Does organic acid adsorption affect alkali-feldspar dissolution rates?

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Abstract

Consideration of alkali-feldspar dissolution rates [1] taken from the literature suggests that in the absence of organic ligands and at far from equilibrium conditions they can be represented by $r_+ = k(a_{H^+}^3 / a_{Al^{+3}})^n$, where r_+ refers to the far from equilibrium dissolution rate, k designates a rate constant, a_i stands for the activity of the subscripted aqueous species, and n refers to a stoichiometric coefficient. Dissolution rates of these minerals have also been observed to increase substantially with increasing aqueous organic acid concentration. To assess if this latter effect is the result of either the change in aqueous aluminum activity due to aqueous aluminum–organic acid anion complex formation or organic acid anion adsorption to the mineral surface, dissolution rates predicted using the above equation are compared to measured alkali feldspar dissolution rates. A close correspondence between these predictions and the experimental data are found, providing strong evidence that organic acid anion adsorption does not affect alkali-feldspar dissolution rates. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic acids are suspected to enhance feldspar dissolution rates during both surface and diagenetic processes. Lundström and Öhman (1990) concluded that the presence of organic acids increases feldspar dissolution rates by a factor of 2–3 at the Earth surface conditions; Drever and Vance (1994) suggested the addition of 1 mM of oxalate to organic-free solutions increases feldspar dissolution rates by a factor of 1.5 at 25°C. Dissolution rate enhancement such as this may play a role in the atmospheric CO_2 content and therefore climate (Schwartzman and Volk, 1989; Brady, 1991; Brady and Carroll, 1994; Berner, 1995; Gislason et al., 1996). Feldspar dissolution rates are of particular interest in diagenesis due to its link to secondary porosity formation in sedimentary basins (Heald and Larese, 1973; Parker, 1974). Surdam et al. (1984) proposed that the presence of organic acids in oil field reservoirs might be

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an effective means to enhance feldspar dissolution and aluminum mobility in these systems. This possibility has been disputed by Giles et al. (1994), who found that neither petrographic evidence nor mass balance calculations supported organic acid enhancement of aluminum transport in sedimentary basins. Moreover, aluminum release due to feldspar dissolution in sedimentary basins is intimately connected with aluminum consumption by clay precipitation reactions (Bjørkum and Gjeldsvik, 1988; Bjørkum et al., 1993; Bjørlykke et al., 1995). Nevertheless, because of the possible role of organic acids in surficial weathering and diagenetic processes, exhaustive work has been aimed at characterizing their effect on (1) aqueous aluminum speciation (Fein, 1991a,b; Harrison and Thyne, 1992; Shock, 1993; Fein, 1994; Bénézeth et al., 1994; Palmer and Bell, 1994; Shock and Koretsky, 1995) and (2) feldspar dissolution rates (Mast and Drever, 1987; Bevan and Savage, 1989; Gestsdóttir and Manning, 1992; Hwang and Longo, 1992; Manning et al., 1992; Hajash, 1993; Welch and Ullman, 1993; Oxburgh et al., 1994; Blake and Walter, 1996; Stillings et al., 1996). The results of these studies indicate that at mildly acidic to neutral conditions aqueous aluminum–organic acid anion complex formation can substantially enhance feldspar solubility, and, in general, the presence of aqueous organic acids increases constant pH feldspar dissolution rates.

The goal of the present communication is to characterize the elementary mechanisms responsible for enhanced feldspar dissolution rates in the presence of organic acids. The addition of organic acids to aluminum bearing aqueous solutions provokes aluminum–organic acid anion complex formation at mildly acidic to neutral conditions. One of the consequences of this complex formation is to decrease the fraction of aqueous aluminum present as Al^{+3}. As several recent studies have noted that the dissolution rates of numerous aluminosilicate minerals increase with decreasing aqueous Al^{+3} activity (Devidal et al., 1992; Gautier et al., 1994; Oelkers et al., 1994; Oelkers and Schott, 1994, 1995a; Schott and Oelkers, 1995; Oelkers, 1996; Devidal et al., 1997), aqueous aluminum–organic acid anion complex formation will likely increase the dissolution rates of these minerals. The degree to which this single effect accounts for the observed enhancement of alkali-

feldspar dissolution rates in response to the presence of organic acids can be used to evaluate the role of other possible processes, such as anion surface adsorption, on alkali-feldspar dissolution mechanisms. The purpose of this paper is to compute the effect of aqueous aluminum–organic acid anion complex formation on alkali feldspar dissolution rates stemming from changes in aqueous Al^{+3} activity, compare computed results with experimental data available in the literature, and to use this comparison to evaluate the possible role of organic acid anion adsorption on these rates.

2. Theoretical background

The variation of mineral dissolution rates with solution composition and chemical affinity generally consists of two contributions: the forward dissolution rate of the mineral (r_+) and the effect of the reverse reaction (r_-), which in this case is the reprecipitation of the dissolving mineral. Thus, the overall dissolution rate (r) can be expressed as

$$r = r_+ - r_- = r_+ \left(1 - \frac{r_-}{r_+}\right) \qquad (1)$$

Taking account of transition state theory, Aagaard and Helgeson (1977, 1982) and Lasaga (1981) demonstrated that the second term in Eq. (1), which accounts for the effects of inverse reaction, can be expressed as

$$\left(1 - \frac{r_-}{r_+}\right) = \left(1 - \exp(-A/\sigma RT)\right) \qquad (2)$$

where R corresponds to the gas constant, T refers to absolute temperature, σ stands for the average stoichiometric number of Temkin (1963) (Boudart, 1976; Aagaard and Helgeson, 1982), and A signifies the chemical affinity of the overall reaction which is given by

$$A = RT \ln\left(\frac{K}{Q}\right) \qquad (3)$$

where K and Q designate the equilibrium constant and the activity quotient of the overall dissolution reaction. The form of Eq. (2) is such that at far from equilibrium conditions, when $A \gg \sigma RT$, (r_-/r_+)

tends to zero and the overall rate, r, is equal to the forward dissolution rate r_+.

The variation of forward dissolution rates with solution composition can be deduced from the dissolution mechanism. The dissolution of any aluminosilicate mineral is a complex process consisting of a series of elementary reactions. The result of each elementary reaction is to form an unique species at or near the mineral surface. The slowest of the elementary reactions is considered to be rate limiting. The species formed by the elementary reactions prior to the rate limiting elementary reaction are assumed to be in mutual equilibrium. The final species formed in the series of elementary reactions before the rate limiting elementary reaction is called the precursor complex, which is assumed to react irreversibly to form products. The forward dissolution rate is assumed to be the product of the precursor complex ($P^\cdot$) concentration and its destruction rate to form reaction products (Wieland et al., 1988; Stumm and Wieland, 1990). This concept is consistent with

$$r_+ = k_{P^\cdot}\{P^\cdot\} \qquad (4)$$

where $k_{P^\cdot}$ refers to a rate constant consistent with the $P^\cdot$ precursor complex and $\{P^\cdot\}$ stands for the precursor complex concentration. The precursor complex concentration can be determined quantitatively from the law of mass action for the overall reaction forming this complex from the original mineral. The identity of the precursor complex and it forming reactions are generally deduced from a combination of surface titration measurements and mineral dissolution rates obtained as a function of aqueous composition at far from equilibrium conditions.

The dissolution of alkali feldspars in the system $Na_2O–K_2O–Al_2O_3–SiO_2–H_2O–HCl$ involves a three step process consisting of (1) the relatively rapid exchange of hydrogen and alkali ions near the mineral surface, (2) an exchange reaction between three hydrogen atoms in solution with one aluminum atom in the mineral structure resulting in the breaking of Al–O bonds, coupled with the formation of rate controlling Si rich precursor complexes, and (3) the hydrolysis of Si–O bonds releasing the precursor complexes into solution (Oelkers and Schott, 1992; Oelkers et al., 1994; Gautier et al., 1994; Oelkers and Schott, 1995a,b; Gout et al., 1997). Within this

mechanism, the reaction forming the rate controlling precursor complex is given by

$$(3n)H + nAl < = nAl^{+3} + P^\cdot \qquad (5)$$
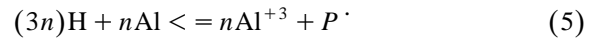
where $Al <$ represents an aluminum atom at the surface of alkali-feldspar, $P^\cdot$ designates the silica rich precursor complex, and n refers to a stoichiometric coefficient. Taking account of the law of mass action for this exchange reaction and the fact that there are a limited number of total possible exchange sites on the aluminosilicate surface, an equation describing the dissolution rates of minerals that follow this mechanism can be expressed as (Oelkers et al., 1994; Oelkers, 1996)

$$r_+ = k_+ \left(\frac{\left(\dfrac{a_{H^+}^3}{a_{Al^{+3}}}\right)^n}{1 + K_5^\cdot \left(\dfrac{a_{H^+}^3}{a_{Al^{+3}}}\right)^n} \right) \qquad (6)$$

where $K_5^\cdot$ designates the equilibrium constant for reaction (5) and k_+ denotes a rate constant. Similar rate expressions were obtained by Sverdrup and Warfvinge (1993, 1995) and Chou and Wollast (1985) for alkali-feldspar dissolution based on the formation of neutral aluminum-depleted precursor complexes. Taking account of experimental data at 150°C on albite (Oelkers et al., 1994) and K-feldspar (Gautier et al., 1994), and that obtained at 25°C for albite (Chou and Wollast, 1985), Oelkers et al. (1994) proposed that $n = 1/3$ at all temperatures. In contrast, consideration of data they obtained at temperatures from 5 to 90°C, Chen and Brantley (1997) argued that the effect of aluminum on alkali-feldspar dissolution rates decreases with decreasing temperature, and no effect of aluminum on alkali feldspar dissolution rates should be measurable at temperatures of less than 50°C. A survey of experimental data at 25°C reveals conflicting results (see below).

Eq. (6) reduces to

$$r_+ = k_+ \left(\frac{a_{H^+}^3}{a_{Al^{+3}}} \right)^n \qquad (7)$$

when the surface contains relatively few precursor complexes $(K_5^\cdot(\frac{a_{H^+}^3}{a_{Al^{+3}}})^n \ll 1)$. The simplified forward rate equation (Eq. (7)) has been demonstrated to

describe the variation of alkali feldspar rates at aluminum concentrations as low as 10^{-7} M (Gautier et al., 1994), suggesting that the denominator in Eq. (6) can be ignored for the interpretation of most experimental alkali-feldspar steady-state dissolution rate data. Note that experimental work reported by Stillings and Brantley (1995) suggests that the exchange reaction between hydrogen and alkali ions may also affect the overall concentration of the aluminum depleted precursor complex. This potential effect is neglected in the present analysis because (1) insufficient experimental data are available to completely characterize its role on feldspar dissolution rates, and (2) aqueous alkali metal–organic complexes are relatively weak (e.g., Fein, 1994; Shock and Koretsky, 1995; Fournier et al., 1998) so that these complexes will not appreciably affect dissolution rates computed with the aluminum depleted precursor complex model described above.

The logarithmic analog of Eq. (7) is given by

$$\log r_+ = \log k_+ + n \log\left(\frac{a_{H^+}^3}{a_{Al^{+3}}}\right) \qquad (8)$$

According to Eq. (8), the logarithms of constant temperature alkali-feldspar dissolution rates should plot as a single a linear function of log $(a_{H^+}^3/a_{Al^{+3}})$ with a slope of n. Plots of this kind are used below to evaluate the mechanism of feldspar dissolution rate enhancement by organic acids. If the logarithms of alkali feldspar dissolution rates measured in both organic acid-free and organic acid bearing aqueous solutions plot as a single function of log $(a_{H^+}^3/a_{Al^{+3}})$, the only effect of the presence of aqueous organic compounds stems from their complexation with aqueous aluminum. If the logarithms of dissolution rates obtained in organic acid bearing solutions plot above the linear relationship indicated by the rates measured in organic acid-free solutions, additional rate enhancement is indicated. Whereas, if the logarithms of dissolution rates obtained in organic acid bearing solutions plot below the linear relationship indicated by the rates measured in the absence of organic acids, additional rate inhibition is indicated. Such additional enhancement or inhibition of alkali feldspar dissolution rates could be a consequence of organic acid adsorption on the mineral surface.

3. Computational results and discussion

The degree to which feldspar dissolution rates in organic acid-free solutions available in the literature are consistent with the dissolution mechanism described above can be evaluated with the aid of Fig. 1. This figure illustrates as a function of log $(a_{H^+}^3/a_{Al^{+3}})$ (a) the logarithms of albite forward dissolution rates reported by Knauss and Wolery (1986) at 70°C as a function of pH and (b) the
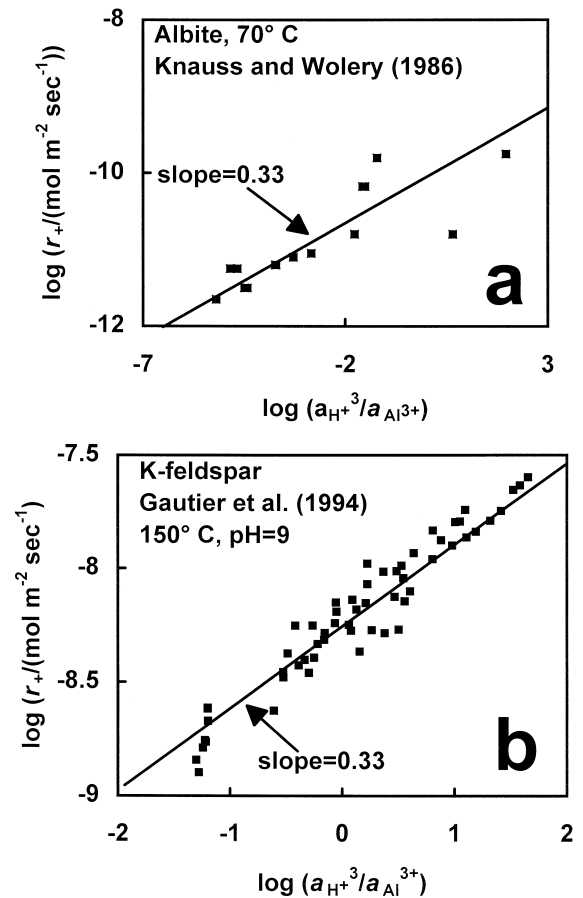

Fig. 1. Logarithms of experimentally measured forward dissolution rates as a function of log $(a_{H^+}^3/a_{Al^{+3}})$: (a) albite at 70°C and (b) K-feldspar at 150°C. Values of $(a_{H^+}^3/a_{Al^{+3}})$ in diagram a were generated from gibbsite saturation indexes reported by Knauss and Wolery (1986). The symbols represent rate data reported in the indicated references, whereas the linear curves correspond to the variation of these rates according to Eqs. (7) and (8), and $n = 0.33$, see text.
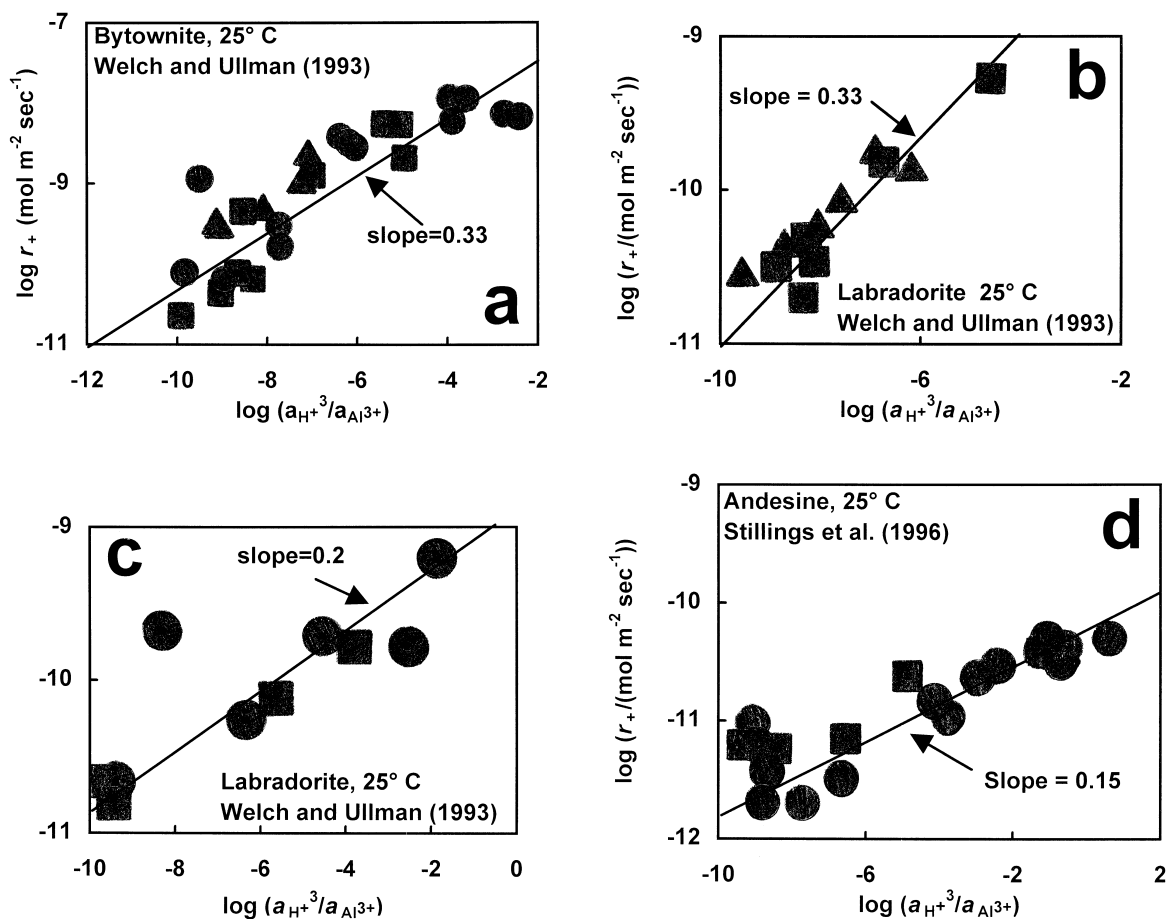
Fig. 2. Logarithms of experimentally measured forward dissolution rates at 25°C as a function of log $(a_{H^+}^3/a_{Al^{+3}})$: (a) bytownite (An56), (b) labradorite (An76), (c) labradorite (An76), and (d) andesine (An47). The filled squares, triangles, and circles correspond to data obtained in organic acid-free, acetic acid bearing, and oxalic acid bearing solutions, respectively; the linear curve corresponds to a fit of these data to Eq. (8). In the few instances where aqueous aluminum concentration was not reported, stoichiometric dissolution was assumed. The pH of these experiments ranged from 3 to 10. According to thermodynamic calculations performed using parameters reported by Pokrovskii and Helgeson (1995), reacting solutions are in equilibrium with gibbsite, boehmite, and diaspore when log $(a_{H^+}^3/a_{Al^{+3}})$ = −7.76, −7.56, and −7.16, respectively; data that plot at lower log $(a_{H^+}^3/a_{Al^{+3}})$ are supersaturated with respect to these minerals. This observation may account for the increased scatter apparent in the left side of these diagrams.

logarithms of K-feldspar forward dissolution rates reported by Gautier et al. (1994) at 150°C and pH 9 as a function of aqueous aluminum and silica concentration. [2] Values of the aqueous activity quotient

were calculated from reported solution compositions using the EQ3 computer code (Wolery, 1983) together with dissociation constants for aluminum hydroxide species taken from Pokrovskii and Helgeson (1995). The linear curve in these figures have a slope of 0.33, which is consistent with that proposed by Oelkers et al. (1994). The close correspondence between the symbols and these linear curves support strongly the mechanism outlined above for feldspar dissolution in organic acid-free aqueous solutions.

[2] Although Gautier et al. (1994) reported K-feldspar dissolution rates at chemical affinities as low as 4.7 kcal/mol, only rates for which $A > 14$ kcal/mol are depicted in Fig. 1b because at close to equilibrium conditions, r_+ is significantly greater than the measured overall rate (see Eqs. (1) and (2)).

Table 1
Equilibrium constants used to compute the stability of aqueous metal–organic acid anion complexes at 25°C in the present study

Reaction	log K	Ref.
$H_2C_2O_4^0 = H^+ + HC_2O_4^-$	−1.252	Martell and Smith (1977)
$HC_2O_4^- = H^+ + C_2O_4^{2-}$	−4.266	Martell and Smith (1977)
$CH_3COOH^0 = H^+ + CH_3COO^-$	−4.5	Archer and Monk (1964)
$AlC_2O_4^+ = Al^{+3} + C_2O_4^{2-}$	−6	Sjöberg and Öhman (1985)
$Al(C_2O_4)_2^- = Al^{+3} + 2C_2O_4^{2-}$	−11	Kharaka et al. (1988)
$Al(CH_3COO)^{+2} = Al^{+3} + CH_3COO^-$	−2.8	Palmer and Bell (1994)
$Al(CH_3COO)_2^+ = Al^{+3} + 2CH_3COO^-$	−4.6	Palmer and Bell (1994)
$Ca(CH_3COO)^+ = Ca^{+2} + CH_3COO^-$	−1.1	Archer and Monk (1964)
$NaC_2O_4^- = Na^+ + C_2O_4^{2-}$	−1.0	Kharaka et al. (1988)
$Na(CH_3COO)^0 = Na^+ + CH_3COO^-$	0.4	Archer and Monk (1964)

The degree to which the observed alkali-feldspar dissolution rate enhancement in the presence of organic acids can be accounted for by the aluminum-depleted precursor mechanism described above can be assessed by an evaluation of the experimental data reported by Welch and Ullman (1993) and Stillings et al. (1996). These experimental studies are considered because they report feldspar steady state dissolution rates (1) over a wide range of pH, (2) in both organic acid-free, and oxalic and acetic acid bearing solutions, and (3) provide the aqueous aluminum concentrations of the reacting fluids. Logarithms of rates reported in these studies are depicted as a function of log $(a_{H^+}^3/a_{Al^{+3}})$ in Fig. 2. Values of this aqueous activity quotient were calculated from reported solution compositions using the EQ3 computer code (Wolery, 1983) together with dissociation constants for aluminum hydroxide species taken from Pokrovskii and Helgeson (1995) and those for possible organo-metallic complexes given in Table 1. It can be seen in Fig. 2 that the logarithm of feldspar dissolution rates measured in organic acid-free solutions (as indicated by the solid circles) plot as a linear function of log $(a_{H^+}^3/a_{Al^{+3}})$ and that the symbols representing the logarithm of rates measured in the presence of oxalic and acetic acid fall on the same linear curves. The linear curves in Fig. 2a and b have a slope of 0.33 which is consistent with that suggested by Oelkers et al. (1994). In contrast, the linear curves consistent with the data in Fig. 2c and d have slopes of 0.2 and 0.15, respectively. One possible reason for the lower slopes in the latter two plots is that some of these experimental data were obtained from experiments performed in solutions that

were supersaturated with respect to secondary phases. For example, if the data shown in Fig. 2d obtained in solutions that were supersaturated with respect to diaspore were removed from the regression calculations, one obtains a slope of greater than 0.2.

The extent to which the scatter apparent in Fig. 2 is due to the effect of organic acid concentration can be assessed with the aid of Fig. 3. According to Eq. (8), if the variation of r_+ with solution composition stems only from the aluminum depleted precursor complex mechanism described above, log r_+ −
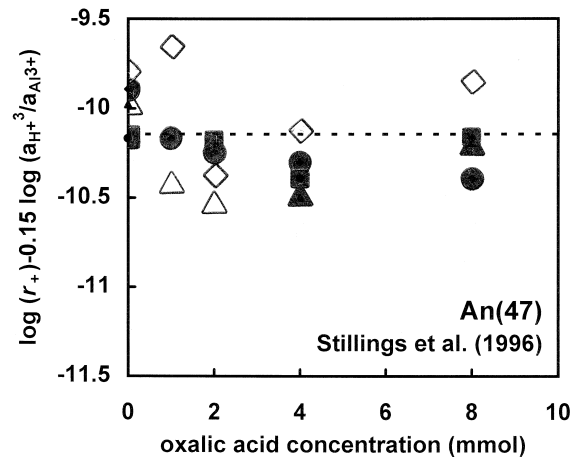

Fig. 3. log $r_+ - 0.15 \log(a_{H^+}^3/a_{Al^{+3}})$ depicted as a function of the reactive fluid oxalic acid concentration. The symbols correspond to data reported by Stillings et al. (1996) and the line represents the average value of these data. The circles, squares, triangles, and diamonds correspond to data obtained at pH = ~ 3, ~ 4, ~ 5, and ~ 7, respectively; open and filled symbols represent data obtained in solutions supersaturated and undersaturated with respect to diaspore (see text).

$n \log(a_{H^+}^3/a_{Al^{+3}})$ should be constant. This term is plotted as a function of the oxalic acid concentration of the reactive fluids investigated by Stillings et al. (1996) in Fig. 3. Only the data of Stillings et al. (1996) are considered in this figure because this is the only study that provides feldspar dissolution rates at a variety of different organic acid concentrations and at fixed pH. It can be seen in this figure that although there is scatter of up to 0.5 log units around the average, no systematic variation in the symbols are apparent with oxalic acid concentration. It should be emphasized that the scatter in the data obtained in solutions that were supersaturated with respect to aluminum bearing solids is significantly greater than that obtained in undersaturated solutions.

The plots illustrated in Figs. 2 and 3 indicate that the logarithms of alkali-feldspar forward dissolution rates can be described as a single linear function of $\log(a_{H^+}^3/a_{Al^{+3}})$ in both the presence and absence of organic acids. This observation strongly supports the concept that enhanced alkali-feldspar dissolution in the presence of aqueous organic acids stems directly from the aluminum deficient precursor complex mechanism described above. The adsorption of organic acid anions to this surface, if it indeed occurs, has a negligible affect on alkali-feldspar dissolution rates. This conclusion is in contrast with models proposed by Amrhein and Suarez (1988) and Stillings et al. (1996), who suggest that this dissolution rate enhancement is a consequence of organic acid anion adsorption to aluminum surface sites. These models are based on: (a) the observation that the tendency of metal–organic anion surface complex formation on simple oxides (e.g., Al_2O_3, and Fe_2O_3) is correlated with the tendency to form the corresponding aqueous metal–organic anion complex (Ikeda et al., 1982; Schindler and Stumm, 1987; Stumm and Furrer, 1987) and (b) the observation by Furrer and Stumm (1986) of a marked enhancement of δ-Al_2O_3 dissolution rates in the presence of aqueous oxalate, malonate, and salicylate anions. This latter effect was attributed by the authors to the formation of bidentate bonds at the solid–liquid interface that polarize adjoining Al–O bonds, thereby facilitating metal detachment. Such a mechanism is not likely to operate for alkali feldspar dissolution, however, as this mineral develops Al-depleted surface regions in solution as shown by surface analysis

(Casey et al., 1989; Casey and Bunker, 1990; Hellmann et al., 1990; Oelkers and Schott, 1992; Gout et al., 1997) and titrations (Schott, 1990, Oelkers et al., 1995). As organic acid anions exhibit only weak aqueous and surface complexation with silica (Pokrovski, 1996; Poulson et al., 1997; Pokrovski and Schott, 1998), organic acid cations cannot adsorb on the silica-rich/Al-depleted surface of dissolving alkali-feldspars. [3]

Forward albite dissolution rates in the system HCl–NaCl–Al_2O_3–SiO_2–organic acid–H_2O computed using Eq. (7) and $n = 1/3$ together with the results of solute speciation calculations performed using the EQ3 computer program are illustrated in Fig. 4. All calculations were performed assuming a 10^{-2} M NaCl solution and 10^{-6} M total dissolved Al; pH is controlled by adding the appropriate quantities of HCl or NaOH. The curves in Fig. 4a illustrate computed forward albite dissolution rates with and without added oxalic acid. The computed results indicate that oxalic acid affects forward albite dissolution rates only over the pH range 2–7; at higher or lower pH aqueous aluminum oxalate complexing is negligible. The maximum effect of oxalic acid is predicted to occur at a pH of 4–5, where the addition of 10^{-3} M oxalic acid is predicted to raise forward albite dissolution rate at a constant total aqueous aluminum concentration by close to two orders of magnitude. As can be seen in Fig. 4b, the effect of acetic acid on forward albite dissolution rates is also limited to mildly acidic conditions, but this effect is far lower than the corresponding effect of oxalic acid. The maximum increase in the forward albite dissolution rate for the addition of 10^{-2} M acetic acid and a total aqueous aluminum concentration of 10^{-6} M is only a factor of two at pH = 5.2. These computed results are closely consistent with the experimental results of Welch and Ullman (1993)—see also Oelkers and Schott (1995a). It should additionally be noted that aqueous aluminum–organic anion complexing will affect the chemical affinity of the overall dissolution reaction, which itself will affect overall alkali-feldspar dissolution rates at near to

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[3] This conclusion is in agreement with recently performed, but yet to be published surface titration experiments (Brady, personal communication).
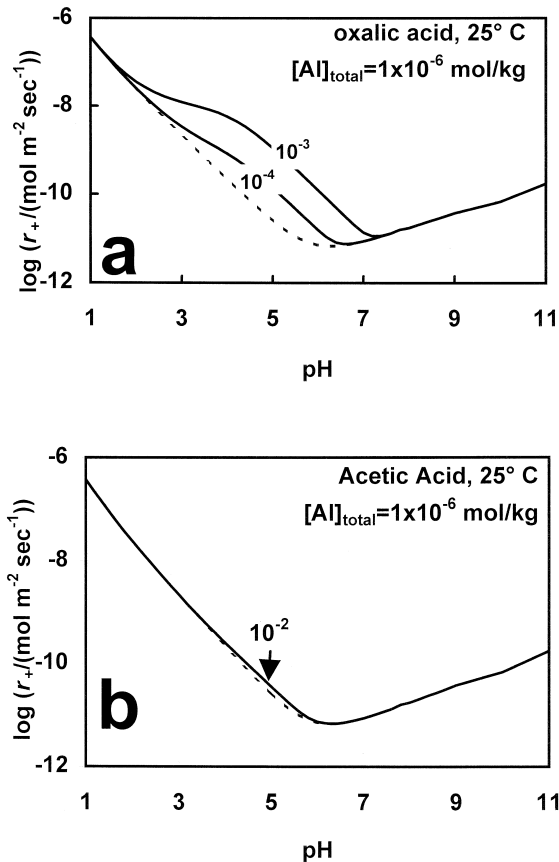
Fig. 4. Predicted albite forward dissolution rates in a 10^{-2} M NaCl solution containing 10^{-6} M total dissolved Al as a function of pH, generated using Eq. (7) and $n = 0.33$ together with the results of solute speciation calculations performed using the EQ3 computer code and thermodynamic parameters given in Table 1. The dashed curves correspond to results computed for organic acid-free solutions, whereas the solid curves in (a) and (b) represent results for oxalic acid bearing and acetic acid bearing solutions, respectively. The numbers on the curves correspond to the organic acid concentrations in mol/kg. Although some of these solutions are supersaturated with respect to some aluminum bearing minerals at near neutral pH they are included in this figure because they are representative of conditions considered during laboratory experiments.

equilibrium conditions. This later effect may dominate in some natural systems (Drever et al., 1996).

4. Conclusions

The analysis and comparisons presented above indicate that the observed enhancement of constant pH alkali-feldspar forward dissolution rates by the presence of aqueous organic acids can be accurately described using the aluminum deficient precursor complex dissolution mechanism. As this mechanism considers only the effect of precursor complex concentration on alkali-feldspar surfaces to compute rates, this observation suggests strongly that organic acid anion surface adsorption, if it does occur, has a negligible effect on alkali feldspar dissolution rates. Owing to the success of the aluminum deficient precursor complex dissolution mechanism to the description of alkali-feldspar dissolution rates in both organic acid-present and organic acid-free aqueous solutions it seems likely that this mechanism may be used for the accurate prediction of rates in a wide variety of solution compositions present in natural systems.

References

Aagaard, P., Helgeson, H.C., 1977. Thermodynamic and kinetic constraints on the dissolution of feldspars. Geol. Soc. Am. 9, 873, Abstracts with Program.

Aagaard, P., Helgeson, H.C., 1982. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions: I. Theoretical considerations. Am. J. Sci. 282, 237–285.

Amrhein, C., Suarez, D.L., 1988. The use of a surface complexion model to describe the kinetics of ligand-promoted dissolution of anorthite. Geochim. Cosmochim. Acta 52, 2785–2793.

Archer, D.W., Monk, C.B., 1964. Ion-association constants of some acetates by pH (glass electrode) measurements. J. Chem. Soc. 1964, 3117–3122.

Bénézeth, P., Castet, S., Dandurand, J.L., Schott, J., 1994. Experimental study of aluminum acetate complexing between 60 and 200°C. Geochim. Cosmochim. Acta 58, 4561–4571.

Berner, R.A., 1995. Chemical weathering and its effect on atmospheric CO_2 and climate. Rev. Mineral. 31, 565–583.

Bevan, J., Savage, D., 1989. The effect of organic acids on the dissolution of K-feldspar at conditions relevant to burial diagenesis. Mineral. Mag. 53, 415–425.

Bjørkum, P.-A., Gjeldsvik, N., 1988. An isochemical model for formation of authigenic kaolinite, K-feldspar, and illite in sediments. J. Sed. Pet. 58, 506–511.

Bjørkum, P.-A., Walderhaug, O., Aase, N.E., 1993. A model for the effect of illitization on porosity and quartz cementation of sandstones. J. Sed. Pet. 63, 1089–1091.

Bjørlykke, K., Aagaard, P., Egenerg, P.K., Simmons, S.P., 1995. Geochemical constraints from formation water analyses from the North Sea and the Gulf Coast Basins on quartz, feldspar and illite precipitation in reservoir rocks. In: Cubitt, J.M., England, W.A. (Eds.), The Geochemistry of Reservoirs, Geochemical Soc. Spec. Pub., 86, pp. 33–50.

Blake, R.E., Walter, L.M., 1996. Effects of organic acids on the dissolution of orthoclase at 80°C and pH 6. Chem. Geol. 132, 91–102.

Boudart, M., 1976. Consistency between kinetics and thermodynamics. J. Phys. Chem. 80, 2869–2870.

Brady, P.V., 1991. The effect of silicate weathering on global temperature and atmospheric CO_2. J. Geophys. Res. B 96, 18101–18106.

Brady, P.V., Carroll, S.A., 1994. Direct effects of CO_2 and temperature on silicate weathering. Geochim. Cosmochim. Acta 58, 1853–1856.

Casey, W.H., Bunker, B., 1990. Leaching of mineral and glass surfaces during dissolution. Rev. Mineral. 23, 397–426.

Casey, W.H., Westrich, H.R., Massis, T., Banfield, J.F., Arnold, G.W., 1989. The surface chemistry of labradorite feldspar after acid hydrolysis. Chem. Geol. 78, 205–218.

Chen, Y., Brantley, S.L., 1997. Temperature and pH dependence of albite dissolution rate at acid pH. Chem. Geol. 135, 275–290.

Chou, L., Wollast, R., 1985. Steady state kinetics and dissolution mechanisms of albite. Am. J. Sci. 285, 963–993.

Devidal, J.L., Dandurand, J.L., Schott, J., 1992. Dissolution and precipitation kinetics of kaolinite as a function of chemical affinity ($T = 150°C$, $pH = 2$ and 7.8). In: Kharaka, Y.K., Maest, A.S. (Eds.), Water Rock Interaction. A.A. Balkema, Rotterdam, 1, pp. 93–96.

Devidal, J.L., Schott, J., Dandurand, J.L., 1997. An experimental study of the dissolution and precipitation kinetics of kaolinite as a function of chemical affinity and solution composition at 150°C, 40 bars, and pH 2, 6.8, and 7.8. Geochim. Cosmochim. Acta 61, 5165–5186.

Drever, J.I., Vance, G.F. 1994. Role of soil organic acids in mineral weathering processes. In: Pittman, E.D., Lewan, M.D. (Eds.), Organic Acids in Geological Processes. Springer Verlag, Berlin, pp. 138–161.

Drever, J.I., Poulson, S.R., Stillings, L.L., Sun, Y. 1996. The effect of oxalate on the dissolution rate of quartz and plagioclase feldspars at 20–25°C. In Geochemistry of Crustal Fluids: Water/Rock Interaction During Natural Processes, Seefeld, Austria, 6–11 December 1996, Conference Abstracts, pp. 39.

Fein, J.B., 1991a. Experimental study of aluminum-, calcium-, and magnesium-acetate complexing at 80°C. Geochim. Cosmochim. Acta 55, 955–964.

Fein, J.B., 1991b. Experimental study of aluminum–oxalate complexing at 80°C: implications for the formation of secondary porosity within sedimentary reservoirs. Geology 19, 1037–1040.

Fein, J.B., 1994. Porosity enhancement during clastic diagenesis as a result of aqueous metal–carboxylate complexation: experimental studies. Chem. Geol. 115, 263–279.

Fournier, P., Oelkers, E.H., Gout, R., Pokrovski, G., 1998. Experimental determination of aqueous sodium-acetate dissociation constants at temperatures from 20° to 240°C. Chem. Geol. 151, 69–84.

Furrer, G., Stumm, W., 1986. The coordination chemistry of weathering: dissolution kinetics of Al_2O_3 and BeO. Geochim. Cosmochim. Acta 50, 1847–1860.

Gautier, J.-M., Oelkers, E.H., Schott, J., 1994. Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150°C and pH 9. Geochim. Cosmochim. Acta 58, 4549–4560.

Gestsdóttir, K., Manning, D.A.C., 1992. An experimental study of the dissolution of albite in the presence of organic acids. In: Kharaka, Y.K., Maest, A.S. (Eds.), Water–Rock Interaction WRI-7. A.A. Balkema, pp. 315–318.

Giles, M.R., de Boer, R.B., Marshall, J.D., 1994. How important are organic acids in generating secondary porosity in the subsurface. In: Pittman, E.D., Lewan, M.D. (Eds.), Organic Acids in Geological Processes. Springer Verlag, Berlin, pp. 449–470.

Gislason, S.R., Rose, N.M., Oelkers, E.H., 1996. Chemical weathering, glaciers and the carbon cycle. In: Botterell, S.H. (Ed.), 4th International Symposium on the geochemistry of the Earth's surface, University of Leeds, United Kingdom, pp. 574–577.

Gout, R., Oelkers, E.H., Schott, J., Zwick, A., 1997. The surface structure of acid leached albite—new Insights on the dissolution mechanism of alkali feldspars. Geochim. Cosmochim. Acta 61, 3013–3018.

Hajash, A., 1993. Comparison and evaluation of experimental studies on dissolution of minerals by organic acids. In: Pittman, E.D., Lewan, M.D. (Eds.), Organic Acids in Geological Processes. Springer Verlag, Berlin, pp. 201–225.

Harrison, W.J., Thyne, G.D., 1992. Predictions of diagenetic reactions in the presence of organic acids. Geochim. Cosmochim. Acta 56, 565–586.

Heald, M.T., Larese, R.E., 1973. The significance of feldspar in porosity development. J. Sed. Pet. 43, 458–460.

Hellmann, R., Eggleston, C.M., Hochella, M.F., Crerar, D.A., 1990. The formation of leached layers on albite surfaces during dissolution under hydrothermal conditions. Geochim. Cosmochim. Acta 54, 1267–1281.

Hwang, W.-L., Longo, J.M., 1992. The effects of organics on feldspar dissolution under hydrothermal conditions. Chem. Geol. 98, 271–292.

Ikeda, T., Sasaki, M., Hachiya, K., Astumian, R.D., Yasunaga, T., Schelly, Z.A., 1982. Adsorption–desorption kinetics of acetic acid on silica–alumina particles in aqueous suspensions using the pressure-jump relaxation method. J. Phys. Chem. 86, 3861–3866.

Kharaka, Y.K., Gunter, W.D., Aggarwal, P.K., Perkins, E.H., DeBrall, J.D., 1988. SOLMINEQ.88: A computer program code for geochemical modeling of water–rock interactions. U.S. Geol. Sur. Water Res. Invest. Rep. 88-4227.

Knauss, K.G., Wolery, T.J., 1986. Dependence of albite dissolution kinetics on pH and time at 25°C and 70°C. Geochim. Cosmochim. Acta 50, 2481–2497.

Lasaga, A.C., 1981. Transition state theory. Rev. Mineral. 8, 135–169.

Lundström, U., Öhman, L.-O., 1990. Dissolution of feldspars in the presence of natural organic solutes. J. Soil Sci. 41, 359–369.

Manning, D.A.C., Gestsdottir, K., Rae, E.I.C., 1992. Feldspar dissolution in the presence of organic acid anions under diagenetic conditions: an experimental study. Adv. Org. Geochem. 19, 483–492.

Martell, A.E., Smith, R.M. 1977. Critical Stability Constants, Vol. 3, Other Organic Ligands, Plenum.

Mast, M.A., Drever, J.L., 1987. The effect of oxalate on the dissolution rates of oligoclase and tremolite. Geochim. Cosmochim. Acta 51, 2559–2568.

Oelkers, E.H., 1996. Summary and review of the physical and chemical properties of rocks and fluids. Rev. Mineral. 34, 131–191.

Oelkers, E.H., Schott, J., 1992. The dissolution rate of albite as a function of chemical affinity and the stoichiometry of activated complexes in aluminosilicate dissolution reactions. Geol. Soc. Am. 24, A207, Abstracts with program.

Oelkers, E.H., Schott, J., 1994. Experimental study of kyanite dissolution rates as a function of Al and Si concentration. Miner. Mag. 58A, 659–660.

Oelkers, E.H., Schott, J., 1995a. The dependence of silicate dissolution rates on their structure and composition. In: Kharaka, Y.K., Chudaev, O.V. (Eds.), Water Rock Interaction. A.A. Balkema, pp. 153–156.

Oelkers, E.H., Schott, J., 1995b. Experimental study of anorthite dissolution and the relative mechanism of feldspar hydrolysis. Geochim. Cosmochim. Acta. 59, 5039–5053.

Oelkers, E.H., Schott, J., Devidal, J.-L., 1994. The effect of aluminum, pH, and chemical affinity on the rates of aluminosilicate dissolution reactions. Geochim. Cosmochim. Acta 58, 2011–2024.

Oelkers, E.H., Schott, J., Ward, D.B., Brady, P.V., Gout, R., 1995. The dissolution rates of single and multi-(hydr)oxide silicate minerals: I. Experimental observations. Geol. Soc. Am. 27, A–43, Abstract with programs.

Oxburgh, R., Drever, J.I., Sun, Y.-T., 1994. Mechanism of plagioclase dissolution in acid solution at 25°C. Geochim. Cosmochim. Acta 58, 661–669.

Palmer, D.A., Bell, J.L.S., 1994. Aluminum speciation and equilibria in aqueous solution: IV. A potentiometric study of aluminum acetate complexation in acidic NaCl brines to 150°C. Geochim. Cosmochim. Acta 58, 651–660.

Parker, C.A., 1974. Geopressures and secondary porosity in the deep Jurassic of Mississippi. Gulf Coast Assoc. Trans. 29, 69–80.

Pokrovski, G., 1996. Etude expérimentale du comportement du germanium, du silicium et de l'arsenic et de la complexation de l'aluminium avec la silice dans les solutions naturelles. Thèse Université Paul Sabatier, Toulouse, France, 174 pp.

Pokrovskii, V.A., Helgeson, H.C., 1995. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system Al_2O_3–H_2O–NaCl. Am. J. Sci. 295, 1255–1342.

Pokrovski, G., Schott, J., 1998. Experimental study of the complexation of silicon and germanium with aqueous organic species. Implications for Ge and Si transport and the Ge/Si ratio in natural waters. Geochim. Cosmochim. Acta, (in press).

Poulson, S.R., Drever, J.I., Stillings, L.L., 1997. Aqueous Si–oxalate complexing, oxalate adsorption onto quartz, and the effect of oxalate upon quartz dissolution rates. Chem. Geol. 140, 1–7.

Schindler, P.W., Stumm, W. 1987. The surface chemistry of oxide, hydroxide and oxide minerals. In: Stumm, W. (Ed.), Aquatic Surface Chemistry. Wiley-Interscience, New York, pp. 83–110.

Schott, J., 1990. Modelling of dissolution of strained and unstrained multiple oxides: The surface speciation approach. In: Stumm, W. (Ed.), Aquatic Chemical Kinetics, Wiley-Interscience, New York, 337–366.

Schott, J., Oelkers, E.H., 1995. Dissolution and crystallization rates of silicate minerals as a function of chemical affinity. Pure Appl. Chem. 67, 603–610.

Shock, E.L., 1993. Application of thermodynamic calculations to geochemical processes involving organic acids. In: Pittman, E.D., Lewan, M.D. (Eds.), Organic Acids in Geological Processes. Springer Verlag, Berlin, pp. 270–318.

Shock, E.L., Koretsky, C.M., 1995. Metal–organic complexes in geochemical processes: Estimation of standard partial molal properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 1497–1532.

Schwartzman, D.W., Volk, T., 1989. Biotic enhancement of weathering and the habitability of earth. Nature 340, 457–460.

Sjöberg, S., Öhman, L.-O., 1985. Equilibrium and structural studies of silicon (IV) and aluminum (III) in aqueous solution: Part 13. A potentiometric and 27Al nuclear magnetic resonance study of speciation and equilibra in the aluminum (III)–oxalic acid–hydroxide system. J. Chem. Dalton Trans. 1985, 2665–2669.

Stillings, L.L., Brantley, S.L., 1995. Feldspar dissolution at 25°C and pH 3, reaction stoichiometry and the effect of cations. Geochim. Cosmochim. Acta 59, 1483–1496.

Stillings, L.L., Drever, J.I., Brantley, S.L., Sun, Y., Oxburgh, R.,

1996. Rates of feldspar dissolution at pH 3–7 with 0.8 mM oxalic acid. Chem. Geol. 132, 79–89.

Stumm, W., Furrer. G., 1987. The dissolution of oxides and aluminum silicates; Examples of surface-coordination controlled kinetics. In: Stumm, W. (Ed.), Aquatic Surface Chemistry. Wiley-Interscience, New York, pp. 197–219.

Stumm, W., Wieland, E., 1990. Dissolution of oxide and silicate minerals: Rates depend on surface speciation. In: Stumm, W. (Ed.), Aquatic Chemical Kinetics. Wiley-Interscience, New York, pp. 367–400.

Surdam, R.C., Boese, S.W., Crossey, L.J., 1984. The chemistry of secondary porosity. In: McDonald, D.A., Surdam, R.C., (Eds.), Clastic Diagenesis, Am. Assoc. Pet. Geol. Mem. 37, pp. 127–150.

Sverdrup, H., Warfvinge, P., 1993. Calculating field weathering rates using a mechanistic geochemical model-PROFILE. J. Appl. Geochem. 8, 273–283.

Sverdrup, H., Warfvinge, P., 1995. Estimating field weathering rates using laboratory kinetics. Rev. Mineral. 31, 485–541.

Temkin, M.I., 1963. The kinetics of stationary reactions. Akad. Nauk SSSR Doklady 152, 782–785, (in Russian).

Welch, S.A., Ullman, W.L., 1993. The effect of organic acids on plagioclase dissolution rates and stoichiometry. Geochim. Cosmochim. Acta 57, 2725–2736.

Wieland, E., Werhli, B., Stumm, W., 1988. The coordination chemistry of weathering: III. A potential generalization on dissolution rates of minerals. Geochim. Cosmochim. Acta 52, 1969–1981.

Wolery, T.J., 1983. EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: Users guide and documentation. UCRL-53414. Lawrence Livermore National Laboratory, Livermore, CA.