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## **ROLE OF ACETIC ACID IN SILICICLASTIC DIAGENESIS: AN EXPERIMENTAL STUDY**

Gina Bagnetto Waters

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ROLE OF ACETIC ACID IN  
SILICICLASTIC DIAGENESIS: AN EXPERIMENTAL STUDY

A Thesis

Submitted to the Undergraduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
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in

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by  
Gina Bagnetto Waters  
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**ABSTRACT**

Organic acid anions, known to be present in some formation waters, are thought to enhance silicate mineral solubility by complexing with Si and Al. In turn, these organic acid complexes may play a role in creating secondary porosity in clastic rocks during diagenesis. A series of experiments was performed to investigate the reactions that occur between clastic sediment, with and without calcite, and acetic acid in varying concentrations at 25°C and 1 bar. The results of these experiments show that at 25°C and 1 bar and over a time frame of 60 days, acetic acid has no appreciable affect on mineral hydrolysis at acetic acid concentrations below 1000 mg/L. However, at mineral concentrations of 1000 mg/L or greater, the degree of mineral hydrolysis increases significantly as shown by the high concentrations of Na, K, Mg, Ca, Sr, Ba, and Si detected in the aqueous solutions.

Despite the observed increase in Si concentration above 1000 mg/L of acid in the calcite free experiments, Si did not complex to a significant degree. Had Si been complexed by acetate, one would expect to find higher concentrations of Si in solution than detected in these experiments. One would also expect to find Si in appreciable amounts in the experiments containing calcite, whereas this was not the case in these experiments. At elevated acetate concentrations, the pH of the solutions was still acidic. It is proposed that this lower pH enhanced Si solubility, rather than the organic acid anion complexing Si as suggested by other investigators. Many workers promote the idea that Al is also complexed by organic acid anions. However, that theory is not borne out by these experiments. Dissolved Al was not present above the limits of detection (0.01 mg/L) in any run, which contradicts the traditional interpretation that acetate should complex Al.

The experimental fluids were largely oversaturated with respect to quartz an apparently buffered by metastable equilibrium with respect to albite-K-feldspar and calcite-dolomite, similar to waters in some natural siliciclastic water systems. This suggests that organic acid anions, such as acetate, may have no unique influence over bicarbonate or chloride on mineral stability or on mineral hydrolysis.

## **INTRODUCTION**

The role of dissolved organic acids in fluid/mineral reactions has been studied and debated for over a decade. Organic acids are reported to be found in oil field brines in concentrations up to 10,000 mg/L and thus appear to be important constituents in some sedimentary fluids (Carothers and Kharaka, 1978; Hanor and Workman, 1986; MacGowan and Surdam, 1988). Table 1 lists the commonly reported carboxylic organic acids found in natural waters. The relative concentrations of individual species in oilfield brines vary. In most cases, however, acetate appears to be the dominant species (Surdam et al., 1984). Many experiments have been performed in order to understand the role that organic acids play in fluid/mineral reactions. Experiments have been carried out under elevated pressure and temperature conditions to evaluate the stability of organic acids under diagenetic conditions (Manning et al., 1994; Barth et al., 1990; Reed and Hajash, 1992). Other experiments have been conducted at 25°C and 1 bar to evaluate the role of organic acids during weathering at the earth's surface, especially the acids that act as contaminants (Bennett et al., 1988; Bennett and Siegel, 1987).

Many investigators within the last few years have concentrated their studies on the dissolution of feldspar in various organic acids and on the presumed enhanced solubility of alumino-silicates by organic acids (Manning et al., 1994; Harrison and Thyne, 1992; Reed and Hajash, 1992; Bennett, 1991; Barth et al., 1989; and Bennett et al., 1988). Results of these

Table 1. Selected carboxylic organic acids and their structural formula

Common Name	Structural Formula
<i>Monofunctional</i>	
Acetic acid	$\text{CH}_3\text{COOH}$
Propionic acid	$\text{CH}_3\text{CH}_2\text{COOH}$
Isobutyric acid	$(\text{CH}_3)_2\text{CHCOOH}$
n-butyric acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
<i>Difunctional</i>	
Oxalic acid	$(\text{COOH})_2$
Malonic acid	$\text{CH}_2(\text{COOH})_2$
Succinic acid	$(\text{CH}_2)_2(\text{COOH})_2$
<i>Trifunctional</i>	
Citric acid	$\text{COH}(\text{CH}_2)_2(\text{COOH})_3$

experiments have been used to infer the potential effect of organic acids during diagenesis of sedimentary rocks. Of particular interest has been the role that organic acids may have in creating secondary porosity in clastic rocks. It has been suggested that the presence of organic acids in pore fluids may account for precipitation of cements located far from the implied source of mineral dissolution (Crossey, 1991; Surdam et al., 1984, 1989). Another important observation regarding organic acid anions has been the apparent increased solubility of some metals in the presence of some organic acid pore fluids (Tan, 1980; Harrison and Thyne, 1992).

There is debate over the relative importance of organic acids in silicate diagenesis. It is not clear whether the observed increase in silica concentration in organic acid solutions represents complexing by the organic anions, which in turn enhances silicate solubility, or whether this observed increase in silica concentration is a result of enhanced reaction rates (Manning et al., 1994). Questions also arise regarding the credibility of previous experimental analysis. Manning et al. (1994) criticize the integrity of some experimental studies, arguing that the systems were not maintained at constant conditions throughout experimentation. Kharaka et al. (1986), however, suggest that the true role of organic acids is simply to buffer the pH and Eh of pore water fluids, which in turn strongly affects mineral diagenesis.



There has been very little documentation of the behavior of cations other than Al and Si during reaction of sediments with organic acids. In addition, a number of recent studies have excluded acetic acid, the dominant naturally occurring organic acid, from their research. The aim of this study was to gain a better overall understanding of the behavior of minerals in contact with varying concentrations of acetic acid and to evaluate the relative importance of this organic acid in comparison with other fluid systems without organic acid components. While most studies involving organic acids concentrate upon the dissolution of a single mineral phase, e.g., feldspar, this study involved observing a system containing multiphase sediments reacting with organic acids in solution. The results can potentially be applied to surface weathering studies and may contribute important information regarding the behavior of ions in acetic acid solutions during diagenesis.

## **PROCEDURE**

### **Experimental Set-Up**

The experiments were designed to determine the chemical behavior of acetic acid solutions in contact with siliciclastic sediments. The concentration of initial acetic acid varied between setups while the volume of sediment was kept constant. Calcite was included in some experiments to observe how the fluid systems changed when a carbonate phase was present.

Twenty-one experimental runs were prepared, each containing a mixture of siliciclastic sediment, with or without calcite, and an acetic acid solution. The experiments were housed in capped, 125 mL polyethylene bottles.

The sediments utilized were collected from the bank of the Mississippi River in Baton Rouge, Louisiana by L. Esch and J.S. Hanor. These sediments have also been used by L. Esch for his experimental research on NaCl brines reacting with siliciclastic sediments (Esch and Hanor, 1993). The basic mineralogy of the sediments was determined, and the results of the analyses are summarized in Table 2 (Esch, pers. comm., 1994).

### **Sample Preparation**

The sediments were rinsed with deionized and distilled water and then dried in an oven at 60°C for 2-3 days. The mass of sediment was then removed from the oven, broken into smaller pieces (approximately 2-3 cm in diameter) with a mortar and

Table 2. Sediment Mineralogy determined by X-ray diffraction

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**Mineral Phase**

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Quartz

Kaolinite

Smectite

Illite - weathered detrital muscovites

K-feldspar (m)

Plagioclase (m)

(m) = minor phase

pestle, and placed back into the oven for another 2-3 days. These pieces were crushed further with the mortar and pestle until they ranged in size from powder to several millimeters in diameter. The amount of sediment which was crushed to powder was minimized to preserve the crystal structure of the minerals. The prepared sediment was placed in a desiccator until it was ready to be transferred to the sample bottles.

Seven different concentrations of acetic acid solution were prepared. The solutions were made from glacial acetic acid and distilled, deionized water using volumetric flasks and calibrated pipets. The acetic acid concentrations of the solutions were 10 mg/L, 30 mg/L, 100 mg/L, 300 mg/L, 1000 mg/L, 3000 mg/L, and 10,000 mg/L. These concentrations cover the reported range of acetate concentrations in natural waters.

Twenty-one 125 ml polyethylene sample bottles were prepared by soaking in a 2% soap solution for 24 hours, rinsing with deionized, distilled water, soaking with 2% HCl solution for 24 hours, and rinsing 3 times with deionized, distilled water. The bottles were then dried at 60°C overnight to remove all water.

27.00 g of sediment were added to each of the sample bottles. The samples were divided into three sets of seven experiments. In addition to the acid, the first set of experiments contained clastic sediment only. The second set contained sediment plus 1.00 g of reagent grade  $\text{CaCO}_3$  determined to be calcite by X-ray diffraction (L. Esch, pers. comm., 1994). The third set of experiments initially contained sediment, but

1.00 g of the same reagent grade  $\text{CaCO}_3$  as calcite was added after 30 days of reaction time. Calcite was added to observe whether the behavior of the cations would be different in solutions with calcite.

The mass of sediment was chosen to fit conveniently in the sample bottles. Because the density of the sediment was approximately  $2.7 \text{ g/cm}^3$ , 100 mL of acetic acid solution of different concentrations were added to each bottle, providing a 10:1 volumetric ratio of acetic acid solution to sediment. The concentrations of acetic acid increased logarithmically in seven steps from 10 mg/L up to 10,000 mg/L.

The amount of calcite added to sample groups 2 and 3 was determined by calculating the amount of calcite required for calcite saturation in the acetic acid solutions. 0.005 g of calcite were required to saturate the 10 mg/L solution; 0.5 g were required to saturate the 10,000 mg/L solution. Therefore, 1.00 g of calcite was added to all of the samples in groups 2 and 3 to insure complete saturation.

The bottles were then capped and stored at an ambient temperature of approximately  $25^\circ\text{C}$  (room temperature) and 1 bar pressure. The bottles were gently agitated daily, and all of the bottles in groups 1 and 2 remained sealed throughout the experimental run until alkalinity measurements were taken after 60 days. However, the bottles in group 3 were briefly opened to add calcite after 30 days.

## Analytical Techniques

### *Alkalinity Titrations*

After 60 days of reaction time, the liquid phase of each experiment was analyzed to determine pH and major anion and cation concentrations. Total alkalinity was determined using the standard method described by Brown et al. (1970). The solution was titrated with a standard solution of sulfuric acid, but rather than simply using an indicator to reach the desired pH endpoint, a titration curve was constructed. Titration continued until the pH of the solution fell to between 2.2-2.5. Finishing with a low pH ensured that no  $\text{CO}_2$  would reenter the system; this was required to ensure the accuracy of the reverse titrations for acidity to be performed later. Once the titration was completed, the acidified solution was sealed and was retained for later acetate alkalinity measurements. The data collected was then used in a Gran function (Drever, 1988) to identify precise end points where all alkalinity had been titrated.

Reverse titrations were conducted to determine the portion of alkalinity contributed by acetate ion. This was a much more difficult parameter to calculate because organic anions do not reach precise pH stability and are not easily detected in alkalinity titrations. The acetate alkalinity titrations were performed following the method described by Brown et al. (1970). The acid solutions were titrated with a standard solution of NaOH to a pH of 8.3. Again, a titration curve was constructed, and

the Gran function for reverse titrations was employed to determine the precise end point for acetate alkalinity (Stumm and Morgan, 1981). After the volumes of acid used for total alkalinity and the volumes of base used for acetate alkalinity were calculated from their corresponding Gran functions, total alkalinity was calculated using the equation from Brown et al. (1970):

$$\frac{1000}{\text{mL}_s} \times \text{mL}_a = \text{total alkalinity as } \text{HCO}_3^-$$

where  $\text{mL}_s$  is the volume of the experimental solution and  $\text{mL}_a$  is the volume of acid added to the solution to reach its end point as determined by the Gran Plot. The calculation for acetate alkalinity is more complicated because it must take into account the addition of acid to the solution before reverse titration:

$$[\text{mL}_a \times \text{acid } N] - [\text{mL}_b \times \text{base } N] \times 60,030 = \text{mg/L organic acids as acetic acid}$$

where  $\text{mL}_b$  is the volume of base added to the solution to reach its end point, and  $N$  is the normality of the acid and base solutions (Collins, 1975).

However, some of the values needed adjustment because at low concentrations of acetic acid, the acetate was difficult to detect. In the experiments with low initial acetic acid concentrations, the calculations performed for acetate alkalinity yielded unreasonable or negative results. In the experiments with an appreciable amount of initial acetic acid, enough acetate was released into the system to allow calculation.

The acetate alkalinity values for the low concentrations in each set of solutions required adjustment if the experiments were to be considered in alkalinity analyses. Adjustments to the acetate alkalinity calculations were based upon the constant relationship between acetate alkalinity and total alkalinity at higher concentrations of acetic acid. For the carbonate free series, Acetate alkalinity = Total alkalinity; for the sample 2 series, Acetate alkalinity = (2/3) Total alkalinity; and for the sample 3 series, Acetate alkalinity = (1/2) Total alkalinity.

*Analyses of Cations using Inductively Coupled Plasma (ICP)*

The following cations in solution were analyzed using the ICP: Na, K, Ca, Mg, Si, Fe, Mn, Pb, Zn, Al, Ba, and Sr. In preparation for analyzing the cations on the ICP, each experimental solution underwent a 10x dilution with a 2% HCl solution. The acid dilution was necessary to preserve the ions in solution, and it also served to dilute the experiments, which potentially had large concentrations of cations and acetate, down to the approximate concentration of the standard solutions for analysis.

Five standard solutions were made. It was more accurate to analyze a few (<5) cations in a given ICP run than many (>5). Therefore, the cations incorporated into the standards were grouped for convenience of testing. The cations in each standard were grouped based upon their compatibility with respect to wavelength and relative concentration in solution. The cation



choices and their corresponding wavelengths are shown in Table 3. The first standard was a blank solution composed of 100 mg/L acetic acid in a 2% HCl acid solution. The blank was created with acetic acid and HCl to provide a consistent baseline for the matrix of the experiments. The second standard was composed of 10 mg/L Fe, 100 mg/L Ca, 100 mg/L Mg, 10 mg/L Mn, and 10 mg/L Si in a matrix composed of a portion of the blank solution. The third standard was composed of 75 mg/L Ba, 10 mg/L Sr, 10 mg/L Pb, and 10 mg/L Zn in the same blank matrix. The fourth standard was composed of 100 mg/L K and 100 mg/L Na in the blank matrix. K and Na were combined in a separate standard solution because their wavelengths are detectable at much greater wavelengths than the others (the visible light spectrum). The fifth standard was composed of a 1 mg/L Al solution, again with the same matrix as the others. Al required a separate standard due to its difficulty in detectability in that it is generally found in only trace amounts.

The limits of detection for the cations analyzed by the ICP as reported by the manufacturer are listed in Table 4. Through previous experience with this ICP unit, however, the true limit of detection for each of the cations analyzed has been determined to be approximately 0.01 mg/L (Esch, pers. comm., 1994). The calculated coefficient of variation from the analytical results, based upon multiple analyses, were below 5-8 percent. This information appears to verify the precision of the results. Error bars were not calculated for these experiments.

Table 3. ICP Standards and their chosen wavelength analyzed

Standard 2		Standard 3		Standard 4		Standard 5	
Fe	-- 259.940nm	Ba	-- 455.403nm	K	-- 766.491nm	Al	-- 308.215nm
Ca	-- 422.673nm	Sr	-- 407.771nm	Na	-- 589.592nm		
Mg	-- 285.213nm	Pb	-- 220.353nm				
Mn	-- 257.610nm	Zn	-- 213.856nm				
Si	-- 251.611nm						

Table 4. ICP Limits of detection as reported by the  
VARIAN guide

Element	VARIAN guide ICP values (mg/L)
Al	0.0015
Ba	0.00007
Ca	0.00003
Fe	0.0015
K	0.01
Mg	0.0001
Mn	0.0003
Na	0.001
Pb	0.014
Si	0.005
Sr	0.00002
Zn	0.0009

*SOLMINEQ88*

After all of the analytical data were recorded, the pH, alkalinity, and cationic information were entered and evaluated using the SOLMINEQ88 program (Kharaka et al., 1988). This program uses that information to calculate charge balance, activities, activity coefficients, activity ratios, and  $p\text{CO}_2$ . These results were then used to plot fluid compositions on phase diagrams for the experiments in question.

## **RESULTS**

Table 5 summarizes the measured solute concentrations in the solutions at 25°C and 1 bar pressure. The sample 1 series is the set of solutions that did not contain calcite. The sample 2 series contained calcite throughout the experiment, and in the sample 3 series calcite was added to the system after 30 days of reaction time. Table 6 summarizes the calculated activities and activity ratios from the SOLMINEQ 88 program.

As the experiments reacted, an unexpected phenomena occurred. In some of the experiments, the reaction bottles and their contents were yellow or grey colored. Upon closer observation, some small bubbles were recognized on the sediment grains. While laboratory analyses were not conducted to explain the phenomenon, it is known that some respirative bacteria consume acetate. Two genus of microorganisms known to consume acetate are *Bifidobacterium* and *Clostridium* (Chapelle, 1993). One or more species of these bacteria may have been growing in the bottles and may have contributed to the discoloration of the bottles.

### **pH**

Figure 1 shows pH as a function of acetic acid concentration. The initial pH values of the acetic acid solutions prior to their reaction with mineral phases were approximately 4.00 at the lowest concentration of acetic acid and

Table 5. Ionic concentrations

Sample Numbers	Acetic Acid Conc. *	pH	Total Alkalinity	Acetate Alkalinity
1-1	10	7.00	85.02	85.02
1-2	30	6.65	118.8	118.8
1-3	100	7.20	101.8	101.8
1-4	300	7.70	134.6	134.6
1-5	1000	6.01	450.6	450.6
1-6	3000	4.38	680.8	680.8
1-7	10000	3.96	846.8	846.8
2-1	10	7.40	221.2	132.7
2-2	30	7.33	219.2	131.5
2-3	100	7.92	249.0	149.4
2-4	300	8.41	316.4	189.8
2-5	1000	8.21	991.0	594.6
2-6	3000	7.89	2393	1436
2-7	10000	7.72	7498	4499
3-1	10	8.18	178.9	89.46
3-2	30	8.20	186.1	93.03
3-3	100	8.25	201.6	100.8
3-4	300	8.49	224.0	112.0
3-5	1000	7.90	756.2	378.1
3-6	3000	8.30	2264	1132
3-7	10000	7.67	7820	3910

\* All concentrations are reported as mg/L

Table 5. Ionic concentrations

Sample Numbers	Carbonate Alkalinity (as HCO <sub>3</sub> <sup>-</sup> )	K	Na	Ca	Mg	Sr	Ba
1-1	0.00	6.20	24.40	26.10	4.70	0.10	0.10
1-2	0.00	7.40	26.60	26.60	5.50	0.10	1.40
1-3	0.00	5.40	22.30	26.30	4.90	n.d.	n.d.
1-4	0.00	5.30	21.90	31.40	6.60	n.d.	n.d.
1-5	0.00	7.30	29.40	110.8	26.10	0.30	n.d.
1-6	0.00	17.60	33.80	211.3	51.20	0.70	0.30
1-7	0.00	28.30	38.50	408.7	84.90	1.40	0.90
2-1	88.48	7.30	28.80	83.60	16.80	0.20	n.d.
2-2	87.68	6.90	26.60	62.70	13.00	0.20	0.10
2-3	99.60	35.70	27.80	72.70	14.70	0.20	0.30
2-4	126.56	35.80	27.90	94.00	18.50	0.20	n.d.
2-5	396.40	34.00	31.90	275.4	49.10	0.60	0.10
2-6	957.28	6.90	37.50	821.6	99.60	1.40	0.30
2-7	2999.20	29.20	46.40	2851	170.1	3.10	0.70
3-1	89.46	9.80	30.70	127.8	25.40	0.40	0.20
3-2	93.03	10.70	30.30	100.8	20.40	0.30	0.20
3-3	100.80	12.50	32.00	121.5	24.80	0.30	0.00
3-4	112.00	8.90	29.50	105.7	22.90	0.30	0.10
3-5	378.10	4.10	32.10	265.7	50.50	0.60	n.d.
3-6	1132.00	13.50	35.70	299.7	105.2	1.60	0.30
3-7	3910.00	32.20	41.10	2923	183.8	3.30	1.50

Table 5. Ionic concentrations

Sample Numbers	Si	Fe	Mn	Zn	Pb
1-1	10.30	0.20	n.d.	n.d.	n.d.
1-2	11.20	0.10	n.d.	0.20	n.d.
1-3	11.00	n.d.	n.d.	n.d.	n.d.
1-4	11.50	0.20	n.d.	n.d.	0.30
1-5	22.10	6.10	12.60	n.d.	0.10
1-6	47.80	0.00	7.30	n.d.	0.20
1-7	61.30	0.40	15.10	n.d.	0.30
2-1	7.60	0.10	n.d.	n.d.	n.d.
2-2	7.90	0.10	n.d.	n.d.	n.d.
2-3	8.10	0.20	n.d.	n.d.	n.d.
2-4	8.10	0.10	n.d.	n.d.	n.d.
2-5	10.50	4.40	24.00	n.d.	0.20
2-6	15.10	4.30	49.00	n.d.	n.d.
2-7	11.80	0.30	17.30	n.d.	n.d.
3-1	8.30	n.d.	n.d.	n.d.	n.d.
3-2	8.40	n.d.	n.d.	n.d.	n.d.
3-3	9.30	0.20	n.d.	n.d.	n.d.
3-4	10.10	0.10	5.90	n.d.	n.d.
3-5	17.30	15.50	26.00	n.d.	0.30
3-6	18.90	13.20	31.60	n.d.	0.20
3-7	16.90	1.30	21.60	0.60	0.40



Table 6. Activity Data from SOLMIN88.

Sample Numbers	TDS	pCO <sub>2</sub>	ACTIVITIES				
			Ca	Mg	Na	K	HCO <sub>3</sub>
1-1	157.12	n.d.	5.07E-04	1.51E-04	9.99E-04	1.49E-04	n.d.
1-2	198.63	n.d.	5.05E-04	1.73E-04	1.09E-03	1.77E-04	n.d.
1-3	171.72	1.12E-03	5.07E-04	1.57E-04	9.12E-04	1.30E-04	2.70E-04
1-4	211.84	5.24E-04	5.89E-04	2.06E-04	8.91E-04	1.27E-04	4.00E-04
1-5	665.4	3.40E-03	1.67E-03	6.62E-04	1.14E-03	1.66E-04	5.18E-04
1-6	1051	n.d.	3.11E-03	1.28E-03	1.29E-03	3.93E-04	n.d.
1-7	1486.6	n.d.	5.46E-03	1.96E-03	1.42E-03	6.10E-04	n.d.
2-1	365.6	3.35E-03	1.41E-03	4.74E-04	1.14E-03	1.70E-04	1.28E-03
2-2	336.7	3.95E-03	1.08E-03	3.76E-04	1.06E-03	1.62E-04	1.29E-03
2-3	408.7	1.12E-03	1.22E-03	4.12E-04	1.10E-03	8.30E-04	1.42E-03
2-4	501	4.27E-04	1.49E-03	4.95E-04	1.10E-03	8.25E-04	1.67E-03
2-5	1392	1.94E-03	3.35E-03	1.03E-03	1.09E-03	1.59E-04	4.79E-03
2-6	3428	8.88E-03	7.45E-03	1.59E-03	1.30E-03	1.40E-04	1.05E-02
2-7	10627.9	3.47E-02	1.62E-02	1.75E-03	1.46E-03	5.34E-04	2.78E-02
3-1	381.52	5.18E-04	2.06E-03	6.92E-04	1.20E-03	2.25E-04	1.19E-03
3-2	357.16	5.24E-04	1.67E-03	5.68E-04	1.19E-03	2.47E-04	1.27E-03
3-3	402.2	4.93E-04	1.95E-03	6.74E-04	1.25E-03	2.87E-04	1.34E-03
3-4	407.5	3.04E-04	1.70E-03	6.23E-04	1.16E-03	2.05E-04	1.43E-03
3-5	1168.3	3.96E-03	3.41E-03	1.12E-03	1.20E-03	8.96E-05	4.79E-03
3-6	2802.6	4.29E-03	2.84E-03	1.77E-03	1.28E-03	6.78E-04	1.30E-02
3-7	11045.7	5.09E-02	1.65E-02	1.88E-03	1.29E-03	5.88E-04	3.63E-02

TDS - reported in mg/L

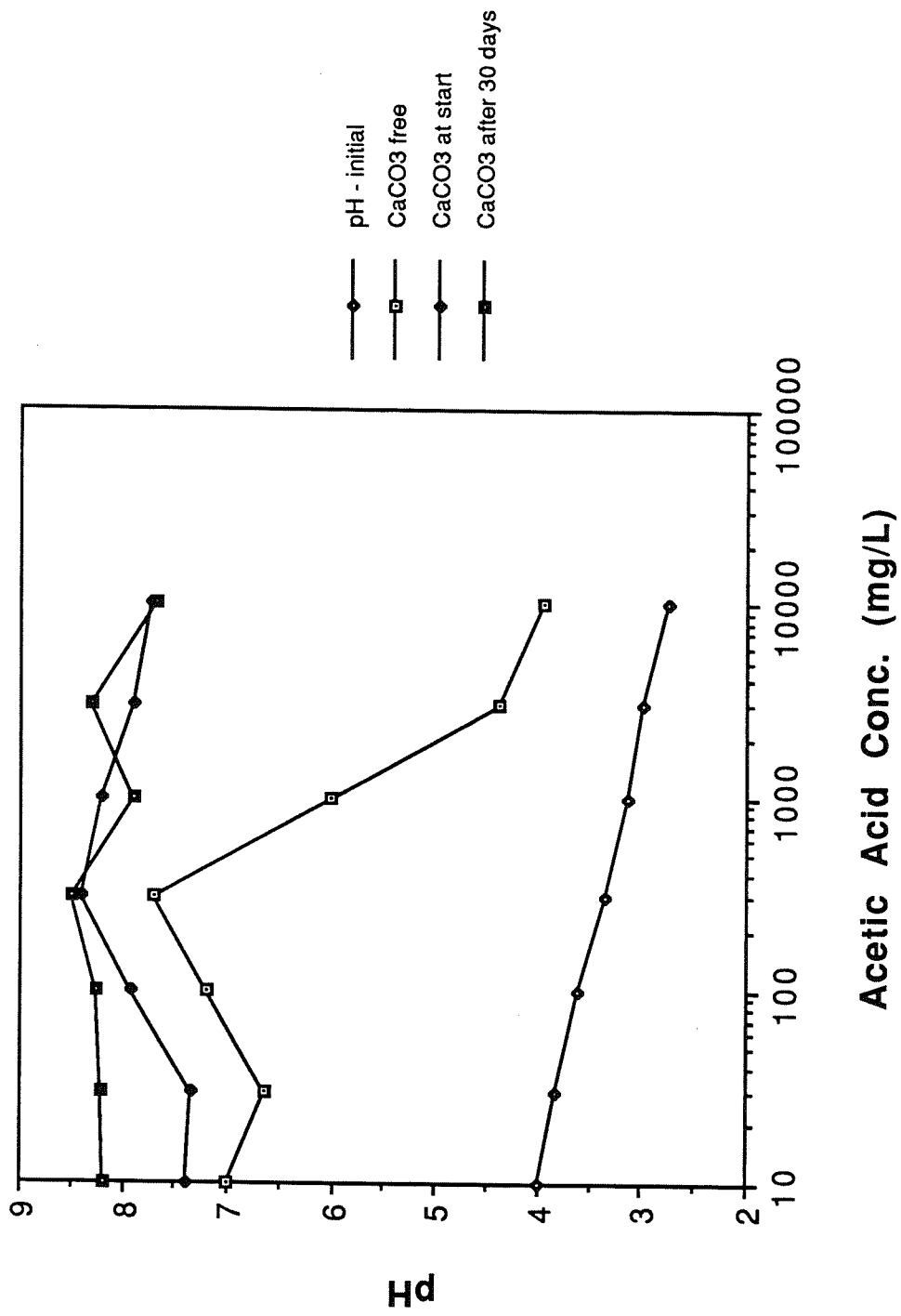
Table 6. Activity Data from SOLMIN88.

Sample Numbers	ACTIVITIES						
	H	OH	H4SiO4	Ba	Fe	Mn	Pb
1-1	1.00E-07	1.02E-07	2.08E-04	5.66E-07	2.81E-06	n.d.	n.d.
1-2	2.24E-07	4.57E-08	2.27E-04	7.77E-06	1.38E-06	n.d.	n.d.
1-3	6.31E-08	1.62E-07	2.22E-04	n.d.	n.d.	n.d.	n.d.
1-4	2.00E-08	5.13E-07	2.31E-04	n.d.	2.71E-06	n.d.	3.07E-08
1-5	1.00E-07	1.02E-07	4.48E-04	n.d.	6.89E-05	1.49E-04	3.74E-08
1-6	4.17E-05	2.45E-10	9.71E-04	1.28E-06	n.d.	8.13E-05	4.02E-07
1-7	1.10E-04	9.33E-11	1.25E-03	3.43E-06	3.88E-06	1.50E-04	6.21E-07
2-1	3.98E-08	2.57E-07	1.53E-04	n.d.	1.23E-06	n.d.	n.d.
2-2	4.68E-08	2.19E-07	1.60E-04	4.97E-07	1.27E-06	n.d.	n.d.
2-3	1.20E-08	8.51E-07	1.62E-04	1.44E-06	2.44E-06	n.d.	n.d.
2-4	3.89E-09	2.63E-06	1.56E-04	n.d.	1.13E-06	n.d.	n.d.
2-5	6.17E-09	1.66E-06	2.07E-04	3.48E-07	4.17E-05	2.34E-04	1.96E-09
2-6	1.29E-08	7.94E-07	3.04E-04	7.47E-07	3.26E-05	3.69E-04	n.d.
2-7	1.91E-08	5.35E-07	2.44E-04	1.04E-04	1.62E-06	8.94E-05	n.d.
3-1	6.61E-09	1.55E-06	1.63E-04	9.30E-07	n.d.	n.d.	n.d.
3-2	6.31E-09	1.62E-06	1.65E-04	9.54E-07	n.d.	n.d.	n.d.
3-3	5.62E-09	1.82E-06	1.82E-04	n.d.	2.29E-06	n.d.	n.d.
3-4	3.24E-09	3.16E-06	1.93E-04	4.67E-07	1.12E-06	7.12E-05	n.d.
3-5	1.26E-08	8.13E-07	3.46E-04	n.d.	1.53E-04	2.56E-04	5.97E-09
3-6	5.01E-09	2.04E-06	3.70E-04	8.07E-07	1.10E-04	2.58E-04	7.02E-10
3-7	2.14E-08	4.77E-07	3.51E-04	2.12E-06	7.13E-06	1.05E-04	2.34E-09

Table 6. Activity Data from SOLMIN88.

Sample Numbers	ACTIVITIES		LOG		ACTIVITY		RATIOS	
	Zn	Sr	Ca/H2	Mg/H2	Na/H	K/H		
1-1	n.d.	8.87E-07	1.07E+01	1.02E+01	4.00E+00	3.17E+00		
1-2	n.d.	8.68E-07	1.00E+01	9.54E+00	3.69E+00	2.90E+00		
1-3	n.d.		1.11E+01	1.06E+01	4.16E+00	3.31E+00		
1-4	n.d.		1.22E+01	1.17E+01	4.65E+00	3.80E+00		
1-5	n.d.	2.06E-06	1.12E+01	1.08E+01	4.06E+00	3.22E+00		
1-6	n.d.	4.66E-06	6.25E+00	5.87E+00	1.49E+00	9.74E-01		
1-7	n.d.	8.36E-06	5.66E+00	5.21E+00	1.11E+00	7.45E-01		
2-1	n.d.	1.53E-06	1.20E+01	1.15E+01	4.46E+00	3.63E+00		
2-2	n.d.	1.57E-06	1.17E+01	1.12E+01	4.36E+00	3.54E+00		
2-3	n.d.	1.52E-06	1.29E+01	1.25E+01	4.96E+00	4.84E+00		
2-4	n.d.	1.45E-06	1.40E+01	1.35E+01	5.45E+00	5.33E+00		
2-5	n.d.	3.35E-06	1.40E+01	1.34E+01	5.25E+00	4.41E+00		
2-6	n.d.	5.71E-06	1.37E+01	1.30E+01	5.00E+00	4.04E+00		
2-7	n.d.	7.79E-06	1.37E+01	1.27E+01	4.89E+00	4.45E+00		
3-1	n.d.	2.94E-06	1.37E+01	1.32E+01	5.26E+00	4.53E+00		
3-2	n.d.	2.26E-06	1.36E+01	1.32E+01	5.28E+00	4.59E+00		
3-3	n.d.	2.20E-06	1.38E+01	1.33E+01	5.35E+00	4.71E+00		
3-4	n.d.	2.21E-06	1.42E+01	1.38E+01	5.55E+00	4.80E+00		
3-5	n.d.	3.48E-06	1.33E+01	1.29E+01	4.98E+00	3.85E+00		
3-6	n.d.	7.08E-06	1.41E+01	1.39E+01	5.41E+00	5.13E+00		
3-7	2.24E-09	8.11E-06	1.36E+01	1.26E+01	4.78E+00	4.44E+00		

Figure 1.



decreased systematically down to 2.74 as the concentration of the acid increases. The final pH values for each set of reacted samples were significantly higher. Series 3, in which calcite was added to the system after 30 days, had the largest pH values, and maintained on average a pH of 8.14. The sample 2 series pH values were lower than the sample 3 series. However, the pH values seemed to increase slightly with increasing initial acetic acid concentration, peak at 300 mg/L acetic acid, then slowly decline as concentration increased. The carbonate free series follows a similar pattern as the sample 2 series but with lower pH values. There is a significant drop in pH at acetic acid concentrations greater than 300 mg/L acetic acid. It appears that some mechanism hindered the progress of the reaction in those experiments.

### Alkalinity

Total alkalinity of the samples are below 250 mg/L and are approximately equal for all 21 samples up to 1000 mg/L acetic acid (Figure 2). At that concentration, alkalinity values in the samples that contained calcite in them (series 2 & 3) logarithmically increase with increasing initial acetic acid concentration. The alkalinity of the carbonate-free runs increases moderately with increasing acid concentration.

Calculated acetate alkalinity concentrations (Figure 3) follow a similar trend as total alkalinity. Figures 1 and 2 show how total alkalinity and acetate alkalinity vary with increasing

Figure 2.

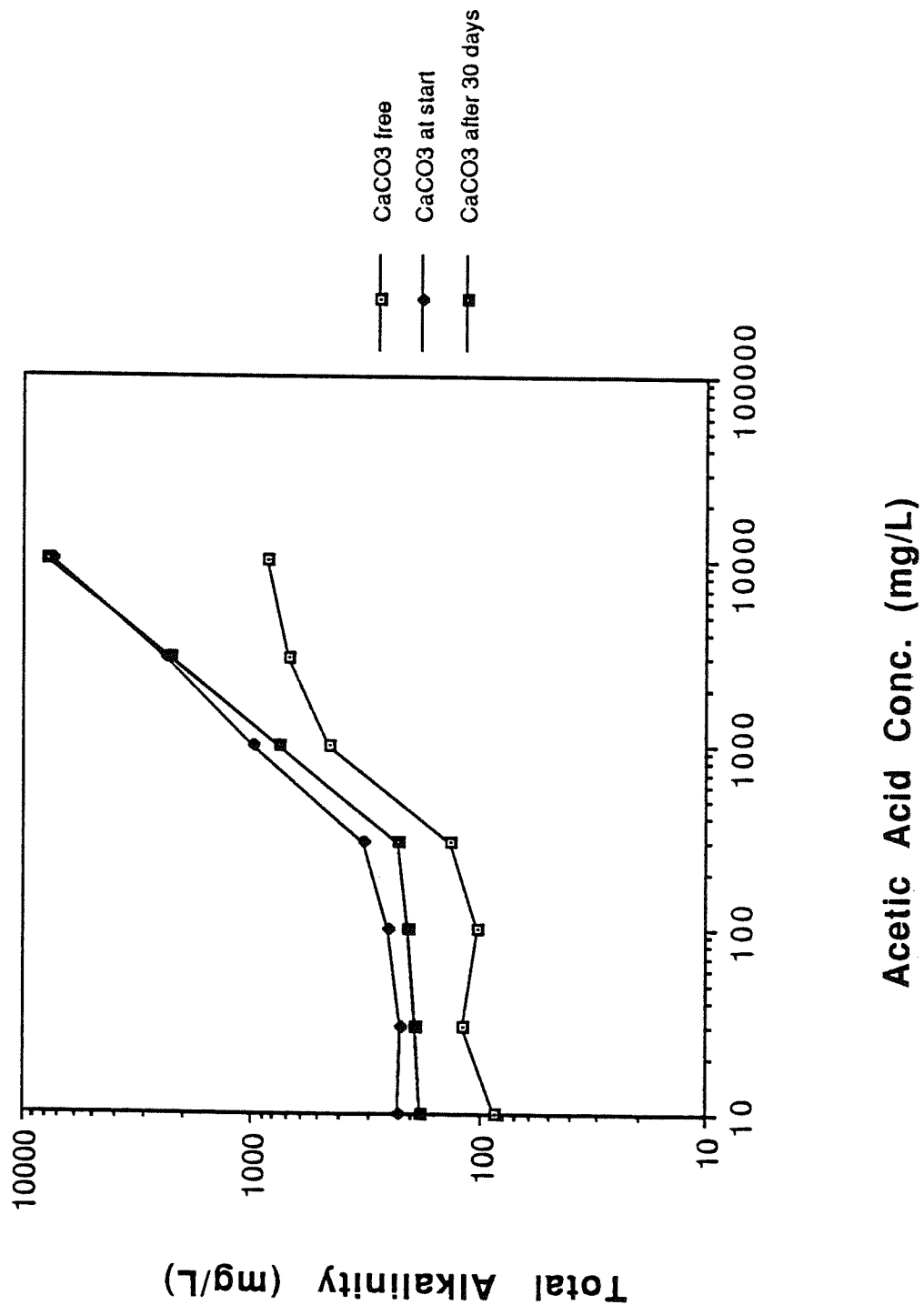
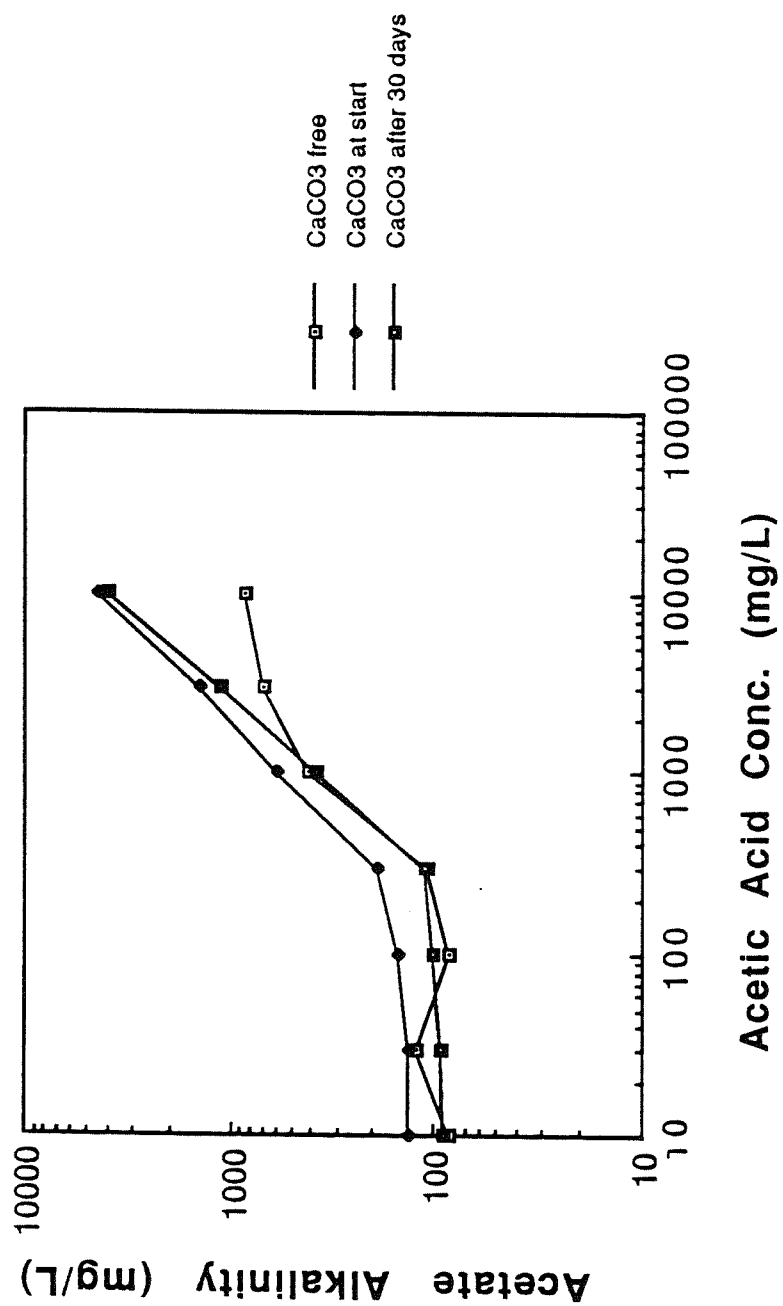


Figure 3.



acetic acid concentration. It is evident from these graphs that the presence of calcite greatly increases the alkalinity of the system, but only at acetic acid concentrations greater than 1000 mg/L does any significant increase occur with increasing acid concentration.

#### Na and K

Figures 4 and 5 show variation of Na and K with increasing initial acetic acid concentration. For both Na and K, the concentrations in each sample series are moderately low up to 1000 mg/L of initial acetic acid. At 1000 mg/L initial acetic acid, concentration levels for both Na and K increase systematically by approximately 20 mg/L with increasing acid concentration.

Figure 4 illustrates the behavior of Na in solution. Na values, at every acid concentration in the carbonate free series, are relatively lower than in series 2 and 3 at comparable initial acid concentrations. Na in the sample 3 series is highest at a given acetic acid concentration at low acid concentrations. Above 1000 mg/L, however, the sample 2 series has the highest concentrations of Na. In Figure 5, dissolved K values in the carbonate free series are shown to be lower than the dissolved K in the other two sets of solutions for low acid concentrations. However, at 1000 mg/L, K in the carbonate free samples is present in larger amounts than the other two sample series. Conversely, K in the sample 2 and sample 3 series is present in higher



Figure 4.

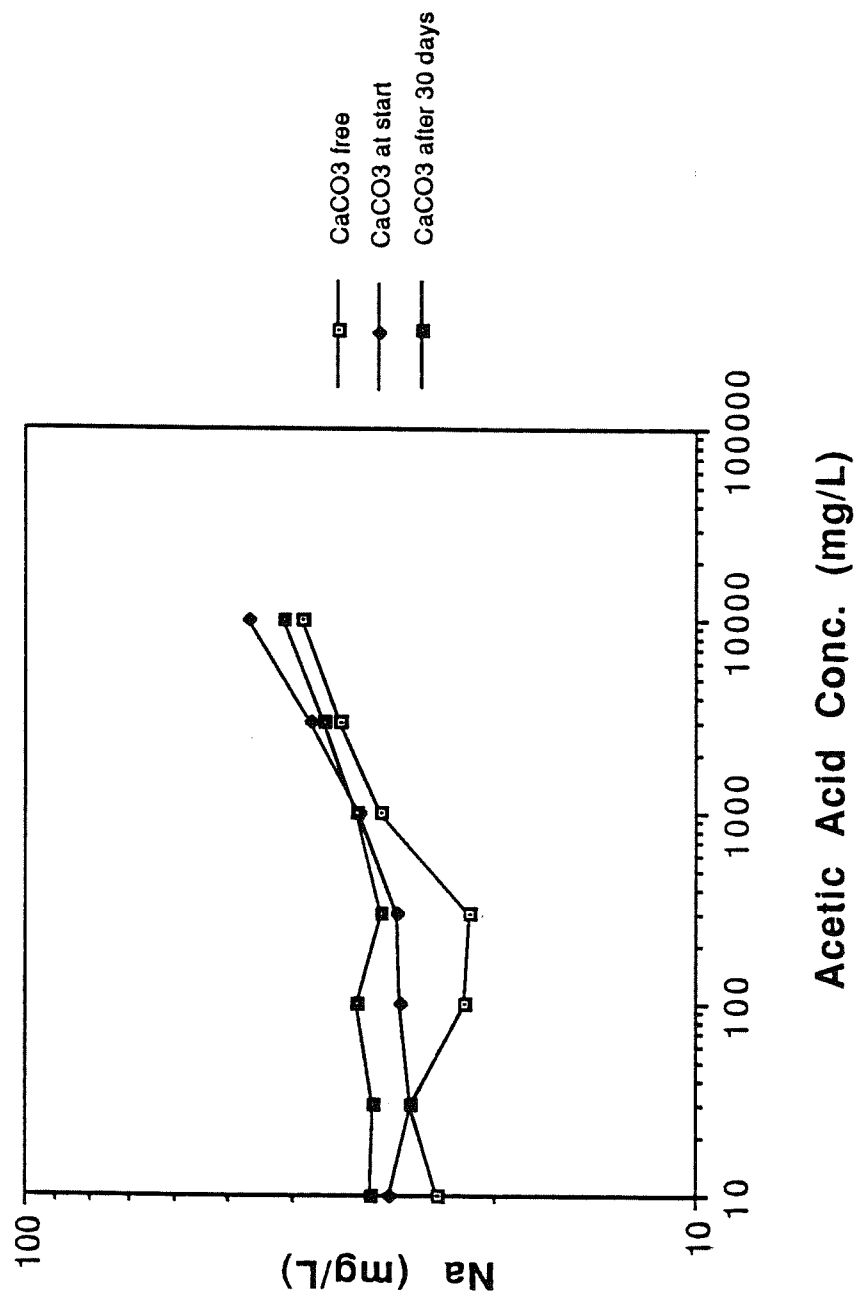
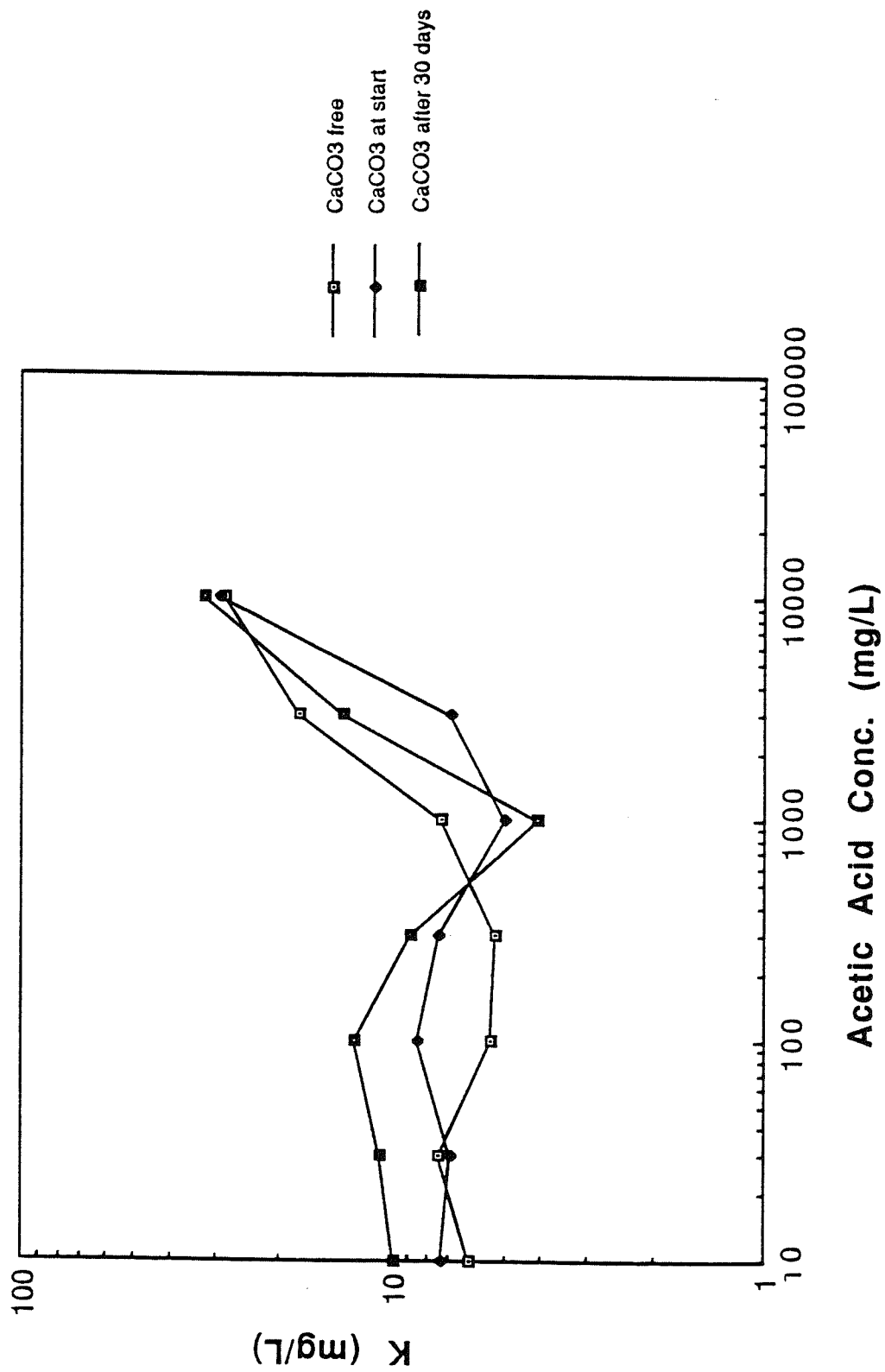


Figure 5.



concentrations over the sample 1 series at comparable acid concentrations, but at 1000 mg/L acid and beyond, the concentration of K detected in the series 2 and 3 samples is slightly lower than detected in the carbonate free samples at the same given concentration.

#### Mg and Ca

Figures 6 and 7 show the variation of Mg and Ca with initial acetic acid concentration. Mg and Ca have similar trends of low concentration at low levels of acetic acid for all three sample series and significant increases in concentrations above 1000 mg/L acetic acid. Mg and Ca concentrations are consistently lowest in the carbonate free samples and are consistently highest in the sample 3 series. However, Ca in the sample 2 and sample 3 series at 10,000 mg/L acetic acid is present in amounts well over 1000 mg/L. Figure 6 shows that while Mg begins to increase at 1000 mg/L acetic acid like Ca, the Mg concentrations are always lower than Ca at a given acetic acid concentration, and its maximum concentration in solution is less than 200 mg/L.

#### Sr and Ba

Sr and Ba add more information about the system (Figures 8 and 9). Both the concentrations of Sr and Ba increase logarithmically with increasing acetic acid concentration. The concentration of Sr in the carbonate-free series is lower than the concentration of Sr in both the sample 2 and sample 3 series

Figure 6.

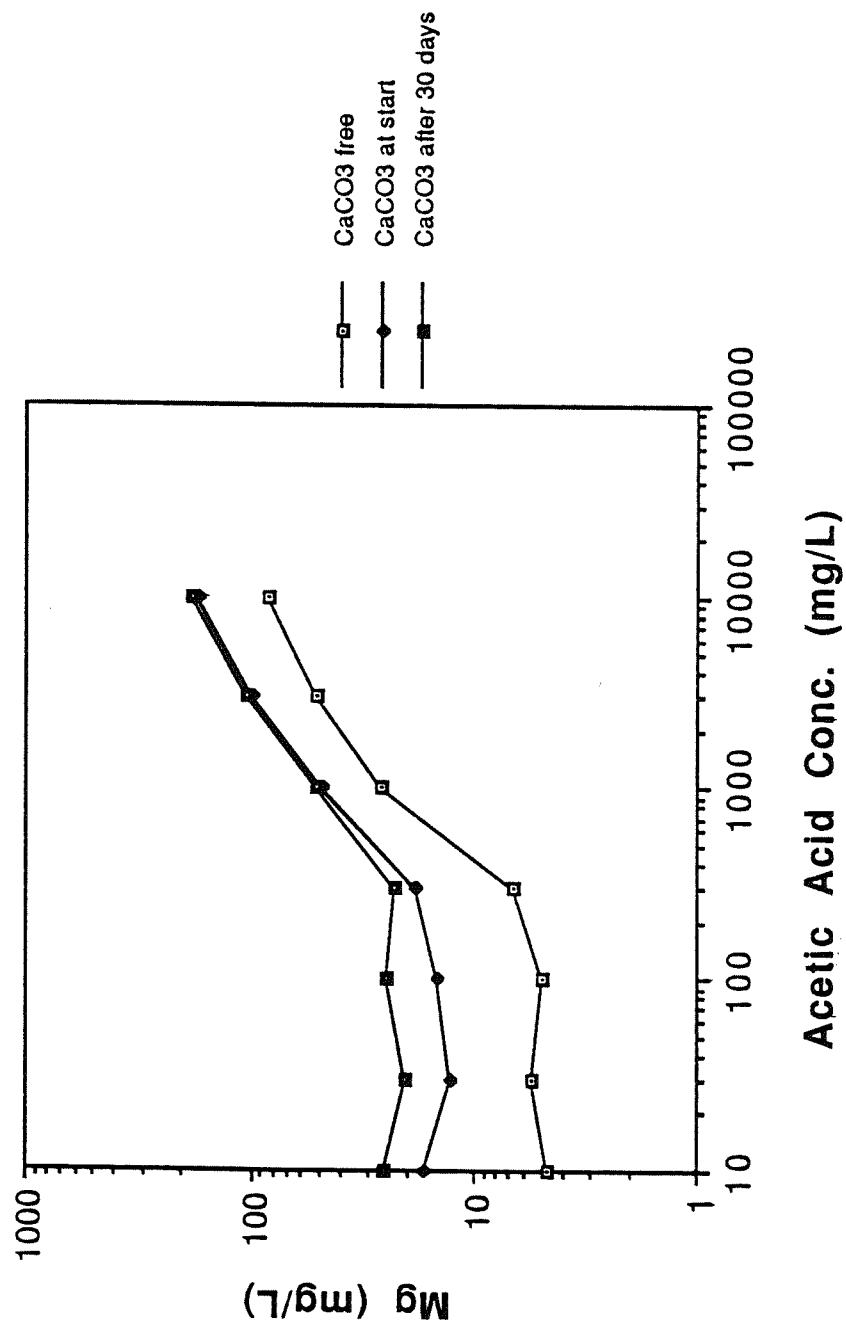


Figure 7.

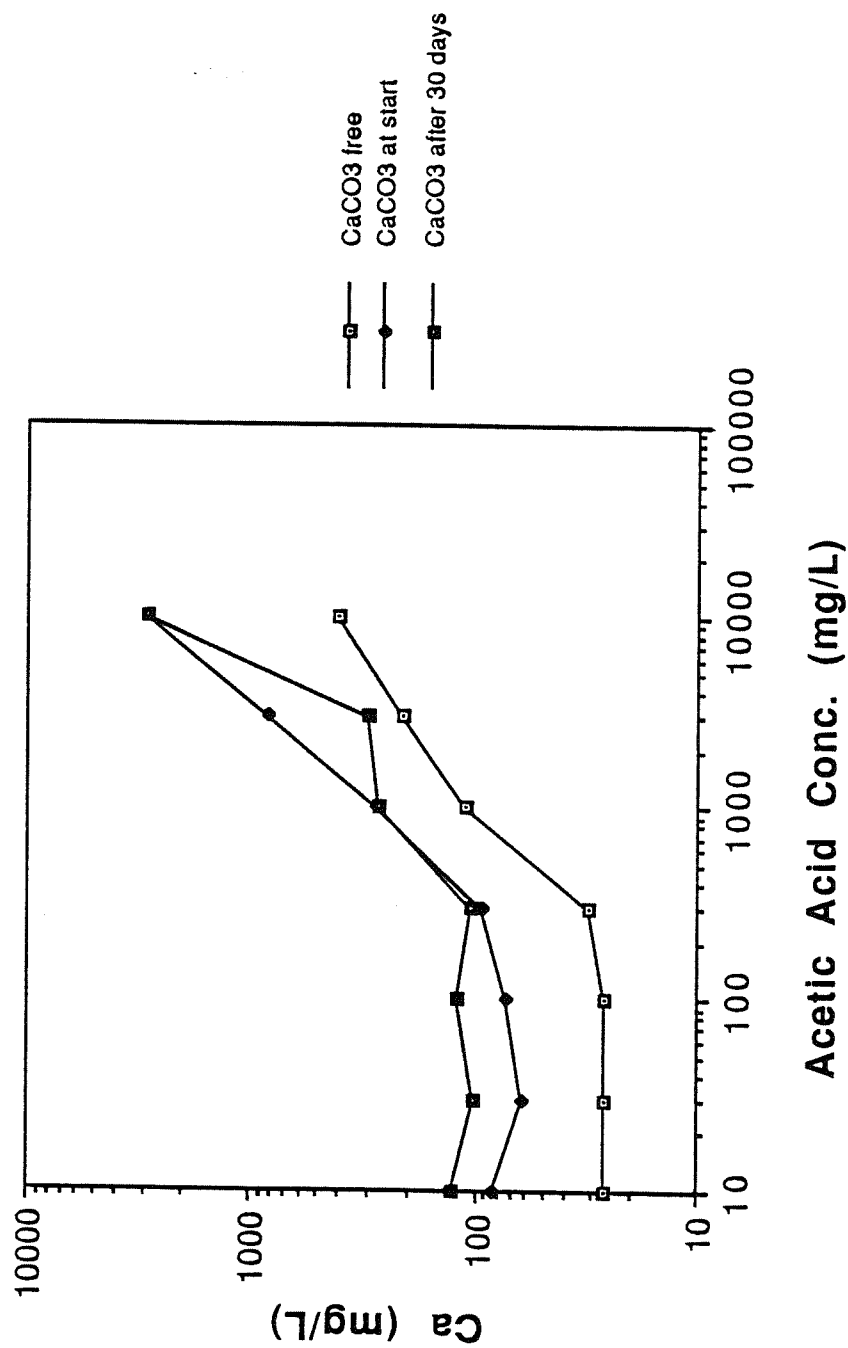


Figure 8.

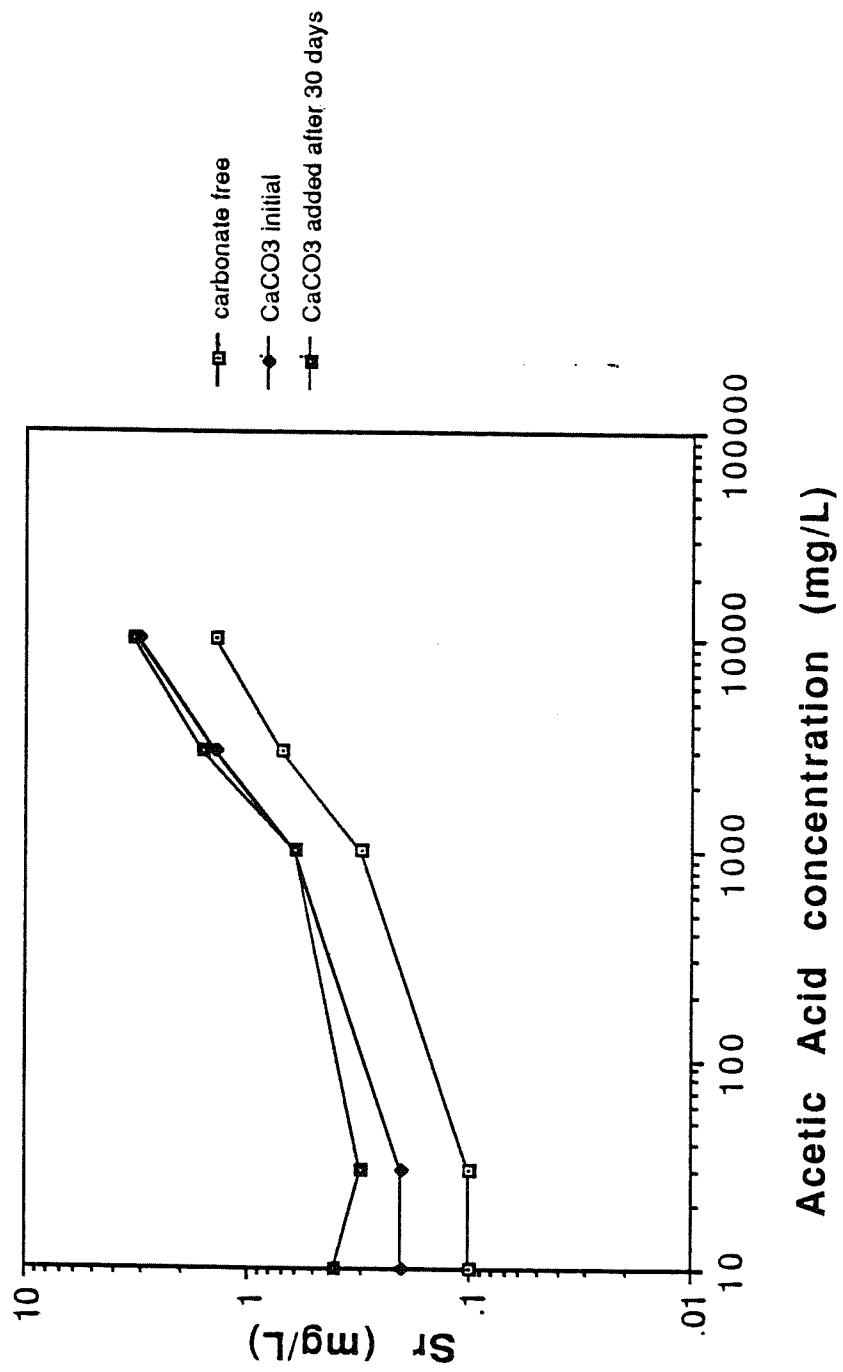
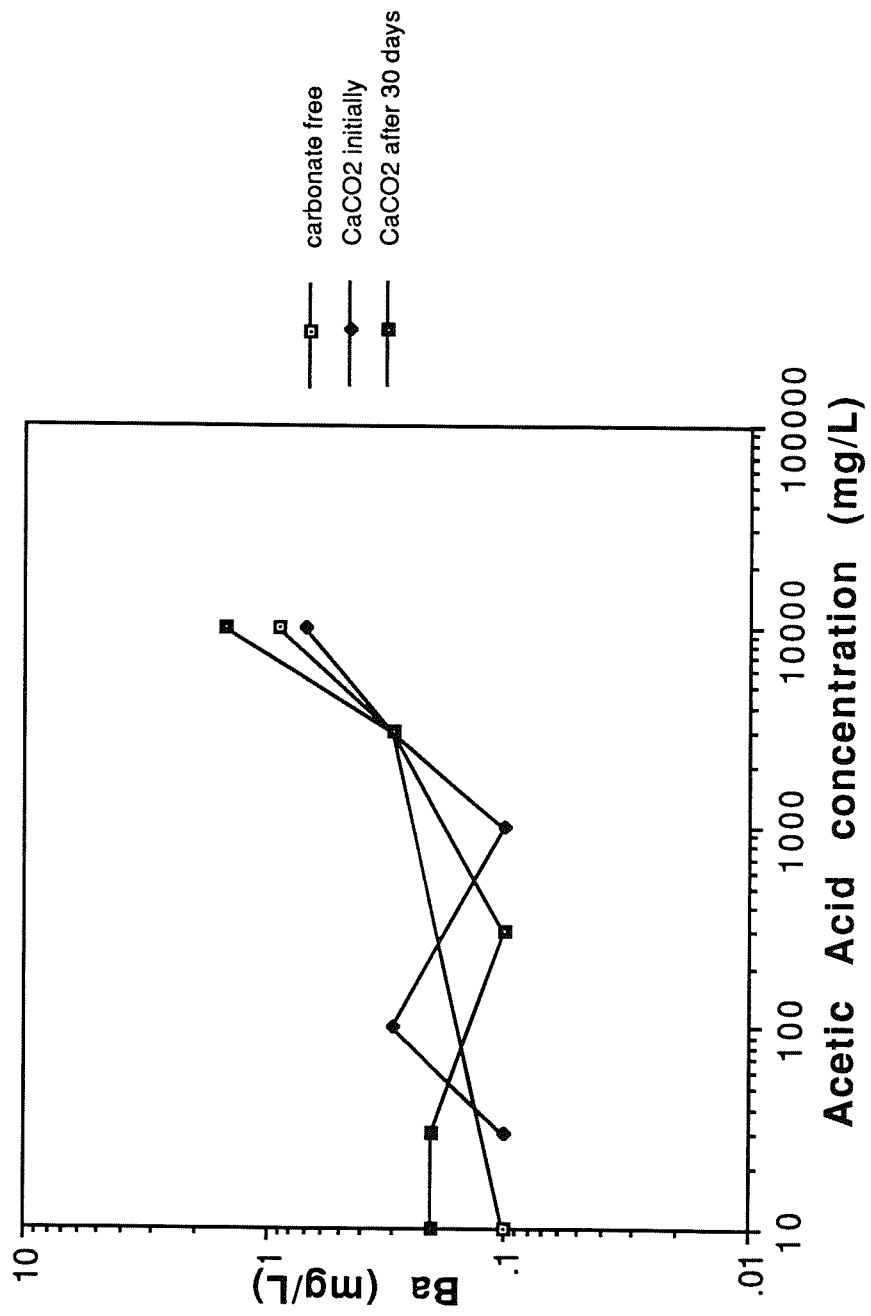


Figure 9.



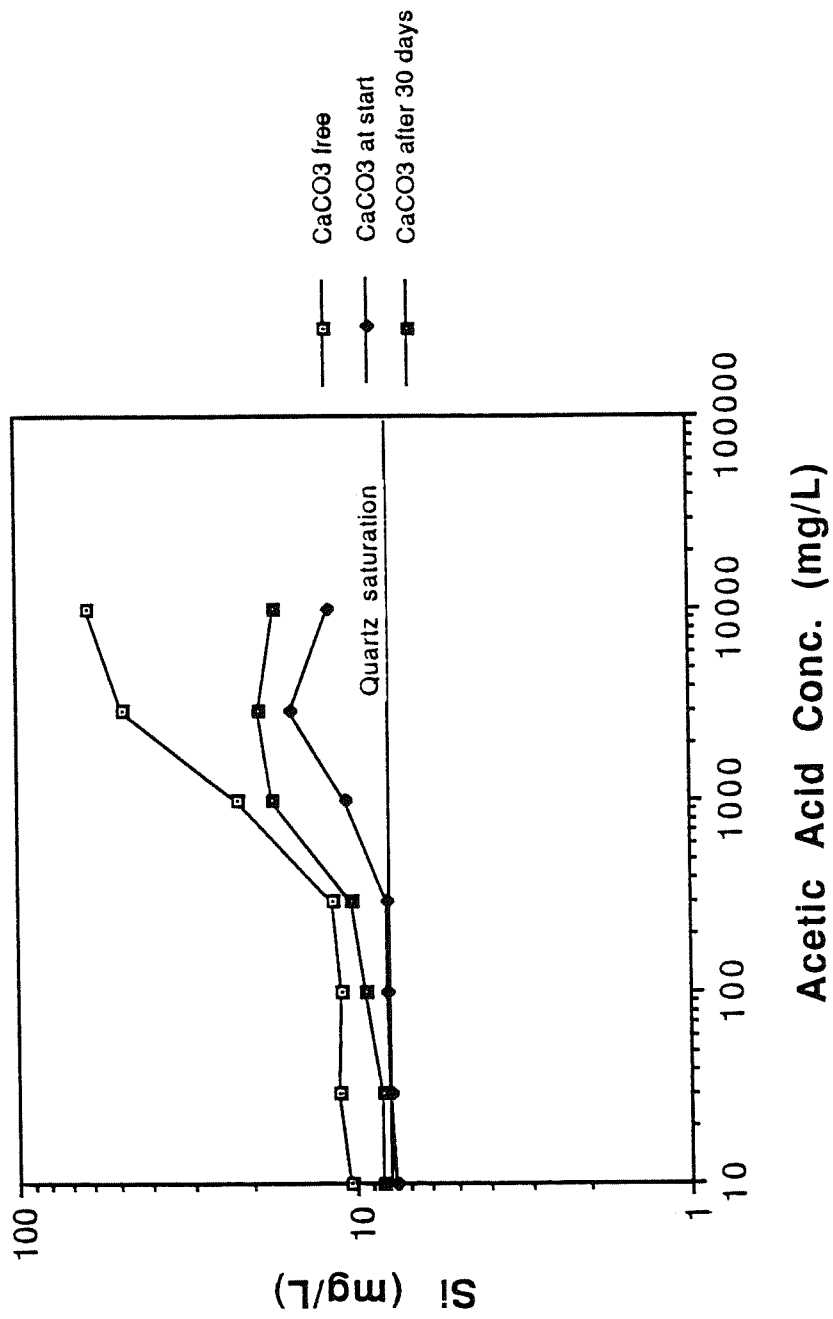
at all initial acetic acid concentrations. The highest detected concentration of Sr in the carbonate-free samples was 1.4 mg/L. The Sr levels in series 2 and 3 approximately are approximately twice the series 1 values, with the levels in sample series 3 slightly higher than in sample series 2. While Ba follows the same basic pattern as Sr, with concentration increasing with increasing acid concentration, the data are less precise. All three sample series have approximately the same concentration (0.30 mg/L) for each concentration of acetic acid. At 10,000 mg/L acid, though, series 3 contains the greatest amount of Ba found in solution, 1.5 mg/L.

### Silica

The behavior of dissolved Si is both similar to and different from the previous cations in the response of Si to the various concentrations of acetic acid (Figure 10). At the low values of acetic acid Si maintains low concentrations in solution, like the other cations. At 1000 mg/L, Si increases with increasing acid concentration. In contrast to the behavior of Na, K, Mg, and Ca, which are consistently higher in the carbonate bearing systems, the highest dissolved silica values are found in the carbonate free series. The increase in concentration for carbonate-free series is significantly more than the increase for series 2 and 3. Si in the sample 2 and sample 3 series increases by only a small amount with increasing initial acid concentration, then its concentration decreases at



Figure 10.



10,000 mg/L acid. At every acid concentration, the sample 2 series has the lowest Si values. The Si values for the sample 3 series are higher than series 2, but they are still significantly lower than the Si concentration in the carbonate free samples.

#### Fe and Mn

Figures 11 and 12 show the results for the metals Fe and Mn, respectively. Fe and Mn are especially interesting because the samples from the highlighted region contained growing bacteria. The presence of the bacteria caused the bottle, solution, and possibly the sediment to be discolored yellow. More important, it appears that the presence of the bacteria correlates with the elevated concentrations of Fe and Mn within the acetic acid concentrations of 500 mg/L - 5000 mg/L. The increase of Fe in the acetic acid range of 500 mg/L - 5000 mg/L was greatest for the sample series 3 at every acid concentration, but at 1000 mg/L acid the sample 1 series increased more than series 2. At 3000 mg/L the series 2 maintained an increase in Fe concentration while series 1 contained no bacteria and Fe was below the detection limit. At 10,000 mg/L acid Fe is greatest in series 3 at 1.3 mg/L Fe, and at all other acid concentrations, Fe is below the detection limit.

Mn also showed maximum concentrations within the range where bacteria lived. The carbonate free series was the least affected group of samples in the increase of Mn concentration. At 1000 mg/L acid, Mn in the sample 3 series is increased the most, but

Figure 11.

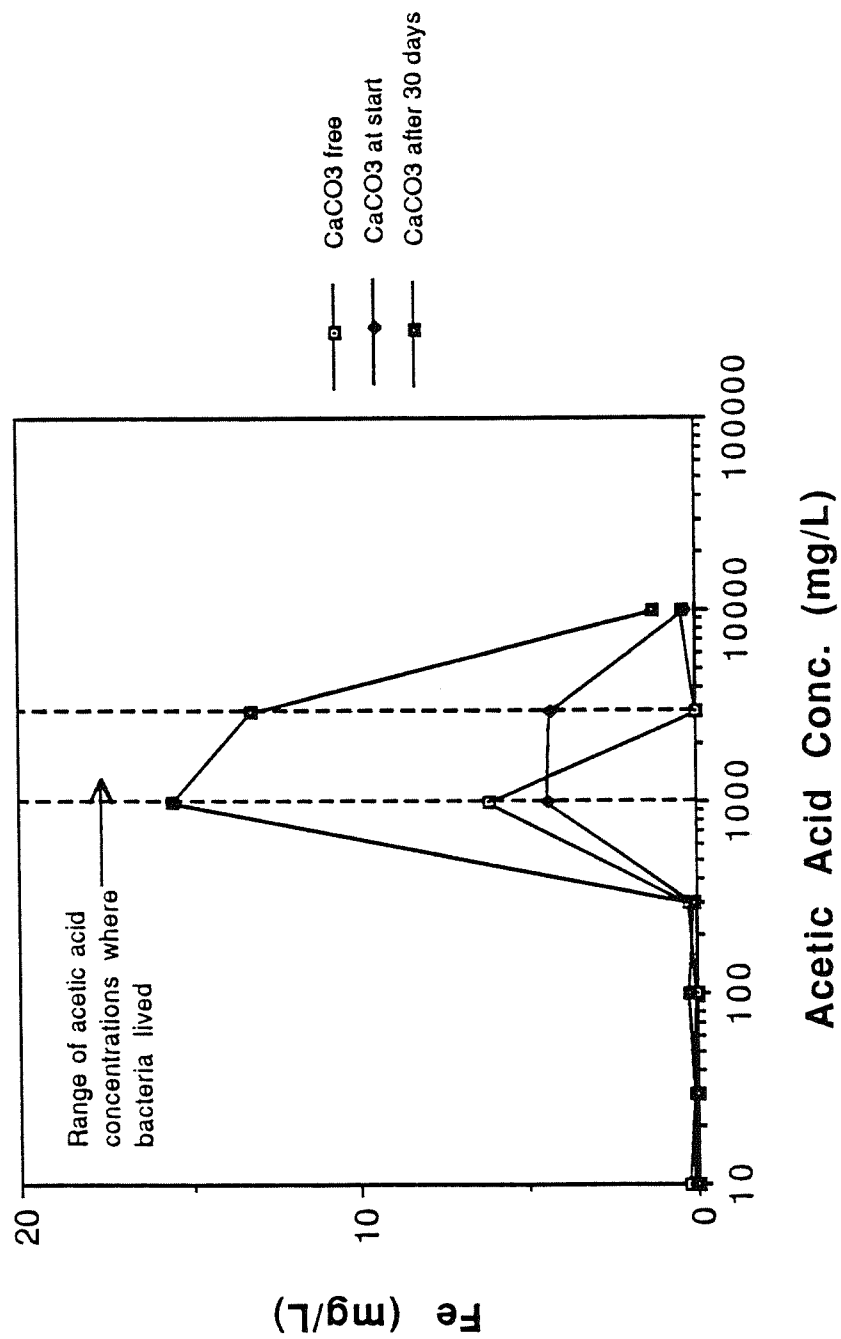
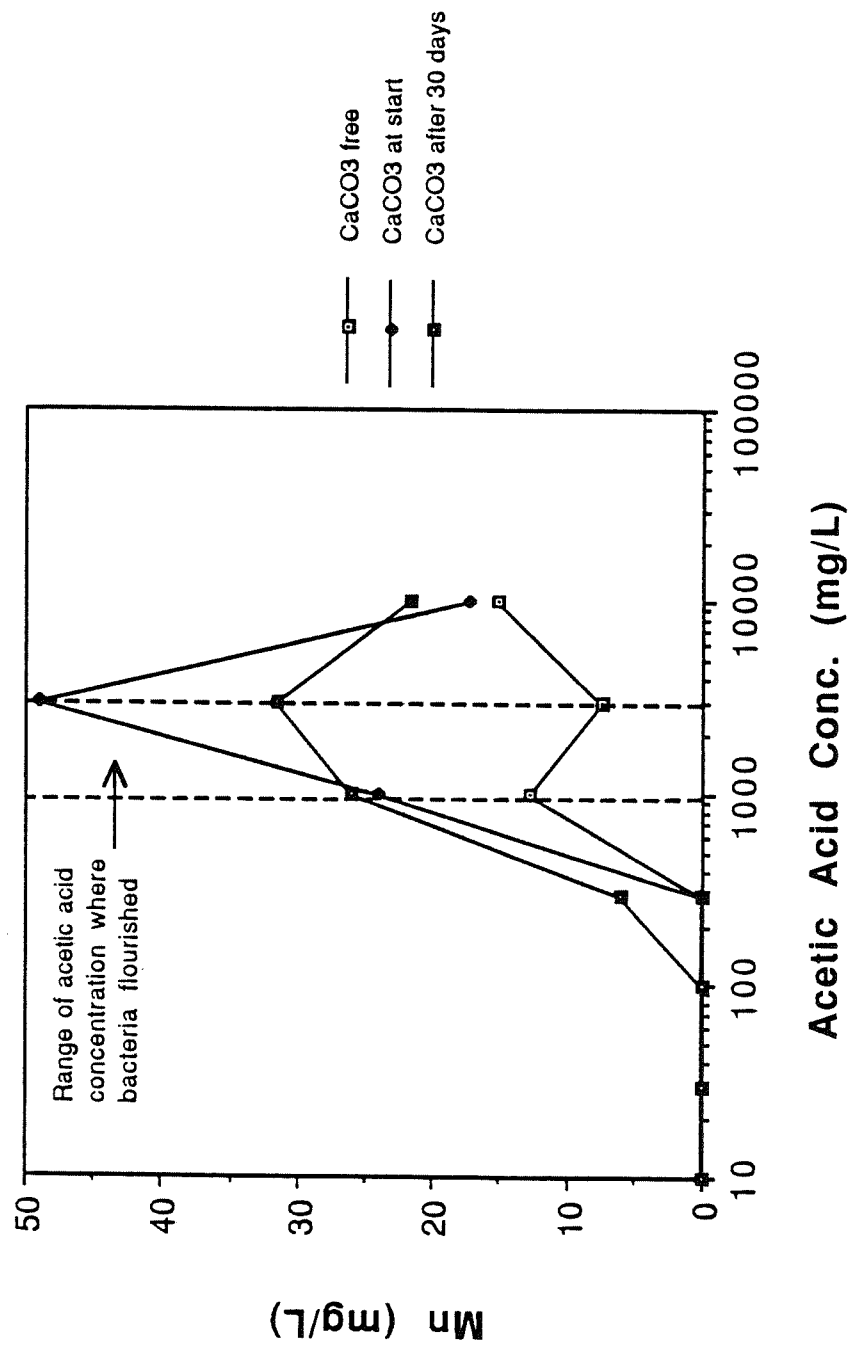


Figure 12.



at 3000 mg/L acid Mn in series 2 dramatically increases beyond levels in series 1 and series 3. Like Fe, Mn is not present in any appreciable amount at low acid concentrations. However, at 10,000 mg/L acid, Mn increases to approximately 20 mg/L for all three sample series.

#### Pb and Zn

It is difficult to comment on the role of Pb in the system (Figure 13). At many acid concentrations Pb is not present in measurable concentrations while at others it only appears in trace amounts varying between 0.1 and 0.4 mg/L Pb. Zn was not detected in the system except in an insignificant amount (0.06 mg/L) at 10,000 mg/L acid in the sample 3 series.

#### Al

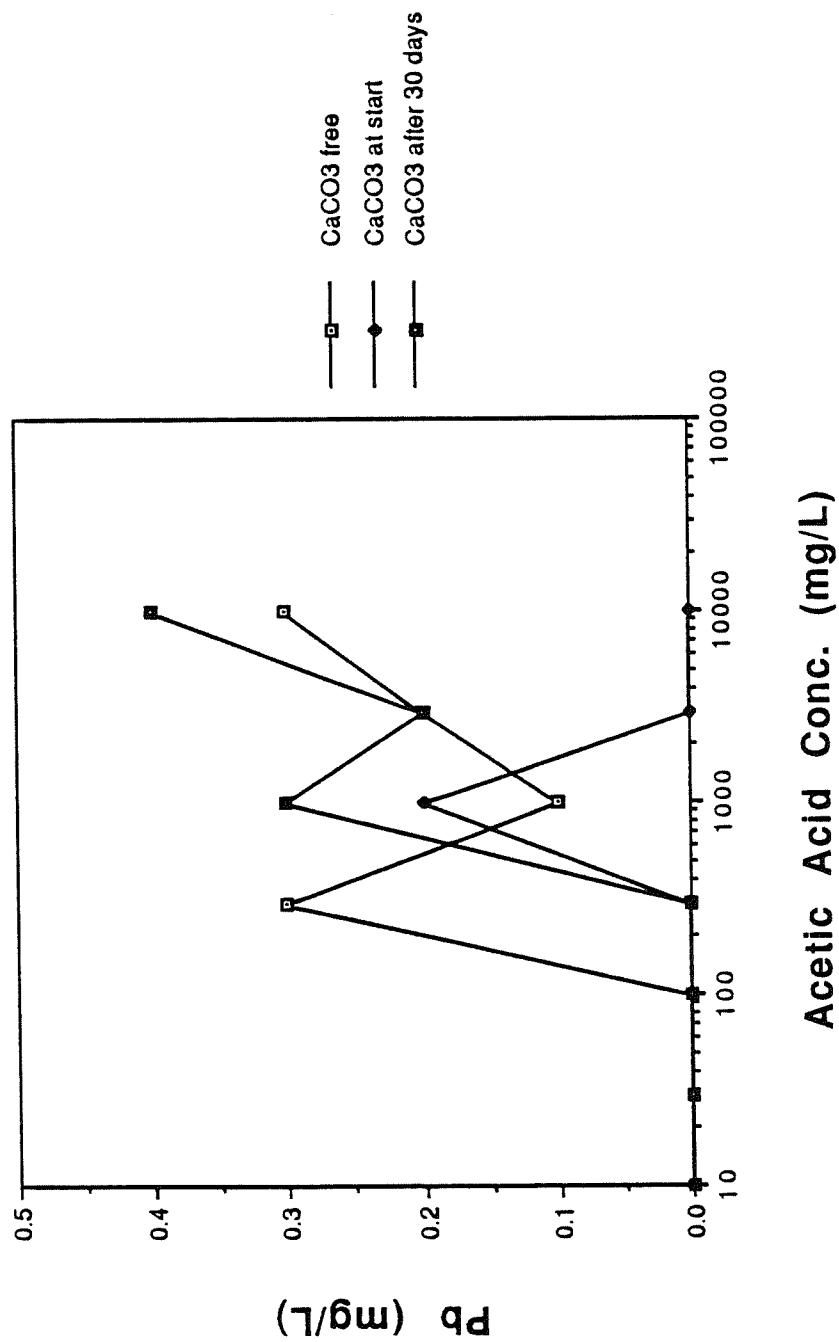
Al was below the detection limit ( $<0.01$  mg/L) for all samples and could not be analyzed as part of the system.

#### Activity Plots

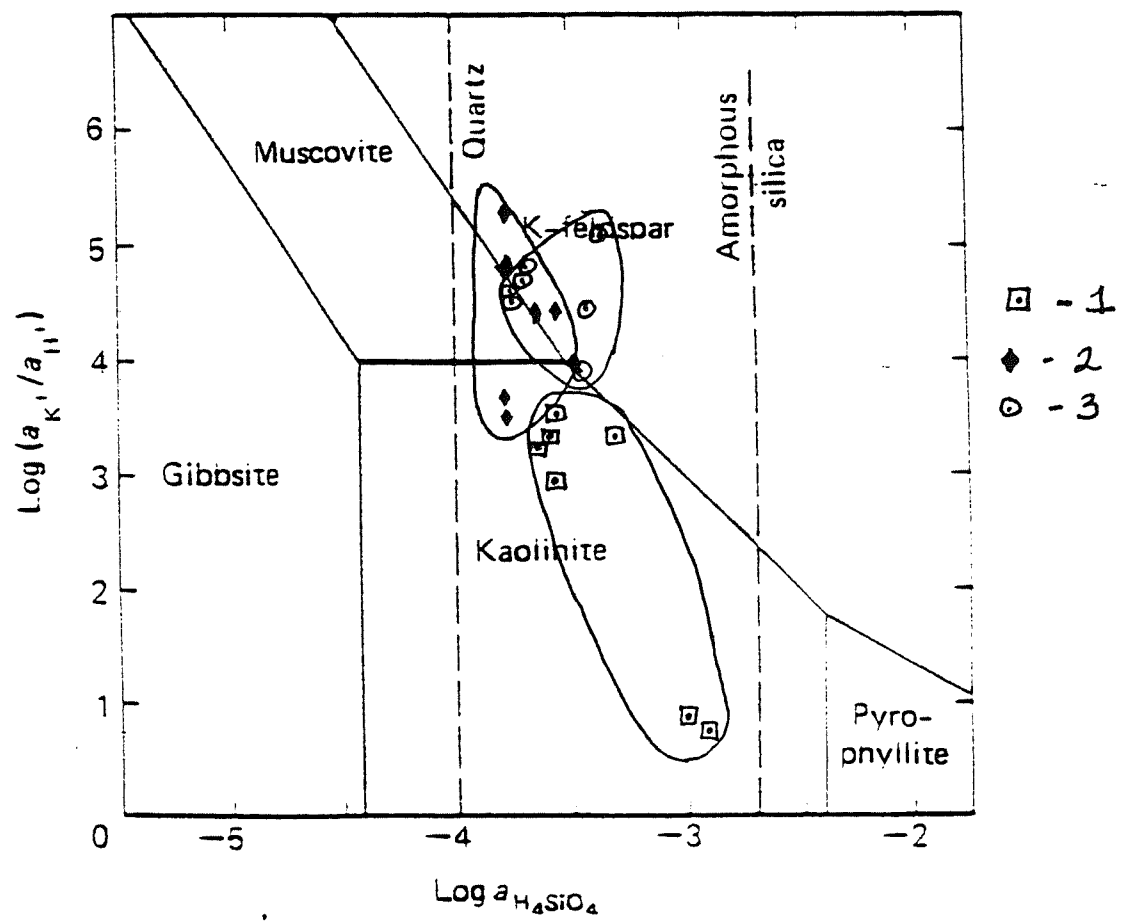
An estimate of the approach toward chemical equilibrium of a fluid with respect to one or more mineral phase can be made by plotting solute activities on conventional activity-activity stability diagrams (see Drever, 1988, for an extended discussion of how these diagrams are constructed).

Figures 14,15, and 16, show the calculated values of  $\log[a(K^+/H^+)]$ ,  $\log[a(Na^+/H^+)]$ , and  $\log[a(Ca^{2+}/H^+)]$  versus

Figure 13.



**T = 25°C**



**Figure 14.**

$T = 25^{\circ}\text{C}$

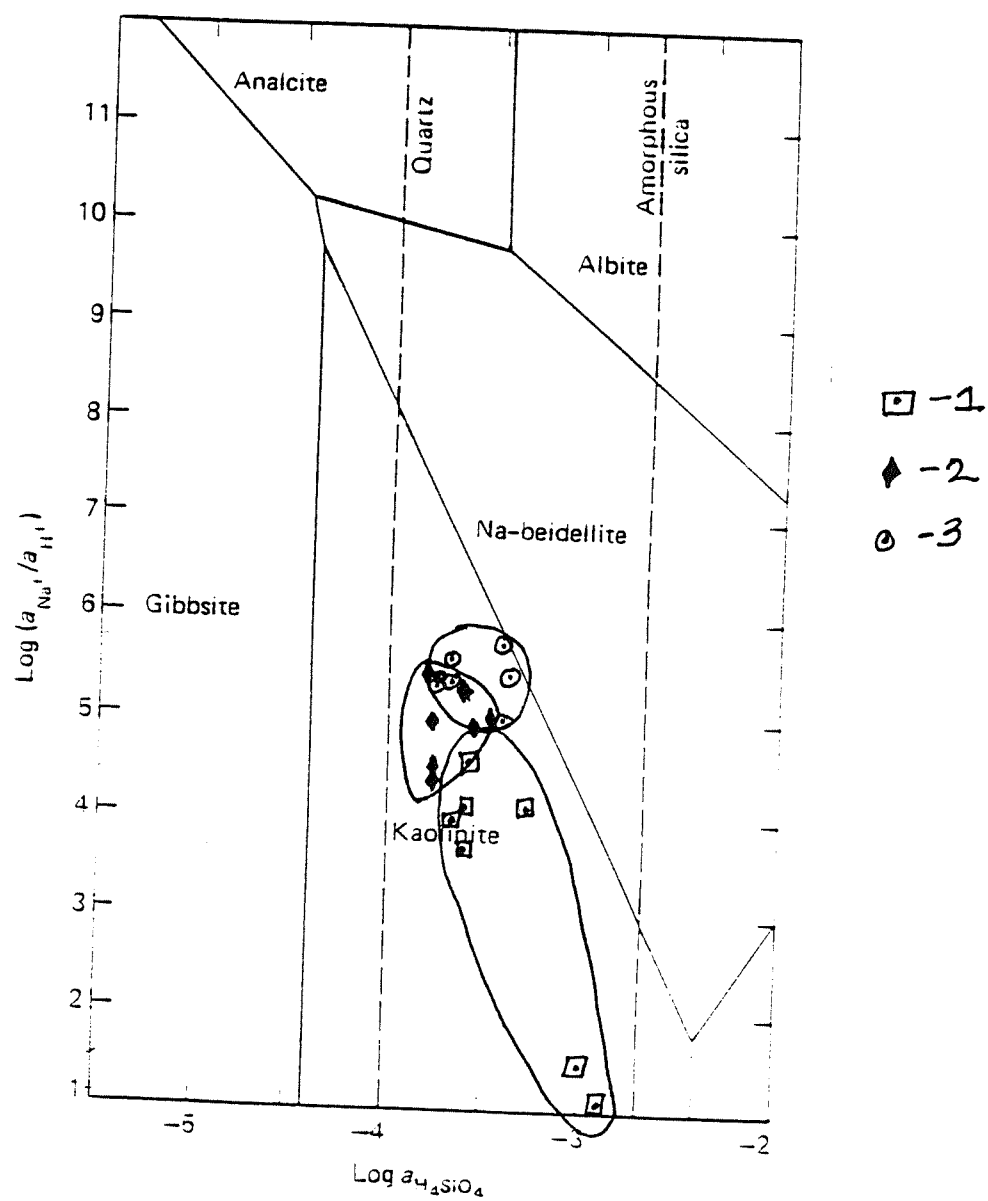
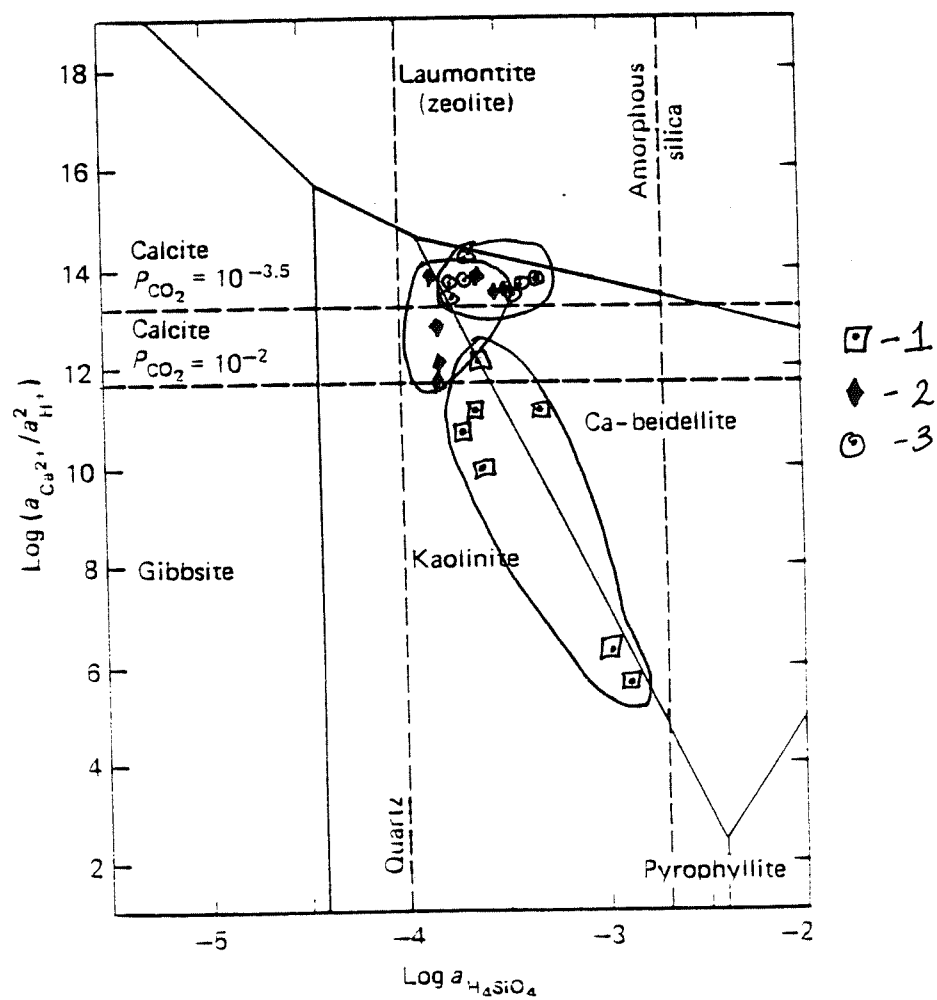


Figure 15.



$T = 25^{\circ}\text{C}$



**Figure 16.**

$\log(H_{4SiO_4})$  for the acetic acid solutions with respect to predicted values for fluids in equilibrium with common sedimentary mineral phases at 25°C and 1 bar (Drever, 1988).

All fluids are supersaturated with respect to quartz. The carbonate-free series plot in compositional fields suggesting equilibrium with respect to kaolinite and Ca-beidellite. The carbonate-bearing fluids plot in fields suggesting approximate equilibrium with respect to muscovite, K-feldspar, Ca-beidellite  $\pm$  kaolinite.

A different perspective of possible controls on fluid compositions is shown in Figures 17 and 18. Figure 17 shows the stability fields of the solutions with respect to calcite and dolomite. Equilibrium between calcite and dolomite was calculated following the same guidelines as for the phase diagrams (Drever, 1988). All of the fluids regardless of sediment composition lie on the equilibrium line between calcite and dolomite. Figure 18 shows the stability fields of the solutions with respect to K-feldspar and albite. All of the fluids, regardless of sediment composition, lie on the equilibrium line between K-feldspar and albite.

Figure 17.

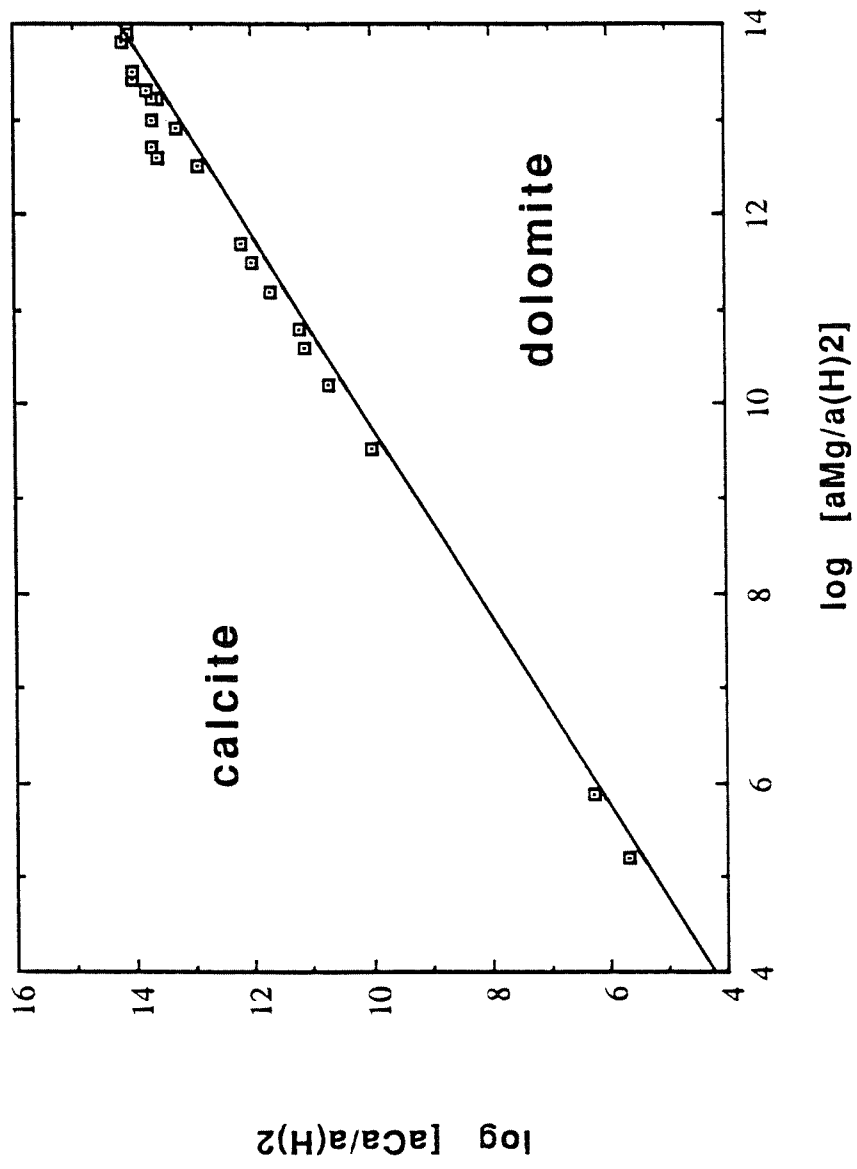
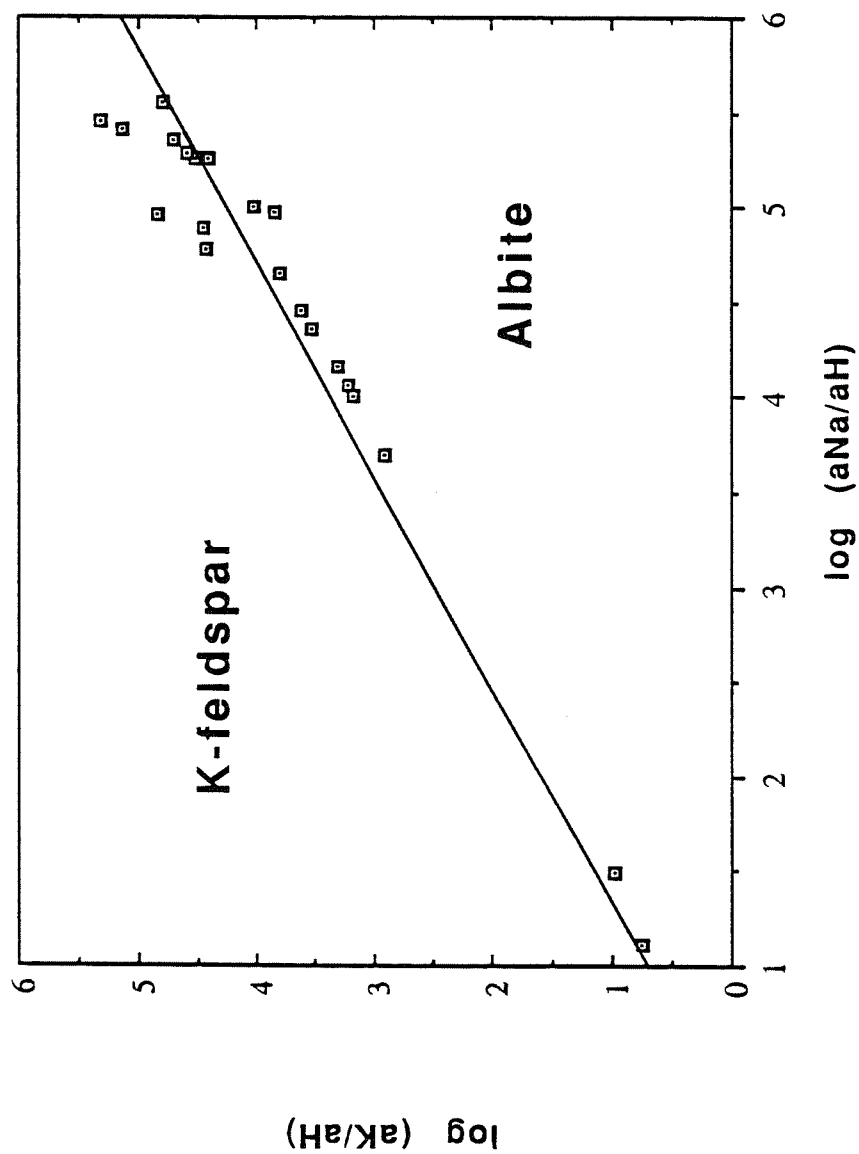


Figure 18.



## **DISCUSSION**

### **Effect of Variable Acid Concentration**

In each series of solutions, the solute concentrations remained relatively low and nearly constant until the concentrations of acetic acid exceeded 1000 mg/L. At acid concentrations of 1000 mg/L and above, dissolution of minerals and release of solutes appeared to increase for all ions except the metals. The metals were unaffected by increasing acid concentration because they were involved in redox reactions rather than acid/base reactions. Therefore, at low temperatures (25°C) and high concentrations of acetic acid it is reasonable to conclude that solute concentration is enhanced by the presence of acetic acid.

While Manning et al. (1994) argue that there is no reliable laboratory evidence for increased mineral solubility in the presence of organic acids, Surdam et al. (1984) showed that organic acids present in brines may enhance dissolution of alumino-silicates by complexing Al. However, those and other studies were conducted at 100°C and 345 bars, and the results from those studies cannot be directly compared to the present study.

Bennett et al. (1988) set up similar experiments to those of Manning et al. and Surdam et al. but at 25°C and 1 bar. Their conclusions suggest that organic acids do indeed have an influence upon mineral solubility and they do play an important

role in the earth's surface weathering. The latter conclusions are consistent with the findings of these experiments; therefore, the assumption that acetic acid influences solubility is accepted.

Dissolved aluminum in these experiments was below the detection limit in all samples. Although it is thought that Al is typically complexed by organic anions (Surdam et al., 1989), this is not always true. Surdam et al. (1984) suggest that the solubility of Al decreases when solutions are at approximately neutral pH and when calcite is in the system. One or both of these conditions exist in all of the samples tested. While this may not be the explanation for the absence of detectable Al in solution, it does not preclude the possibility of Al complexing by organic acids under other conditions.

#### Solubility of Silicate Minerals - Effect of Calcite

These results suggest that acetic acid in large concentrations promotes the release of cations in solution at 25°C and 1 bar, the role of added calcite in the system can be evaluated. The samples that contained calcite in the system had approximately neutral to slightly basic values of pH in each of the experiments. This appears to be a direct result of having CO<sub>2</sub> in the system.

In contrast to the samples containing calcite, pHs of the carbonate free series were neutral to acidic. At low concentrations of acid (up to 300 mg/L acetic acid) the pH of the

solutions was approximately neutral. However, at larger acid concentrations, the pH of each sample was acidic. The predicted pH of an acetic acid-acetate buffer is 4.75 (Dickerson et al., 1984), and the pH values for samples 1-5, 1-6, and 1-4 were 6.01, 4.38, and 3.96, respectively. This observation of pH supports the theory that organic acid ions provide an internal pH buffer (Barth et al., 1990).

The presence of calcite in some of the samples greatly increased the concentrations of several solutes at high levels of acetic acid. As one might predict, Ca is present in high concentrations in the calcite bearing series relative to the carbonate free systems. For the 10,000 mg/L acetic acid level in sample series 2 and 3, the Ca concentrations were 7.5 times higher than in the carbonate free series. Similarly, total alkalinity values were approximately an order of magnitude higher in the samples with calcite versus the carbonate free samples. In the samples that had calcite in the system, Mg, Sr, and acetate alkalinity were also higher than were detected in the carbonate free series. All of the Mg and Sr ions must have come from the standard river sediment because the reagent grade calcite contained no significant amount of Mg or Sr. One theory to explain this phenomenon is that as the amount of initial acid increased, the concentration of acetate anions in solution increased. Therefore, more cations went into solution to maintain the charge balance in the system. In addition, cation exchange on the clay surfaces may have occurred between Ca and Mg

in all of the samples. However, more ions were available for exchange in the samples with added calcite and increased levels of Mg in solution (Drever, 1988).

Silica shows an inverse trend in concentration with increasing acetic acid concentration among the samples with calcite and the samples without calcite. The samples with calcite show five times less silica in solution than the samples without calcite. One might expect to see decreased concentrations of silica in the solutions without calcite, but instead, the carbonate free experiments show levels of silica in solution which are much greater than those solutions containing calcite. This point is of significance with regard to increased solubility of silicates due to organic acid. Quartz is a relatively insoluble mineral, and only at high pH values are total dissolved silica values large (Drever 1988). Similar increased solubilities of quartz in the presence of organic acid have been observed by other investigators (Bennett and Siegel, 1987; Bennett, 1988; Williams et al., 1985).

Two accepted models for enhanced dissolution of silicate minerals by organic acid involve the complexing of free cations, especially Al (Boyle et al., 1974), or the increase of proton availability from the organic acids (Tan 1980). These models depend upon the dissolution of alumino-silicates at low pH and the diagenetic conditions exclusively and do not explain the rapid weathering of quartz which is seen in shallow groundwater environments (Bennett and Siegel, 1987). Bennett et al. (1988)



explain that silica solubility in oxalic acid concentrations of approximately 1000 mg/L, under conditions of 25 °C and 1 bar and neutral pH may be enhanced by the direct interaction of organic acid anions with frame work Si-O-Si bonds. The organic anion interacts with the surface of quartz and will consequently donate a partial charge to the framework silica atoms. The extra charge increases the density of electrons at the Si-OH bond. At that site, the bond becomes stronger and thus weakens the framework of the Si-O-Si bond. The Si-OH bonds are more susceptible to hydrolysis, therefore increasing the rate of dissolution.

The reactions in the present experiments may have followed the processes described above with regard to silica solubility because the conditions of this experiment approximately paralleled the conditions of the experiments described by both Bennett et al. (1988) and Tan (1980). The conditions of this experiment were 25°C and 1 bar, however as the concentration of acid increased the pH of the solution was buffered and unlike the Bennett et al. model, pH remained relatively low. In the samples with low pH, the solubility of Si increased. While Si-OH bonds may form in some experiments as a result of added charge at Si-O-Si bond sites and in turn release more Si into solution, it cannot be denied that acidic solutions affect the solubility of silica in systems without calcite.

The remaining cations in solution were not significantly affected by the addition of calcite into the system, although they did increase in concentration with increasing acetic acid

strength. K and Na do not exchange with Ca on cation sites as readily or as easily as does Mg (Drever, 1988). Therefore, the added opportunity for cation exchange by the addition of calcite is not greatly enhanced for the monovalent cations. Ba is not found in significant amounts in either silicates or carbonates (Drever, 1988), and appears unaffected by the addition of calcite.

Fe and Mn were present in trace amounts in all but a few of the experiments. However in the experiments containing acetic acid at concentrations between 1000-3000 mg/L, the solutions were enriched with Fe and Mn. In these ranges of acid concentration, bacteria apparently thrived. It is known that some respirative bacteria consume acetate (Chapelle, 1993). Two common genus involved in such processes are *Bifidobacterium* and *Clostridium*. *Bifidobacterium* consume and produce acetate in fermentation and may, in fact, produce acetic acid as an end product. During their fermentation of acetate, *Clostridium* typically reduce Fe using special proteins, called ferredoxins, that act as electron carriers. A byproduct of the fermentation is hydrogen; thus it is not surprising that some gas was observed in these experiments. Mn is another metal that can be reduced with Fe (Drever, 1988). The same conditions that reduce Fe should also reduce Mn. It is seen that at the same acid concentrations where Fe was reduced, Mn was reduced also.

Unlike Fe and Mn, Pb does not participate in redox reactions; therefore the marginal increase at high levels of acid

concentration must be explained in a different manner. It has been suggested that trace amounts of Pb in acetic acid solutions may act as an indicator of feldspar dissolution (Manning et al., 1991). This idea is not a satisfactory explanation because the increase in Pb concentration is not systematic with increasing acid concentration. The values for Pb appear to have no correspondence with acetic acid concentration, nor do they appear to be affected by the addition of calcite into the system. It is thought that the amount of Pb detected in the experiment solutions is dependent upon the amount of Pb in the particular feldspars used in experimentation.

#### Mineral Stability Diagrams

Figures 14, 15, and 16 show that all of the fluids tested are oversaturated with respect to quartz, and most of the fluids are clustered at or near the equilibrium boundaries between kaolinite and K-feldspar or smectite. This observation suggests that in a relatively short amount of time and under moderate PT conditions, the waters have approached mineral equilibrium. Upon closer examination of mineral stability, Figures 17 and 18 show that the fluids analyzed are in apparent or metastable equilibrium with both calcite and dolomite. Similarly, the fluids are also in equilibrium with K-feldspar and albite. These observations are important in light of the original mineral composition of the sediment; although K-feldspar was reported as only a minor mineral phase, and calcite was added to only some of

the fluid systems, all of the systems eventually approached equilibrium with K-feldspar and calcite.

#### Comparison with Natural Waters

It is interesting to compare these experimental fluids to natural waters. In a report on the composition of shallow groundwaters from Natchitoches, Louisiana, the ionic activity ratios that were plotted on mineral activity-activity stability diagrams fell on the equilibrium lines between kaolinite and K-feldspar and smectite (Su, 1993). The same stability relations which were observed in the natural water system were also observed in the experimental fluid systems of this report. This fact seems to suggest that the experimental fluids mimic the behavior that is seen in natural water systems and that these results can be applied to at least some studies of natural water systems containing acetate.

**CONCLUSIONS**

Many workers have theorized that organic acid anions may affect the solubility of silicate minerals, particularly feldspar, at varying temperatures and pressures. Instead of using pure feldspar, however, the experiments in this study were conducted using multiphase sediments; therefore hydrolysis produced by organic acid anions were studied instead of solubility.

The results of these experiments show that at 25°C and 1 bar and over a relatively short time frame, acetic acid has no appreciable affect on mineral hydrolysis at acid concentrations below 1000 mg/L. However, at acid concentrations of 1000 mg/L or greater, the degree of mineral hydrolysis increased significantly as shown by the relatively high concentrations of Na, K, Mg, Ca, Sr, Ba, and Si detected in the solutions. In contrast, Fe, Mn, and Pb did not exhibit a strong correlation with acetic acid concentration. Zn and Al were analyzed but were below the detection limit in all of the fluids.

While many workers promote the idea that Al is complexed by organic acid anions, this theory is not borne out by these experiments. The observed absence of Al above the 0.01 mg/L limit of detection in solution is consistent with data presented by Surdam et al. (1984), who show that at approximately neutral pH and in the presence of calcite Al solubility decreases in organic acids. The solutions of the experiments in this study, like Surdam et al. (1984), were at nearly neutral pH, and many of

the solutions contained calcite.

The addition of calcite to some experiments seemed to have an effect on the ionic concentrations of acetate, Mg, Ca, Sr, and Si. The addition of calcite to some of the experiments added more cations to the solutions. To maintain charge balance as more Ca was released into solution, acetate anions also went into solution; this explains the increased concentration of acetate in the calcite-containing experiments. In addition, divalent cations are usually involved in cation exchange on clays; therefore, as the Ca concentration increased, more opportunity for exchange existed, and the concentration of Mg and Sr in solution increased as a result. These ions also contributed to the charge balance of the solutions.

Silica was influenced, inversely, by the addition of calcite because in the solutions with calcite, silica concentrations were lower than the silica concentrations in the experiments without calcite. The increased concentrations of silica in the carbonate free experiments are attributed to the presence of high concentrations of acetic acid. The large acid concentration caused the concentration of acetate to increase. To maintain charge balance, the concentration of silica increased in the carbonate free solutions because additional Ca was not present due to the addition of calcite. The silica concentration in the experiments with calcite were low because other cations were in solution to account for the charge balance.

The experimental fluids behaved similarly to natural waters.

After 60 days of reaction, the experiments at 25°C and 1 bar approached equilibrium with kaolinite, K-feldspar, and smectite. Also, all of the fluids plotted on the equilibrium boundary between calcite and dolomite. This trend in mineral equilibrium is typical of many solutions in contact with siliciclastic sediments. This is an important observation because it indicates that many solutions in contact with siliciclastic sediments regardless of organic components approach the same mineral equilibrium status.

It appears from this study that more investigation is necessary to determine whether organic components truly make any significant contributions in mineral solubility/hydrolysis when encountered in fluids. The results of this study support only some previous observations regarding organic anions in solution: (1) acetic acid buffers the pH of the solution, (2) moderate increases in silica solubility is observed in the presence of organic acids, and (3) bacteria that feed on organic material increase trace metal concentrations. Beyond these observations, it appears that these mineral/fluid reactions proceed in the same general manner as mineral/fluid reactions involving fluids without acetic acid. The mineral assemblages remain stable across the acid concentration range, and the cations, excluding Si to a minor extent, behave similarly in solutions without organic material.

**REFERENCES**

- Barth, T., A.E. Borgund, and M. Riis, 1990, Organic acids in reservoir waters-relationship with inorganic ion composition and interactions with oil and rock: *Organic Geochemistry*, v. 16, p. 489-496.
- Bennett, P.C., 1991, Quartz dissolution in organic-rich aqueous systems: *Geochimica et Cosmochimica Acta*, v. 55, p. 1781-1797.
- Bennett, P., M.E. Melcer, D.I. Siegel, and J.P. Hassett, 1988, The dissolution of quartz in dilute aqueous solutions of organic acids at 25°C: *Geochimica et Cosmochimica Acta*, v. 52, p. 1521-1530.
- Bennett, P. and D.I. Siegel, 1987, Increased solubility of quartz in water due to complexing by organic compounds: *Nature*, v. 326, p. 684-688.
- Boyle, F.R., G.K. Voigt, and B.L. Sawhney, 1974, Chemical weathering of biotite by organic acids: *Soil Science*, v. 117, p. 42-45.
- Brown, E., M.W. Skougstad, and M.J. Fishman, 1970, Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases: *Techniques of Water-Resources Investigations of the United States Geological Survey*, 160 p.
- Carothers, W.W., and Y.K. Kharaka, 1978, Aliphatic acid anions in oil-field waters-implications for origin of natural gas:



AAPG Bulletin, v. 62, p. 2441-2453.

Chapelle, F.H., 1993, Ground-water Microbiology and Geochemistry, first ed., John Wiley & Sons, Inc., 424 p.

Collins, A.G., 1975, Geochemistry of Oilfield Waters, Elsevier Scientific Publishing Co., 496 p.

Crossey, L.J., 1991, Thermal degradation of aqueous oxalate species: *Geochimica et Cosmochimica Acta*, v.55, p.1515-1527.

Dickerson, R.E., H.B. Gray, M.Y. Darensbourg, and D.J. Darensbourg, 1984, Chemical Principles, fourth ed., The Benjamin/Cummings Publishing Company, Inc., 930 p.

Drever, J.I., 1988, The Geochemistry of Natural Waters, second ed., Prentice Hall, Inc., 437 p.

Esch, L. and Hanor, J.S., 1993, Reaction of NaCl brines with siliciclastic sediments: an experimental study: *Geologic Society of America, Abstracts with Programs*, 1993 Annual Meeting, Boston, p. A322.

Hanor, J.S. and A.L. Workman, 1986, Distribution of dissolved volatile fatty acids in some Louisiana oil field brines: *Applied Geochemistry*, v. 1, p. 37-46.

Harrison, W.J. and G.D. Thyne, 1992, Predictions of diagenetic reactions in the presence of organic acids: *Geochimica et Cosmochimica Acta*, v. 56, p. 565-586.

Kharaka, Y.K., W.D. Gunter, P.K. Aggarwal, E.H. Perkins, and J.D. DeBraal, 1988, SOLMINEQ 88: A Computer Program for Geochemical Modeling of Water-Rock Interactions: USGS

Water-Resources Investigations Report 88-4227, 420 p.

- Kharaka, Y.K., L.M. Law, W.W. Carothers, and D.F. Goerlitz, 1986, Role of organic species dissolved in formation waters from sedimentary basin in mineral diagenesis, in Roles of organic matter in sediment diagenesis (ed. D. Gautier): SEPM Special Publication 38, p. 111-123.
- MacGowan, D.B. and R.C. Surdam, 1988, Difunctional carboxylic acid anions in oilfield waters: Organic Geochemistry, v. 12, p. 245-259.
- Manning, D.A.C., E.I.C. Rae, and K. Gestsdottir, 1994, Appraisal of the use of experimental and analogue studies in the assessment of the role of organic acid anions in diagenesis: Marine and Petroleum Geology, v. 11, p. 10-19.
- Reed, C.L. and A. Hajash, 1992, Dissolution of granitic sand by pH-buffered carboxylic acids: a flow-through experimental study at 100°C and 345 bars: AAPG Bulletin, v. 76, p. 1402-1415.
- Stumm, W. and J.J. Morgan, 1981, Aquatic Chemistry: An introduction emphasizing chemical equilibria in natural waters, John Wiley & Sons, Inc., 780 p.
- Su, S., 1993, Hydrogeochemistry of shallow groundwater in Natchitoches Parish, Louisiana, unpublished.
- Surdam, R.C., S.W. Boese, and L. Crossey, 1984, The chemistry of secondary porosity, in Clastic Diagenesis (eds. D.A. McDonald and R.C. Surdam): AAPG Memoir 37, p. 127-151.

Surdam, R.C., L.J. Crossey, E.S. Hagen, and H.P. Heasler, 1989,  
Organic-inorganic interactions and sandstone diagenesis:  
AAPG Bulletin, v. 73, p. 1-23.

Tan, K.H., 1980, The release of silicon, aluminum, and potassium  
during decomposition of soil minerals by humic acid: Soil  
Science, v. 129, p. 5-11.

Williams, L.A., G.A. Parks, and D.A. Crerar, 1985, Silica  
diagenesis. I. Solubility controls: Journal of Sedimentary  
Petrology, v. 55, p. 301-311.