

Dissolution and crystallization rates of silicate minerals as a function of chemical affinity

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Abstract: The variation of silicate dissolution and crystallization rates with chemical affinity and solution composition can be quantified by the identification of the rate controlling precursor complex. The nature of this complex depends on the individual mineral structure. Specifically, the destruction of quartz and anorthite frameworks requires the breaking of only one type of structural group. For these minerals, the rate controlling precursor complex has the composition of the mineral itself plus or minus H^+ , OH^- , and/or H_2O . As a result, the hydrolysis rates of these minerals do not depend on either the aqueous Al/Si ratio or chemical affinity at far from equilibrium conditions. In contrast, the destruction of the kaolinite, albite, K-feldspar, and kyanite frameworks requires the breaking of more than one structural group. For these minerals the rate controlling precursor complex has a different Al/Si ratio from the mineral and their hydrolysis rates have been found to depend on the aqueous Al/Si ratio. These rates thus *appear* to depend on chemical affinity at far from equilibrium conditions. Taking into account the identity of these precursor complexes and the framework of transition state theory leads to equations that can accurately describe the hydrolysis rates of each of these minerals as functions of pH, aqueous aluminum and silica concentration, and chemical affinity.

INTRODUCTION

Detailed knowledge of silicate dissolution/precipitation kinetics at conditions characteristic of geochemical processes is essential to understanding the rate and extent of chemical mass transfer and water/rock interaction both in and on the surface of the Earth. With the exception of some Earth surface systems, for example environmental pollution and chemical weathering, these processes occur at near to equilibrium conditions. Thus, there is a strong need for kinetic rate equations that allow the extrapolation of mineral dissolution and crystallization rates measured in the laboratory at far from equilibrium conditions to the near to equilibrium conditions typical of natural processes.

Prior to 1992, the variation of silicate dissolution/crystallization rates with chemical affinity was generally believed to follow a behavior consistent with transition state theory (TST), and the assumption that 1) a single elementary reaction dominates the dissolution rates at all affinities, and 2) the activated or precursor complex controlling this hydrolysis has the same Al/Si ratio as the reacting mineral. According to these assumptions, the constant pH reaction rates are independent of solution saturation state at far from equilibrium conditions, and a simple function of chemical affinity at near to equilibrium conditions. Recent experimental investigations of silicate dissolution as a function of solution saturation state permit the testing of rate laws derived from TST with the above assumptions. Of the minerals thus far investigated, quartz (ref. 1, 2) and anorthite (ref. 3) were found to obey this rate equation, but albite (ref. 4, 5), K-feldspar (ref. 6), kyanite (ref. 7) and kaolinite (ref. 8-11) dissolution rates were found to exhibit different behaviors. These results imply that the rate-limiting reaction step is not the same for all silicates and depends on the individual mineral structure. The purpose of this communication is to summarize recent experimental results on

silicates and to present new equations, which can accurately describe silicate dissolution/precipitation rates as functions of solution composition and chemical affinity.

BACKGROUND ON TRANSITION STATE THEORY

Within the framework of transition state theory (ref. 12), the rate of an elementary reaction is proportional to the concentration of the activated complex (or free energy maximum that the reactants should pass to be converted into products). Wieland et al. (13) demonstrated that the rate is also proportional to the concentration of the surface species precursor of the activated complex (precursor complex). Although silicate dissolution likely involves several elementary reactions, TST can still be applied to the overall rate if it is controlled by a single elementary rate-limiting step (ref. 14). Within this context, silicate dissolution rates can be described using (ref. 15, 16)

$$r = k_+ \prod a_i^{-n_i} \{1 - \exp(-A/\sigma RT)\} \quad (1)$$

where r defines the net reaction rate, k_+ denotes a dissolution rate constant, a_i corresponds to the activity of the i th aqueous species, n_i signifies the reaction coefficient of the i th species in the reaction forming the precursor complex, σ refers to the reaction order, A denotes the chemical affinity for the overall reaction, T stands for absolute temperature, and R represents the gas constant.

The product $\prod a_i^{-n_i}$ describes the effect on the overall rate of the activities of the aqueous species involved in precursor complex formation. The terms within the brackets describe the effect of solution saturation state. For highly undersaturated solutions, A has a large positive value and the term within the brackets is equal to 1. At these conditions the dissolution rate is independent of chemical affinity (or bulk solution saturation index), but is still dependent on the activities of the aqueous species that participate in the formation of the precursor complex. For small deviations from equilibrium (i.e. when $A/\sigma < RT$), the rate becomes linearly related to chemical affinity.

When applying eq.(1) to silicate dissolution rates, it is commonly assumed that 1) H^+ , OH^- and H_2O are the only aqueous species involved in precursor complex formation, 2) a single reaction mechanism controls the overall rate at all chemical affinities, and 3) $\sigma=1$. These assumptions lead to the following rate equation (ref. 17)

$$r = k'_+ (a_{H^+})^{n_{H^+}} \{1 - \exp(-A/RT)\} \quad (2)$$

where k'_+ refers to the dissolution rate constant for the hydrolytic process. This rate law has been used extensively to model water-rock interactions in the crust (ref. 18-22). The adoption of eq.(2) leads to predictions of mineral dissolution/crystallisation rates as a function of chemical affinity at constant pH as illustrated in Fig.1. It can be seen in this figure that eq.(2) implies that silicate dissolution rates are independent of chemical affinity at far from equilibrium conditions (i.e. $A > 10$ kJ/mol at 150°C) and decrease with A at close to equilibrium conditions.

SUMMARY AND ANALYSIS OF EXPERIMENTAL DATA ON THE FREE ENERGY DEPENDENCE OF QUARTZ AND ALUMINOSILICATE DISSOLUTION

The degree to which eq.(2) can describe the variation of silicate dissolution rates can be evaluated by comparison of Fig 1 with recently obtained experimental data. All the experimental data described in this study are steady state hydrolysis rates, which were obtained in fluid-flow reactors. The main advantages of flow-reactors over batch reactors is that they 1) allow direct measurement of steady-state rates in aqueous solutions, and 2) permit measurement of these rates at specific fluid compositions and chemical affinities by either changing the inlet solution composition or the flow rate, without dismantling the reactor.

The constant pH dissolution/crystallization rates of quartz and several aluminosilicates are shown in Fig. 2 as a function of chemical affinity. A comparison of Figs. 1 and 2 indicates that, among the minerals studied,

only quartz and anorthite obey eq.(2). The dissolution rates of kaolinite, albite, K-feldspar and kyanite are apparent¹ functions of chemical affinity at constant pH and far from equilibrium conditions. Moreover, the experiments of Devidal (11), Oelkers and Schott (5, 7) and Gautier et al. (6) performed with various Al/Si ratios in the inlet solution show, without ambiguity, that kaolinite, albite, K-feldspar and kyanite dissolution rates also depend strongly on the value of this ratio.

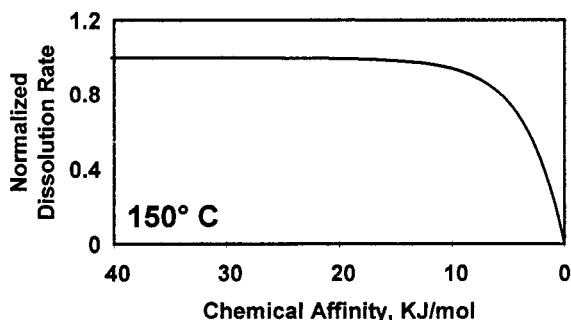


Fig. 1. Variation of mineral dissolution rates with chemical affinity as predicted with eq.(2).

Within the context of TST, these behaviors can be accounted for by the concept that quartz and anorthite dissolution is controlled by precursor complexes that have the same composition than the reacting mineral plus or minus H^+ , OH^- , and/or H_2O , however, this is not the case for the other aluminosilicates. It follows that the simplified rate equation derived from TST (eq.2) cannot be applied to silicate dissolution without caution. As the hydrolysis of mixed oxide silicates is a multi-step process involving the breaking of a number of different bonds, it is likely that the stoichiometry of the surface precursor depends on the structure of each mineral.

IDENTIFICATION OF THE SURFACE PRECURSOR OF THE ACTIVATED COMPLEX AND IMPLICATIONS FOR MINERAL RATE LAWS

Quartz

It is generally agreed that the general limiting step for quartz dissolution in acidic and near neutral conditions is the hydrolysis of the Si-O-Si structural unit at the surface of the solid (ref. 23) :



The attack of water consists of two molecular steps. The first step involves the adsorption of water near a Si-O-Si group. The second step involves the formation of a new Si-O bond by the oxygen of the adsorbed water and the cleavage of the Si-O-Si group (ref. 23). The activated complex believed to induce silica dissolution is associated with this step. It follows that the surface precursor can be represented by $(SiO_2 \cdot nH_2O)^*$. This stoichiometry implies that water molecules are the only aqueous species involved in precursor complex formation. For this reason quartz dissolution obeys eq.(2) and is independent of chemical affinity in highly undersaturated solutions.

Albite and K-feldspar

The structure of alkali feldspars (ref. 24) contains exchangeable cations (Na, K) along with two hydrolyzable sites in the oxide polymer (silicate and aluminate groups). The crosslink density of alkali feldspars is the same as quartz but, unlike quartz, one third of the crosslinks are relatively reactive Al-O-Si bonds. In accord with Oelkers et al. (25) and Gautier et al. (6), the dissolution of alkali feldspars can be considered as a three step process, as outlined in Fig.3. The first of these steps is the relatively rapid equilibration between hydrogen and alkali ions on the mineral surface (Fig 3a). This exchange, which may be reversible (ref.26), leads to an alkali deficient surface layer several unit cells deep into the surface (ref. 27-30). The second step (Fig. 3b) is the reversible exchange of hydrogen with aluminum on this surface

¹ The word apparent is used in this context, as it is not possible in Fig.2 to unambiguously distinguish the effects of changing chemical affinity from changing aqueous Si or Al

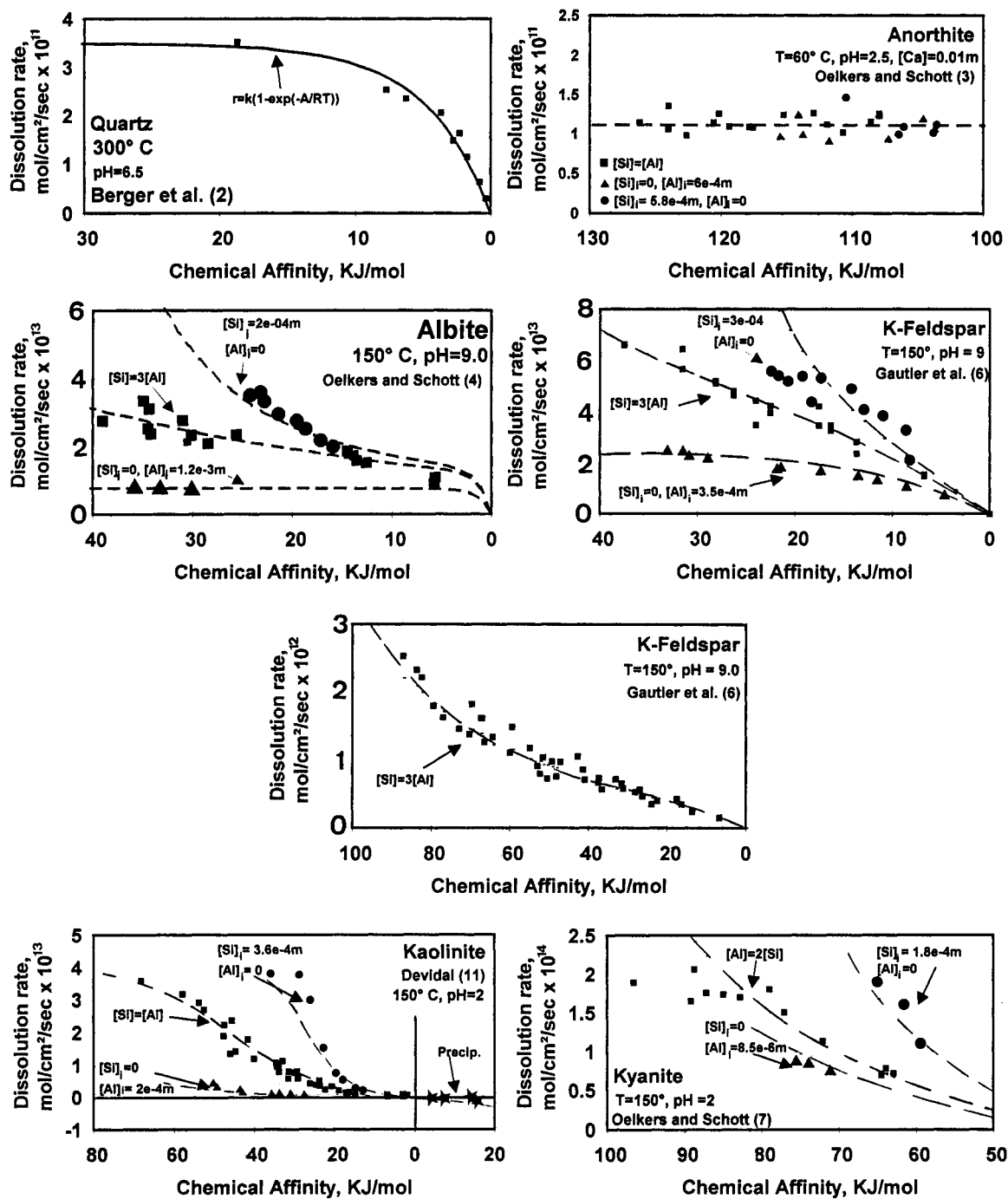


Fig. 2. Experimentally generated steady state dissolution rates of quartz, kaolinite, albite, K-feldspar, anorthite and kyanite as a function of chemical affinity. The various symbols correspond to experimental data obtained in fluids of different Al/Si ratios: squares denote data obtained in solutions having the same Al/Si ratio as the individual mineral, circles represent data obtained in solutions having lower Al/Si ratios than the mineral, triangles represent data obtained in solutions having higher Al/Si ratios than the mineral, and stars designate precipitation rate data. The composition of these fluids are noted in the figure, where [Al] and [Si] refer to the total solute concentration of the indicated species in the reactor during the experiments, but [Al]_i and [Si]_i denote the total indicated solute concentration of the inlet solution. The curves drawn through these data were generated from equations given in the text. Chemical affinities depicted in this figure were computed using the EQ3 computer code (ref 42) and equilibrium constants generated from SUPCRT92 (ref. 43) -- see text.

involving the breaking of Al-O bonds of Al-O-Si groups and leaving the surface of the alkali feldspar enriched in silica both at acidic (ref. 28) and basic conditions (ref. 4, 29). This mechanism is consistent with the results of *ab initio* calculations (ref.31) which indicate that within the tetrahedral framework, Al-O-Si bonds are weaker than Si-O-Si bonds. The final and rate limiting step of dissolution is, as for quartz, the hydrolysis of Si-O-Si bonds (Fig.3c). This implies that the rate controlling precursor complex of the alkali feldspars is the same as that of quartz.

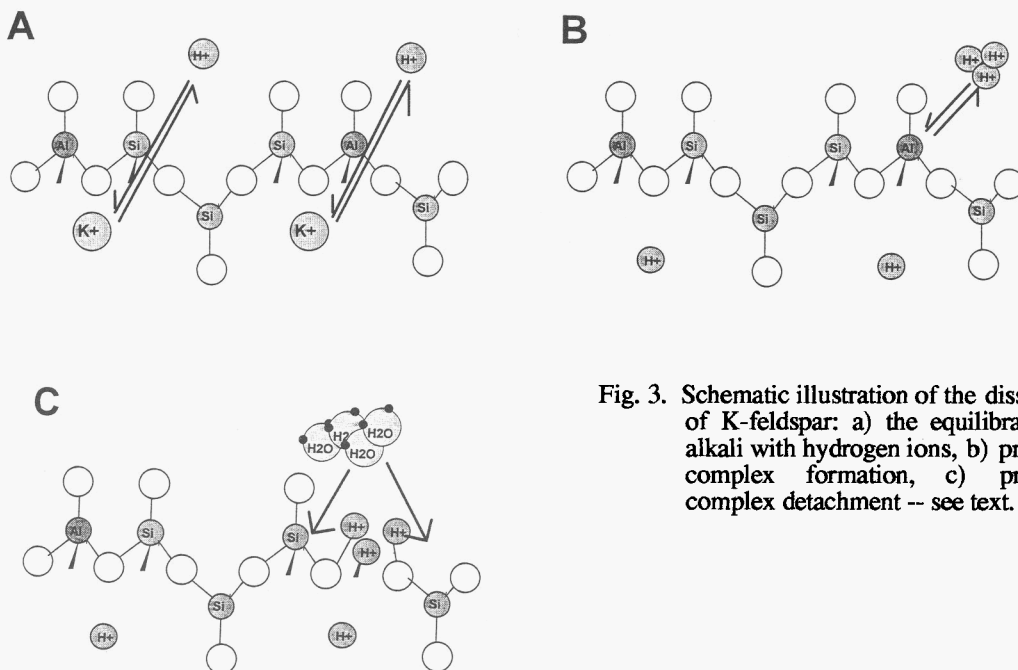
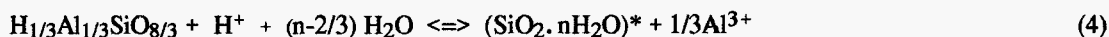


Fig. 3. Schematic illustration of the dissolution of K-feldspar: a) the equilibration of alkali with hydrogen ions, b) precursor complex formation, c) precursor complex detachment -- see text.

At acidic conditions the reaction to form this precursor complex is consistent with



where $\text{H}_{1/3}\text{Al}_{1/3}\text{SiO}_{8/3}$ designates a hydrogenated feldspar normalized to one Si atom, $(\text{SiO}_2 \cdot n\text{H}_2\text{O})^*$ stands for the silica rich, aluminum deficient precursor complex, and n refers to the number of moles of H_2O contained in each mole of precursor complex. Expressing the law of mass action for reaction (4)

$$K = \frac{a_{(\text{SiO}_2 \cdot n\text{H}_2\text{O})^*} a_{\text{Al}^{3+}}^{1/3}}{a_{\text{H}_{1/3}\text{Al}_{1/3}\text{SiO}_{8/3}} a_{\text{H}^+}} \quad (5)$$

and assuming that the total number of sites available per unit surface area for reaction (4) to occur is equal to S ($S = \{\text{H}_{1/3}\text{Al}_{1/3}\text{SiO}_{8/3}\} + \{(\text{SiO}_2 \cdot n\text{H}_2\text{O})^*\}$ where $\{\}$ denotes the concentration of the surface species per unit surface area) the precursor complex concentration can be quantified leading to a rate expression for the dissolution of alkali feldspars given by (ref. 6, 25)

$$r = k'_+ S \left[\frac{K \left(\frac{a_{\text{H}^+}^3}{a_{\text{Al}^{3+}}} \right)^{.33}}{1 + K \left(\frac{a_{\text{H}^+}^3}{a_{\text{Al}^{3+}}} \right)^{.33}} \right] (1 - \exp(-A/3RT)) \quad (6)$$

where k'_+ refers to a dissolution rate constant. This equation implies that the dissolution of the alkali feldspars at constant pH exhibits three types of behavior depending on saturation state: 1) the rates are at a maximum, independent of chemical affinity and aluminum concentration, extremely far from equilibrium

where the mineral surface is saturated with precursor complexes, 2) the rates are controlled by aqueous aluminum concentration in an intermediate region where fewer precursor complexes are present at the mineral surface, and 3) the rates are dominated by the effects of chemical affinity in the near to equilibrium region where $A/3RT \leq 5$.

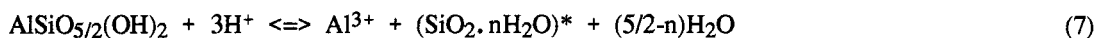
The degree to which eq.(6) can be used to describe the dissolution of albite and K-feldspar can be assessed in Fig.2. Note there is no apparent maxima in the alkali feldspar rate data depicted in this figure as a function of affinity, indicating that the mineral surfaces were not saturated with precursor complexes in these experiments ($K \approx 0$). Such is not the case for kaolinite (see below). The curves depicted in figure 2 for the alkali feldspars were computed with eq.(6), and $k'_+ = 2.9 \times 10^{-12}$ mol/cm²/sec for albite and $k'_+ = 5.5 \times 10^{-13}$ mol/cm²/sec for K-feldspar. The close correspondence between the curves and the experimental data represented by symbols in Fig.2 demonstrates their consistency with eq.(6), and supports the hypothesis that these rates are controlled by Si-rich, Al-deficient surface precursor complexes. Eq.(6) has also been demonstrated to accurately describe the variation of the dissolution rates of several aluminosilicate minerals, as a function of pH (ref. 25). A further support to the concept that both quartz and alkali feldspars hydrolysis is controlled by the same limiting step (breaking of Si-O-Si structural units) and precursor complex is that both the alkali feldspars and quartz hydrolysis have similar activation energies: $E_a \sim 80$ kJ/mol (ref. 1, 17, 32-37)

Anorthite

The structure of calcium feldspar is similar to that of the alkali feldspars described above with the exception that the aluminosilicate framework consists of an equal number of Al and Si atoms, which exhibit essentially complete ordering (ref. 24). Consequently, this framework does not contain relatively non-reactive Si-O-Si groups, but only relatively reactive Al-O-Si groups. It follows that anorthite dissolution is fundamentally different from alkali feldspar dissolution, which is controlled by the hydrolysis of these Si-O-Si groups. In contrast, as the destruction of the anorthite requires only the destruction of a single structural unit (Al-O-Si), the rate controlling precursor complex for this mineral consists of this structural unit plus or minus H⁺, OH⁻ and/or H₂O. Thus, the precursor complex has the same Al/Si ratio as the mineral, and anorthite dissolution at constant pH is independent of aqueous Al and Si concentration at far from equilibrium conditions. This is demonstrated in Fig. 2, where the steady state dissolution rates of anorthite obtained in aqueous solutions of various Al and Si concentrations at 60° C and pH=2.5 are depicted as a function of chemical affinity. It can be seen in this figure that these rates, all of which are at far from equilibrium conditions, are independent of the aqueous Al/Si ratio. Anorthite dissolution data also confirms the relative reactivity of Al-O-Si groups in the feldspar structure, as 1) its reaction rate is approximately 2.5 orders of magnitude greater than corresponding rates for K-feldspar at 25° C and pH=5 (ref. 38), and 2) the activation energy for anorthite dissolution has been found to be ~18 kJ/mol (3) which is lower than corresponding values of the alkali feldspars by a factor of ~4.

Kaolinite

The fundamental unit of the kaolinite structure is an extended sheet consisting of a silica-type layer (Si₄O₁₀)⁴⁻ and a gibbsite-type layer (OH)₆—Al₄—(OH)₂⁴⁺ (ref.39). Three morphological planes of different chemical composition exist at the kaolinite surface: the gibbsite and siloxane surfaces (basal surfaces) and a complex oxide of the two constituents Al(OH)₃ and SiO₂ at the edge surface. Because of this complex surface chemistry, multi-site and multi-step models have been proposed to describe the dissolution of kaolinite (ref. 40). However, recent observations of stoichiometric kaolinite dissolution at acidic and alkaline pHs (ref. 11), and the relatively high 'reactivity' of octahedral aluminum compared to tetrahedral aluminum and silicon suggest that the dissolution mechanism of kaolinite is less complex than previously thought and that, as for quartz, the rate limiting step is the hydrolysis of the relatively unreactive Si-O-Si bonds. Within the framework of TST, the reaction of formation of a Si-rich, Al-deficient precursor complex at acidic conditions can be written as (ref. 11) :



where $\text{AlSiO}_{5/2}(\text{OH})_2$ designates a kaolinite normalized to one Si atom. Combining of the law of mass action for reaction (7), the conservation of the total number of surface sites, and the principle of detailed

balancing yields a rate expression for kaolinite dissolution/crystallization similar to eq.(6), in which the exponent of the term ($a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$) equals unity (each Si atom in the kaolinite structure forms a precursor complex) and the expression within the exponential is $-A/2RT$ (there are two Si atoms in kaolinite formula). The close agreement in Fig.2 between experimental points and the curves generated from this expression strongly supports the validity of eq.(6 and 7) and thus the control of kaolinite dissolution by Si-rich, Al-deficient surface precursor complexes. At far from equilibrium conditions ($A > 60$ kJ/mol), kaolinite dissolution rates become independent of affinity, owing to the fact that essentially all the possible surface sites contain precursor complexes. This behavior contrasts with that of the alkali feldspars where the dissolution rate does not become independent of A , even for chemical affinities as high as 90 kJ/mol ($m_{\text{Al}} < 5 \times 10^{-7}$ N). This reflects a stronger tendency of aluminum to reattach itself to feldspar surface than to kaolinite surface and to add crosslinks to the silicate framework that destroy surface precursor complexes.

In alkaline solutions there is a competition between reaction (7) and the adsorption of aqueous silica on surface precursors which forms siloxane groups (ref. 11) :



Taking account of reaction (8) yields a rate equation analogous to eq.(6) but in which aqueous silica concentration is an additional parameter. In agreement with experimental data, the predicted rates exhibit an inverse dependence on the concentration of both dissolved aluminum and silica.

Precipitation rates of kaolinite computed from eq.(6) are substantially lower than predictions of near equilibrium precipitation rates obtained using eq.(2). These lower computed precipitation rates are consistent with field observations and precipitation rates of kaolinite reported in the literature (ref. 8-11)

Kyanite

Kyanite consists of chains of aluminum octahedra that are crossed linked by Si tetrahedra and additional Al octahedra (ref. 41). The distribution of steady state dissolution rate data depicted in Fig. 2 for kyanite dissolution at 150° C and pH=2 indicates that these far from equilibrium rates are proportional to the reciprocal square root of aqueous aluminum concentration. This observation is consistent with the concept that one aluminum atom must be removed from the kyanite structure to form two silica rich precursor complexes on the mineral surface. Taking account of the composition of this precursor complex and TST, an equation to describe kyanite dissolution as a function of fluid composition can be derived, which is similar to eq. (6) but for which the exponent of the term ($a_{\text{H}^+}^3/a_{\text{Al}^{3+}}$) equals 0.5. The results of a fit of this equation is represented as dashed curves in Figure 2; these curves were computed with this equation by assuming $K(a_{\text{H}^+}^3/a_{\text{Al}^{3+}})^{0.5} \ll 1$.

CONCLUSIONS

The results presented above demonstrates that the hydrolysis of mixed oxide silicates is a multi-step process involving the breaking of several different bonds. Thus the rate laws controlling these reactions depend on the structure and chemistry of the mineral's near-surface region. The key to the hydrolysis of most aluminosilicates is the destruction of the oxide polymer composed of silicate and aluminate groups. As aluminate groups are much more reactive than silicate groups, the Al/Si ratio exerts an important control on the mechanism of polymer framework destruction. When the Al/Si ratio is small, like in alkali feldspars, aluminate sites can be completely removed without dramatically increasing the porosity of the solid and the rate limiting step for dissolution, as for quartz, is the breaking of Si-O bonds. At the other structural extreme, in minerals like olivines exhibiting a crosslink density of zero, the hydrolysis of modifier cation-oxygen bonds is likely rate limiting, permitting isolated silicate units to be directly converted to aqueous silica.

It is possible from structural considerations, surface chemistry determinations and measurements of reaction rates as a function of chemical affinity and solution composition, to characterize the rate limiting step and the precursor complex stoichiometry of several aluminosilicates. Taking account of precursor complex forming

reactions and TST leads to equations that can accurately describe the variation of these rates with respect to solution composition and chemical affinity. The stoichiometry of these rate controlling Si-rich, Al-deficient precursor complexes has two important applications for geochemical processes: 1) in agreement with observations made on natural hydrothermal and sedimentary systems, the dissolution/crystallization rates predicted by this revised interpretation are up to several orders of magnitude lower than previously postulated and, 2) crystallization rate constants of many aluminosilicate minerals may be similar to that of quartz.

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