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KAOLINITE DISSOLUTION AT 25°, 60°, AND 80°C

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ABSTRACT. The constant dissolution rates, k_r in moles Si per cm^2 per second, of kaolinite at 25°, 60°, and 80°C are dependent on solution pH and temperature. At all three temperatures, k_r decreases from acid to near neutral pH and increases from near neutral to alkaline pH. For instance at 80°C, $\log_{10} k_r$ is −14.6, −16.5, and −14.4 at pH 1.5, 7.5, and 12.1, respectively. Based on the dissolution behavior of kaolinite as a function of time, solution pH, and temperature we conclude that during constant congruent dissolution Al detachment is rate determining at low pH, and Si detachment is rate limiting at high pH.

The calculated activation energies, E_a, of the constant kaolinite dissolution rate are dependent on solution pH. E_a decreases from 16.0 to 1.7 (kcal $mole^{-1}$) from pH = 1 to 7 but increases from 3.4 to 9.8 (kcal $mole^{-1}$) from pH = 8 to 12.

INTRODUCTION

The temperature and pH-dependencies of the dissolution behavior of aluminosilicates are not well understood. It is generally agreed that reactions occurring at the mineral-solution interface play key roles in the overall dissolution behavior of silicate minerals near the Earth's surface. The pH-dependency of aluminosilicate dissolution has been ascribed to the net adsorption of H^+ and OH^- ions to aluminum and silicon reaction sites (Blum and Lasaga, 1988; Carroll-Webb and Walther, 1988; Brady and Walther, 1989), as well as to the formation of positively, neutral, and negatively charged aluminosilicate activated complexes at acid, near neutral, and alkaline pH, respectively (Aagaard and Helgeson, 1982; Chou and Wollast, 1985; Knauss and Wolery, 1986). In addition, diffusion of the elements through an amorphous surface layer may also affect the overall rate of dissolution. Feldspar surfaces dissolved in very acid and alkaline solutions analyzed by X-ray photoelectron spectroscopy (Eggleston and Hochella, 1988) and Rutherford backscattering (Casey, Westrich, and Arnold, 1988) are enriched with an amorphous silica surface.

In this communication we evaluate the observed dissolution rate behavior of kaolinite at 25° and 60° from Carroll-Webb and Walther (1988) and 80°C, reported in this study, by analyzing its temperature and pH-dependencies. Evaluation of dissolution rate behavior as a function of temperature and solution pH allows the pH-dependence of the activation energy to be determined.

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DISSOLUTION EXPERIMENTS

Well crystallized kaolinite from Washington County, Georgia, was used in the kaolinite dissolution experiments. The starting material was checked for purity by X-ray diffraction with CuK_α radiation. No minerals other than kaolinite were indicated in the diffraction pattern, which scanned from 5° to 65° 2-θ. Kaolinite was examined with a Hitachi S-570 scanning electron microscope. The hexagonal kaolinite platelets measured 0.2 μm thick and varied from 0.4 to 1.0 μm in diameter.

The surface area for kaolinite (11.2 m^2/g) was determined by the B.E.T. static volume method (Brunauer, Emmet, and Teller, 1938) using krypton adsorption. The surface areas of starting material and the end products were found to be equal within the accuracy of the gas adsorption techniques, ± 10 percent. All end products were washed in distilled and deionized water to remove any buffer salts, then dried at 60°C in isobutyl alcohol solution to prevent coagulation of the suspension particles prior to measurement.

One gram of kaolinite was placed directly into polypropylene reaction vessels filled with 500 ml of the pH buffer solution. The pHs of the experiments were controlled by the following buffering agents: KCl, HCl (pH = 1 to 2), KH phthalate, HCl (pH = 2 to 4), succinic acid, NaOH (pH = 4 to 6), tris(hydroxymethyl) aminomethane, HCl (pH = 7 to 9), sodium borate, NaOH or $NaHCO_3$, NaOH (pH = 9 to 11), and KCl and NaOH (pH = 11 to 12) (Perrin and Dempsey, 1974). Mallinckrodt analytical reagent grade chemicals were used for the buffer solutions. These buffers were chosen because they do not significantly complex aluminum in solution (Sillen and Martell, 1971). In previous kaolinite dissolution studies at 25°C using the same buffers, Carroll-Webb and Walther (1988) found no significant effect of organic ligand concentration on the overall dissolution rate. The pHs of the buffer solutions were measured at temperature periodically throughout the dissolution experiments and did not vary by more than ±0.02 pH units.

The temperature of the experiments was maintained at 80°C by placing the batch reactors in water baths heated to an accuracy of 0.2°C. Possible temperature gradients within the bath were eliminated by continuously agitating it on a shaker table. Great care was taken to remove aliquots of a uniform suspension from the reaction vessel in order to avoid changing the total surface area to solution ratio. The suspensions were filtered through an 0.2 μm Nuclepore membrane into previously cleaned polypropylene bottles. As the samples passed through the filter, they were diluted by a factor of 2 with distilled and deionized water or 0.02 N HCl in order to avoid precipitation of an aluminum phase as the samples cooled to room temperature.

The solutions were analyzed for aluminum and silicon with a direct current plasma (DCP) Beckman SpectraSpan VB emission spectrometer. The detection limits for aluminum and silicon are 0.002 and 0.01 ppm, respectively. The high and low standards were made with the buffer solutions in order to correct directly for any possible matrix effects from

elements in the buffer solutions. Analysis of blank buffer solution yielded aluminum and silicon concentrations at the detection limits of the analytical technique.

RESULTS AND DISCUSSION

Kaolinite dissolution at 80°C and fixed pH is plotted for representative experiments as a function of release of Si and time in figure 1. At pH < 5, kaolinite dissolves congruently and at a constant rate after about 24 hrs (fig. 1A). At pH > 9, two periods of dissolution rate are observed: a period of rapid congruent dissolution during the first ~100 hrs (short-term dissolution), followed by a slower constant congruent dissolution period (long-term dissolution (fig. 1B). The measured release rates of Al and Si during the long-term constant dissolution period are shown in table 1. Al release rates at some pH's are not given because there was too much scatter to derive an accurate rate constant. The long-term Si dissolution rates are plotted versus pH in figure 2A. The Si dissolution rates decrease with increasing pH in the acid pH region to pH 6, are at a dissolution rate minimum from pH 6 to 8, and increase with increasing pH at pH > 8. From pH 5.7 to 8.6, kaolinite dissolves incongruently throughout the duration of the experiment; the Al rates being as much as 1.5 orders of magnitude less than the Si rates. The samples in this pH range were filtered directly into 0.02 M HCl solutions. No aluminum complexing agents were used in this study. These solutions are calculated to be supersaturated with respect to gibbsite using the speciation code EQ3 (Wolery, 1983). No gibbsite was found by X-ray diffraction analysis of the solid at the end of the experiment. The calculated amount of gibbsite which may have precipitated is extremely small. It seems reasonable that from pH 5.7 to 8.6 the Al dissolution rates represent the difference between a forward kaolinite dissolution rate and a backward precipitation rate of an amorphous aluminum phase at 80°C.

The long-term kaolinite Al and Si dissolution rates at 25° and 60°C from Carroll-Webb and Walther (1988) are also given in table 1. The same experimental techniques were used. In addition to long-term dissolution, rapid short-term periods of dissolution are observed during the first few hours of dissolution, where Al is preferentially removed over Si at acid pH and Si is preferentially removed over Al at alkaline pH. In order to avoid complications due to the possible precipitation of aluminous phases in the near neutral pH region in these studies, only the Si dissolution rates are compared as a function of temperature (fig. 2B, C). Despite the fact that the effect of ionic strength is negligible at 25°C, we will only use the dissolution rates determined in solutions of I = 0.05M in this comparison. At 60°C (fig. 2B), the rates behave similarly to the 80°C rates. However, the dependence of k_r on pH is somewhat less at near neutral pH and the rates at a similar pH are as much as half an order of magnitude lower than at 80°C. At 25°C, the near neutral pH rates show even less of a pH dependence, and the rate constants are

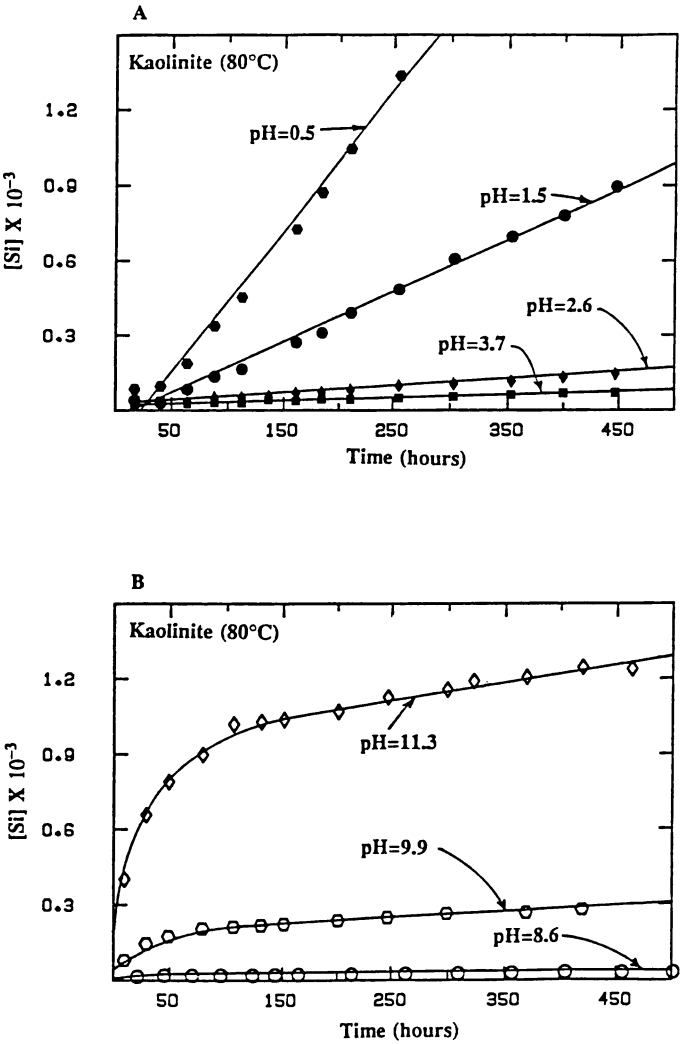

Fig. 1. Kaolinite dissolution at 80°C, plotted as the Si (moles $L^{-1} \times 10^{-3}$) versus time (hrs). (A) In the acid pH region the solid hexagons, circles, diamonds, and squares correspond to dissolution experiments at pH = 0.5, 1.5, 2.6, and 3.7, respectively. (B) In the alkaline pH region, the open diamonds, hexagons, and circles correspond to dissolution experiments at pH = 11.3, 9.9, and 8.6, respectively.

approximately half to two orders of magnitude less than the 80°C dissolution rates in the near neutral pH region and at very low and high pH, respectively. At 25°C, kaolinite dissolves slightly incongruently for the entire length of the experiments ($\log k_{r,Al} - \log k_{r,Si} = 0.2 \pm 0.1$); aluminum dissolution rates being consistently lower than the silicon

TABLE 1

Kaolinite long-term dissolution rates at 80°, 60°, and 25°C

pH	Buffering Agent	Ionic Strength (M/L)	Log_{10} Rate (moles Si $cm^{-2}s^{-1}$)	Log_{10} Rate (moles Al $cm^{-2}s^{-1}$)
80°C				
0.50	KCl,HCl	0.05	-14.10	-14.11
1.50	KCl,HCl	0.05	-14.58	-14.60
2.63	KHPthalate,HCl	0.05	-15.47	-15.45
3.67	KHPthalate,HCl	0.05	-15.83	-15.87
4.93	Succinic Acid,NaOH	0.05	-16.31	-16.67
5.73	Succinic Acid,NaOH	0.05	-16.68	
5.98	Succinic Acid,NaOH	0.05	-16.74	-17.39
7.49	Tris,HCl	0.05	-16.59	
7.50	Tris,HCl	0.05	-16.48	-18.02
8.56	Tris,HCl	0.05	-16.51	-17.12
8.60	Tris,HCl	0.05	-16.50	
9.93	NaBorate,NaOH	0.05	-15.60	-15.64
11.26	NaOH,KCl	0.05	-15.01	-15.10
12.13	NaOH,KCl	0.05	-14.37	-14.28
60°C				
2.14	KCl,HCl	0.05	-15.70	-15.76
3.64	Succinic Acid,NaOH	0.05	-16.43	-16.31
3.72	Succinic Acid,NaOH	0.05	-16.17	-15.99
4.04	Succinic Acid,NaOH	0.05	-16.23	-16.41
4.56	Succinic Acid,NaOH	0.05	-16.72	-16.55
4.58	Succinic Acid,NaOH	0.05	-16.62	-16.52
4.58	Succinic Acid,NaOH	0.05	-16.31	
4.59	Succinic Acid,NaOH	0.05	-16.31	-16.73
5.19	Succinic Acid,NaOH	0.05	-16.95	
5.38	Succinic Acid,NaOH	0.05	-16.44	
5.42	Succinic Acid,NaOH	0.05	-17.00	-17.31
5.55	Succinic Acid,NaOH	0.05	-16.38	
6.43	Tris,HCl	0.05	-17.43	-17.47
7.16	Tris,HCl	0.05	-16.90	
7.40	Tris,HCl	0.05	-17.44	
8.20	Tris,HCl	0.05	-16.84	
9.54	NaBorate,NaOH	0.05		-16.65
10.80	NaBorate,NaOH	0.05	-15.84	-16.08
25°C				
0.99	KCl,HCl	0.05	-16.49	-16.47
2.03	KCl,HCl	0.05	-16.78	-16.59
2.99	KHPthalate,HCl	0.05	-16.87	
4.00	KHPthalate,HCl	0.05	-16.85	-16.76
4.01	Succinic Acid,NaOH	0.05	-16.55	-16.89
4.01	Succinic Acid,NaOH	0.05	-16.95	-16.88
4.85	Succinic Acid,NaOH	0.05	-16.98	-17.03
5.78	Succinic Acid,NaOH	0.05	-16.98	
6.93	Tris,HCl	0.05	-17.01	-17.29
7.89	Tris,HCl	0.05	-16.90	-17.33
8.18	Tris,HCl	0.05	-17.13	
8.18	Tris,HCl	0.05	-17.28	
8.51	Tris,HCl	0.05	-17.53	
8.53	Tris,HCl	0.05	-17.25	
8.63	Tris,HCl	0.05	-17.29	
9.33	Tris,HCl	0.05	-17.43	-17.70
9.35	Tris,HCl	0.05	-17.22	-17.59
9.37	Tris,HCl	0.05	-17.40	-17.60
9.48	$NaHCO_3$,NaOH	0.05	-17.18	
10.26	NaBorate,NaOH	0.05	-17.30	
12.17	KCl,NaOH	0.05	-15.85	-15.81

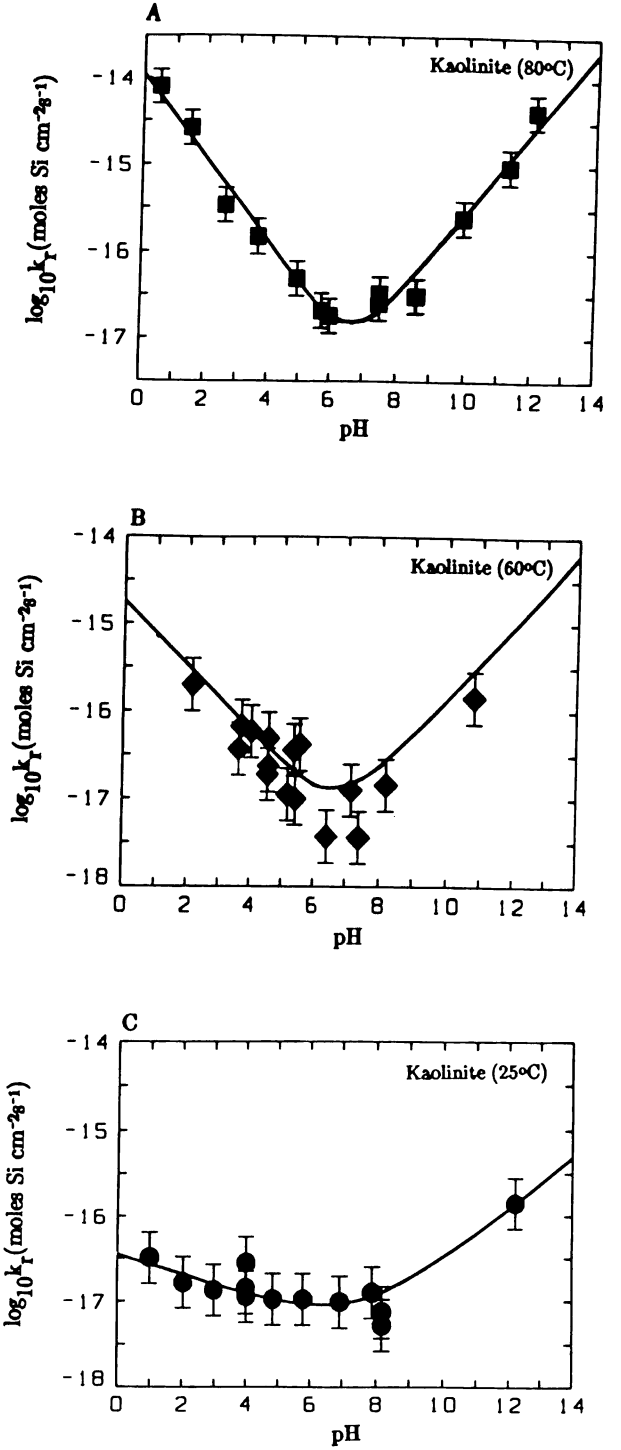

Fig. 2. Kaolinite dissolution plotted as the $\log_{10} k_r$ (moles Si $cm^{-2}s^{-1}$) versus solution pH at (A) 80°, (B) 60°, and (C) 25°C. The solid curves (A) and (C) consist of two linear segments fitted to the experimental data in the acid and alkaline pH regions. At near neutral pH we assume the rates of the linear segments are additive. The solid curve in (B) represents the calculated rates derived from E_a determined from the 25° and 80°C data.

dissolution rates from pH 2 to 9. The dissolution rate data at 25°C from pH 8.5 to 10.5 may reflect the precipitation of a smectite-type phase (see Carroll-Webb and Walther, 1988). These data are not shown in figure 2C and were not used in our analysis.

Reactions at the mineral-solution interface.—Transition state theory (Wynne-Jones and Eyring, 1935), has been used to explain dissolution processes occurring at the mineral-solution interface (Dibble and Tiller, 1981; Lasaga, 1981; Aagaard and Helgeson, 1982). For dissolution reactions far from equilibrium the rate limiting elementary reaction is the detachment of a metal-cation or a complex consisting of more than one metal-cation from the mineral-solution interface to the bulk solution. It is the irreversible breakdown of this activated complex to the reaction products that controls the overall rate of dissolution.

Surface complex reaction theory (Stumm and Morgan, 1981) describes the equilibrium between ions in the bulk solution and ions adsorbed to surface metal-cation reaction sites. The pH-dependencies of slightly soluble oxide and silicate dissolution rates are promoted by the adsorption of H^+ and OH^- ions to reaction sites exposed on the mineral-solution interface (Bales and Morgan, 1985; Furrer and Stumm, 1986; Zinder, Furrer, and Stumm, 1986; Blum and Lasaga, 1988; Carroll-Webb and Walther, 1988; and Brady and Walther, 1989).

The sequence of short-term incongruent dissolution periods followed by constant congruent dissolution at 25° and 60°C indicates that aluminum and silicon are removed from the mineral-solution interface by two different types of complexes, which are not completely independent of one another. During the short-term dissolution period in the acid pH region, aluminum is preferentially released into solution indicating that aluminum complexes are more easily detached. Through the near neutral pH region to pH 9 or 10, silicon is preferentially released into solution indicating that silicon complexes are more easily detached. With increasing time the release rates of both aluminum and silicon decrease and approach stoichiometric dissolution. The change from higher short-term dissolution to lower constant dissolution cannot be explained by the rapid dissolution of fines. If this were the case, then the release of aluminum and silicon would be congruent during the short-term period of dissolution. Nor is it an artifact of the batch dissolution experimental technique. The pH-dependence of the short-term dissolution has been observed as non-stoichiometric peaks of aluminum and silicon in fluidized bed reactor studies of albite when the solution pH was abruptly changed (Chou and Wollast, 1985).

The aluminum and silicon rates become interrelated as the bonding between the aluminum and silicon layers prevents continued independent detachment of the metal-cations resulting in stoichiometric dissolution. Aluminum and silicon cations in kaolinite are bonded to a common oxygen anion. The initial faster detachment of an aluminum cation, resulting from the breaking of an Al-O bond where the oxygen is also bonded to a silicon cation, increases the probability of the detach-

ment of the silicon cation as well. If the detachment of every aluminum cation is accompanied by the detachment of a silicon cation and vice versa, then kaolinite dissolution would be congruent from the beginning of dissolution, and the rate limiting complex would consist of a one to one Si:Al stoichiometry. However, the short-term dissolution is incongruent. If the Al and Si layers dissolve independently from one another, then the dissolution of kaolinite would not approach constant congruent dissolution (the incongruency observed in the short-term dissolution period would be maintained in the long-term dissolution period). However, dissolution approaches congruency with increased reaction time.

As discussed by Brady and Walther (1989), the high pH dissolution rates of silicate minerals are generally controlled by Si activated complexes even though Si release is initially greater than stoichiometric. This implies that relative changes in the energetics of the activated complexes are most important. If this is also true at acid pH for kaolinite, similar analysis may be used. At acid pH the dominant Al complex is positively charged $>AlOH_2^+$, and this likely controls the rate. Detachment of Al leads to the exposure of more Si sites and likely lowers the activated site energy for Si by decreasing the oxygen coordination and allowing bond weakening at the Si site. Therefore, detachment of Si is controlled by the rate of Al detachment at low pH.

The importance of the short-term dissolution period should not be overlooked. Approx 50 percent of the total dissolution observed in the 25° and 60°C experiments at pH < 6 and in the 25°, 60°, and 80°C experiments at pH > 6 occurred during the short-term periods. The duration of the 25°, 60°, and 80°C dissolution experiments were 1000, 600, and 500 hrs, respectively. For example, the dissolution of kaolinite at 25°C and pH = 2 during the first 200 hrs of dissolution is incongruent to approx 1 unit cell, corresponding to Si and Al detachment across the entire surface of approx 4 and 8 angstroms, respectively. At the end of the experiments approximately two unit cells of kaolinite have been dissolved. In order to model accurately the macroscopic observations of kaolinite dissolution better understandings of the short-term dissolution mechanisms, of the formation and concentration of the aluminum and silicon surface complexes at constant dissolution, and of the critical bonding between the Al-Si framework bonds are required.

Temperature dependence of kaolinite dissolution.—At constant pH, the kaolinite long-term dissolution rates increase with increasing temperature. We are not able to give a molecular description of the overall dissolution behavior of kaolinite because we don't know the exact mechanism or stoichiometry of the rate determining steps. For this reason, molecular descriptions such as transition state theory are difficult to apply to the temperature dependence of the overall dissolution behavior of kaolinite. We use instead the classical Arrhenius equation to describe the temperature dependence at constant pH:

$$k_r = A \exp \frac{-E_a}{RT} \tag{1}$$

where A (moles $cm^{-2}s^{-1}$) is the pre-exponential factor, and E_a (cal $mole^{-1}$), the activation energy, is a measure of the energy with which the reactants must collide in order for the reaction to occur. The activation energy of the overall reaction consists of the combined effects of the activation energies from all the elementary reactions. Assuming E_a is independent of temperature it follows from eq (1) that:

$$E_a = -R \frac{\partial \ln k_r}{\partial(1/T)} \tag{2}$$

The pH-dependence of the dissolution rates indicate that the dissolution of kaolinite is controlled by two different mechanisms. At low pH and high pH, the dissolution rates are proportional to activity of H^+ and OH^- ions in the bulk solution, respectively. In the near neutral pH region, both mechanisms contribute to the overall dissolution rate. Previous investigators studying feldspar dissolution (Helgeson, Murphy, and Aagaard, 1984; Knauss and Wolery, 1986) have used line segments through the acid, near neutral, and alkaline pH regions that correspond to three differently charged activated complexes as the rate limiting molecular step. They assumed E_a was constant for each pH region, such that the pH-dependence of the dissolution rates within a pH region is the same with increasing temperature. One should note that our data suggest the rates become more pH-dependent with increasing temperature. The fits to the 80° and 25°C data were made using linear regressions of the data in the acid and alkaline pH regions. The contributions of each mechanism were added together to fit the data in the near neutral pH region. The pH-dependence of the 80°C data is well defined over the entire pH range. The 25°C data are well defined at pH < 7 but defined by one experiment at alkaline pH and three data points at pH 7.5 to 8.5. The slope derived from a linear regression of these data is 0.30, which is identical to the pH-dependence of quartz and other silicate minerals at alkaline pH and 25°C (Brady and Walther, 1989). The good agreement of the pH-dependencies in the alkaline pH region between kaolinite and other silicate minerals allows us to calculate E_a over this pH region. There is an obvious pH-dependence of the 60°C dissolution rate data; however, the uncertainty is quite large (fig. 2B). For this reason, we have chosen to use only the 25° and 80°C data sets to derive E_a as a function of solution pH.

We determined E_a for kaolinite dissolution at constant pH with eq (2) from the fits of the 80° and 25°C dissolution rate data (table 2). The changes in log k_r at constant pH as a function of 1/T are shown in figure (3). The solid line in figure 2B is the pH-dependence of kaolinite dissolution rates at 60°C calculated from the E_a. The calculated rates are well within the uncertainty of the 60°C data in the acid pH region and only slightly higher than the uncertainty at alkaline pH. Note that E_a derived by using data from all three temperatures decreases by less than 0.6 (kcal $mole^{-1}$).

The calculated values of E_a for kaolinite dissolution range from 1.7 to 16.0 (kcal $mole^{-1}$). The lowest values are at near neutral pH but

TABLE 2

E_a and A as a function of pH

pH	E_a (±0.6) (kcal/mole)	pH	E_a (±0.6) (kcal/mole)
1	16.0	7	1.7
2	13.3	8	3.4
3	10.3	9	5.3
4	7.7	10	7.0
5	4.9	11	8.5
6	2.3	12	9.9

increase with both increasing and decreasing pH. The E_a values of surface controlled reaction rates have been generally reported to vary from 10 to 20 (kcal/mole). The upper limit for E_a of aqueous diffusion controlled reactions is 5 (kcal/mole) (Lasaga, 1981). The faster rates of kaolinite dissolution at low and high pH are surface controlled. The same pH-dependencies are observed at near neutral pH. Therefore, it is likely that these dissolution rates are also surface controlled. The low E_a values determined from pH 5 to 9 cannot be indicative of aqueous diffusion controlled reactions, because the suspensions were continuously agitated. Furthermore, aqueous diffusion controlled reactions have dissolutions rates on the order of 10^{-5} (moles mineral $cm^{-2}s^{-1}$).

Comparison of previously determined E_a.—While the E_a values of several minerals have been detemined over the temperature range of 25 to 200°C (Rickard, 1975; Rimstidt and Barnes, 1980; Ohmoto and Lasaga, 1982; Schott, Berner, and Sjoborg, 1981; Grandstaff 1977 and 1980; among others), very few investigators have determined the E_a associated with silicate dissolution as a function of solution pH. Tole and others (1986) studied the dissolution of nepheline at 25°, 60°, and 80°C. At pH = 3, 5, 7, and 11, they obtained E_a values of 17.4, 12.7, 15.2, and 18.4 (kcal $mole^{-1}$), respectively.

Assuming that the rate determining reaction for feldspar dissolution involved the detachment of a positively, neutral, and negatively charged activated complex at acid, neutral, and alkaline pH, Helgeson, Murphy, and Aagaard (1984) analyzed the dissolution rate data of several investigators for albite and K-feldspar studies. At 25°C, they obtained E_a values equal to 19.6, 9.1, and 21.2 (kcal $mole^{-1}$) in the acid pH-dependent, near neutral pH-independent, and alkaline pH-dependent regions, respectively. Knauss and Wolery (1986) studied the dissolution kinetics of albite at 70°C from acid to alkaline pH and at 25°C from pH 4 to 10. Using the same approach as Helgeson, Murphy, and Aagaard (1984), E_a values were calculated to be 29.1, 13.5, and 8.3 (kcal $mole^{-1}$) in the acid, neutral, and alkaline pH regions, respectively. The acid pH region E_a value obtained by Knauss and Wolery (1986) was calculated from their 70°C data and the 150°C albite dissolution data of

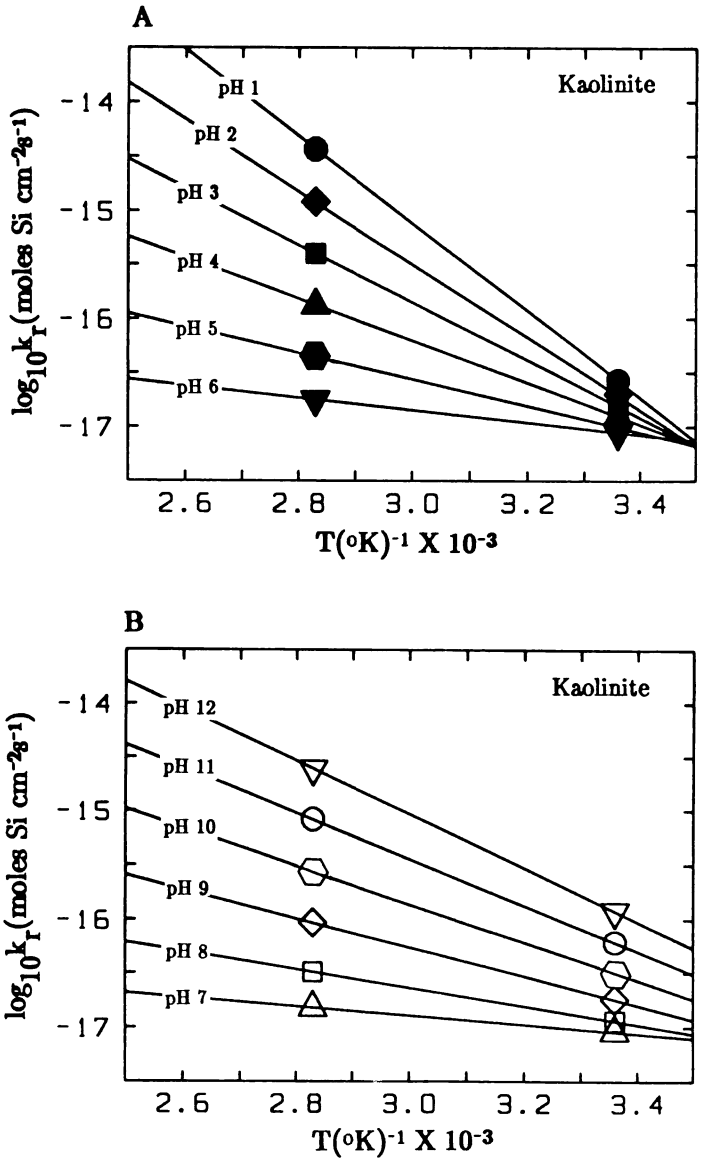

Fig. 3. Temperature dependence of kaolinite dissolution plotting the $\log_{10} k_r$ (moles Si $cm^{-2}s^{-1}$), calculated from the curves fitted to the experimental data, versus $T^{-1} \times 10^{-3}$. (A) In the acid pH region, the solid circles, diamonds, squares, triangles, hexagons, and downward triangles correspond to the dissolution rate constants at pH = 1, 2, 3, 4, 5, and 6, respectively. (B) In the alkaline pH region, the open triangles, squares, diamonds, hexagons, circles, and downward triangles correspond to the dissolution rate constants at pH = 7, 8, 9, 10, 11, and 12, respectively.

Lagache (1965). The pH of the Lagache data is, however, not well known.

Knauss and Wolery (1988) determined the dissolution rates of quartz at 70°C as a function of pH. Using their 70°C data and the estimated quartz dissolution rate constants of Rimstidt and Barnes (1980) at 25°C in the alkaline pH region and of van Lier, deBruyn, and Overbeek, (1960) and Stober (1967) at 25°C in the pH-independent region, they calculated E_a of 21.8 and 25.9 (kcal mole^{-1}) for the pH-independent and alkaline regions, respectively. There has been some discussion (Gaffney, Marley, and Janecky, 1989; Knauss and Wolery, 1989) of the 70°C rates below pH 6.2. The rates may be higher, resulting in a higher E_a for the pH-dependent region. Brady and Walther (1990) studied the dissolution kinetics of quartz at 25° and 60°C. They calculated E_a at pH < 7 to be 11 (kcal mole^{-1}); at pH > 8, E_a increases from 13 to 23 (kcal mole^{-1}).

Walther and Wood (1986) compared the dissolution rate constants of a variety of silicate minerals at near neutral pH where the rates are not substantially pH-dependent from 25° to 900°C. At temperatures greater than 300°C the logarithm of the rate constants varied linearly with T^{-1}°K yielding a E_a = 13.3 (kcal mole^{-1}) (Wood and Walther, 1983). However, at 25°C the rate constants of different minerals differ by as much as five orders of magnitude.

CONCLUDING REMARKS

The dissolution rate constants of kaolinite at 25°, 60°, and 80°C are surface reaction controlled and dependent on solution pH. At all three temperatures, the pH-dependencies of kaolinite dissolution behavior are similar; rate constants decrease with increasing pH in the acid pH region, approach a dissolution rate minimum in the near neutral pH region, and increase with increasing pH in the alkaline pH region.

Kaolinite dissolution is controlled by the detachment of Al and Si reaction sites at low and high pH, respectively. Initially the detachment of aluminum and silicon from the kaolinite-solution interface are somewhat independent of one another at 25° and 60°C and perhaps at 80°C. With increasing time, the dissolution of kaolinite approaches congruency, requiring the detachment of aluminum and silicon to become interdependent. The number and energetics of aluminum and silicon activated complexes at the kaolinite-solution interface must adjust themselves so that congruent dissolution can be observed. At 80°C, dissolution is congruent throughout the duration of the experiment, indicating that the time required for adjustment of the Al and Si complexes at the interface decreases with increasing temperatures.

The temperature and pH dependence of the constant kaolinite dissolution rates were evaluated with the Arrhenius equation. From pH 1 to 7, E_a decreases with increasing pH from 16.0 to 1.7 (kcal mole^{-1}).

From pH 8 to 12 E_a increases with increasing pH from 3.4 to 9.8 (kcal $mole^{-1}$).

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