pH and high pH solutions significant leached layers of the slow detaching cations can be produced during this early non-stoichiometric dissolution phase until the dissolution becomes stoichiometric. For sheet silicates at low temperature this non-stoichiometric reaction period can be extensive because much of the dissolution at the rapidly detaching cation sites at the edge of a sheet will expose the same cation rather than a cation of the other type.

In order to predict the steady-state stoichiometric rates of mineral dissolution as a function of pH from the concentration of charged surface sites, one needs to know the relative concentration of Al and Si surface sites at the time when stoichiometric dissolution has occurred. This relative concentration of Al and Si surface sites is pH dependent. Surface titrations of aluminosilicates, which could be used to put constraints on this ratio, are typically done on unreacted surfaces or on those that have been prepared by reacting them in strong acid or base. These surfaces are unlikely to have the ratio of Si and Al sites present at the pH and time when stoichiometric dissolution is achieved. These surfaces will then dissolve non-stoichiometrically. Xie and Walther (1992) have, however, attempted to predict the Si/Al ratio as a function of pH for stoichiometric
dissolution of kaolinite. Only future investigations will demonstrate if the predicted ratio of Si/Al as a function of pH is realistic. The minimum in long-term steady-state rates of dissolution as a function of pH can not be determined by averaging the sum of oxide components but appears to correspond to the pH where the sum of the absolute value of negative plus the absolute value of positive charge at both Al and Si sites is a minimum.

It can be shown that there is a linearity between pH rather than a\textsubscript{H} and the concentration of charged surface sites between a mole fraction of charged sites of 0.2 to 0.8. The activity of H\textsuperscript{+} is a constant from the double layer to the bulk solution, but the concentration of H\textsuperscript{+} is not. With this understanding the relation between the thermodynamic equilibrium constants for the reactions between surface sites, K\textsubscript{(1)} and K\textsubscript{(2)} and the equilibrium concentration ratios, K\textsubscript{(1)}\textsuperscript{app} and K\textsubscript{(2)}\textsuperscript{app} can be determined.

As temperature increases the charge on surface sites on aluminosilicates and therefore their rates of dissolution become more pH dependent, controlled by increases in [\textsuperscript{[\textsuperscript{Al-OH}\textsuperscript{+}]}] and [\textsuperscript{[Si-O\textsuperscript{−}]}] in acid and alkaline solutions, respectively. This requires that the activation energy of the overall dissolution reaction for an aluminosilicate be pH dependent increasing at low pH with a decrease in pH and increasing in alkaline solutions with increasing pH. However, this change in rate with pH (that is, slope) as a function of temperature appears to obey an Arrhenius relation (fig. 13). It is argued that this is controlled by the pH dependent surface reaction to form charged surface complexes. Because of this increase in pH dependence with increasing temperature the concentration of charged surface complexes at near neutral pH becomes exceeding small, and therefore a mechanism of dissolution based on the neutrally charged surface complexes appears to occur increasingly with increasing temperature. The mechanism involving neutrally charged surface complexes is then pH independent and occurs over an increasingly large pH range with increasing temperature. The rates of dissolution of aluminosilicates will then become nearly pH independent in most solutions. Judging from the limited data this begins to happen by 300°C (Lagache, 1965; Hellmann, 1994). Therefore, the rate expression of Wood and Walther (1983) is probably a reasonable estimate for far from equilibrium dissolution rates in supercritical H\textsubscript{2}O solutions at all but extreme pH conditions.

The analysis given here is for the effects of protonation and deprotonation of the surface. Other surface complexes besides those due to surface protonation and deprotonation may become important, particularly at lower temperatures. These complexes can have dramatic effects on rates and need to be accounted for (Wogelius and Walther, 1991, 1992). Also, there should be somewhat of an increase in surface charge and therefore rates of dissolution with increased ionic strength. This effect has yet to be quantified.
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