Secondary Porosity Revisited: The Chemistry of Feldspar Dissolution by Carboxylic Acids and Anions[1]

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ABSTRACT

Carboxylic acids in subsurface waters have been proposed as agents for dissolving feldspars and complexing aluminum to create secondary porosity in sandstones. Previously published experimental work indicated high aluminum mobility in the presence of carboxylic acid solutions. In order to further evaluate aluminum mobility, alkali feldspar dissolution experiments were run at 100°C and 300 bars in the presence of mono- and dicarboxylic acids and their anions. Experimental results imply that under reservoir conditions, aluminum-organic anion complexes are insignificant for acetate and propionate and possibly significant for oxalate and malonate. Propionate appeared to inhibit alkali feldspar dissolution and, hence, may retard aluminum mobility. Dissolution of feldspar in the presence of oxalic and acetic acid can be explained by enhanced dissolution kinetics and greater aluminum mobility under low-pH conditions. The general absence of such low-pH fluids in subsurface reservoirs makes this an unlikely mechanism for creating secondary porosity. Also, the thermal instability of oxalate and malonate limits their aluminum-complexing potential in reservoirs at temperatures above 100°C.

PURPOSE OF STUDY

The goal of this study was to follow the dissolution of alkali feldspar for two weeks in different fluids at 100°C

(212°F) and 300 bars (4350 psi), so that the relative differences in aluminum concentrations between experiments would provide qualitative information on the significance of aluminum complexing. The experimental conditions have too low a temperature and too short a reaction time to expect to reach thermodynamic equilibrium with the feldspar. The reaction time and temperature were picked to facilitate comparison with experimental results on organic acids reported by Surdam et al. (1984). One difference between our experiments and the experiments of Surdam et al. was our use of titanium reaction vessels; Surdam et al. used Teflon vessels. The pressure was selected to conform approximately with the expected reservoir fluid pressure (at 9400 ft) in the Gulf Coast at a temperature of 100°C.

INTRODUCTION

Secondary porosity is recognized to be common in sandstones of all ages worldwide (e.g., Hayes, 1979; Schmidt and McDonald, 1979). The origin of secondary porosity, however, is a problem of continuing interest to geochemists and petrologists. Schmidt and McDonald (1979) stressed the dissolution of carbonate cement through the action of carbon dioxide (carbonic acid). This proved to be a popular hypothesis, because experimental work showed that CO_2 was generated by the thermal maturation of organic matter and the cracking of organic acid anions. Additional potential subsurface sources of CO_2 include igneous activity, metamorphic reactions, and diagenetic reactions. The potential role of CO_2 in the dissolution of aluminosilicates was emphasized by Al-Shaieb and Shelton (1981). Meteoric water containing CO_2 is known to dissolve feldspars in sandstone aquifers (Bjørlykke et al., 1979). However, studies by Bjørlykke (1984) and Lundegard et al. (1984) showed that organic matter generally contains insufficient oxygen to generate enough CO_2 to explain the observed amounts of secondary porosity in many basins.

Surdam and his students (e.g., Surdam et al., 1984, 1989) have vigorously supported organic acids, generated by thermal maturation of organic matter, as the agent creating secondary porosity in reservoirs. Organic acids are an attractive agent because of their acidity, which can dissolve aluminosilicate minerals, and their anions, which have the potential to complex aqueous aluminum, thereby hindering back-precipitation reactions. In addition, organic acids are stronger acids than carbonic acid (Meshri, 1986). Nevertheless, the experimental results of this study

and those of Mast and Drever (1987) and Bevan and Savage (1989) question the importance of the organic acid hypothesis, which also has been criticized on other grounds (Giles and Marshall, 1986; Lundegard and Land, 1986, 1989; Lundegard and Sentfle, 1987).

In many situations, the origin of secondary porosity could be due to CO_2, organic acids, or a combination of both agents. For example, Yin and Surdam (1985) explained secondary porosity in sandstones of the Latrobe Group, Gippsland Basin, Australia, as originating from dissolution by organic acids. The Latrobe Group, however, is a major regional aquifer with a fresh water lens extending 60 km offshore and a fresh water–saline water interface at a depth of 2.5 km below sea level (Harrison et al., 1987). Thus, secondary porosity can be explained by either organic acids generated from organic maturation reactions or CO_2-charged fresh water influx in the basin together with CO_2 generated from decarboxylation of the organic acid anions. However, secondary porosity in some sequences is clearly not related to the influx of meteoric waters. Prezbindowski and Pittman (1986) described what may be a unique situation involving a Cretaceous turbidite sequence in DSDP core on the lower continental rise 435 km off Cape Hatteras. In this geologic setting, it is unlikely that the rocks have encountered fresh water, but the feldspars are partly dissolved. Some subsurface process involving organic maturation is probably required to explain this dissolution.

Upon generation from organic-maturation reactions, organic acids would be expected to react quickly with clay-size minerals, which have large surface areas, in shale source beds. Reaction time is a general problem with inorganic acids involving acid treatments of reservoirs through wellbores. The acids (HCl and HCl/HF mixtures) are quickly spent in the near vicinity of the perforations where they react rapidly with fine particles. Engineers are constantly searching for a means of retarding the reaction so the acid can penetrate more deeply into the formation before becoming spent (Clark et al., 1982). By analogy, we would expect organic acids to be spent within the source beds, leaving only the water-soluble organic acid anions to migrate into the reservoir fluids.

Petrographic aluminum mass balances (using the available core samples) on mineral dissolution and precipitation in reservoir rocks (e.g., Milliken, 1988; Milliken et al., 1989) commonly show a net loss of aluminum. Other studies (e.g., Boles, 1984; Thomson and Stoessell, 1985), however, have shown conservation of aluminum. Aluminum mobility in the subsurface is not indicated by measured formation-fluid aluminum concentrations, which are generally less than 1 ppm (e.g., Kharaka et al., 1986). One exception is Ca-rich reservoir fluid in the Stevens sandstones at Paloma field in the San Joaquin basin, California, which contain up to 6 ppm Al (Fisher and Boles, 1990). The calculated slow rates of fluid movement, resulting from compaction in deeply buried reservoirs, range from microns to millimeters per year (Giles, 1987; Bethke, 1985). The combination of very slow rates of fluid movement updip in a reservoir and very low measured aluminum concentrations argues against significantly enhancing porosity by aluminum silicate dissolution. Some authors have proposed convection as a means of

more rapid fluid movement (Wood and Hewett, 1984); however, conditions for convection are not generally fulfilled in clastic reservoirs (Bjørlykke et al., 1988). The contradiction between "observed" aluminum mobility in the rocks versus "observed" immobility in the fluids has not been resolved.

The thermal generation and subsequent destruction of organic acid anions has been documented in reservoirs between 80° and 200°C (Carothers and Kharaka, 1978; Kharaka et al., 1986). Thermal destruction of the anions involves decarboxylation and hence is an important source of CO_2 and acidity in the reservoirs. The thermal destruction takes place at lower temperatures (up to 120°C) for dicarboxylic anions than for monocarboxylic anions (up to 200°C) (Crossey, 1985). The monocarboxylic acetate anion is generally the predominant organic acid anion in subsurface fluids (Carothers and Kharaka, 1978), followed by propionate and then sometimes by the dicarboxylic malonate anion (Surdam et al., 1989, their Table 1; Fisher and Boles, 1990).

Surdam et al. (1989) emphasized the potential complexing of organic anions with aluminum between 80° and 120°C, when secondary porosity commonly forms in clastic reservoirs. This temperature range corresponds to the range where the maximum organic anion concentrations occurred in water samples analyzed by Carothers and Kharaka (1978). The organic complexing would provide a mechanism for aluminum mobility in subsurface fluids. Surdam et al. (1984) reported results from two-week, 100°C (at fluid-vapor equilibrium pressure) feldspar dissolution experiments that produced aluminum concentrations in excess of 1000 ppm through dissolution with oxalic acid, and lesser, but still significant, concentrations through dissolution with acetic acid. They proposed the formation of organic anion-aluminum complexes to explain the high aluminum concentrations, arguing that kaolinite would otherwise precipitate (MacGowan et al., 1988). The resulting SiO_2 concentrations were in excess of amorphous silica solubility, implying that kinetic inhibitions were important in preventing precipitation of that phase during the two-week duration of the experiments. We suggest that similar kinetic inhibitions on the rapid precipitation of gibbsite and kaolinite could also explain high aqueous aluminum concentrations.

There is a major inconsistency in the experimental results by Surdam et al. (1984), which report aluminum concentrations of about 1000 ppm in their Table 2. They report a fluid:rock ratio of 1000:1; thus, total dissolution could only produce 1000 ppm of dissolved salts. Crossey (1989, personal communication) reported the actual ratio was 5 mL of fluid to 50 mg of solids, corresponding to a fluid:rock mass ratio of about 100:1. However, the inconsistency is still present because the weight percents of aluminum contents of feldspar are only 9.7%, 10.3%, and 19.4%, respectively, for K-feldspar, albite, and anorthite. Hence, total dissolution of, for example, andesine with 40% anorthite could yield only about 1400 ppm Al, and the authors did not report total dissolution of the feldspars. Crossey (1989, personal communication) explained the discrepancy by revealing that the reacted solid residues had been analyzed and found to be unknown solids of low-
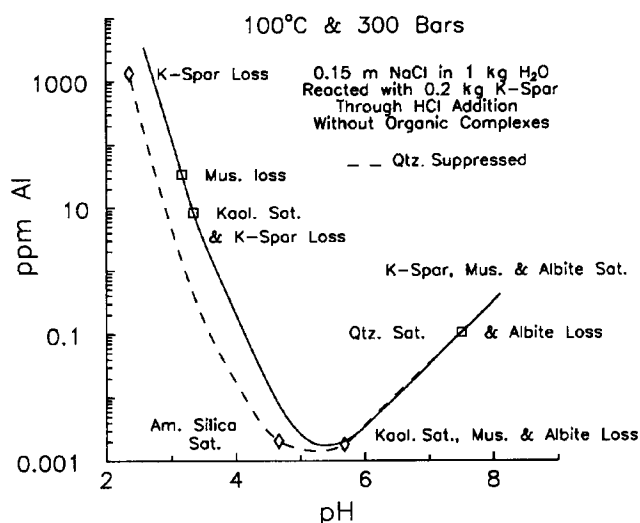
100°C & 300 Bars

Figure 1—Computer simulation of K-feldspar dissolution in 0.15 molal NaCl through the addition of HCl at 100°C and 300 bars. Reaction paths begin at the high pH end and move toward lower pH with the addition of HCl. Two reaction paths are shown: the solid line follows the path that includes quartz as a precipitate, and the dashed line follows the path that allows amorphous silica to equilibriate in the absence of quartz. Muscovite was used as a substitute for illite, and pyrophyllite was suppressed in the presence of amorphous silica.

aluminum content, thereby implying nearly complete feldspar transformation had occurred into different solids in two-week experiments at 100°C. However, this information was not reported by Surdam et al. (1984). Instead, they showed a reacted-grain surface in their Figure 7 and label it as an andesine fragment, not a low-aluminum solid.

In the experiments in our study, only a few per cent of the alkali feldspar actually dissolved, reacted aluminum concentrations were below 70 ppm in oxalic acid and below 3 ppm in acetic acid, and there was no transformation to a solid of low-aluminum content. These results directly contradict those of Surdam et al. (1984), in which they report 150, 1300, 790, and 1400 ppm Al in their Table 2 for microcline, andesine, albite, and laboradorite dissolution, respectively, as well as their now amended report of feldspar transformation (Crossey, 1989, personal communication) during those two week experiments.

The sampling procedure of Surdam et al. (1984) provides a plausible explanation of their high Al concentrations in plagioclase dissolution. Crossey (1989, personal communication) reported that fluids from those experiments were centrifuged but not filtered before analysis and that aluminum was analyzed by flame atomic absorption using nitrous oxide flame. Fine solid particles of aluminum silicates, not removed by centrifuging, would contribute to higher values of aluminum, explaining their results.

Surdam et al. (1984, their Figure 4) attempted to establish the state of supersaturation with respect to gibbsite in the absence of considering organic complexes, using this as an indication of the potential magnitude of such complexes. However, accurate supersaturation calculations for

samples from acid solutions (pH between 1 and 2 in oxalic acid solutions and between 2 and 3 in acetic acid solutions at 25°C) depend critically on the accuracy of back-computed pH measurements in the experiments at 100°C and (to a lesser extent) on the "low" activity coefficient of the trivalent aluminum ion, points not addressed by Surdam et al. (1984). High aluminum concentrations do not necessarily indicate organic complexing because thermodynamic calculations predict high concentrations in acid solutions, without the presence of organic anions, in equilibrium with kaolinite (Stoessell, 1987, his Figure 1) (Figure 1 and the discussion below). Kaolinite was used on these diagrams rather than gibbsite because its solubility is lower for the experimental conditions.

Two additional problems exist in relating Surdam et al.'s laboratory experiments to subsurface conditions. The first problem is the unusual low pH conditions of the organic acids. Low pH fluids must be uncommon in reservoir rocks because of the general persistence in sandstones of minerals such as albite, chlorite, and illite. On Figure 1, a computer simulation of reacting K-feldspar with HCl is shown, obtained using thermodynamic modeling of inorganic reactions (described in "Results and Discussion"). As shown in Figure 1 for albite and illite, in which muscovite is used to approximate illite stability, these minerals would be totally destroyed at quartz saturation under such acid conditions. The second problem is the reaction fluids lacked significant concentrations of competing cations (for the organic anions) commonly found in subsurface fluids, such as calcium, which forms an insoluble oxalate compound (Hillebrand et al., 1953, p. 619–621).

MacGowan et al. (1988) explained the lack of significant concentrations of aluminum in reservoir fluids, particularly those with abundant organic anions from North Coles Levee field in the southern San Joaquin Basin, California, as due to loss by precipitation and/or filtration during production. However, no actual field evidence is offered to support this process taking place. They also disputed the thermodynamic modeling results of Kharaka et al. (1986). Those results indicate organic anion-aluminum complexes may not be significant in subsurface fluids because other, more abundant, cations also form complexes with organic anions. MacGowan et al. (1988) offered no thermodynamic modeling results using organic complexes to support high aluminum mobility in reservoirs.

REACTANT MATERIAL AND EXPERIMENTAL CONDITIONS

Alkali feldspar dissolution was first measured in a 0.15-molal sodium chloride solution, which served as the baseline experiment. Subsequent experiments (using fluids of similar anion normality) were run with four organic sodium salts (acetate, oxalate, propionate, and malonate) and with two organic acids (acetic acid and oxalic acid). The sodium oxalate experiment was run twice, because the first time most of the oxalate was destroyed. The effect of aqueous calcium from calcite dissolution was tested in two additional experiments involving sodium chloride and sodium oxalate. To investigate further an apparent inhibit-

a

b

c

Figure 2—Scanning electron photomicrographs of reacted K-feldspar grain surfaces in several different solutions: (A) from experiment 1 in sodium chloride, (B) from experiment 2 in sodium acetate, and (C) from experiment 6 in acetic acid. Magnification = 2000×.

Table 1. Aqueous Sample Compositions in PPM[†]

Experiment 1a. Microcline reacted with 0.15-molal NaCl fluid (5270 ppm Cl and 3420 ppm Na). The 25°C pH was initially 5.72; the final value was 5.70 on a 1:20 mass-diluted and degassed (i.e., pressure reduced from 300 bars to atmospheric pressure) sample.

Reaction hours	Al	SiO$_2$	K	Na	Ca	Mg	Cl
0	*	0.01	0.12	3600	0.24	0.02	5580
170	0.22	2.22	1.6	3500	4.9	0.72	5350
340	0.28	2.96	2.0	3470	5.3	0.72	5320

Experiment 1b. Microcline and calcite reacted with 0.15-molal NaCl fluid (5270 ppm Cl and 3420 ppm Na). The 25°C pH was initially 5.35; the final value was 6.49 on a 1:20 mass-diluted and degassed sample and 8.83 on a degassed sample. The final sample had 74 ppm HCO$_3$.

Reaction hours	Al	SiO$_2$	K	Na	Ca	Mg	Cl
0	*	b.d.	0.15	3410	0.13	0.03	5070
170	0.26	5.49	3.6	3370	18.6	1.02	5140
340	0.22	7.61	3.4	3400	20.8	0.98	5180

Experiment 1c. Microcline reacted with 0.075-molal NaCl fluid (2650 ppm Cl and 1720 ppm Na). The 25°C pH was initially 5.41; the final value was 5.85 on a 1:20 mass-diluted and degassed sample and 7.58 on a degassed sample.

Reaction hours	Al	SiO$_2$	K	Na	Ca	Mg	Cl
0	*	0.02	0.04	1740	0.09	0.10	2660
170	0.04	4.31	2.0	1760	5.6	0.61	2660
340	0.27	5.13	7.0	1870	8.8	0.92	2710

Experiment 2. Microcline reacted with 0.15-molal NaCH$_3$CO$_2$ fluid (8750 ppm CH$_3$CO$_2$ and 3410 ppm Na). The 25°C pH was initially 7.64; the final value was 6.80 on a 1:20 mass-diluted and degassed sample.

Reaction hours	Al	SiO$_2$	K	Na	Ca	Mg	CH$_3$CO$_2$
0	*	0.27	b.d.	3420	0.04	0.01	8690
170	0.24	4.94	1.9	3440	4.7	0.61	8690
340	0.19	6.17	1.6	3440	4.7	0.70	8690

Experiment 3a. Microcline reacted with 0.075-molal $Na_2C_2O_4$ fluid (6540 ppm C_2O_4 and 3410 ppm Na). The 25°C pH was initially 6.87; the final value was 7.04 on a 1:20.83 mass-diluted and degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	$C_2O_4^{\#}$
0	*	0.04	b.d.	3500	0.06	0.02	6250
170	1.53	5.64	1.4	3470	2.4	2.1	630
340	1.34	6.65	2.5	3430	2.8	2.1	0

Experiment 3b. Microcline reacted with 0.075-molal $Na_2C_2O_4$ fluid (6540 ppm C_2O_4 and 3410 ppm Na). The 25°C pH was initially 6.83; the final value was 7.12 on a 1:20 mass-diluted and degassed sample and 9.17 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	C_2O_4
0	*	b.d.	0.03	3430	0.04	0.03	*
170	0.63	9.59	2.1	3500	10.1	4.0	6470
340	0.80	11.10	3.1	3530	8.9	4.2	6340

Experiment 3c. Microcline and calcite reacted with 0.075-molal $Na_2C_2O_4$ fluid (6540 ppm C_2O_4 and 3410 ppm Na). The 25°C pH was initially 6.83; the final value was 8.33 on a 1:20 mass-diluted and degassed sample and 9.92 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	C_2O_4
0	*	b.d.	0.03	3430	0.04	0.03	*
170	0.81	9.72	4.5	3370	4.0	2.1	6100
340	1.01	19.3	4.8	3360	4.5	4.5	6300

Experiment 4a. Microcline reacted with 0.15-molal $NaC_2H_5CO_2$ fluid (10,800 ppm $C_2H_5CO_2$ and 3400 ppm Na). The 25°C pH was initially 7.74; the final value was 7.06 on a 1:20 mass-diluted and degassed sample and 7.56 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	$C_2H_5CO_2$
0	*	0.27	0.32	3470	0.43	0.25	10,950
170	0.14	4.67	4.0	3440	4.2	0.60	10,950
340	0.08	5.73	3.8	3470	4.2	0.64	10,950

Experiment 4b. Microcline reacted with 0.075-molal $NaC_2H_5CO_2$ fluid (5440 ppm $C_2H_5CO_2$ and 1710 ppm Na). The 25°C pH was initially 7.14; the final value was 6.90 on a 1:20 mass-diluted and degassed sample and 7.67 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	$C_2H_5CO_2$
0	*	0.35	b.d.	1740	0.25	0.14	5580
170	0.07	3.59	4.4	1780	5.6	0.76	5310
340	0.18	4.62	3.5	1830	4.4	0.59	5380

Experiment 5. Microcline reacted with 0.075-molal $Na_2CCH_2O_2CO_2$ fluid (7570 ppm $CCH_2O_2CO_2$ and 3410 ppm Na). The 25°C pH was initially 8.25; the final value was 7.61 on a 1:20 mass-diluted and degassed sample and 8.33 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	$CCH_2O_2CO_2^{\#}$
0	*	b.d.	0.19	3370	1.2	0.02	7900
170	0.67	4.61	1.7	3390	6.5	0.92	320¶
340	0.64	5.70	3.8	3450	7.0	0.86	280¶

Experiment 6. Microcline reacted with 0.15-molal HCH_3CO_2 fluid (8780 ppm CH_3CO_2). The 25°C pH was initially 2.77; the final value was 3.58 on a 1:20 mass-diluted and degassed sample and 3.19 on a degassed sample.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	CH_3CO_2
0	*	0.01	0.08	b.d.	0.08	b.d.	8870
170	2.39	16.3	2.3	13.2	4.3	2.0	7810§
340	2.76	22.5	3.7	13.6	27.1	7.4	7740§

Experiment 7. Microcline reacted with 0.075-molal $H_2C_2O_4$ fluid (6560 ppm C_2O_4). The 25°C pH was initially 1.48; the final value was 3.01 on a 1:40 mass-diluted and degassed sample and 1.67 on a degassed sample. Titanium concentrations from samples 7-1 and 7-2 were 460 and 290 ppm, respectively, due to leaching of the titanium reaction vessel.

Reaction hours	Al	SiO_2	K	Na	Ca	Mg	$C_2O_4^{\#}$
0	*	b.d.	0.04	b.d.	0.08	b.d.	6630
170	35.1	231.	48.2	25.1	1.9	1.9	2120
340	67.0	365.	74.2	18.9	5.4	1.8	3020‡

b.d. = below detection.

†See Appendix for a description of analytical methods and estimates on accuracy.

*The initial reactant solution was used to make the standards to measure concentrations in the reacted solutions.

#Deficiencies in organic anion normalities in solution are due to anion destruction by decarboxylation plus hydrogen reduction to form bicarbonate ions in experiments 3a and 5 and carbonic acid in experiment 7. Measured alkalinities did not change in experiments 3a and 5.

¶110, 470, and 540 ppm of formate, acetate, and propionate were measured, respectively, by ion chromatography in the sample taken at 170 reaction hours, and were 150, 440, and 650 ppm, respectively, in the sample taken at 340 reaction hours.

§330 and 500 ppm of formate were measured by ion chromatography in the samples taken at 170 and 340 reaction hours, respectively.

‡The increase in oxalate concentration between 170 and 340 reaction hours in experiment 7 is assumed due to analytical error in the ion chromatographic measurements. Lack of sufficient sample prevented the analyses from being repeated.

ing effect on feldspar dissolution by propionate anions, an additional baseline experiment was run at 0.075-molal sodium chloride and compared with a sodium propionate experiment of similar anion normality. The experiments and results are described in "Results and Discussion."

A single alkali feldspar (microcline) specimen from a pegmatite at Keystone, South Dakota, obtained from Ward's Natural Science Establishment, served as the source of feldspar reactant for all the experiments. It was crushed and sieved to produce a size fraction between 1 and 2 mm. Heavy liquids were used to separate non-

feldspar grains, and the remaining grains were washed with distilled water to remove fine material. Residual impurities included trace quartz and mica (predominately muscovite) in distinct domains on some of the grains. The amount of albite in the K-feldspar was determined by photographing backscattered electron images, which showed a gray contrast between feldspars. A Zeiss ZIDAS digitizing tablet was then used to measure the area of the two minerals. Albite constituted 14% of the K-feldspar crystal used in the experiments. As an additional reactant, Iceland spar (calcite) was crushed and sieved to obtain the 1 to 2-mm-size fraction, then washed with distilled water to remove fine material.

Typical grain surfaces showed only minor dissolution between the unreacted grain surfaces and the reacted surfaces from the experiments involving organic salts or sodium chloride (Figure 2A, B). Etch pits and other evidence of dissolution were more pronounced in the two experiments involving organic acids (Figure 2C).

The grains were reacted for two weeks in rocking, titanium-lined reaction vessels at 100°C and 300 bars. Three hundred grams of fluid were reacted with 3 g of 1–2 mm diameter alkali feldspar grains in each experiment. In addition, 3 g of 1–2 mm diameter calcite grains were added as a reactant mineral in two of the experiments. Aqueous samples were taken at 170 and 340 hours, reducing the fluid:feldspar mass ratio from 100:1 to 90:1 during the second week of each experiment. The measured aqueous concentrations are reported in Table 1. The laboratory procedures, including sampling procedures, analytical techniques, and estimated analytical accuracies, are discussed in detail in the Appendix.

RESULTS AND DISCUSSION

The initial reaction fluids are listed in the headings in Table 1 for the 12 experiments and are summarized below for easy reference.

Experiments 1a, b, and c:
> 0.15-molal (1a, b) and 0.075-molal (1c) NaCl (sodium chloride), containing 5270 ppm Cl (1a, b) and 2650 ppm Cl (1c).

Experiment 2:
> 0.15-molal $NaCH_3CO_2$ (sodium acetate), containing 8750 ppm CH_3CO_2.

Experiments 3a, b, and c:
> 0.075-molal $Na_2C_2O_4$ (sodium oxalate), containing 6540 ppm C_2O_4.

Experiments 4a and b:
> 0.15-molal (4a) and 0.075-molal (4b) $NaC_2H_5CO_2$ (sodium propionate), containing 10,805 ppm $C_2H_5CO_2$ (4a) and 5440 ppm $C_2H_5CO_2$ (4b).

Experiment 5:
> 0.075-molal $Na_2CO_2CH_2CO_2$ (sodium malonate), containing 7570 ppm $CO_2CH_2CO_2$.

Experiment 6:
> 0.15-molal HCH_3CO_2 (acetic acid), containing 8780 ppm CH_3CO_2.

Experiment 7:
> 0.075-molal $H_2C_2O_4$ (oxalic acid), containing 6560 ppm C_2O_4.

Relative to reservoir fluids, these pH unbuffered reaction solutions correspond to dilute NaCl fluids and high concentrations of organic salts and organic acids.

The solid reactants included the alkali feldspar grains in all experiments and calcite grains in experiments 1b and 3c. With the exception of experiments 1c and 4b, all the fluids initially had identical normalities of anions and of either sodium or hydrogen ions. The reaction fluids for experiments 1c and 4b had half the anion normalities of the remaining ten experiments and were run to check an apparent inhibiting effect on the release of aluminum by propionate during feldspar dissolution. Experiments 3a and b are duplicate experiments in which oxalate was destroyed in 3a but not in 3b.

Experiments 3a, b, and c, involving sodium oxalate, and experiment 7, involving oxalic acid, are difficult to relate to reservoir conditions because calcium, normally present in significant concentrations in reservoir fluids, forms an insoluble oxalate compound. If strontium were present, it would partially precipitate as an oxalate (Hillebrand et al., 1953, p. 626). In addition, the organic acid solutions in experiments 6 (acetic acid) and 7 (oxalic acid) have a much lower pH than reservoir fluids. Although organic acids are directly generated from kerogen in source beds, the H+ ions should be neutralized by reaction with minerals in source beds or along migration routes, making low pH fluids unlikely in reservoirs. However, the organic anions are present until destroyed with increasing temperature by decarboxylation reactions.

To investigate the concentration range of aluminum expected in the absence of organic complexes, a computer simulation was run using the baseline fluid composition of 0.15-molal NaCl. The fluid was reacted to equilibrium with K feldspar, and then the pH was lowered through the addition of HCl. The reaction path is shown on Figure 1 in terms of the aluminum concentration versus pH for two conditions: with and without allowing quartz to precipitate. The computer simulation was run with REACT, a FORTRAN program written by the senior author for use on IBM-compatible personal computers and has been described in Stoessell et al. (1989). A description of the assumptions used in the program and the aqueous complexes considered in the simulation may be obtained from the senior author upon request. The major points shown on the figure are the large aluminum concentrations that are possible at pH values less than 2.6 for a fluid in equilibrium with kaolinite and the very minor concentrations expected in fluids having a pH of about 5. These aluminum concentrations do not include "colloidal" aluminum, which probably contributes significantly (even after filtering through a 0.45-μm filter) to the total aluminum concentrations measured in the experiments. A potential source of error in Figure 1 is the computed activity coefficient of Al^{3+} in fluids with a pH below 2.6. In such fluids, the coefficient decreases rapidly with increasing ionic strength.

Total aqueous concentrations of Al and SiO_2 are plotted in Figure 3 as a function of reaction time. In Figure 3a and d, Al and SiO_2 concentrations, respectively, are shown for the eight experiments with only alkali feldspar as a reactant and having initial anion normalities of 0.15/kilogram
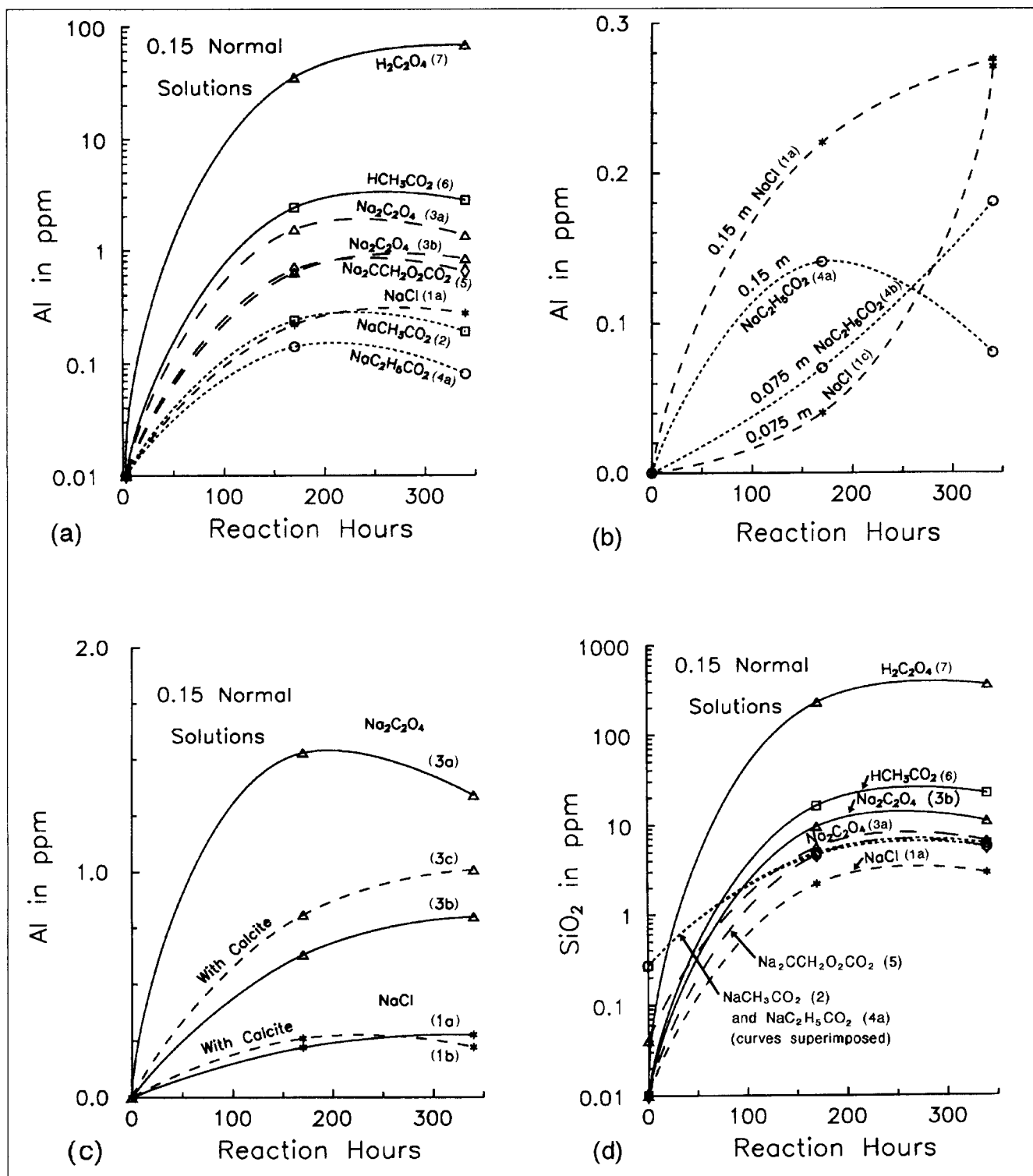
Figure 3—Concentrations of Al (a, b, and c) and aqueous SiO_2 (d) as a function of reaction time. Numbers on curves refer to experiments listed in Table 1.

of water. Total concentrations of aqueous Al are plotted in Figure 3b for the two Na-propionate experiments (4a and b) and their appropriate NaCl baseline experiments (1a and c). On Figure 3c, total aqueous concentrations of Al are plotted for the two experiments containing calcite as

an additional reactant (experiments 1b and 3c), and for the equivalent experiments lacking calcite as a reactant (experiments 1a and 3a and b).

The mineral dissolution is controlled by complex kinetics; however, increases in the degree of undersaturation

through decreases in pH and in the formation of aqueous complexes should increase the dissolution rate (Aagaard and Helgeson, 1982). Experiments 1a–c, involving sodium chloride, are baseline experiments for looking at the effects of acidity and of organic anion complexing. Experiment 1b differs from experiments 1a and c in having both alkali feldspar and calcite as a reactant, adding aqueous calcium through calcite dissolution to the system. Experiment 1c differs from experiments 1a and b in having half the NaCl concentration. Aluminum concentrations are expected to be greater in the seven sodium salt experiments (experiments 2, 3a–c, 4a and b, and 5) if significant amounts of aluminum complex with the organic anions and in the two organic acid experiments (experiments 6 and 7) because of both the lower reaction pH as well as the potential formation of aluminum complexes.

Aluminum concentrations are not greater in experiments 2 (sodium acetate) or 4 (sodium propionate), relative to experiment 1a (sodium chloride), implying aluminum is not significantly complexed by the monocarboxylic acetate and propionate anions. In addition, the decrease in aluminum concentrations in experiment 4a relative to experiment 1a suggests propionate may actually inhibit feldspar dissolution. Aluminum concentrations are enhanced by factors of 3 and 2.5, respectively, in experiment 3b (sodium oxalate) and experiment 5 (sodium malonate) relative to experiment 1a, implying the dicarboxylic oxalate and malonate anions form aluminum complexes in the absence of cations other than sodium. However, aluminum concentrations were enhanced by a factor of 5 in experiment 3a in which most of the oxalate was destroyed, so other factors must also contribute. Also, as noted above, some divalent cations (e.g., Ca and Sr) not present in significant concentrations in these reaction fluids would be expected to precipitate oxalate. As shown in Table 1, calcium was not released in the mineral dissolution reactions in sufficient quantities, even in experiment 3c, which contained calcite as a reactant, to affect the oxalate concentrations. However, the final concentration of aqueous calcium in experiment 3c is one half that in experiment 1b, the corresponding NaCl baseline experiment which also had calcite as one of the reactants. This decrease is probably due to the precipitation of calcium oxalate.

Both oxalate and malonate anions were destroyed at 100°C in the reaction chamber during the course of experiments 3a and 5. Experiment 3a was repeated with and without calcite as a reactant in experiments 3b and c in a different reaction vessel. The destruction of oxalate was insignificant in the second reaction vessel, which was constructed similarly to the first reaction vessel. The kinetics controlling the destruction of the oxalate and malonate are not known; however, Surdam et al. (1984, their Tables 2–4) also reported destruction of oxalate anions in their oxalic acid experiments. The destruction probably represents decarboxylation combined with aqueous hydrogen reduction. The overall reactions can be written as $C_2O_4^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2$ for oxalate and $CO_2CH_2CO_2^{2-} + 2H_2O \rightarrow 2HCO_3^- + CH_4$ for malonate. The titanium walls of the chamber may have had a catalytic effect on the decarboxylation reactions; however, Palmer and Drummond (1986) showed that titanium has only a minimal effect on the decarboxylation of organic anions such as acetate.

The decarboxylation process may affect the feldspar dissolution, accounting for much of the increase in aluminum concentrations in experiments 3a and 5 rather than aluminum complexing with anions. This follows from the inverse correlation of aqueous aluminum with the amount of oxalate present at the end of experiment 3. The correlation argues against aluminum-oxalate complexing as the only reason for the increase in aqueous aluminum concentrations.

The potential effect of propionate inhibiting feldspar dissolution, perhaps by a surface poisoning effect, was further tested in experiments 1c (sodium chloride) and 4b (sodium propionate) by varying the anion concentration. A new baseline experiment using 0.075-molal NaCl was run in experiment 1c for comparison with results in experiment 4b using a starting reaction fluid of 0.075-molal Na-propionate solution. The aluminum concentrations were one third lower at the end of 340 hours in the experiment involving sodium propionate relative to the baseline experiment using sodium chloride. A plot of the experimental results for aluminum in experiments 1a and c (the two sodium chloride runs) and in experiment 4a and b (the two sodium propionate runs) is shown in Figure 3b.

Aluminum concentrations were greater (at 340 hours) by factors of about 14 in experiment 6 (acetic acid) relative to experiment 2 (sodium acetate), and 84 in experiment 7 (oxalic acid) relative to experiment 3b (sodium oxalate). The enhancements were increasing at the end of the experiments, indicating the low pH solutions were continuing to aggressively react with the minerals. In experiment 7, a precipitate of amorphous titanium oxide occurred on the sides of the reaction chamber and on many of the grain surfaces, implying that dissolution would have been even greater in the absence of this precipitate. Also in experiment 7 more than half of the oxalate was destroyed and the overall reaction can be written as $H_2C_2O_4 + 2H_2O \rightarrow 2H_2CO_3 + H_2$. A similar reaction involving reduction of the hydrogen in water could account for the oxidation of the titanium liner.

The greater increases in aluminum concentrations between experiments 3b and 7 relative to those between experiments 2 and 6 correlate with the lower pH values, as suggested by initial 25°C pH of 1.48 for the oxalic acid fluid in experiment 7 vs. 2.77 for the acetic acid fluid in experiment 6. This correlation suggests that the reason for the enhancements is the low pH and not aluminum complexing with organic anions, since decreasing the pH decreases the unprotonated organic anion concentrations. The large increases in aqueous aluminum and other components in experiment 7 do not extend to calcium, apparently because of the presence of aqueous oxalate.

Increases in SiO_2 concentrations in the organic salt solutions in experiments 2, 3a and b, 4a, and 5, relative to experiment 1a (sodium chloride), are by a factor of 2–3 for all four experiments; final increases in SiO_2 concentrations between experiments 6 and 2 and between experiments 7 and 3b are by factors of 4 and 33, respectively (Figure 3c). The concentration increases in the organic salt solutions relative to experiment 1 may not be significant because two of the baseline experiments, 1b and c, which had a lower concentration of sodium chloride, produced SiO_2 concentrations comparable to those generated in the

organic salt experiments. The concentration increases in the organic acid solutions are, as in the case of aluminum, at least partially due to the enhanced dissolution of feldspar in low pH fluids. Of all the experiments, the molar SiO_2:Al ratios in experiments 6 and 7 (organic acids) approach most closely the expected value of 3 for congruent alkali feldspar dissolution.

Surdam et al. (1984) ran their experiments on feldspar dissolution in Teflon reaction chambers. They reported running experiments on feldspar dissolution using Na-acetate and Na-oxalate, but they did not give any results. However, they did report results from acetic acid and oxalic acid experiments. In two week experiments, microcline and albite were reacted separately with 10,000 ppm acetate (0.171 molality acetic acid). These experiments reported 21 and 14 ppm aluminum, respectively, as compared to 3 ppm in our experiment 6. Their experimental procedure used a fluid:mineral mass ratio of about 100:1 (Crossey, 1989, personal communication, correcting the reported ratio of 1000:1) in which the grain size was not given. Their reported pH values are 25°C values and are not back-calculated reaction pH values (Crossey, 1989, personal communication). Their acetic acid solutions were 1.14 times more concentrated than those used in experiment 6, perhaps explaining the higher aluminum concentrations due to the resulting lower initial pH values.

In two week experiments, microcline and albite were also reacted separately with 10,000 ppm oxalate (0.115 molal oxalic acid), obtaining 150 and 790 ppm aluminum, respectively, and albite with 1,000 ppm oxalate (0.011 molal oxalic acid), obtaining 75 ppm (Surdam et al., 1984). These concentrations are greater than the 67 ppm for microcline dissolution in our experiment 7 obtained using 6560 ppm oxalate (0.075 molal oxalic acid); however, as noted in the Introduction, the reported value of 790 ppm Al in Surdam et al.'s experiments is probably incorrect. The aluminum concentrations in our study would probably have been higher in experiment 7 in which titanium oxide precipitated as a coating on the feldspar surface and presumably inhibited feldspar dissolution. Surdam et al. (1984) also reported the formation of a gel precipitate in their oxalic acid experiments with andesine, but they did not provide any information on gels forming with other feldspars. In their experiments and in our experiment 7, much of the oxalate was destroyed during the experiments, although not to the extent of our experiment 3a, one of the sodium oxalate experiments. The destruction of the oxalate in experiment 3a and also malonate anions in experiment 5 suggests that we have underestimated the significance of these anions in forming Al-complexes. However, as previously noted and as discussed below, there was less aluminum released in experiments 3b and c in which oxalate was not destroyed. The destruction of oxalate and malonate (although kinetically controlled) implies a limited presence in reservoir fluids above 100°C (Bevan and Savage, 1989), limiting their effect on aluminum mobility regardless of their ability to complex aluminum. Perhaps the general low values of these difunctional anions in reservoir fluids is simply due to their continued destruction resulting from catalytic effects of various mineral surfaces.

Aluminum silicate experiments are notoriously difficult to reproduce, much less compare between two researchers using reaction chambers of different designs and materials, different reactant grain compositions, somewhat different fluid compositions, and different(?) grain sizes. Yet both studies clearly show that aluminum concentrations are enhanced (relative to NaCl solutions) in the presence of acetic and oxalic acids. However, our results, when taken in conjunction with the lack of enhancement in the presence of sodium acetate and the minor enhancement in the presence of sodium oxalate experiment, imply that most of the increases (actually, all of the increases for the acetic acid solutions) represent a pH effect that would occur without the presence of organic anions.

Boles (personal communication, 1990) suggested that Ti-organic-anion complexing might have occurred due to the use of Ti-lined reaction vessels in our study. We suggest that Al-Fl complexing might have occurred in the experiments reported by Surdam et al. (1984) due to their use of Teflon-lined reaction vessels. However, we do not believe the different results of the two studies are due to the use of different reaction vessels.

The complexing effect of oxalate on aluminum could explain some of the enhancement of aluminum in experiment 3b and c relative to experiment 1a. However, the relative aluminum concentrations in experiments 3a–c are inversely related to the amount of oxalate remaining in solution, implying other processes are at work. In addition, the aluminum concentrations in experiments 3b and c only approach 1 ppm, hardly a significant amount.

The major soluble organic anions in reservoir formation waters are the acetate and propionate ions, and they did not appear to form (in our study) significant concentrations of aluminum complexes. In addition, the presence of propionate ions appeared to retard feldspar dissolution, implying a surface poisoning effect which would work against aluminum mobility.

Our results support the experimental work on K-feldspar dissolution at 70 and 95°C by Bevan and Savage (1989). They ran their experiments in pH-buffered solutions and actually detected a decrease in dissolution rates at pH 1 with oxalic acid relative to HCl solutions. This observation does not support the formation of aluminum-oxalate complexes as being important in the acidic solutions. At a buffered pH of 4 and of 9, they report enhanced dissolution of the K-feldspar of similar magnitude as shown in experiments 3a–c relative to experiment 1a.

SUMMARY

Sandstones commonly have feldspars that are partially dissolved to form secondary porosity. Feldspar dissolution requires that the released aluminum be transported away from the dissolution sites, possibly as aqueous aluminum-organic complexes. The concentration of aluminum in solution is an indication of aluminum mobility. Formation waters in sandstones commonly have aluminum concentrations measured in parts per billion. Experimental results using alkali feldspar suggest that, under reservoir conditions, aqueous aluminum-organic anion complexes are insignificant for acetate and propionate and possibly sig-

nificant for oxalate and malonate. The feldspar was soluble in organic acids due to the low pH and the associated enhanced dissolution kinetics resulting in increased aluminum mobility. However, such low-pH fluids are unlikely in the subsurface. These experimental results question the importance of the organic acid/acid anion hypothesis as related to the dissolution of feldspars.

Alkali feldspar dissolution experiments of two weeks duration were run at 100°C and 300 bars in the following fluids (each having 0.15 normality, per kilogram H_2O, of anions): sodium chloride, sodium acetate, sodium oxalate, acetic acid, oxalic acid, sodium propionate, and sodium malonate. The sodium chloride and sodium oxalate experiments were repeated in the presence of calcite as a reactant. The sodium chloride experiment was considered a baseline to determine if aluminum mobility was affected by the anions and/or the low pH solutions of the acids. Relative to the baseline experiment, aluminum concentrations were nearly identical in the sodium acetate experiment, were only one third (showing apparent inhibition of dissolution) in the sodium propionate experiment, and enhanced by factors of about 2 and 3 in the sodium malonate and sodium oxalate experiments. In the two low-pH organic acid solutions, aluminum concentrations were enhanced by factors of about 10 and 240, respectively, in acetic acid and oxalic acid (calcium-poor) experiments.

To further test the apparent inhibiting effect of propionate on feldspar dissolution, sodium chloride and sodium propionate experiments were run at 0.075 molality at 100°C and 300 bars. The aluminum released in the sodium propionate experiment was two thirds the aluminum released in the sodium chloride experiment. The depletion was less than that observed at the higher molality and needs to be further examined.

The results imply concentrations of aluminum–organic anion complexes were insignificant in the sodium acetate and sodium propionate experiments, and could have been significant in the sodium oxalate and sodium malonate experiments. The high aluminum concentrations in the acetic acid and oxalic acid experiments appeared to correspond to the more rapid feldspar dissolution in low-pH (1 to 3 at 25°C) solutions and the higher solubility of aluminum at low pH values. The absence of low-pH solutions in reservoir fluids limits the importance of this affect in aluminum mobility in the subsurface. Furthermore, the thermal destruction of dicarboxylic oxalate and malonate anions (noted in both subsurface fluids and in several experiments at 100°C) limits their aluminum complexing and hence, their importance in aluminum mobility during the formation of secondary porosity. The monocarboxylic acetate and propionate anions do not appear to form significant concentrations of aluminum complexes under subsurface conditions. Furthermore, the propionate anion appears to retard feldspar dissolution and, hence, may inhibit the formation of secondary porosity.

APPENDIX

The grains were reacted for about two weeks (340 hours) in one of two 0.5 L, titanium-lined (rocking in a 90° cycle every 2 sec) LECO TEM-Pres

reaction vessel at 100°C (electric wire furnace, ± 1°C) and 300 bars (argon gas pressure in headspace of vessel, ± 3 bars) with an initial fluid:rock mass ratio of 100:1 (300 g of solution to 3 g of grains). The reaction vessels and sampling apparatus and procedure have been previously described (Stoessell et al., 1987). The only difference was the use of monel tubing and titanium valves in the two (low pH) experiments involving organic acids (experiments 6 and 7) and in some of the organic salt and sodium chloride experiments (experiments 1b, 3b and c, 4a and b, and 5).

Several problems were encountered during the experiments: a slow gas leak reduced the pressure from 300 to 150 bars during the first 170 hours of experiment 6, and the titanium was etched in the reaction chamber in experiment 7, causing precipitation of amorphous titanium oxide. Because the feldspar dissolution is not expected to be pressure sensitive in the absence of CO_2 gas, the pressure decrease probably did not significantly affect the results in experiment 6. In experiment 7, the precipitate covered most of the feldspar grains (as well as the interior sides of the reaction chamber), presumably slowing down the rate of dissolution. A final problem was the destruction of dicarboxylic anions during the experiments in acid and in some sodium salt solutions. The destruction of oxalate was sensitive to the reaction vessel used in the experiments; for example, malonate was destroyed in experiment 5 and oxalate was destroyed in experiments 3a and 7 but not in 3b and c, which were run in a different reaction vessel. To all outward appearances, the two reaction vessels were identical. The destruction also occurred in the Teflon reaction chambers used in the experiments reported by Surdam et al. (1984) and probably represents, in our study, a catalytic effect of the titanium surfaces of the reaction chamber.

Aqueous samples were taken at 170 and 340 hours. The fluid:rock mass ratio dropped to 90:1 between the first and second samples. Sampling was done at reaction pressure by displacing distilled water in a sample tube in which the tube temperature was not controlled. The pH measurements listed in Table 1 were measured at 25°C on the diluted and degassed (unfiltered) samples. In addition, some pH values are listed for 25°C degassed and undiluted samples. None of these values are the actual pH values under reaction conditions and are listed so that other researchers may attempt to back-calculate the reaction pH when the sample was taken.

Aqueous samples for analysis were mass diluted by 1:20 (except those in experiment 7, which were diluted 1:40) with distilled water as they were removed from the sample tube. All samples were filtered through a #42 Whatman filter and, in addition, samples used for analysis of aluminum were filtered through a 0.45-μm filter and stored in 2% nitric acid (reagent grade) solutions.

The concentrations of the samples listed in Table 1 have an estimated accuracy within 10% for titanium (experiment 7) and aluminum, and 5% for other cations, chloride, and acetate and propionate (determined by acid and base titrations on the reacted solutions and compared with the initial unreacted solutions). In addition, oxalate, malonate, and acetate (in one experiment) were determined by ion chromatography at the Amoco Research Center with a reported estimated accuracy of within 10%. Colorimetric techniques used to measure oxalate concentrations have an estimated accuracy within 5%.

An Instrumentation Laboratory atomic absorption spectroscopy system (IL S12 spectrophotometer, IL 755 graphite furnace, and a Fastac II automatic sampler) was used to analyze for aluminum, sodium, potassium, magnesium, calcium, and titanium. Aqueous aluminum concentrations were determined by furnace and flame spectroscopy in which all standards were made up in 2% nitric acid with an identical matrix in terms of major salt components as that in the unknowns. Concentrations of titanium, sodium, potassium, calcium, and magnesium were analyzed by flame atomic absorption spectroscopy. Excesses of alkali (1000 ppm) were added to control ionization in standards and samples for sodium and potassium, and strontium (1000 ppm) was added to control interferences for calcium and magnesium. Samples containing large concentrations of oxalate were acidified after the addition of strontium to dissolve the resulting precipitates. Aluminum and titanium have larger uncertainties due to the use of the furnace for aluminum and the use of flame spectroscopy for titanium on samples already diluted by a factor of either 20 or 40.

Nonpolymerized SiO_2 concentrations were measured using the standard molybdate blue method. The assumption was made that the nonpolymerized SiO_2 concentrations represented the major amounts of SiO_2 in these, generally, acidic to neutral solutions. Chloride concentrations were analyzed using a Buchler 4-2500 chloridometer. The pH measurements and titrations (mentioned below) were made using a combination Orion #91-05 pH electrode with an Orion Model 601A pH meter in which

pH buffers of 4.00 and 7.00 were used to calibrate the meter and electrode.

The organic anion concentrations were measured using several methods. Acetate and propionate concentrations in experiments 2 and 4a and b were determined by titration with a standard acid (HCl). Acetate and oxalate concentrations in experiments 6 and 7, respectively, in the starting solutions were checked for accuracy by titration with a standard base (NaOH). Similar titrations were not performed on the reaction samples from experiments 6 and 7 because of the prior development of a precipitate in the nonacidified samples after two weeks of storage. Concentrations of oxalate in experiments 3a and 7 were determined by J.B. Fisher using ion exclusion chromatography (Dionex AS4 separator). The low values in the reaction samples in experiment 3a were verified by R. K. Stoessell using the ferric-salicylate colorimetric technique (Snell et al., 1961, p. 358). Yang Chen measured the oxalate concentrations in experiments 3b and c using the technique of Snell et al. (1959). Fisher measured the concentrations of acetate in the reaction samples from experiment 6 (Dionex HPICE separator) and the concentrations of malonate in reaction samples from experiment 5 (Dionex HPICE separator).

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