The effect of organic acids on the dissolution of K-feldspar under conditions relevant to burial diagenesis

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Abstract

The mechanism by which secondary porosity in sandstone reservoirs is produced is poorly understood. Previous hypotheses to account for the increased dissolution of framework silicates have invoked the introduction of acidic and/or organic-rich fluids capable of complexing metals. In order to evaluate the relative effects of these factors, the rates of K-feldspar dissolution have been measured at 70 °C and 95 °C, at pH values of 1, 4, and 9, with and without oxalic acid, at a total pressure of 50 MPa, using direct sampling autoclaves. The presence of oxalic acid increased the dissolution rate of K-feldspar at pH 4 and 9, but decreased the rate at pH 1 at both temperatures. The maximum increase in dissolution rate was observed at pH 4, 95 °C, by a factor ~4. In oxalic-free experiments, the rate of dissolution increased an order of magnitude with each unit decrease in pH in the pH regime 1–4. In the presence of oxalic acid, this dependency of dissolution upon pH decreased to approximately an order of magnitude increase with each decrease in pH by 2 pH units. The dissolution process was observed to be stoichiometric under all conditions, indicating that the mechanism by which rates are increased was not due to preferential complexation of aluminium, but rather by an increase in the overall solubility of feldspar in the neutral pH region. This regime of increased rate of reaction of feldspar coincides with that expected to be naturally buffered by the introduction of organic acids into a sandstone reservoir system.

KEYWORDS: organic acids, K-feldspar, dissolution, diagenesis.

Introduction

THE dissolution of feldspar in reservoir sandstones undergoing burial diagenesis may be an important factor in creating extra porosity in such formations (Schmidt and MacDonald, 1979). Potash feldspar, $KAlSi_3O_8$, is a significant constituent of many sandstones, and can account for up to 30% of the detrital components. Deeply buried reservoir sandstones commonly have a much reduced feldspar content—oversized pores containing grain remnants (seen in thin section) indicate that this is due to dissolution (Moncure et al., 1984). Since K-feldspar is such a common component of sandstones, its dissolution can create significant levels of secondary porosity. A closer understanding of the way in which this dissolution occurs may lead to greatly refined models of porosity prediction in the subsurface (e.g. Scherer, 1987).

The amount of porosity created in the subsurface by feldspar dissolution is determined by the rate and magnitude (solubility) of feldspar reaction with pore fluids, coupled with the volumetric flow rate of such pore fluids through the reservoir formation. The rate and magnitude of feldspar removal is intimately linked with the ability to transport aluminium in solution. Aluminium is least soluble in the neutral pH 5–7 regime characteristic of most oilfield brines, due to its amphoteric chemical behaviour (Curtis, 1978; Kharaka et al., 1986). The problem of increasing feldspar dissolution then becomes one of enhancing Al mobility within the fluid phase. There are two major hypotheses which have been proposed to account for this phenomenon.

Firstly, the expulsion of acidic pore waters from underlying shales has been suggested as a major cause of increased mobility of Al (Curtis, 1978; Irwin and Hurst, 1983; Siebert et al., 1984). These

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pore fluids may contain large volumes of carbon dioxide derived from the thermal decarboxylation of organic matter. Carbon dioxide is quickly converted to carbonic acid, which then lowers the pH of the expelled fluids (Curtis, 1983). Hydrogen ions may also be produced in the expelled pore fluids by the alteration of unstable clay minerals to illite (Bjorlykke, 1984).

More recently, the association of organic acids with the pore fluids expelled from underlying shales has been invoked as a means of complexing the aluminium, thus increasing aluminosilicate solubility (Surdam et al., 1984; Surdam and Crossey, 1985). Oilfield brines are known to contain a range of organic acids of variable concentration (Carothers and Kharaka, 1978; Kharaka et al., 1986). The experiments of Surdam et al. (1984) showed that organic acids such as acetic and oxalic are generated by compacting muds, particularly in the temperature range 70–100 °C. Acetic acid was found to enhance the solubility of aluminosilicates by one order of magnitude, and oxalic acid (difunctional and thus a better chelating agent) by up to three orders of magnitude. The increased dissolution of feldspar via Al-complexation by organic acids has been widely invoked as a means of generating large-scale secondary porosity in reservoir sandstones (Burley, 1986; Goodchild and Whitaker, 1986; Edman and Surdam, 1986; Meshri, 1986).

Evaluations of these hypotheses have been attempted by a number of authors (e.g. Giles and Marshall, 1986; Lundegard et al., 1984), although ultimately, these assessments have been inhibited by a lack of experimental data relating to feldspar dissolution under controlled conditions relevant to deep burial. The present study was designed to remedy this situation.

Previous dissolution studies

Early experimental studies of feldspar were conducted to examine the dissolution mechanism. The papers by Wollast (1967), Busenberg and Clemency (1976) and Siegel and Pfannkuch (1984) are all examples of this type of study conducted at earth surface conditions (25 °C, 1 atmosphere pressure).

Although laboratory experiments investigating feldspar behaviour with organic acids have been conducted previously, they have not always been carried out under well controlled conditions, in order to separate the effects of temperature, pH, and the presence of organic acids. Huang and Kiang (1972) found organic acids to increase the dissolution rates of plagioclase feldspars significantly. Their experiments, however, conducted

at room temperature, failed to buffer the pH, which may well have had an overriding effect on the dissolution behaviour. More recently, Manley and Evans (1986) observed the effects of organic acids on feldspars at 13 °C, a temperature typical of temperate weathering conditions. Although observing an increase in element release by the addition of organic acids, they concluded that it was the strength of the acids, rather than their complexing abilities, that was causing the increased dissolution. Mast and Drever (1987) investigated the dissolution behaviour of oligoclase and tremolite under controlled conditions of pH and temperature (22 °C), using a fluidized bed reactor of the type developed by Chou and Wollast (1984). These authors noted no increase in dissolution rate due to the addition of oxalate at 0.5 and 1 mM.

All of the above studies examined the effect of organics under atmospheric conditions. The experiments of Surdam et al. (1984) were designed to investigate the effects of organics upon aluminosilicate dissolution under conditions appropriate to burial diagenesis, but these authors did not buffer pH conditions, nor monitor changing fluid composition with time in their experiments. Only the initial and final readings of element concentrations and pH were made, and the P_{CO_2} was not buffered. However, the results of these experiments revealed increased solubility of Al in the presence of organic acids.

The present study was aimed at clarifying the findings of these past investigations by investigating the dissolution behaviour of K-feldspar at buffered pH values of 1, 4, and 9 under physical conditions appropriate to burial diagenesis (temperatures of 70° and 95 °C, 500 bars pressure), and both with, and without, the presence of organic acids. The temperatures employed are on either side of the organic acid generation 'window' suggested by Surdam et al. (1984).

Mechanisms of feldspar dissolution

Most authors now concur that feldspar dissolution under conditions far from chemical equilibrium proceeds via a surface-controlled chemical reaction, catalysed by the activities of certain chemical species (particularly the hydronium and hydroxide ions) in the fluid phase (Lagache, 1965; Holdren and Berner, 1979; Aagaard and Helgeson, 1982; Helgeson et al., 1984; Lasaga, 1984; Chou and Wollast, 1984; Knauss and Wolery, 1986; Murphy and Helgeson, 1987). Although the initial stages of dissolution appear to be non-stoichiometric, involving preferential release of alkali cations and possibly aluminium (Chou and
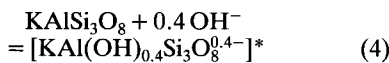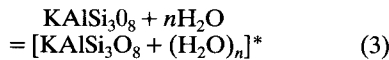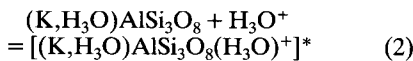
Wollast, 1985; Holdren and Speyer, 1986), under steady-state conditions dissolution is stoichiometric (i.e. alkali cations, aluminium and silica are released to solution in proportion to the chemical composition of the feldspar).

The rate of dissolution has also been observed to be directly proportional to the amount of 'effective surface area' (that portion of the total surface area active as sites for dissolution e.g. dislocation outcrops, twin boundaries etc.) exposed to the fluid phase (Holdren and Speyer, 1985). Accordingly we may write a rate law as follows:

$$r = s k (a_{H^+})^n \qquad (1)$$

where r and k represent the rate and rate constant for dissolution, respectively, s is the effective surface area, and n is some exponent.

Modifications of transition state theory (Eyring, 1935) have been applied to derive a mechanistic understanding of mineral dissolution processes (Aagaard and Helgeson, 1982; Helgeson et al., 1984; Wolery, 1986; Murphy and Helgeson, 1987). These interpretations require the formation of an activated complex on the surface of the mineral grain, the rate of destruction of which then governs the dissolution rate of the mineral. Three types of activated complex for feldspar dissolution have been invoked, in the pH regimes 0–3, 3–9, and 9–14. The reactions describing the stoichiometry of the respective activated complexes for these pH regimes may be written as (Aagaard and Helgeson, 1982; Helgeson et al., 1984; Wolery, 1986; Murphy and Helgeson, 1987):

$$(K,H_3O)AlSi_3O_8 + H_3O^+$$
$$= [(K,H_3O)AlSi_3O_8(H_3O)^+]^* \qquad (2)$$

$$KAlSi_3O_8 + nH_2O$$
$$= [KAlSi_3O_8 + (H_2O)_n]^* \qquad (3)$$

$$KAlSi_3O_8 + 0.4\,OH^-$$
$$= [KAl(OH)_{0.4}Si_3O_8^{0.4-}]^* \qquad (4)$$

where * indicates the activated complex.

The stoichiometry of the above activated complexes is in accord with observed pH dependencies of feldspar dissolution of -1.0, 0, and 0.4 in the respective pH regimes (Chou and Wollast, 1985; Knauss and Wolery, 1986).

Methods

Experiments have been conducted in direct-sampling autoclaves (Seyfried et al., 1979, 1987). These autoclaves have the facility to extract fluid samples from an experiment without disturbing P–T conditions. The

extraction of dissolution kinetics data from experiments conducted in batch-type autoclaves may be complicated by the precipitation of secondary solids as steady-state or equilibrium is approached (Rimstidt and Dove, 1986). Efforts have been made in this study to derive kinetic information from those time portions of the experiments where the dissolution reaction was believed to be unaffected by secondary precipitation reactions. In addition, three experiments were carried out using an adapted direct-sampling autoclave fitted with a piston pump enabling continuous flow through a packed bed of feldspar grains to be carried out (Dibble and Potter, 1982; Potter et al., 1987). This configuration contrived to minimise precipitation effects by careful choice of fluid flow rate, so that the results from these latter experiments served as a useful constraint on those carried out under batch conditions. In the flow reactor the feldspar was confined within a 5 mm diameter, 7.5 cm long gold tube, through which the reservoir of buffer solution was constantly drawn by the pump at an accurately monitored flow rate. A flow rate of $\sim 0.012\,\text{ml/min}^{-1}$ was used for these experiments.

2 g of prepared perthitic orthoclase feldspar together with 200 ml of buffer solution were used for each experiment carried out under batch conditions. Run durations lasted up to one month for these experiments. Fluid samples were extracted at regularly spaced intervals throughout this period. Experiments carried out under flow conditions were of the order of 100 hours' duration, fluid samples being collected twice daily for subsequent chemical analysis.

A pink orthoclase feldspar from Norway was used for all experiments. SEM petrography and microprobe analysis revealed the orthoclase to include some 17% albite exsolution lamellae. Average microprobe analyses of the two phases are shown in Table 1.

Table 1. Average microprobe analysis of the orthoclase feldspar and albite exsolution lamellae used in the experiments.

% Oxide	Orthoclase	Albite
SiO_2	64.15	68.4
Al_2O_3	17.91	19.77
Na_2O	0.78	11.43
K_2O	16.39	0.1
Total	99.2	99.7

Ca, Ti, Mg, Fe, Sr, & Ba were all found to be below detection levels.

The mineral sample was mechanically crushed and sieved until a large proportion of it was collected in the 125–250 µm size range (fine sand grain size). In order to remove surface fines, the grains were carefully washed in deionised water with spells in an ultrasonic bath until SEM (Cambridge Stereoscan 250) examination showed the grains to be free from surface debris. This was done to ensure that there were no fine particles left adhering to the grain surfaces, and to carefully

characterise the grains for comparison with the grains from the dissolution experiments. A typical grain surface prior to dissolution is shown in Fig. 5(*a*). The surface area of the crushed feldspar was then determined by the BET Argon method as $0.474\,m^{-2}g^{-1}$. Reacted feldspars from the experiments were air-dried and then re-examined by SEM for the effects of dissolution.

The buffer solutions used were as follows:

> pH 1   0.2 M HCl/NaCl
> pH 3.6   0.2 M Na acetate/acetic acid
> pH 9   0.2 M boric acid/NaCl/NaOH

Buffer solutions were formulated using the methods of Perrin and Dempsey (1974). These methods were slightly modified—NaCl used instead of KCl in order to detect K release—but this did not impair the effectiveness of the buffers. pH was monitored with every sample taken from the experiments, and remained constant ±0.2 pH units. The acetic acid/acetate buffer was used in this series of experiments as if it was 'inorganic' in its behaviour. This was due to the unavailability of a suitable inorganic buffer at this pH. At the dilute concentrations employed here, its complexation abilities were minimised, and acetic acid has been shown to be comparable in behaviour to carbonic acid at this concentration level (Huang and Longo, 1987).
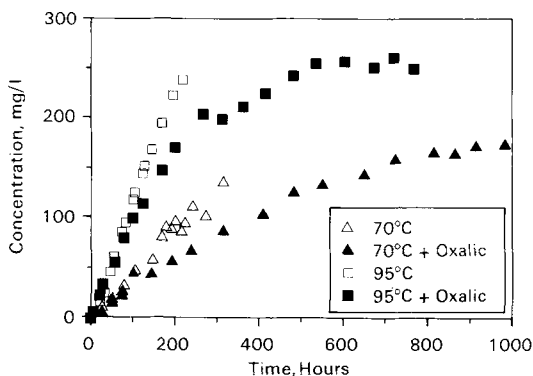
instance, oxalic acid has been used because it is one of the simplest difunctional acids and will illustrate behaviour of such molecules. In order to accommodate the addition of oxalic acid, the buffers had to be modified slightly as follows:

> pH 1   made up to pH 1.1 before adding oxalic
> pH 3.6   made up to pH 4.4 before adding oxalic
> pH 9   made up to pH 9.5 with strengthened solutions
>   of 1 M.

At each sampling stage in an experiment, 1 ml was withdrawn by syringe and discarded, to flush out the sampling tube. Approximately 5 ml of sample were then removed. 1 ml of this was used to measure the pH, the rest being drawn through a $0.2\,\mu m$ filter and acidified with HCl (1%) for ICP analysis (Perkins Elmer Plasma 2 Spectrometer). Two ICP samples were prepared, both with ×5 dilutions—one for an immediate check of the Si level (to determine sampling intervals) and the other to run in a batch once the run was completed. The samples were analysed for Si, Al, and K, for which the ICP has detection levels of 0.08 ppm, 0.065 ppm, and 0.1 ppm, respectively. This relatively high detection limit for potassium meant an often incomplete set of potassium data, particularly for the earliest samples of some experiments. Analysis of sodium release was not possible, as all buffers contained Na.
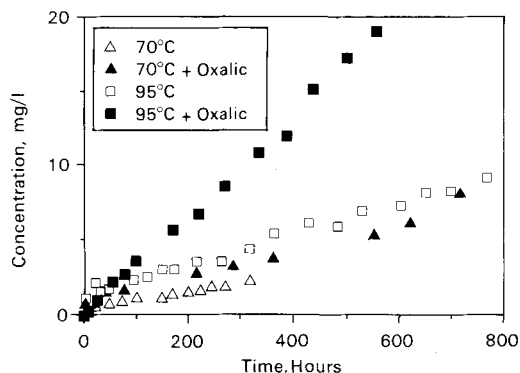

FIG. 1. Silica concentration–time data for batch runs at pH 1.

FIG. 2. Silica concentration–time data for batch runs at pH 3.6.

Oxalic acid was added at the strength of 0.02 M. This is similar to values in oilfield waters (Carothers and Kharaka, 1978). A trial batch experiment was carried out to determine the temperature tolerance of the buffers with oxalic acid. The oxalate was found to begin breaking down above 100 °C. The availability of oxalic acid in a natural system is open to some question, as experiments by Huang and Longo (1987) have shown that it is preferentially complexed by Ca and Mg, rather than Al, forming very insoluble salts. However, in this

Results and discussion

Calculation of rate constants. Concentration–time profiles for the experiments are shown in Figs 1, 2 and 3. Broadly, three regions may be discerned. Firstly, there is an initial rapid release. This feature is especially pronounced in the pH 3.6 runs (Fig. 2), when this period of dissolu-

tion occupies roughly 50 hours. An initial rapid rate is also visible in the pH 9 experiments (Fig. 3), lasting up to 100 hours of run duration. The pH 1 data show no such enhanced early rate. These early rapid rates are interpreted as being due to solution of the disturbed surfaces of the grains caused by the disaggregation process. Another possible cause may be the initial rapid formation of a leached layer on the grain surfaces (Chou and Wollast, 1984). During the pH 1 experiments, the early effect is completely masked by the overall rapid dissolution rate. Secondly, a linear increase in concentration with time is observed. Finally, a third portion of the concentration–time curve is observed as the dissolution rate nears steady-state. This latter behaviour is ascribed to the precipitation of a secondary solid phase.
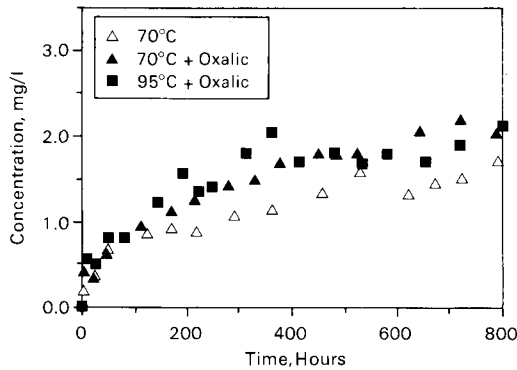

Fig. 3. Silica concentration–time data for batch runs at pH 9.

Rate constants for dissolution have been calculated from the linear portions of the concentration–time data assuming a zero-order reaction rate at constant pH and temperature (e.g. Lasaga, 1984):

$$\frac{\delta c_i}{\delta t} = \frac{A}{V} \nu_i k \qquad (5)$$

where $\delta c_i / \delta t$ = rate of release in concentration with time of component i

A = surface area of orthoclase
V = volume of solution
k = bulk dissolution rate of orthoclase
ν_i = stoichiometric content of component i in orthoclase (3 for Si, 1 for K and Al)

Equation (5) has the following solution, assuming that the concentration of component i in the fluid is zero at time = 0 (e.g. Lasaga, 1981):

$$c_i = \frac{A}{V} \nu_i k t \qquad (6)$$

Equation (6) may be re-arranged as follows:

$$k = \frac{V}{A} c_i \frac{1}{\nu_i t} \qquad (7)$$

Since the volume of fluid within the batch reactor decreased progressively with time in each experiment, equation (7) must be corrected as follows (e.g. Robinson, 1982):

$$k = \frac{c_i}{\nu_i A} \int_0^t \frac{V}{\delta t} \qquad (8)$$

Since the volume decrease with time was known, the integral term

$$\int_0^t \frac{V}{\delta t} \qquad (9)$$

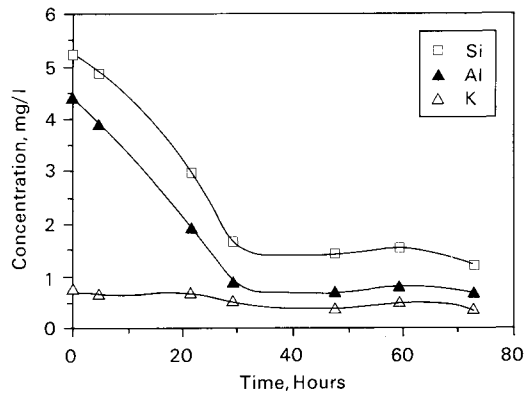was calculated at each sample interval. Rate constants were determined using equation (8).

Fig. 4. Silica, potassium and aluminium concentration––time data for flow through run at pH 3.6, 95 °C.

Typical analytical data for the fluid samples collected from the flow-through experiments are presented in Fig. 4. An initial high output concentration is observed, due to the reaction of disturbed surfaces on the feldspar grains, followed by a decrease to what is interpreted as steady state dissolution. Rate constants were also calculated using equation (8).

Deviations from ideal plug-flow behaviour have been shown to be minimal for the flow-through

apparatus under the conditions employed in these experiments (Savage *et al.*, in prep.), so that corrections for non-ideal flow behaviour have a negligible effect upon the calculated rate constants. Since chemical conditions can be maintained far from equilibrium by a judicious choice of flow rate, data from these experiments served as a useful constraint upon those derived by batch methods.

Rate constants determined with respect to bulk surface area by both experimental techniques are presented in Table 2 and graphically in Fig. 7. It was not possible to determine a dissolution rate for K-feldspar in the batch experiment at 95 °C, pH 9, as concentrations of Si, K, and Al in the fluid samples from this experiment were time-invariant, suggesting the rapid precipitation of a secondary solid phase. However, a dissolution rate was determined for K-feldspar under these conditions by use of the flow-through technique.

Table 2. Rate constants calculated from Si release versus time data.

Runs at pH 1	Rate (mol m^{-2} sec^{-1})
70°C	1.76×10^{-10}
70°C with oxalic	1.47×10^{-10}
95°C	7.46×10^{-10}
95°C with oxalic	5.05×10^{-10}
Runs at pH 3.6	
70°C	3.09×10^{-12}
70°C with oxalic	4.89×10^{-12}
95°C	4.68×10^{-12}
95°C with oxalic	1.84×10^{-11}
Runs at pH 9	
70°C	9.34×10^{-13}
70°C with oxalic	1.45×10^{-12}
95°C	not determined
95°C with oxalic	2.37×10^{-12}
Flow-through Runs	
pH 1/95°C with oxalic	4.13×10^{-11}
pH 3.6/95°C	5.14×10^{-12}
pH 9/95°C	1.92×10^{-12}

Bulk dissolution rates calculated from Al and K data give very similar values to those calculated by Si release, in experiments both with and without organic acids. These values are illustrated for pHs 1 and 3.6 in Fig. 6a and b. This observation implies a stoichiometric dissolution process for the feldspar under the conditions of the experiments, although in the pH 1 experiments (Fig.

6a), K was found to be released at a slightly slower rate than Si and Al. This behaviour may be an indication of the albite lamellae being dissolved more rapidly than the bulk of the K-feldspar.

The flow-through experiments produced dissolution rates that were slightly greater than their batch run counterparts (apart from the pH 9/95 °C run, for which there is no equivalent rate determination). This phenomenon may be attributed to the removal of precipitation effects in the flow-through system.

SEM examination. After completion of each experiment, the feldspar residue was air dried and then re-examined for the effects of dissolution. It was found that only the pH 1 runs had produced visible effects of the dissolution process. These effects took the form of prismatic etch pits, and were commonly seen to follow the cleavage directions of the orthoclase. The pH 1/70 °C runs showed minor signs of etching, whilst those at pH 1/95 °C were most severe, with every grain displaying some evidence of dissolution. A typical example of the etching observed is shown in Fig. 5b.

Another aim of post-experiment SEM examination was to detect any secondary products that may have formed. In the pH 1/95 °C/oxalic acid run, an amorphous grain coating was observed, similar in form to the gel described by Surdam *et al.* (1984). The solids retrieved from the pH 9/95 °C run displayed no evidence of a precipitate, despite the evidence from the fluid data, although the precipitate may have been of such a small amount that it remained undetected.

Effects of pH variation. From Fig. 7 it may be seen that the rate of Si release at pH 1 is an order of magnitude greater than at the other two pH values. Below pH 4 the rates increase by an order of magnitude for each decrease in unit pH. Similar pH variation was observed at both 70 °C and 95 °C, and thus is not dependent on temperature within the range tested.

The variation of dissolution rate with pH is similar to that observed in previous studies of albite dissolution (Chou and Wollast, 1985; Knauss and Wolery, 1986), and K-feldspars (Helgeson *et al.*, 1984; Murphy and Helgeson, 1987). Although the range of pH and density of coverage of this study makes it difficult to make definitive conclusions concerning the pH dependency of dissolution, or the stoichiometry of potential activated complexes, the results are in general agreement with the pH-regimes developed by these authors.

The rates determined in the pH 9 experiments are somewhat smaller than expected. The previous studies of feldspar dissolution mentioned
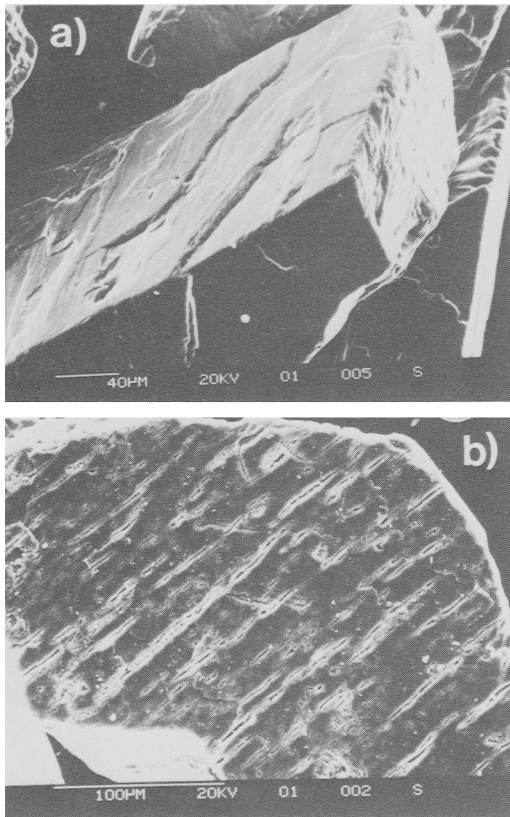
FIG. 5(a). Surface of cleaned orthoclase grain prior to experiments. (b) Etched surface of orthoclase grain after dissolution.
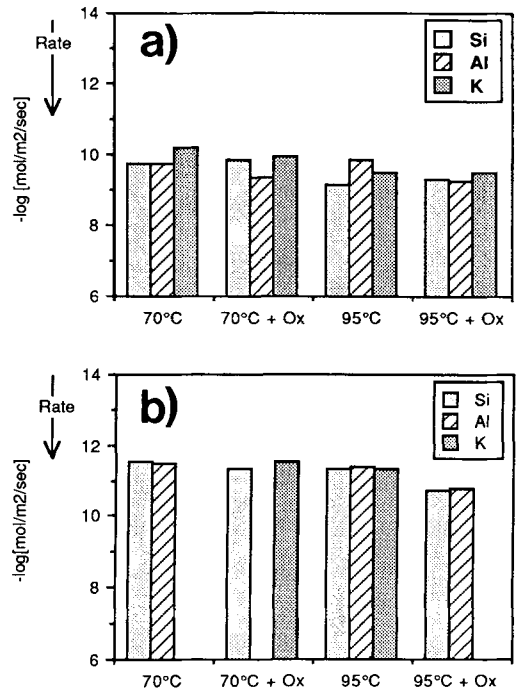

FIG. 6(a). Bulk dissolution rates at pH 1, calculated from silica, potassium and aluminium. (b) Bulk dissolution rates at pH 3.6, calculated from silica, potassium and aluminium.

above have shown that owing to the amphoteric nature of aluminium, feldspar dissolution rates increase with increasing activity of the hydroxyl ion in solution at pH values above about pH 8 at 25 °C. Helgeson *et al.* (1984), and Knauss and Wolery (1986) suggest that this threshold pH increases with temperature up to pH~9.5 at 95 °C. Evidence from this study indicates a similar behaviour for orthoclase, so data at pH 4 and 9 should thus fall into the pH-independent regime. The experiments at pH 9, however (Fig. 3), give the lowest release rates and display the broadest scatter, possibly due to precipitation effects. The resultant rate values may thus be considered less reliable than those at the pH values 1 and 3.6. Further experiments in the alkali pH range would be needed to verify these conclusions.

Effects of oxalic acid. The addition of oxalic acid to the buffer solutions had a varying effect on the dissolution behaviour depending upon the pH of the experiment. At pHs 9 and 3.6, the pres-

ence of oxalic acid caused an increase in the rate of dissolution (Figs 2 and 3, Table 2), by a factor of 2–4, whereas at pH 1 (Fig. 1) the resultant rates are actually slightly lower than for those runs without oxalic acid. Therefore, the presence of oxalic acid at pH 1 marginally inhibits the dissolution of the feldspar.

The greatest increase of feldspar dissolution rate due to the presence of oxalic acid was observed at 95 °C and pH 3.6 (Fig. 3, Table 2). More experiments would be needed at intermediate pHs and temperatures to determine the optimum level of enhancement of feldspar dissolution caused by the addition of oxalic acid.

The preferential release of aluminium relative to potassium and silicon was not observed in the experiments with oxalic acid (Fig. 6a and b), indicating that any increased rate of K-feldspar dissolution in the presence of oxalic acid was not accompanied by a non-stoichiometric dissolution process. The presence of organic acids increases the rate of release of K and Si as well as Al, indicating that the oxalic acid affects the overall dissolution mechanism, rather than causing selective complexation. A change in the dissolution mecha-

nism is also implied by the calculated activation energy for dissolution (see below).

Effects of temperature. Mineral dissolution rates generally have an exponential temperature dependence, as expressed by the Arrhenius equation:

$$k = A_e e^{-E_a/RT} \qquad (10)$$

where:

E_a = activation energy

A_e = pre-exponential factor

R = gas constant

T = temperature (°Kelvin)

Determining the activation energy (E_a) for a given reaction may give an indication of the nature of the reaction mechanism. Values below about 5 kcal mol^{-1} generally indicate that the reaction is diffusion controlled, limited by the rate at which products diffuse away from the mineral surface. Higher values imply that the reaction is surface-reaction controlled (Lasaga, 1981). The dissolution behaviour of the majority of minerals falls into the latter category. Lasaga (1984) quotes an average activation energy for the dissolution of silicates as 14 kcal mol^{-1}.

Table 3. Activation Energies of Orthoclase dissolution.

	E_a (kJ mol^{-1})	E_a (kcal mol^{-1})
pH 1	57.66	13.78
pH 1 + oxalic acid	48.28	11.54
pH 3.6	14.44	3.45
pH 3.6 + oxalic acid	58.06	13.88

Activation energies for the dissolution of orthoclase have been calculated using equation (10). The activation energies calculated by this method are presented in Table 3. Values have not been presented for the data at pH 9, as the data are incomplete.

It may be seen from Table 3 that the calculated activation energies cover a wide range of values, varying with pH and with or without oxalic acid. The greatest activation energy is for the experiments at pH 3.6 with oxalic acid (13.9 kcal mol^{-1}), whereas the lowest value (3.5 kcal mol^{-1}) is for the experiment at the same pH *without* oxalic acid. Clearly, the presence or absence of oxalic acid makes a considerable difference to the activa-

tion energy for the dissolution process, and by inference, a difference to the reaction mechanism. The activation energy of 3.5 kcal mol^{-1} was obtained in the oxalic acid-free experiments at pH 3.6. It is very difficult to explain this very low activation energy in terms of a surface-controlled reaction mechanism. More probably, the rate constant determined at pH 3.6 at 70°C may be in error due to the scatter of the concentration–time data.

The variation of activation energy with pH in the oxalic-free experiments is consistent with observations by Helgeson *et al.* (1984) and Knauss and Wolery (1984), who noted that the activation energy for the pH-dependent regime (pH 1–4 at 70–95 °C) of feldspar dissolution is approximately half that observed in the pH-independent regime (pH 4–10 at 70–95 °C). However, Helgeson *et al.* (1984) quote values of 8.5 and 19.0 kcal mol^{-1} for the activation energies in these regimes, respectively, which compares with values of 3.5 and 13.8 kcal mol^{-1} from this study.
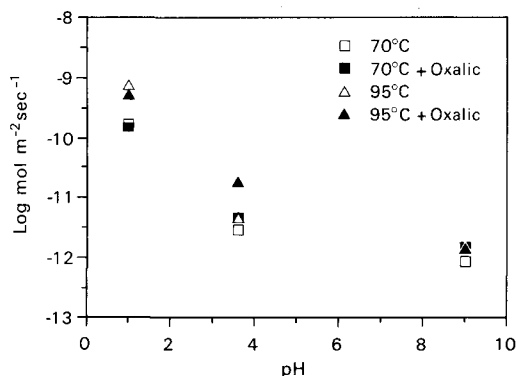

FIG. 7. All orthoclase dissolution rates from batch runs, calculated from silica release.

The presence of oxalic acid in the experiments described here decreases the activation energy necessary for dissolution in the pH-dependent region, from 13.8 to 11.5 kcal mol^{-1}, whereas its presence in the pH-independent region increases the activation energy, from 3.5 to 13.9 kcal mol^{-1}. This behaviour is related to the change in pH dependence of feldspar dissolution which occurs with the addition of oxalic acid. Without oxalic acid, a line connecting the rate constants at pH 1 and 4 at 95 °C (Fig. 7) has a slope ~ 1, i.e. $n \sim 1$ (equation 1). The comparable data at 70 °C have a slope <1 (~ 0.67), but this may be due to the rate determination at pH 3.6 for this temperature

being in error. The 95 °C data would be consistent with the model of pH dependency of feldspar dissolution outlined by previous authors. However, with the introduction of oxalic acid into the experiments, the pH dependency of the dissolution constant at both 70° and 95 °C is 0.55 in each case, indicating a reduced dependency upon pH. This would explain the dissolution rate of K-feldspar in the presence of oxalic acid being greater than without oxalic acid at pHs >1.5, and the converse being true at pH values <1.5.

Although further data in the pH range 4–8 are required, this conclusion suggests that the effect of organic acids upon feldspar dissolution is most pronounced in the mildly acidic-neutral pH conditions, which may be typical of those buffered naturally in sandstone reservoirs. More data points would be required to fully 'map' the various pH-dependent regimes, but it is clear from the available data that the dissolution mechanism of K-feldspar is changed significantly due to the addition of oxalic acid.

Table 4. Comparison of rate constants (mol m^{-2} sec^{-1}) of K feldspar dissolution (all at 25°C)

Orthoclase		Reference
1.67 x 10^{-12}	(pH 5)	Busenberg and Clemency, 1976.
1.58 x 10^{-12}	(pH 4)	This study
1.40 x 10^{-11}	(pH 1)	This study
Microcline		
1.74 x 10^{-12}	(pH 5)	Busenberg and Clemency, 1976.
1.86 x 10^{-12}	(pH 5)	Siegel and Pfannkuch, 1984.

Comparison with previous data. For the purposes of comparison, rate constants for K-feldspar dissolution determined in previous experimental studies are presented in Table 4, together with the rate constants determined here. In order to compare our data with experimental studies at other temperatures, our data have been extrapolated to the relevant temperatures by means of the Arrhenius expression, using the determined activation energy at the relevant pH. It can be seen that the rate constants determined in this study are very similar to those determined by Busenberg and Clemency (1976) and Siegel and Pfannkuch (1984) for orthoclase and microcline.

Regarding the effect of organic acids, our findings support the conclusions of Manley and Evans (1986) and Mast and Drever (1987), that organic acids do not increase the dissolution rates of feld-

spar by the preferential complexing of Al. Instead, our results suggest that organic acids are capable of increasing the effective solubility of feldspar (as suggested by Surdam *et al.*, 1984). Mast and Drever (1987) noted no increased rate of oligoclase feldspar dissolution due to the addition of oxalic acid in the pH range 4–9. However, they added oxalic acid in the concentration range 0.5–1.0 mM, which is considerably less (×20–40) than the concentration employed in the study described here. Also, the effect of oxalic acid appears to be greater at 95° than 70 °C, whereas Mast and Drever's study was at 25 °C. The differences in our and their conclusions could be explained by the differences in the concentration of organic acids and temperature.

Conclusions and implications

The results of these experiments indicate that the effect of oxalic acid on K-feldspar dissolution is most significant at mildly acid pH values (pH ~4). At lower pH values (which may be difficult to sustain in the natural environment under diagenetic conditions), the presence of oxalic acid decreases the dissolution rate of orthoclase. The addition of 0.02 M oxalic acid increases the rate of dissolution of orthoclase at pH ~4 by a factor of approximately ×4, which is equivalent to the same rate increase produced by a temperature increase of 25 °C.

The presence of the oxalic acid does not change the stoichiometric dissolution process of the feldspar, i.e. the increased dissolution of the feldspar is not effected by preferential complexation of aluminium and/or silica. It appears that the enhanced dissolution rate produced at pH ~4 by the presence of oxalic acid is due to a change of the pH-dependent mechanism of feldspar dissolution from a dependence roughly proportional to a unit change in pH to one proportional to a change of two pH units. Further experiments in the pH range 2–7 would be necessary to further delineate this regime.

The optimum pH regime of increased orthoclase dissolution due to the presence of oxalic acid coincides with that naturally buffered by an influx of organic acids into a sandstone reservoir system. The role of organic acids in the production of secondary porosity may be envisaged not only as a pH buffer (Kharaka *et al.*, 1986), but also as a means by which the intrinsic rate of feldspar reaction may be increased. It is a combination of these effects which may serve to produce secondary porosity during burial diagenesis.

One route to improved understanding of the diagenetic evolution of sandstones is through the

development of hydrogeochemical mass balance models. Such quantitative modelling (e.g. Bath et al., 1987) is still in its infancy, and requires, amongst many factors, accurate kinetic data as well as a knowledge of mineral solubilities, fluid composition, flow rates and sand-body geometries. The study of secondary porosity creation by framework grain dissolution will always be hampered by our lack of knowledge of the primary pre-diagenetic composition of sandstones. Petrographic observations can be misleading— secondary porosity created by feldspar dissolution may not always lead to an overall increase in porosity, but rather a re-distribution, as authigenic clay minerals may be precipitated in primary pore spaces (Bjorlykke, 1984; Giles and Marshall, 1986). To achieve increased porosity, flow rates must be great enough to remove products from the sites of dissolution. The spatial and temporal distributions of possible sources of organic acids (e.g. interlaminated shales) and increased acidity must also be considered in the development of accurate predictions of diagenetic histories.

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