

An exploratory study of acetate decomposition and dissolution of quartz and Pb-rich potassium feldspar at 150 °C, 50 MPa (500 bars)

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Abstract

Experiments to explore the dissolution behaviour of Pb-rich orthoclase (1% PbO) and quartz have been carried out in the presence of pH buffered and unbuffered potassium acetate and lithium acetate solutions at 150 °C and 50 MPa (500 bars). In pH-unbuffered potassium acetate solutions Pb and Na solubilities (and pH) increase with increasing fluid acetate content, reflecting increased bulk dissolution of the feldspar; silica solubility decreases despite an increase in measured pH from 7.5 to 8.9. Similarly, in experiments at pH 6 using a potassium acetate pH buffer, quartz solubility decreases with increasing acetate content. The use of lithium acetate pH buffers (pH 6 at 25 °C) in experiments with orthoclase plus quartz results in the precipitation of the lithium chlorite cookeite, complicating interpretation of the fluid chemistry. It is also apparent that in the presence of orthoclase plus quartz (but not albite alone) acetate decarboxylation takes place at much higher rates than expected for the experimental configuration used. The observed effects are unlikely to be due to the presence of acetate alone; the influence of species produced by acetate decay (especially carbonate) must also be considered. This study provides little support for models which call upon acetate to enhance the solubility of aluminosilicate minerals, and suggests that acetate decarboxylation in nature may limit its involvement in dissolution processes. It emphasises the potential of feldspars as sources of elements for mineralisation, such as Pb.

KEYWORDS: acetate, decomposition, quartz, potassium feldspar, dissolution.

Introduction

ALIPHATIC organic acid anions, dominated by acetate (ethanoate), are widely recognised to be essential components of waters hosted by sedimentary rocks in the presence of solid organic matter or petroleum (Carothers and Kharaka, 1978; Fisher, 1987; MacGowan and Surdam, 1988). They provide additional components to be considered in the modelling of mass transport during diagenesis and associated ore mineralisation. In particular, it has been suggested that they may be responsible for the enhanced secondary porosity known to occur within petroleum reservoir sandstones, and several studies have been carried out to investigate the solubility and stability of aluminosilicate minerals in their presence (Mast and Drever, 1987; Bevan and Savage, 1989; Surdam *et al.*, 1989; Surdam and Crossey, 1985). In these studies, the development of secondary porosity essentially involves the

dissolution of feldspar, and this provides a link with the generation of ore fluids of Mississippi Valley type, which are believed to derive a component of their Pb (and Ba) from clastic sediment hosted feldspars (Doe and Delevaux, 1972; Farquhar *et al.*, 1987), and which are believed to resemble oilfield brines in their composition (Sverjensky, 1984, 1987). In addition, it has been suggested that organic acids may be responsible for enhanced solubilities of silica, above levels appropriate for quartz saturation (Bennett and Siegel, 1987; Bennett *et al.*, 1988), with implications for the transport of material required for diagenetic silica cements. Similarly, complexing between acetate and metals in Mississippi Valley type ore fluids is considered to be a potentially important transport mechanism (Giordano, 1985, 1989; Manning, 1986). Most published mineral solubility determinations assume that the organic components of interest are stable for the duration of the exper-

Table 1. Composition of feldspar starting material.

Orthoclase from Broken Hill, New South Wales			
SiO ₂	65.24	Si	2.992
Al ₂ O ₃	19.42	Al	1.050
Na ₂ O	0.61	Na	0.055
K ₂ O	13.34	K	0.781
CaO	0.16	Ca	0.005
PbO	1.43	Pb	0.018
	-----		(Pb* = PbAl ₂ Si ₂ O ₈)
	100.20		
Cell parameters:			
$a = 8.586\text{Å}, b = 13.004\text{Å}, c = 7.208\text{Å}, \beta = 116.05^\circ$			

iment, if not for geologically significant periods, but the validity of this assumption is questionable in view of the difficulties experienced (due to catalytic effects) in determining decarboxylation rates for acetate in isolation (Palmer and Drummond, 1986), which of all organic acid anions can be regarded as relatively stable in view of its predominance in oilfield brines.

The purpose of this paper is to contribute to the discussion of the role of organic acid anions in feldspar dissolution, and to provide cautionary constraints for models of the development of both secondary porosity and Mississippi Valley type ore-forming fluids. It presents exploratory data for both the dissolution of a natural Pb-rich alkali feldspar, in the presence of quartz, and for the concomitant decomposition of acetate, under conditions of *P* and *T* appropriate for diagenesis.

Experimental procedure

Starting materials. The solid starting materials used comprised Pb-rich potassium feldspar (orthoclase micropertthite) from Broken Hill, Australia (Plimer, 1976), which contains approximately 1% PbO, and quartz (Table 1). The 63–125 μm size fraction was used in all experiments reported here (BET surface areas, using nitrogen: feldspar 0.5 m^2/g ; quartz, 0.3 m^2/g). Charges consisted of approximately 2.5 g feldspar and 1.0 g quartz. Solids were routinely cleaned ultrasonically in distilled water to remove surface particles (cf. Murphy, 1989). Solutions were made up from analytical grade reagents; approximately 180 mL was added to the solid material to make up the experimental charge, with an initial fluid:rock weight ratio of about 50:1. Solutions unbuffered with respect to pH consisted simply of potassium acetate solutions of the required concentration, whilst pH buffered solutions were made up using lithium or potassium acetate and acetic acid to give the required concentration of acetate (Table 2). In the initial, pH unbuffered,

experiments the choice of potassium acetate was made to limit the number of components present.

Equipment. The dissolution experiments were carried out using a double rocking fluid-sampling autoclave system, supplied by Coretest Systems Inc., Mountain View, California, with gold reaction cells and titanium closures, exit tubes and sampling valves (Seyfried *et al.*, 1987). Gold filters were used internally in early experiments, and were subsequently replaced by more robust titanium filters. Fluid samples (between 1 and 8 mL) were taken at intervals measured from the time furnace power was turned on (sampling times quoted include a settling down period of approximately 24 hours), using a disposable syringe, and were made up after further filtering (0.2 μm syringe filter) to 10 mL using initially 10% HCl and subsequently 10% HNO₃ (which improved background for graphite furnace AAS determinations). On completion of an experiment, the residual fluids were filtered and subjected to the same analytical procedure as the samples. Both solid residues and internal filters were recovered for examination by analytical electron microscopy and X-ray diffraction as appropriate.

Analytical. A one-drop electrode (Microelectrodes Inc. with Corning Delta 250 meter) was used to measure pH immediately on sampling; measurements were made under nitrogen in a glove box, and were read at room temperature after a settling down period of 15 minutes. Dominant cations (Si, Na, K and Li) were determined by flame AAS, and Al and Pb also by graphite furnace AAS if necessary. Acetate was determined by ion chromatography, using a Dionex HP-ICE organic anion column.

Solid phase run products were routinely analysed by XRD to monitor any changes to the feldspar diffraction patterns during the experiments. In order to characterise secondary, fine-grained, products a fine fraction was prepared by ultrasonic disaggregation of approx. 0.1 g of sample in 5 mL deionised water, followed by a settling period of 30 minutes to produce a suspension of approximately <1 μm e.s.d. This suspended fine fraction was repeatedly pipetted and dried onto a glass slide to produce an oriented specimen for XRD identification of clay minerals following procedures given in Brindley and Brown (1980). For selected samples a diluted drop of the fine fraction was dried onto a carbon film mounted on a copper TEM grid for analytical TEM (ATEM) study.

Run conditions and strategy. All experiments reported here were carried out at 150°C and 50 MPa (500 bars) pressure. Pressure was con-

tinuously monitored and controlled to ± 1 MPa (10 bars), and temperature to $\pm 5^\circ\text{C}$. The duration of individual experiments extended up

to 1600 hours (two months). Variations in run conditions are summarised in Table 2.

Experiments were initially carried out without

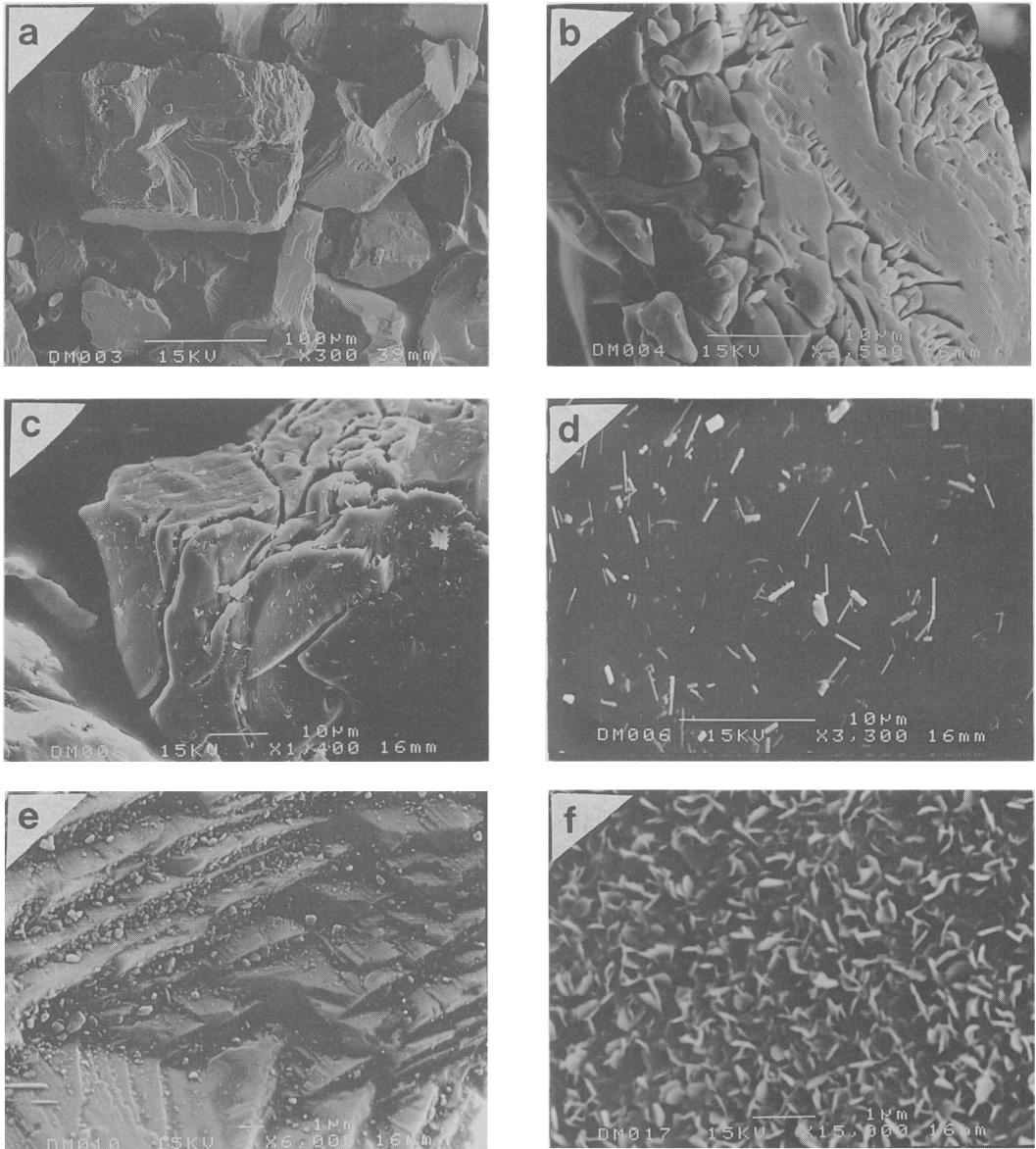


FIG. 1. SEM photomicrographs of feldspar starting material and run products: (a) ultrasonically-cleaned feldspar starting material; (b) etched surface of feldspar from experiment with 0.1 M potassium acetate, pH = 7.5; note lack of secondary mineral products; (c) etched surface of feldspar from experiment with 0.5 M potassium acetate, pH = 9.4, with fibrous secondary phase identified as illite (XRD and ATEM); (d) close-up view of (c) to show fibrous illite; (e) equidimensional secondary K-feldspar on cleavage-defined surface from experiment with 1.0 M potassium acetate, pH 8.1; (f) close up view of cookeite, growing as a coating of orthogonal plates on feldspar, from experiment with 0.5 M lithium acetate, pH 6.

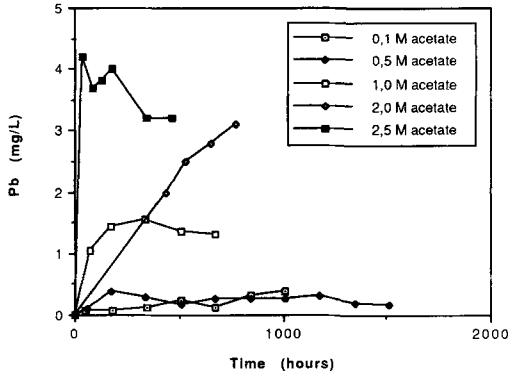


Fig. 2. Pb solubility with increasing potassium acetate content.

buffering fluid pH, and the results are presented here essentially as raw data. Selected experiments were then carried out with fluids buffered at pH 6 using potassium acetate or lithium acetate buffer solutions as run fluids. These experiments involved quartz alone as well as quartz/feldspar mixtures, to help interpret the results for all experiments.

Experimental results

Solid products. Details of the solid products identified as secondary minerals, produced during the course of the experiments, are summarised in Table 2. Typical appearances of residual feldspar and newly-formed secondary phases observed by scanning electron microscopy (SEM) are summarised in Fig. 1. In these photomicrographs, it can be seen that the surfaces of the starting material are free from contamination by fine-grained material, and are defined by the cleavage of the feldspar. Residual feldspars are etched in a manner similar to that reported by Murphy (1989). Where observed, secondary phases occurred within etch pits and as coatings on grain surfaces, but were not evenly distributed within residual solid material.

XRD investigation of bulk samples of residual solids shows no significant change in the feldspar diffraction pattern and no detectable secondary phases. XRD analysis of the fine fraction however reveals secondary clay minerals in both the K-acetate and Li-acetate experiments. In the K-acetate run 17, a sharp 10 Å and weaker 5 Å and 3.3 Å peaks are observed, consistent with basal reflections from a mica-type structure. Similar peaks of weaker intensity are also observed for the fine fractions of experiments 11 and 22. Single crystal ATEM analyses of second-

ary clays from experiment 22 are presented as mica formulae in Table 3; these analyses are typical of published dioctahedral illite analyses (Newman, 1987) and confirm the interpretation of the XRD data. A species with equidimensional grains observed by SEM (Fig. 1e) was identified as K-feldspar by ATEM, and is believed to have formed during the experiment rather than to represent contamination by fines, which were effectively removed by ultrasonic cleaning of the starting material (Fig. 1a).

In the case of the Li-acetate experiments broad diffraction peaks are observed at 7.09 Å and 3.68 Å, which could be produced by either kaolinite or a 7 Å chlorite structure. A TEM study was undertaken to further identify this secondary phase. Electron diffraction patterns were obtainable from clay plates oriented normal to the electron beam and produce the characteristic pseudo-hexagonal pattern confirming the phase is a layer silicate. ATEM results are presented in Table 3 calculated as atomic proportions with Si normalised to 3.0. These analyses are consistent in showing a Si/Al atomic ratio of approximately 3/5, and this clearly indicates that the clay is not kaolinite (for which atomic Si/Al = 1/1). The analyses are however consistent with the Li-chlorite mineral cookeite ($\text{LiAl}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$) if it is assumed that 1 atom of Li is present, lithium being undetectable by ATEM (energy dispersive analysis). Indirect evidence of the formation of a Li-bearing secondary phase is provided by the decrease with time in the Li content of fluids sampled during the experiments (see later; Fig. 9). Small amounts of iron and potassium were detected by ATEM; iron could quite easily fit into the chlorite structure, whilst potassium is possibly present as an interlayered illite component. Previous XRD studies of naturally occurring

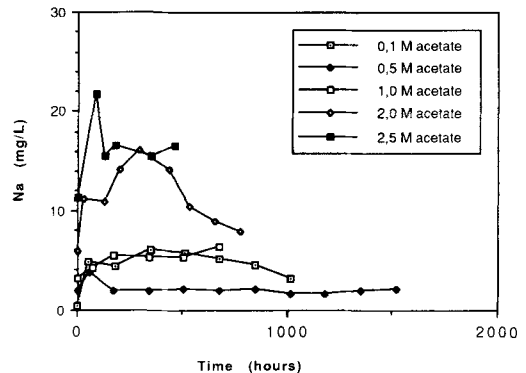


Fig. 3. Na solubility with increasing potassium acetate content.

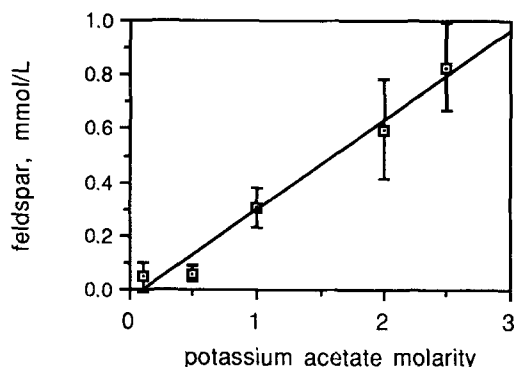


Fig. 4. Orthoclase solubility with increasing potassium acetate content; average values from Pb data.

cookeite (Flehmig and Menschel, 1972; Loughnan and Steggle, 1976; Brindley and Brown, 1980) describe a true 14 Å chlorite structure, rather than the 7 Å structure apparent in this synthetic product. The metastable formation and persistence of the 7 Å chlorite structure in synthetic systems up to 400°C has previously been documented for Mg-chlorites (Nelson and Roy, 1954; Gillery, 1959; Velde, 1973). Similar constraints probably govern the formation of the synthetic 7 Å cookeite.

Attempts to determine the composition of surface and near-surface layers of residual feldspar grains using auger electron spectroscopy have so far been unsuccessful for a number of reasons. Individual grains have proved too small (at the low end of the 63–125 µm range), and have

uneven surfaces defined by marked cleavage terraces (Fig. 1a). In addition, a proportion of the feldspar grains carries coatings of secondary phases (where present), although these are irregularly distributed within the residual solids.

Feldspar solubility as a function of acetate concentration. Initial experiments involved the determination of feldspar solubility in the presence of quartz and potassium acetate solutions, and analytical procedures were unable to detect Al. Consequently the only data available to indicate overall feldspar solubility are those for Pb and Na, present as minor elements within the solid starting material. Summaries of results for Pb and Na are shown in Figs. 2 and 3 respectively.

These data are for solutions which were unbuffered with respect to pH, which generally increases with increasing acetate concentration (Table 2). Within individual experiments, no trend in change of pH was observed for fluids sampled during the experiments, which showed irregular variation within the limits given in Table 2. The pH value for the experiment with 0.5 M potassium acetate is anomalous because this experiment involved the use of solids which were the residue from a failed experiment with 0.1 M potassium acetate, and which may have been contaminated with earlier-formed secondary mineral phases in addition to quartz and feldspar.

Although coarse, the data for Pb and, less clearly, for Na consistently indicate that the total amount of dissolved feldspar tends to increase with increasing acetate concentration (e.g. Fig. 4) and with increasing fluid pH. There is little direct evidence that these elements are controlled by

Table 2. Variable conditions and secondary mineral products for experiments reported in this paper.

run	fluid	solid	pH		secondary	mineral	products	
				+/-	XRD	SEM		ATEM
<i>without buffered pH:</i>								
15	0.1 M K acetate	Or+Q	7.5	0.5	-----	none	identified	-----
17	0.5 M K acetate	Or+Q*	9.4*	0.2	10Å phase	needles	-	-
22	1.0 M K acetate	Or+Q	8.1	0.2	10Å phase	equant grains	illite, K feldspar	-
11	2.0 M K acetate	Or+Q	8.8	0.3	10Å phase	none	identified	-
6	2.5 M K acetate	Or+Q	8.9	0.2	-----	not	determined	-----
<i>with pH buffered using acetic acid/Li or K acetate mixtures:</i>								
29	0.5 M acetate (Li)	Or+Q	6.0	0.1	7Å phase	flakes		cookeite
27	1.0 M acetate (Li)	Or+Q	5.9	0.2	7Å phase	flakes		cookeite
24	0.5 M acetate (K)	Q	6.0	0.1				
23	1.0 M acetate (K)	Q	6.0	0.2				

*solid starting material not pure feldspar-quartz mixture; see text.

Orthoclase size fraction = 63–125µm; BET surface area = 0.5 m²/g

Quartz size fraction = 63–125µm; BET surface area = 0.3 m²/g

Table 3. Average formulae of secondary clay phases calculated from ATEM data.

Experiment 22 (1.0 M K acetate); calculated to 22 oxygens (mica formula):					
Si	Al(4)	Al(6)	Fe(6)	K	ΣocI
6.42	1.58	3.54	0.37	1.84	3.91
Experiments 27 & 29 (Li acetate); atomic proportions normalised to Si = 3:					
Si	Al	Fe	K		
3	5.25	0.07	0.15		

secondary precipitated phases. In contrast, data for Si show a decrease with increasing acetate content (Fig. 5), despite the concomitant increase in pH, and this may reflect the role of secondary precipitates, especially illite, in buffering fluid composition. Expected Si values for quartz saturation at neutral pH are approximately 60 mg/L at 150°C (Rimstidt and Barnes, 1980), and these are exceeded for fluids with 0.5 and 0.1 M acetate; this may be partly due to the elevated pH of these experiments. Because of the complex assemblage of solid phases present in these experiments it is not possible to extract dissolution rate data with confidence.

Quartz and feldspar dissolution in pH 6 acetate buffers. In order to clarify some of the initial results which involved the use of unbuffered fluids, additional experiments have been carried out using acetate solutions buffered at pH 6 for quartz alone (potassium acetate buffer solutions) and for quartz-feldspar mixtures (lithium acetate buffer solutions). Results for the quartz dissolution experiments are shown in Fig. 6. Although the values for dissolved Si are systematically higher than those expected from data for quartz solubility from other studies (this may be due to the use of AAS rather than colorimetry for Si determinations; Rimstidt and Barnes, 1980) the

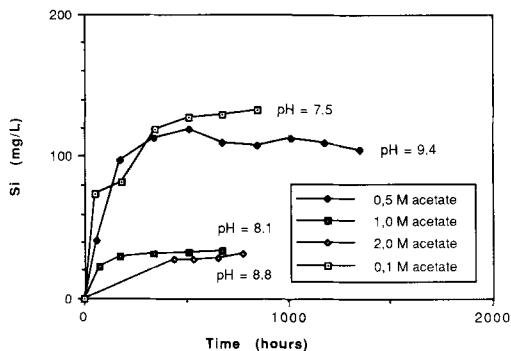


Fig. 5. Silica contents of fluids from experiments to determine the solubility of orthoclase + quartz in potassium acetate solutions.

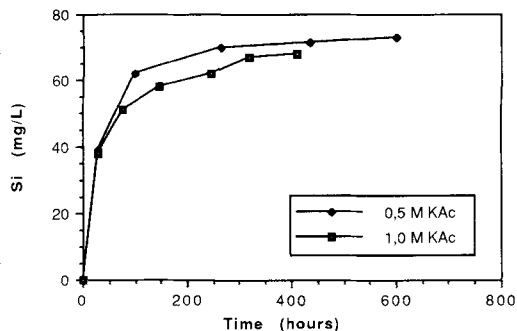


Fig. 6. Quartz solubility in pH 6 potassium acetate buffers.

data are again consistent with a decrease in quartz solubility as acetate content is increased.

Results for experiments involving feldspar-quartz mixtures are shown in Figs. 7 and 8. In these experiments the buffer solution was made up using lithium acetate, so that potassium could be used as an indicator of feldspar dissolution. However, both acetate and (unexpectedly) lithium were removed from solution as the experiments progressed (Fig. 9). Similarly, aluminium was detected in initial samples as a spike of up to 13 mg/L, and subsequently remained close to a detection limit of about 0.5 mg/L. Data for Na (and Pb by default; Pb is below detection for 0.5 M lithium acetate solutions) suggest an increase in total feldspar solubility with increasing acetate content but are not conclusive. Data for K and Si are similar for both experiments and show congruent dissolution of feldspar, with a Si/K molar ratio of close to 3.0.

Acetate decomposition. In early experiments, acetate data were not routinely obtained. Those which were, however, suggested that acetate was not necessarily stable under the experimental

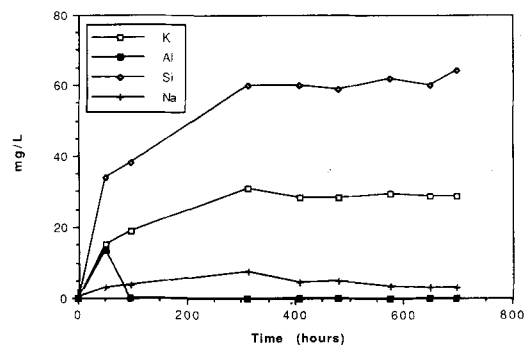


Fig. 7. Feldspar solubility in 0.5 M lithium acetate buffer (pH 6).

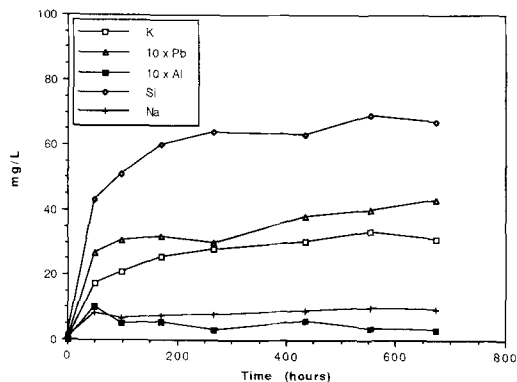


Fig. 8. Feldspar solubility in 1.0 M lithium acetate buffer (pH 6).

conditions. It was observed that in those experiments which show maximum values for Si, acetate clearly decays during the course of the experiment. This is particularly clear for run 15, with 0.1 M potassium acetate as the starting fluid composition, and which yielded Si values of up to 140 mg/L. In Fig. 10 acetate molarity is plotted against time for this experiment, clearly indicating first order decay kinetics. In other experiments in which dissolved Si is low (for 1.0–2.5 M unbuffered acetate solutions) acetate contents appeared to remain relatively stable.

In experiments with pH buffered at 6, acetate was determined routinely and shows variable evidence of decomposition, with less conclusive but similar results for quartz alone (which may be insignificant; Fig. 11a) and for quartz–feldspar mixtures (Fig. 11b). Assuming first-order kinetics, rates of decay are variable, probably reflecting analytical error, with estimates for half lives lying between 45 (1.0 M lithium acetate/orthoclase + quartz) and 170 (1.0 M potassium acetate/quartz) days (Table 4). In both buffered and unbuffered experiments no significant change in run fluid pH, measured under room conditions, could be detected and associated with decarboxylation.

Overall, values for $\log k$ for acetate decarboxylation obtained in all experiments reported here vary from -6.5 to -7.3 , compared with values extrapolated to 150°C by Palmer and Drummond (1986) of between -13 and -18 for acetic acid or sodium acetate in gold or titanium and approximately -7.5 for acetic acid over stainless steel. The values for $\log k$ for acetate decarboxylation with Au/Ti sample containment used in these experiments are expected to be similar to those obtained by Palmer and Drummond (-13 and -18), which are too small to be measured.

Catalytic decarboxylation of acetate in the experiments reported here is therefore clearly greater than expected. However, in more recent experiments in our laboratory, using exactly the same apparatus but with albite instead of orthoclase or quartz (Gestsdotir; pers. comm.), no significant loss of acetate has been observed. It is therefore assumed that the observed decarboxylation is related to the presence of the mineral assemblage, Pb-rich orthoclase plus quartz and its alteration products, rather than the sample containment. It is possible that if present Pb^{4+} may oxidise acetate (as is well known for lead tetraacetate; Carey and Sundberg, 1977), but there is no evidence to suggest that Pb is present within the K-feldspar starting material as anything other than Pb^{2+} . Clearly further work is required to explore this possibility more fully, and experiments are currently in progress to determine the stability of acetate in the presence of end-member albite alone.

Solution modelling

All fluid data derived from the feldspar dissolution experiments have been modelled at 150°C using EQ3NR (version 3245R111) with a steam-saturation database (EQLIB version 3245R136; Wolery, 1983). Limitations inherent in this approach include the model assumption that acetate does not complex with Al or Si, and a lack of thermodynamic data for hydrous lithium minerals such as cookeite. The assumption has been made that thermodynamic data for muscovite within the EQ3 database are appropriate for illite. It has also been assumed that values for pH measured at 25°C will be adequate. For the

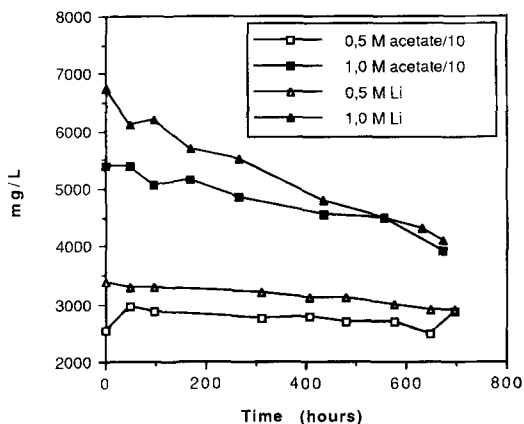


Fig. 9. Decay of Li and acetate with time in pH 6 buffers.

Table 4. Decarboxylation kinetics for acetate at 150°C and 50 MPa (500 bars) pressure.

initial fluid	log k	half life (days)	initial solids present
0.1 M potassium acetate; pH 7.5*	-6.5	20	quartz+feldspar
0.5 M potassium acetate; pH 6	-7.0	95	quartz
1.0 M potassium acetate; pH 6	-7.3	170	quartz
0.5 M lithium acetate; pH 6	-7.2	115	quartz+feldspar
1.0 M lithium acetate; pH 6	-6.8	45	quartz+feldspar

* unbuffered; run 15

experiments using pH 6 buffer solutions, all of which maintain this pH during the experiment, the introduced uncertainties in calculated values for $a(\text{H}^+)$ are unlikely to exceed 0.5 log units. Additional uncertainties arise because of the assumption that activity–composition relationships for acetate solutions can be modelled using Debye–Hückel parameters appropriate for chloride solutions. Nevertheless, the results of solution modelling are consistent with the experimental observations, and can be used as an aid to interpretation and in the design of new experiments.

In Fig. 12 alkali and silica activity data for 150°C, derived from EQ3NR using the Debye–Hückel correction, are plotted for experiments with varying potassium acetate concentration, unbuffered for pH. Relationships for the potassium diagram reflect the use of concentrated solutions of potassium acetate, and indicate that equilibrium between solid and fluid phases, with respect to K, is not achieved. Equilibrium with respect to quartz (assuming $\text{Si}(\text{OH})_4$ speciation) is also not attained in the higher acetate concentration experiments since the data plot well below values appropriate for the quartz saturation line. However, these data plot close to the metastable

extension of the kaolinite–diaspore boundary which perhaps indicates that the observed low silica concentrations in these experiments are controlled by this assemblage. The diaspore component effectively buffers $a(\text{SiO}_2)$ below quartz saturation and could conceivably be present as a precipitate or as a residual leached layer on the feldspar surface; feldspar dissolution appears to be strongly incongruent with respect to aluminium. Illite (muscovite) is the only secondary phase identified in the potassium acetate experiments and is possibly one of the stable phases; further precipitation of illite accompanying dissolution of orthoclase would reduce the $a(\text{K}^+)/a(\text{H}^+)$ ratio. In the analogous case for sodium the fluid data indicate that the assemblage paragonite–kaolinite is stable in the experiments. For the low concentration acetate experiment (0.1 M) silica concentrations are close to but exceed quartz saturation; it is also possible that the kaolinite–pyrophyllite assemblage metastably controls $a(\text{SiO}_2)$ in this case.

Similar data for the experiments with lithium acetate solutions are plotted in Fig. 13. For both Na and K it appears that kaolinite is stable, in the presence of illite, and quartz saturation is achieved. A speculative lithium–silica activity

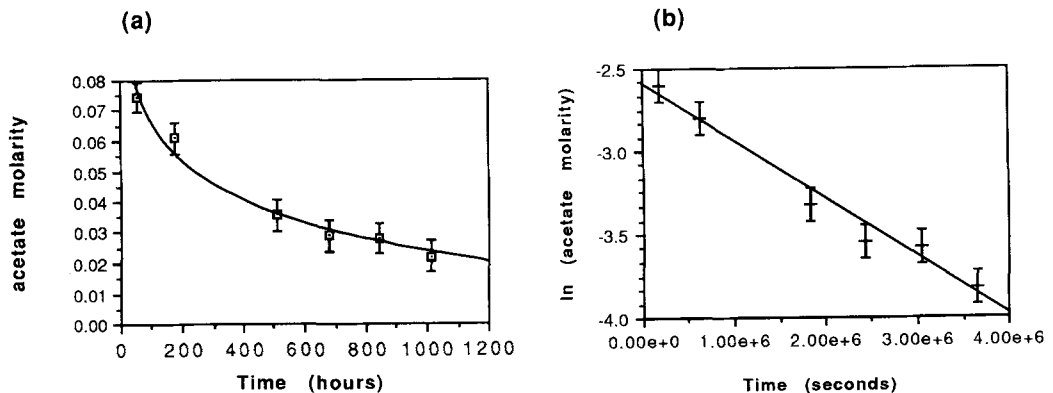


Fig. 10. Decomposition of acetate for run 15, 0.1 M potassium acetate in the presence of orthoclase and quartz (a) raw data; (b) to show first-order kinetics.

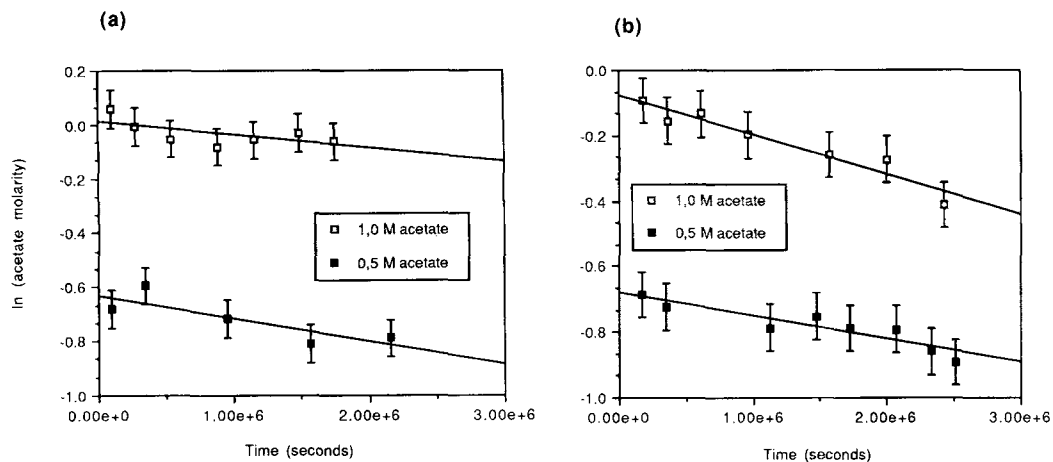
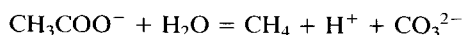


FIG. 11. Decomposition of acetate in the presence of (a) quartz, pH 6 potassium acetate buffer solution and (b) quartz + orthoclase, pH 6 lithium acetate solution.

diagram is shown in Fig. 14; this has been constructed using solubility data for eucryptite, spodumene and petalite derived from the EQ3 database with an arbitrarily chosen value for log K for cookeite solubility ($\log K = 3.88$). This diagram is equivalent to the sodium-silica activity diagram, apart from the use of spodumene rather than bikitaite ($\text{LiAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), which is the Li analogue of analcite. As in the potassium-silica diagram, it appears that equilibrium with respect to lithium is not achieved between the fluid and solid products. This is reinforced by an inability to use these fluid compositional data to estimate log K for the solubility of cookeite.

Discussion

The role of acetate in Si transport under diagenetic conditions. An original intention of this study was to investigate the effect of acetate on dissolution and transport of components derived from potassium feldspar during diagenesis. The results obtained have shown that, from the data for Na and Pb, there does appear superficially to be an overall increase in feldspar solubility with increasing starting fluid acetate content. However, of particular interest is the observation that acetate is unstable in the presence of orthoclase, which suggests that at least a proportion of the observed phenomena may be due to the presence of decay products derived from acetate, such as carbonate/bicarbonate:



The experimental results also suggest an inverse relationship between silica solubility and

fluid acetate content (Fig. 5). This shows that as the acetate content of the starting fluids increases from 0.1 M to 2.0 M there is a reduction in the dissolved silica content from approximately 130 mg/L Si to approximately 30 mg/L Si; an increase would be expected if acetate directly complexed with silica in solution. Furthermore, there is an increase in the pH of the fluid samples as acetate content increases, which would also be expected to enhance further the solubility of silica, rather than be associated with the observed reduction. However, the abundance of secondary mineral precipitates is greater with increasing fluid acetate content, and it is believed to be the presence of these phases which controls the fluid silica contents, rather than the fluid acetate concentration. As the secondary mineral products in pH-unbuffered experiments include illite it can be assumed that in nature the silica content of diagenetic fluids, as they approach equilibrium with quartz, may also be controlled by the presence of secondary phases in addition to feldspars.

Results for the solubility of quartz alone yield no evidence for enhanced dissolution in the presence of acetate. In experiments with both feldspar and quartz with lithium acetate buffer solutions at pH 6, silica contents of fluids match those for corresponding experiments with quartz, suggesting that quartz, rather than feldspar or secondary phases, buffers fluid silica contents. The decomposition of acetate observed for these experiments is apparently associated with, and may be related to, the removal of alkalis from the fluid and the formation of secondary mineral phases, particularly cookeite, on the surface of

etched feldspars. It should be noted that cookeite is reported to occur as a diagenetic mineral (Flehmig and Menschel, 1972), and as discussed above for illite, may help buffer pore fluid compositions.

Taken together, the experiments suggest that there is no increase in silica solubility with increasing fluid acetate content, which implies that acetate alone cannot account for the postulated increases in silica solubility inferred for natural conditions. In the presence of quartz alone there is a slight decrease in silica solubility with increasing acetate content, which may be due to the corresponding reduction in the activity of water. Models for the dissolution of silica include the possible formation of a soluble $\text{Si}(\text{OH})_4$ species which may be hydrated (Walther and Orville, 1983), and relate increases in silica solubility to increases in the activity of water which is conversely reduced by the presence of electrolytes such as chloride, depressing silica solubility (Chen and Marshall, 1982): acetate appears to show similar behaviour.

In contrast to the results for silica, these experiments only provide a tantalising indication of the possible behaviour of aluminium. The observed increase in feldspar solubility with increased fluid acetate concentration and the precipitation of secondary aluminosilicates provide indirect evidence that aluminium is mobilised. However, analytical data for the fluids sampled during individual experiments only report aluminium, if at all, for the earliest samples within a run; it is otherwise below a detection limit of 0.5 mg/L. A possible interpretation is that the aluminium contents of fluids rise rapidly during the initial stages of feldspar dissolution, but are then reduced as soon as secondary clay

minerals, or aluminium oxy-hydroxides, nucleate and start to grow. This behaviour is believed to take place within the first fifty hours of the experiment, approximately half of which includes the time required to reach run temperature. It is possible that the initial secondary precipitates are metastable and transform into more stable assemblages as an experiment proceeds, but the critical point to note is that, in these experiments, aluminium in solution is apparently controlled by the presence or absence of secondary minerals. This suggests that in natural circumstances pore fluid aluminium may also be controlled by the presence of secondary minerals. For significant quantities of aluminium to be transported from a source, rates of mass transport must exceed the rapid rates of precipitation which are suggested by the experimental data.

The stability of acetate: implications for diagenetic transport. It is clear that at 150 °C and 50 MPa (500 bars) pressure there is variation in the stability of acetate; indeed, there are difficulties in determining the thermal stability of acetate in simple experimental systems due to the catalytic effects of certain container materials which enhance decarboxylation (Palmer and Drummond, 1986). Diagenetic systems are naturally complex, involving the presence of several mineral species and complex fluid phases, and so it is to be expected that acetate and other organic anions in solution will be unstable under a wide variety of geological conditions. In order to assess fully the role of acetate, and other organic anions, as potential complexing agents for the transport of inorganic constituents in solution it is necessary to assess their stability under appropriate conditions, both in terms of their rates of formation from organic precursors as well as their rates of

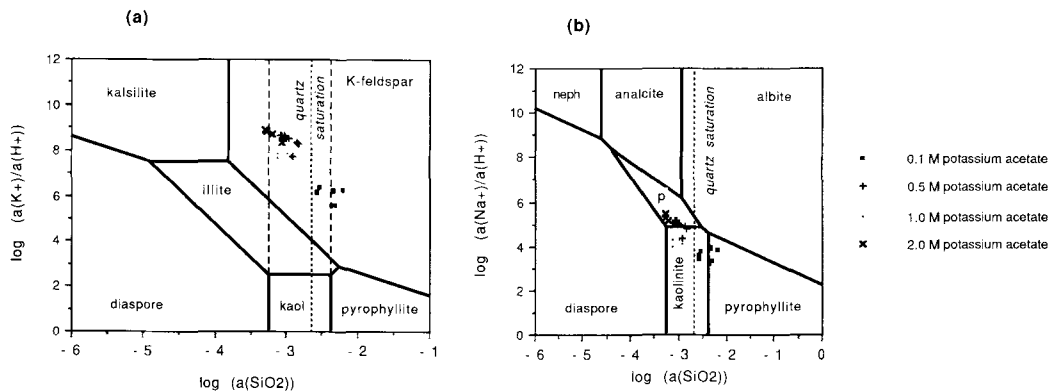


FIG. 12. Plot of $\log a(\text{SiO}_2)$ against (a) $\log a(\text{K}^+)/a(\text{H}^+)$ and (b) $\log a(\text{Na}^+)/a(\text{H}^+)$ for experiments with varying potassium acetate concentration. Abbreviations: kaol = kaolinite; p = paragonite; $T = 150^\circ\text{C}$, pressure = steam saturation.

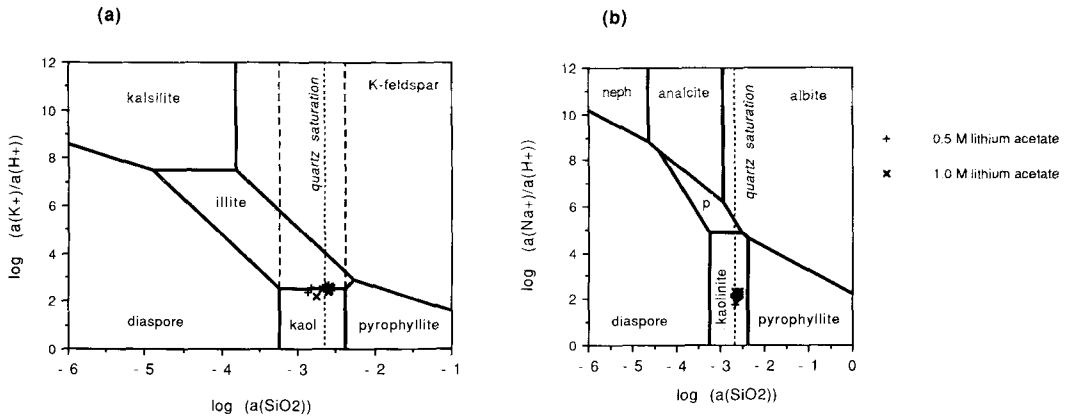


Fig. 13. Plot of $\log a(\text{SiO}_2)$ against (a) $\log a(\text{K}^+)/a(\text{H}^+)$ and (b) $\log a(\text{Na}^+)/a(\text{H}^+)$ for experiments using lithium acetate pH 6 buffer solutions. Abbreviations: kaol = kaolinite; p = paragonite; neph = nepheline; $T = 150^\circ\text{C}$, pressure = steam saturation.

decay. The apparent instability of acetate has major implications for the modelling of solution chemistry involving organic anions (e.g. Shock and Helgeson, 1990) as the kinetics of organic acid decomposition must be taken into account. Current models for silica dissolution mechanisms suggest that if organic species enhance silica solubility they will probably mimic the coordination of hydroxy groups around Si; steric considerations suggest that monodentate species such as acetate (which would require four acetate ligands to be coordinated with a single central Si atom) are unlikely to be stable, while multidentate organic anions may form such complexes. The decomposition of postulated organic complexes of silica in solution as a consequence of the thermal or catalytic decay of the complexing ligands may indeed result in the precipitation of quartz cements, but leave no trace of the organic ligands responsible for enhanced solubilities. The role of organic species in transport could well be

ephemeral, involving metastable equilibria (Shock, 1988) and taking place over periods which are short in geological terms. Organic complexing in aqueous solution may be particularly important in localities close to environments where the maturation of organic matter yields a complex and varied suite of dissolved species of limited stability as components of a geologically immature aqueous pore fluid. Organic-rich mud rocks undergoing petroleum formation represent such an environment, where conditions may favour the formation of unstable soluble species and associated short-lived enhanced fluid solute contents. In contrast, oilfield brines rich in acetate and other monovalent organic acids may be regarded, geologically, as relatively mature pore fluids. Finally, the results of these experiments demonstrate clearly that lead present as a trace element within feldspars can be removed under diagenetic conditions. This emphasises the potential of sedimentary feldspars as potential

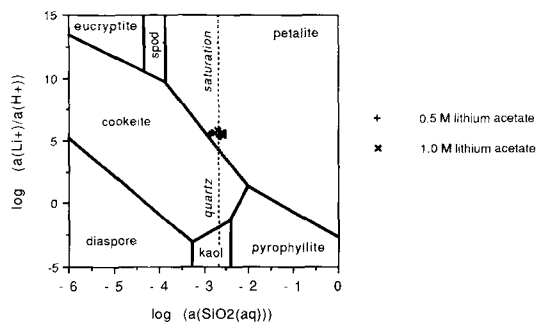


Fig. 14. Speculative plot of $\log a(\text{SiO}_2)$ against $\log a(\text{Li}^+)/a(\text{H}^+)$ for experiments using lithium acetate pH 6 buffer solutions. Abbreviations: kaol = kaolinite; spod = spodumene; $T = 150^\circ\text{C}$, pressure = steam saturation.

sources of cations such as Pb and Ba which are required for Mississippi Valley type and other diagenetic mineralisation.

Conclusions

It is clear that the phenomena observed in these experiments arise as a consequence of several different processes. Overall, the solubility of Pb-rich orthoclase feldspar appears to be enhanced by the presence of acetate and its decay products. However, fluid compositions appear to be influenced by the presence of a complex assemblage of both primary and secondary mineral phases, including illite in K-acetate experiments and cookeite in Li-acetate experiments. No evidence has been found to support the possible role of acetate in enhancing silica solubilities; in contrast, the available experimental data suggest that acetate inhibits quartz dissolution and has little effect on silica transport. It is also clear that the stability of acetate is reduced in the presence of the assemblage orthoclase feldspar plus quartz and secondary precipitates. In all studies of the role of organic anions in aluminosilicate mineral-fluid reaction it is essential to assess their stability, and to monitor the organic acid anion content of the fluid during the course of the experiment. Acetate, and other organic acids, must be regarded as inherently unstable components of natural diagenetic fluids; both their formation and decomposition must be considered in models of diagenetic and ore transport processes.

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References

Bennett, P. C. and Siegel, D. I. (1987) Increased solubility of quartz in water due to complexing by organic compounds. *Nature*, **326**, 684–6.
 — Melcer, M. E., Siegel, D. I., and Hassett, J. P. (1988) The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C. *Geochim. Cosmochim. Acta*, **52**, 1521–30.
 Bevan J. and Savage, D. (1989) The effect of organic

acids on the dissolution of K-feldspar under conditions relevant to burial diagenesis. *Mineral. Mag.*, **53**, 415–25.
 Brindley, G. W. and Brown, G. (1980) *Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society, London.
 Carey, F. A. and Sundberg, R. J. (1977) *Advanced organic chemistry. Part B: reactions and synthesis*. Plenum Press, New York, 521 pp.
 Carothers, W. W. and Kharaka, Y. K. (1978) Aliphatic acid anions in oil-field waters—implications for origin of natural gas. *AAPG Bull.*, **62**, 2441–53.
 Chen, C-T. A. and Marshall, W. L. (1982) Amorphous silica solubilities IV. Behavior in pure water and aqueous sodium chloride, sodium sulfate, magnesium chloride, and magnesium sulfate solutions up to 350°C. *Geochim. Cosmochim. Acta*, **46**, 279–88.
 Doe, B. R. and Delevaux, M. H. (1972) Source of lead in Southeast Missouri galena ores. *Econ. Geol.*, **67**, 409–25.
 Farquhar, R. M., Haynes, S. J., Mostaghel, M. A., Tworo, A. G., Macqueen, R. W., and Fletcher, I. R. (1987) Lead isotope ratios in Niagara Escarpment rocks and galenas: implications for primary and secondary sulphide deposition. *Can. J. Earth Sci.*, **24**, 1625–33.
 Fisher, J. B. (1987) Distribution and occurrence of aliphatic acid anions in deep subsurface waters. *Geochim. Cosmochim. Acta*, **51**, 2459–68.
 Flehmig, W. and Menschel, G. (1972) Über die Lithiumgehalte und das Auftreten von Cookeit (Lithiumchlorit) in permischen Sandsteinene von Nordhessen. *Contrib. Mineral. Petrol.*, **34**, 211–23.
 Gillery, F. H. (1959) The X-ray study of synthetic Mg–Al serpentines and chlorites. *Amer. Mineral.*, **44**, 143–52.
 Giordano, T. H. (1985) A preliminary evaluation of organic ligands and metal-organic complexing in Mississippi Valley-type ore solutions. *Econ. Geol.*, **80**, 96–106.
 — (1989) Anglesite solubility in acetate solutions: The determination of stability constants for lead acetate complexes to 85°C. *Geochim. Cosmochim. Acta*, **53**, 359–66.
 Loughnan, F. C. and Steggle, K. R. (1976) Cookeite and diaspor in the Black Creek pyrophyllite deposit near Pambula, New South Wales. *Mineral. Mag.*, **40**, 765–72.
 MacGowan, D. B. and Surdam, R. C. (1988) Difunctional carboxylic acid anions in oilfield waters. *Org. Geochem.*, **12**, 245–59.
 Manning, D. A. C. (1986) Assessment of the role of organic matter in ore transport processes in low-temperature base-metal systems. *Trans. Instn Min. Metall.*, **95**, B195–200.
 Mast, M. A. and Drever, J. I. (1987) The effect of oxalate on the dissolution rates of oligoclase and tremolite. *Geochim. Cosmochim. Acta*, **51**, 2559–68.
 Murphy, W. M. (1989) Dislocations and feldspar dissolution. *Eur. J. Mineral.*, **1**, 315–26.
 Nelson, B. W. and Roy, R. (1954) Synthesis of the chlorites and their structural and chemical constitution. *Amer. Mineral.*, **43**, 707–25.

- Newman, A. C. D., ed. (1987) *Chemistry of Clays and Clay Minerals*. Mineralogical Society, London, Monograph 6.
- Palmer, D. A. and Drummond, S. E. (1986) Thermal decarboxylation of acetate. Part I. The kinetics and mechanism of reaction in aqueous solution. *Geochim. Cosmochim. Acta*, **50**, 813–23.
- Plimer, I. R. (1976) A plumbian feldspar pegmatite associated with the Broken Hill orebodies, Australia. *Neues Jahrb. Min. Mh.*, 272–88.
- Rimstidt, J. D. and Barnes, H. L. (1980) The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta*, **44**, 1683–99.
- Seyfried, W. E., Janecky, D. R., and Berndt, M. E. (1987) Rocking autoclaves for hydrothermal experiments II. The flexible reaction-cell system. In *Hydrothermal experimental techniques*. (G. C. Ulmer and H. L. Barnes, eds.), Wiley, 216–39.
- Shock, E. L. (1988) Organic acid metastability in sedimentary basins. *Geology*, **16**, 886–90.
- and Helgeson, H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. *Geochim. Cosmochim. Acta*, **54**, 915–45.
- Surdam, R. C. and Crossey, L. J. (1985) Organic-inorganic reactions during progressive burial: key to porosity/permeability enhancement and/or preservation. *Phil. Trans. R. Soc. London, Series A*, **315**, 135–56.
- Hagen, E. S., and Heasler, H. P. (1989) Organic-inorganic interactions and sandstone diagenesis. *AAPG Bull.*, **73**, 1–23.
- Sverjensky, D. (1984) Oil field brines as ore-forming solutions. *Econ. Geol.*, **79**, 23–37.
- (1987) The role of migrating oil field brines in the formation of sediment-hosted Cu-rich deposits. *Ibid.*, **82**, 1130–41.
- Velde, B. (1973) Phase equilibria in the system MgO–Al₂O₃–SiO₂–H₂O: chlorites and associated minerals. *Mineral. Mag.*, **39**, 297–312.
- Walther, J. V. and Orville, P. M. (1983) The extraction-quench technique for determination of the thermodynamic properties of solute complexes: application to quartz solubility in fluid mixtures. *Amer. Mineral.*, **68**, 731–41.
- Wolery, T. J. (1983) *EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: User's guide and documentation*. UCRL-53414. Lawrence Livermore National Laboratory, Livermore, CA.

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