

## Dissolution rates of plagioclase at pH = 2 and 3

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### ABSTRACT

The dissolution rates of plagioclase in acids are very sensitive to the mineral composition. At pH = 2.0 and 25 °C, rates range from  $\approx 1 \times 10^{-15}$  feldspar-mol/cm<sup>2</sup>/s for albite to greater than  $1 \times 10^{-12}$  feldspar-mol/cm<sup>2</sup>/s for anorthite. At pH = 3.0, the respective rates range from  $\approx 3 \times 10^{-16}$  feldspar-mol/cm<sup>2</sup>/s to  $\approx 7 \times 10^{-14}$  feldspar-mol/cm<sup>2</sup>/s. The relationship between mineral composition and dissolution rate, however, is not simple. In order to better define such a relation at pH = 2, rates were measured on eight plagioclase minerals and compared to existing data.

In general, the dissolution rates of a given plagioclase mineral estimated by different researchers generally agree to within a factor of two to five. The uncertainty is much larger for Ca-rich minerals such as bytownite and anorthite, and reasons for the disagreement are unclear. Even with this uncertainty, however, it is apparent that dissolution rates vary nonlinearly with composition and that the rates for the Ca-rich minerals vary more with composition than Na-rich minerals.

### INTRODUCTION

It has long been observed that mineral weathering rates vary considerably with the mineral structure and composition. Goldich (1938), for example, noted that silicate materials that dissolve slowly tend to contain a highly polymerized (e.g., tectosilicate) structure (see also Hurd et al., 1979; Lin and Clemency, 1981). These materials also tend to be selectively leached by aqueous solutions, as there are sufficient unreactive bonds near the mineral surface to maintain integrity once the reactive constituents are removed (Murata, 1943). Under certain conditions, these materials form a thick leached layer adjacent to the aqueous solution. Conversely, silicates with a poorly connected fabric, such as olivine, tend to dissolve rapidly and uniformly (Schott and Berner, 1985; Petit et al., 1989) as long as the adjacent solution is undersaturated with respect to secondary phases.

Both the leaching behavior and bulk dissolution rate of minerals are controlled by the relative concentration of reactive and unreactive sites at the mineral surface. Aluminate ( $\text{AlO}_4^{-5}$ ) sites on an aluminosilicate mineral surface tend to be more rapidly hydrolyzed in a strong acid than the silicate ( $\text{SiO}_4^{-4}$ ) sites (Murata, 1943). Acid treatment, for example, is used to dealuminate zeolites in order to make hydrocarbon-cracking catalysts (e.g., Barner, 1978; Man et al., 1990). Similar dealumination of clay has been proposed as a nonbauxitic source of Al (Aglietta et al., 1988). Acid dealumination reactions also affect the surface of dissolving feldspars (Chou and Wol-

last, 1984, 1985; Holdren and Speyer, 1985; Casey et al., 1988, 1989).

The disparity in reactivity reflects differences in the bonding character of Al and Si to O atoms at the mineral surface. Furthermore, because hydrolysis reactions are catalyzed by H and hydroxyl ions (Wendt, 1973), the disparity in reactivity reflects differences in the acid-base properties of the exposed aluminate and silicate sites. Al is rapidly leached from the surface of feldspar in acid but is not detectable at near-neutral and basic pH conditions (Casey et al., 1988, 1989). The leaching reaction creates an Al-, Na-, and Ca-depleted layer on the surface of some plagioclase minerals in the early stages of a dissolution experiment.

This selective hydrolysis not only affects the chemistry of the mineral surface but should also be manifested in the bulk dissolution rates of minerals, such as plagioclase, which have a wide range in Si and Al concentrations. Plagioclase ranges in composition from albite ( $\text{NaAlSi}_3\text{O}_8$ ) to anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). This variation corresponds to a coupled, isostructural substitution of aluminate ( $\text{AlO}_4^{-5}$ ) groups and  $\text{Ca}^{2+}$  for silicate ( $\text{SiO}_4^{-4}$ ) groups and  $\text{Na}^+$ .

The actual variation in plagioclase dissolution rate at a constant pH is poorly known, as much previous work was limited to a small range of mineral compositions. Even in more comprehensive studies, however, important variables such as the mineral surface area and purity were not determined, or the solution composition was allowed to vary widely during the experiment. These

TABLE 1. Plagioclase compositions

	1	2	3	4	5	6	7
SiO <sub>2</sub>	66.83	62.89	63.74	54.71	52.34	49.45	44.97
TiO <sub>2</sub>	0.00	0.00	0.01	0.05	0.07	0.03	0.01
Al <sub>2</sub> O <sub>3</sub>	19.26	21.95	23.02	27.93	29.17	32.13	34.53
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.05	0.09	0.28	0.31	0.40	0.31
FeO	0.04	0.06	0.09	0.25	0.29	0.36	0.28
MgO	0.01	0.01	0.04	0.23	0.14	0.14	0.02
MnO	0.01	0.01	0.01	0.02	0.02	0.00	0.01
CaO	0.16	4.15	4.47	9.45	12.31	15.49	18.52
NiO	0.12	0.05	0.08	0.10	0.00	0.24	0.10
Na <sub>2</sub> O	11.51	9.05	7.93	5.23	4.30	2.73	0.89
K <sub>2</sub> O	0.11	0.35	1.43	0.93	0.30	0.12	0.02

Note: Separate grains within each powder were analyzed, averaged, and normalized to 100%. Molar Fe concentrations are divided equally between ferric and ferrous oxidation states. The average stoichiometry and the total number of analyses are included as footnotes. In all cases, the analytical precision analysis is less than the compositional variation within a single mineral. 1 = Keystone albite: (Na<sub>0.97</sub>K<sub>0.01</sub>Ca<sub>0.02</sub>Al<sub>0.99</sub>Si<sub>3.00</sub>O<sub>8.00</sub>), 337 analyses. 2 = Mitchell county oligoclase: (Na<sub>0.78</sub>K<sub>0.02</sub>Ca<sub>0.20</sub>Al<sub>1.15</sub>Si<sub>2.85</sub>O<sub>8.00</sub>), 317 analyses. 3 = Bancroft albite: (Na<sub>0.88</sub>K<sub>0.08</sub>Ca<sub>0.21</sub>Al<sub>1.20</sub>Si<sub>2.80</sub>O<sub>8.00</sub>), 266 analyses. 4 = Saranac Lake andesine: (Na<sub>0.46</sub>K<sub>0.05</sub>Ca<sub>0.46</sub>Al<sub>1.50</sub>Si<sub>2.50</sub>O<sub>8.00</sub>), 294 analyses. 5 = Pueblo Park bytownite: (Na<sub>0.38</sub>K<sub>0.02</sub>Ca<sub>0.60</sub>Al<sub>1.58</sub>Si<sub>2.40</sub>O<sub>8.00</sub>), 48 analyses. 6 = Crystal Bay bytownite: (Na<sub>0.24</sub>K<sub>0.01</sub>Ca<sub>0.76</sub>Al<sub>1.74</sub>Si<sub>2.26</sub>O<sub>8.00</sub>), 314 analyses. 7 = Grass Valley anorthite: (Na<sub>0.08</sub>K<sub>0.00</sub>Ca<sub>0.92</sub>Al<sub>1.90</sub>Si<sub>2.08</sub>O<sub>8.00</sub>), 46 analyses.

variations can lead to precipitation of secondary minerals onto the dissolving surface (see review by Helgeson et al., 1984) or to important changes in mineral surface chemistry during the experiment.

The goal of this paper is to define a relation between the dissolution rates and composition of plagioclase feldspars. To achieve this goal it is necessary to supplement the existing data with additional experiments so that rates are available for a wide range of plagioclase compositions. The investigation is restricted to dissolution in strongly acidic solutions where the character of the reaction is relatively well understood (e.g., Chou and Wollast, 1985; Holdren and Speyer, 1985; Casey et al., 1988, 1989) and the precipitation of secondary minerals can be easily suppressed.

## MATERIALS AND TECHNIQUES

### Preparation of samples

All samples except the Pueblo Park bytownite were acquired from Wards Natural Science Establishment, Rochester, New York. The samples and their trace mineralogy are described in the Appendix 1.<sup>1</sup> Two samples of the Mitchell County oligoclase and Saranac Lake andesine were prepared independently. Granular samples were independently prepared from crystals in 1983–1984 (see Holdren and Speyer, 1987) and as part of this study in 1988. The procedures used by each researcher were similar, except that a ball mill was used to crush the material in this study, rather than the disk grinder employed

by Holdren and Speyer (1987). Once prepared, the powders were treated identically.

All of the feldspars except the Grass Valley anorthite were acquired as large crystals. These crystals were ground and wet-sieved to isolate the 25–75 μm size fraction. This powder was repeatedly washed in distilled H<sub>2</sub>O and spectrophotometric-grade acetone in order to remove ultrafine particles that cling to the larger grains. Washing removes most, but not all, ultrafine particles, as determined by scanning electron microscopy.

The anorthite was separated from an anorthosite from Grass Valley, California. This material was crushed in a steel mortar and pestle, followed by sieving to isolate the 25–75 μm size fraction. This powder was washed repeatedly in distilled H<sub>2</sub>O and acetone to remove ultrafine particles. The resulting powder consisted of a mixture of separate grains of mafic minerals and feldspar. These minerals were separated with a Franz Isodynamic Separator, which produced a nearly pure feldspar powder. Final purification was accomplished using high-density liquids. Anorthite grains were then washed with distilled H<sub>2</sub>O and acetone.

### Feldspar compositions and sample purity

The feldspar compositions were measured with an electron microprobe and average compositions are reported in Table 1. The total range of measured compositions is shown on ternary diagrams in Figure 1. The diameter of the electron beam used to analyze these samples was 16 μm.

Each feldspar exhibits some variation in composition as measured with the electron probe, and the traditional name of some samples can be misleading. Specifically, the Pueblo Park bytownite and the Bancroft albite are labradorite and oligoclase, respectively. Much of this variation in composition is attributable to microscopic mineralogic heterogeneities. Zoning, exsolution lamellae, and accessory phases are apparent from microscopic examination of the material (see Appendix). Although all but one of the compositions are consistent with the permissible range of solid solution (Fig. 1), most of these materials contain more than a single feldspar phase (Appendix). The Mitchell County andesine, for example, contains exsolved potassium feldspar (Appendix), which introduces considerable scatter in the ternary plot of composition (Fig. 1).

### Specific surface areas

Specific surface area of each sample was measured prior to dissolution using a Micromeritics Digisorb 2600 device. After degassing overnight at 200 °C, varying mixtures of N and He were adsorbed onto the powder surface. The areas were calculated from the sorption isotherm and the BET theory of area measurement (Brunauer et al., 1938). The precision and accuracy of this technique is generally better than 5%, as determined by repeated measurement of standards and one sample

<sup>1</sup> A copy of Appendix 1 may be ordered as Document AM-91-449 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

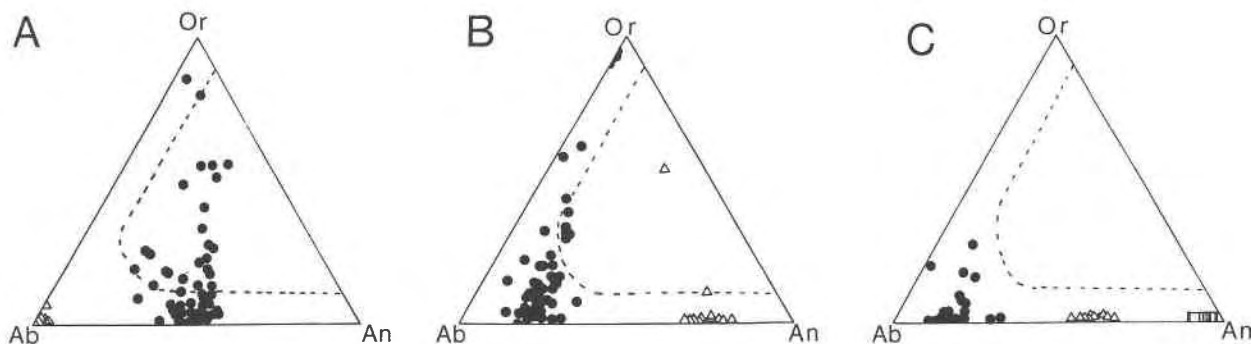


Fig. 1. Variation in feldspar composition for each single powder as a function of the end-member compositions: albite (Ab), anorthite (An), and orthoclase (Or). Analyses for the Keystone albite (unfilled triangle) and Saranac Lake andesine (filled circle) are shown in (A). Analyses for the Bancroft albite (filled circle) and the Crystal Bay bytownite (unfilled triangle) are shown in (B). Analyses for the Mitchell County oligoclase (filled circle), the Pueblo Park bytownite (unfilled triangle) and the Great Valley anorthite (unfilled square) are shown in (C). The dashed line represents the range of feldspar solutions (Smith, 1974).

(Pueblo Park bytownite). Measured areas and uncertainties are listed in Table 2. Because only a small amount of Crystal Bay bytownite was separated, the area was determined by using mixtures of Kr and He rather than N-He mixtures. The precision of area measurements with Kr is comparable to those made with N. The accuracy is only within about 20%, as indicated by repeated measurement of standards.

The exposed area of feldspar probably did not change significantly during the experiment and only a small fraction of the powder mass (typically  $\approx 0.1$  mass%) was consumed. The feldspar areas could not be measured after the experiments because of the artifacts of sample leaching and drying discussed by Casey et al. (1990). Specifically, the leached surfaces partly separate from reacted plagioclase during drying, and this separation exposes new surface area.

#### Dissolution experiments

Batch dissolution experiments were conducted by dispersing each feldspar in a polyethylene bottle containing 0.010 *N* HCl (see Appendix). Solution volumes and masses of mineral powder are compiled in the Appendix. The solutions were continuously agitated at 25 °C. Samples of the solution were periodically extracted from the bottles, pressed through a 0.2  $\mu\text{m}$  filter, and analyzed. The sample volumes varied between 10 and 25 ml. After sampling, an equal volume of unreacted background electrolyte was immediately added to the bottles to maintain a constant total volume. All data are corrected for changes in concentration as a result of sampling. There was negligible drift in pH during the experiments.

Si concentrations were measured using the Heteropoly blue technique (American Public Health Association, 1970). Al concentration was measured with a DC-plasma spectrophotometer. Na and Ca concentrations were determined by atomic absorption spectrophotometry. Precision and accuracy of these techniques are generally bet-

ter than 5%, as determined by repeated analysis of samples and standards.

Dissolution rates were calculated by monitoring the concentrations of Al, Si, Ca, and Na in the solutions (Fig. 2). Rates were calculated by linearly regressing the concentrations against time. Dissolution rates were calculated from the slope of these curves, and from knowledge of the specific surface area and composition of each mineral. The rates are compiled in Table 3. Data used to calculate the rates are given in Appendix 1.

#### RESULTS

The accuracy of any relation between mineral composition and dissolution rate is limited by the abundance and quality of data. The set of plagioclase dissolution rates is illustrated in Figure 3, where results from this study are compared with data from published sources. As one can see, the dissolution rates vary dramatically with mineral composition. Rates increase from  $\approx 1 \times 10^{-15}$  mol/cm<sup>2</sup>/s for albite to well over  $1 \times 10^{-12}$  mol/cm<sup>2</sup>/s for anorthite. All of these data are from experiments conducted in HCl solutions, except possibly for the datum

TABLE 2. Specific surface areas of the feldspar powders

Sample	Area m <sup>2</sup> /g
Bancroft albite	0.405 $\pm$ 0.03
Mitchell County oligoclase no. 1	0.18 $\pm$ 0.01
Mitchell County oligoclase no. 2	0.645 $\pm$ 0.05
Grass Valley anorthite	0.52 $\pm$ 0.02
Keystone albite	0.49 $\pm$ 0.05
Pueblo Park bytownite	0.20 $\pm$ 0.01
Crystal Bay bytownite	0.27 $\pm$ 0.01
Saranac Lake andesine no. 1	0.405 $\pm$ 0.03
Saranac Lake andesine no. 2	0.35 $\pm$ 0.03

Note: The powders range in size from 25 to 75  $\mu\text{m}$ . Uncertainties (one estimated standard deviation) are reported from the BET regression (Lowell, 1979) or the average of repeated measurements of the Pueblo Park labradorite, whichever is larger. The Mitchell County oligoclase no. 2 and the Saranac Lake andesine no. 2 were ground in 1983–1984.

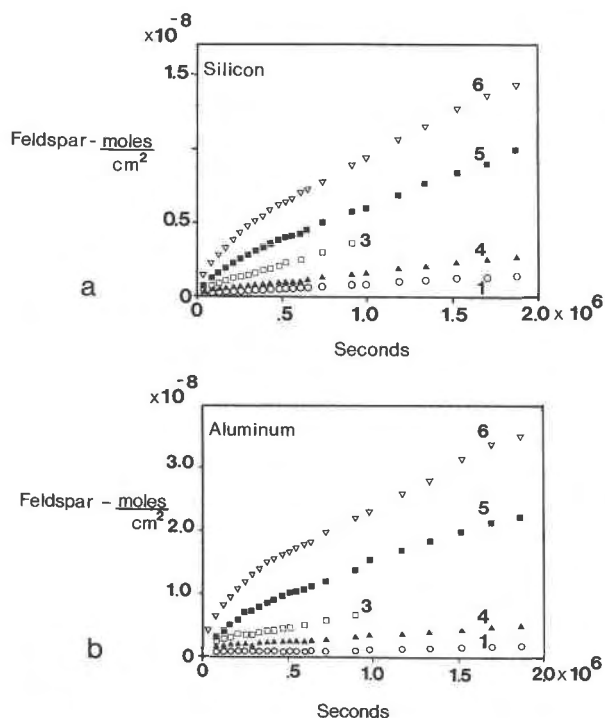


Fig. 2. (a) Concentration of Si in solution as a function of time. The Si concentrations are normalized to the initial powder surface area, the total solution volume, and the composition of the feldspar. The resulting concentrations are plotted in units of feldspar-mol/cm<sup>2</sup>. Expressed in this way, the slope of the curve equals the feldspar dissolution rate in mol/cm<sup>2</sup>/s. The numbers correspond to the samples identified in Table 3. (b) The concentrations of Al in solution as a function of time.

from Brady and Walther (1989). A complete description of this particular experiment by the original authors is in preparation.

In several experiments either separate minerals of similar composition were dissolved (e.g., the Keystone and Amelia albites), or separate experiments were conducted on minerals from the same location (e.g., the Crystal Bay bytownite). In general, the dissolution rates of the plagioclase minerals in the approximate composition range of An<sub>00</sub> to An<sub>60</sub> agree to within a factor of between two and five. Estimates for albite, for example, range from  $1.08 \times 10^{-15}$  to  $2.5 \times 10^{-15}$  feldspar-mol/cm<sup>2</sup>/s. The dissolution rate of the Keystone albite is lower than that reported for Amelia albite at pH = 2.1 by Chou and Wollast (1984, 1985) but compares well with that published by Knauss and Wolery (1986) for an unidentified albite. To make this comparison, data of Knauss and Wolery (1986) were adjusted from 70 °C to 25 °C using the standard Arrhenius relation and the activation energy (8 kcal/mol) measured by Fleer (1982) for anorthite dissolution at pH 2.0. Note also that the batch dissolution rate of albite reported here (Table 3) compares well with experiments conducted in chemostat cells (Knauss and Wolery, 1986; Chou and Wollast, 1985).

There is considerable disagreement, however, about the

TABLE 3. Plagioclase dissolution rates at pH = 2.0

Sample	Rate (feldspar-mol/cm <sup>2</sup> /s) × 10 <sup>15</sup>			
	Si	Al	Ca	Na
1	1.08 ± 0.6	0.47 ± 0.01	—	—
2	1.41 ± 0.2	2.57 ± 0.79	—	—
3	3.62 ± 0.2	4.98 ± 0.14	—	—
4	2.05 ± 1.1	2.51 ± 0.87	—	2.53 ± 0.27
5	6.85 ± 3.0	15.0 ± 7.5	8.46 ± 0.51	8.32 ± 1.20
6	9.88 ± 4.3	26.8 ± 5.7	15.8 ± 0.62	12.9 ± 1.63
7	14.0 ± 3.3	49.2 ± 4.1	42.9 ± 2.08	39.5 ± 3.35
8	212.0 ± 95.0	359.0 ± 174.0	425.0 ± 24.9	419.0 ± 28.8
9	643.0 ± 40.0	600.0 ± 48.0	565.0 ± 48.0	573.0 ± 65.1

Note: Uncertainties for Si and Al fluxes are estimated from duplicate experiments. Uncertainties for Ca and Na fluxes are from the error of the linear regression. All uncertainties correspond to one estimated standard deviation. 1 = Keystone albite, 2 = Mitchell County oligoclase no. 1, 3 = Mitchell County oligoclase no. 2, 4 = Bancroft albite, 5 = Saranac Lake andesine no. 1, 6 = Saranac Lake andesine no. 2, 7 = Pueblo Park bytownite, 8 = Crystal Bay bytownite, 9 = Great Valley anorthite.

dissolution rates of bytownite and anorthite. The rate of dissolution of the Grass Valley anorthite from this study, for example, is approximately 75 times smaller than that reported for the Pacaya anorthite by Fleer (1982) (Fig. 3). Brady and Walther's (1989) rate for anorthite dissolution is also considerably lower than Fleer's (1982) datum, but is also higher than the rate measured in this study for the Grass Valley anorthite. Brady and Walther (1989) dissolved the unnamed anorthite (An<sub>55</sub>) at pH = 1.9. The slight pH differences among the experiments cannot account for such large differences in reported rates.

The discrepancy, however, may be attributable to unique aspects of Fleer's experiments. Most of the data compiled in Figure 3 are from experiments conducted on granular material. The datum of Fleer (1982) is from a batch experiment conducted on a single crystal of anorthite. She estimated the exposed surface area of this crystal geometrically, rather than through the sorption of gases onto exposed surfaces, as was done by the other researchers. If this crystal contained many small fractures, which were accessible to the aqueous solution but too small to be incorporated into the area calculation, her estimate of the dissolution rate would be anomalously high. The total disagreement over anorthite dissolution rates decreases from over a factor of 100 to approximately a factor of four if Fleer's (1982) datum is excluded.

The dissolution rate of the Crystal Bay bytownite reported by Brady and Walther (1989) is lower by almost a factor of ten than is reported here for the same material at pH = 2.0 (Fig. 3). Reasons for this discrepancy are unclear. Although Brady and Walther (1989) conducted their experiments at slightly more basic conditions (pH = 2.15) than those employed here, the large discrepancy in rates cannot be attributed solely to differences in solution pH.

## DISCUSSION

There are two important points to summarize from the preceding section. First, rates vary with plagioclase com-

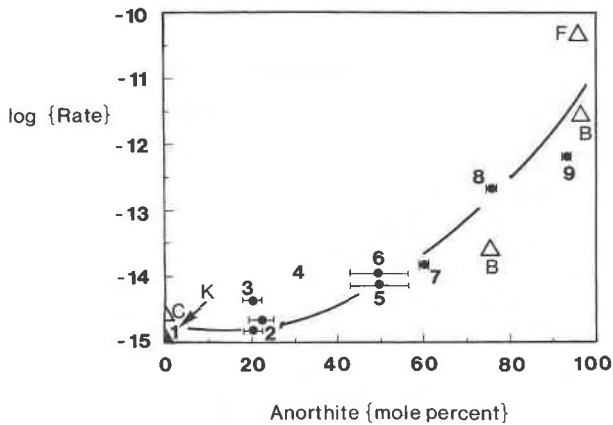


Fig. 3. Specific dissolution rates of plagioclase samples as a function of composition in pH = 2.0 solutions. The numbers correspond to the samples identified in Table 3. Rates are reported as feldspar-mol/cm<sup>2</sup>/s as determined by Si fluxes. Sample C corresponds to the Amelia albite (Chou and Wollast, 1985). Sample F corresponds to the Pacaya anorthite (Fleer, unpublished data). Sample K is an unidentified albite described by Knauss and Wolery (1986). Samples identified with a B correspond to an unidentified anorthite of composition An<sub>95</sub> and the Crystal Bay bytownite (Patrick Brady, personal communication). The curve is an empirical correlation between dissolution rate and feldspar composition.

position by a factor of well over 10<sup>3</sup>. The large difference in dissolution rate of very sodic and very calcic plagioclase has been pointed out before (Lasaga, 1983; Brady and Walther, 1989). The new data presented here for plagioclase minerals of intermediate composition, however, add much detail to the relation (Fig. 3).

Second, this wide variation in rate is much larger than the uncertainty surrounding any single composition. Dissolution rates of a single plagioclase composition from different investigators generally agree to within a factor of approximately 2 to 5 for minerals in the approximate composition range An<sub>00</sub> to An<sub>60</sub>. The disagreement is much larger for more Ca-rich plagioclase, and additional data are critically needed on these compositions.

An empirical correlation of dissolution rate with mineral composition in pH = 2 solutions is given by:

$$\log_{10}[R(X)] = -14.7484 - 0.0135083 \times X + 0.000505238 \times X^2 \quad (1)$$

In Equation 1,  $X$  represents the mole percent anorthite in the plagioclase and  $R(X)$  is the dissolution rate in feldspar-mol/cm<sup>2</sup>/s (Fig. 3). All data shown in Figure 3 are included in this regression, including Fleer's (1982) estimate of the anorthite dissolution rate. No statistical significance is assigned to this nonlinear regression, and the correlation is heavily weighted by the datum of Fleer (1982). The regression is shown as a bold, nearly continuous line in Figure 3.

An important feature of the data is that dissolution rates of calcic plagioclase are apparently more sensitive to variations in composition than sodic materials. The

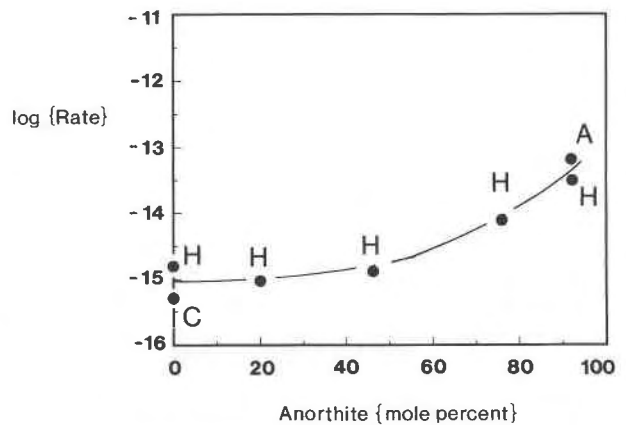


Fig. 4. Dissolution rates of plagioclase samples as a function of mole percent anorthite in pH = 3.0 solutions. Sample C is from Chou and Wollast (1984), sample H is from Holdren and Speyer (1985, 1987), and sample A is from Amrhein and Suarez (1988).

trend of the logarithms of rate vs. composition is not constant, but increases in slope with increased Ca and Al content (Fig. 3). Although the data are scattered, the rates apparently increase more rapidly for the calcic minerals than they do for minerals in the composition range An<sub>00</sub> to An<sub>30-50</sub>. This relation is apparent even if Fleer's (1982) datum is excluded from the set of data. To verify this relation, additional dissolution rates are compiled from experiments at pH = 3 and are shown in Figure 4.

As in the case for experiments at pH = 2, rates increase with anorthite content. The total variation in rates with mineral composition is, however, not as pronounced as in the more acidic solution (Fig. 3). The relation between the logarithm of dissolution rate and mineral composition is nonlinear, however, just as was observed at pH = 2 (Fig. 3). The dissolution rates of plagioclase in the approximate composition range An<sub>40</sub> to An<sub>100</sub> vary more dramatically with composition than plagioclase in the approximate composition range An<sub>00</sub> to An<sub>40</sub>. The relation between plagioclase dissolution rate and mineral composition is, of course, heavily influenced by the few data for calcic compositions. The following empirical correlation describes the distribution of rates:

$$\log_{10}[R(X)] = -15.023 - 0.001131 \times X + 0.0003176 \times X^2 \quad (2)$$

where all variables are as previously defined. All of the experiments used to compile Figure 4 were conducted in HCl solutions.

It is not surprising that the rates of dissolution of plagioclase vary so dramatically and nonlinearly with composition. The structure of albite contains an extensive framework of linked silicate tetrahedra which are resistant to hydrolysis relative to the aluminate sites. Conversely, silicate tetrahedra in ordered anorthite are isolated from one another by aluminate groups. In contrast to albite, selective hydrolysis of the Al from anorthite completely disrupts the structure.

The relationship between dissolution rate and mineral composition is likely to vary with the solution composition. As noted by Wendt (1973), the pH-dependence of hydrolysis rates in simple solutions is controlled by the acid-base properties of the important bonds (see also Bales and Morgan, 1985; Carroll-Webb and Walther, 1988; Blum and Lasaga, 1988). Other sorbed ligands can also promote hydrolysis rates (Amrhein and Suarez, 1988) and the relationships shown in Figures 3 and 4 are not appropriate for solutions containing ligands, such as fluoride ion or certain organic acids, which change the character of hydrolysis from proton-promoted dissolution. Sorption of these ions onto a hydrolyzing bond enhances the rate and may also modify the relation between dissolution rate and mineral composition. Of the data compiled in Figure 3, only Knauss and Wolery (1986) employed a potentially catalytic solute (biphthalate) in their experiment. The close agreement between Knauss and Wolery's rate estimate and those of other investigators suggests that the biphthalate did not affect their result.

Many potential factors may account for the uncertainty of a factor of approximately two to five for minerals in the composition range  $An_{00}$  to  $An_{60}$ . Any single batch rate measurement, for example, is only reproducible to within this factor (Table 3). Furthermore, rates estimated from batch experiments of short duration differ depending upon which element is examined. Rates calculated from the Al flux, for example, are larger than rates calculated from the Si flux (Table 3).

The uncertainty that arises from this nonstoichiometric dissolution is too small to influence dramatically the relation between rate and composition shown in Figure 3. In fact, both Knauss and Wolery (1986) and Chou and Wollast (1985) established stoichiometric dissolution in their chemostat experiments and their rates differ significantly. The discrepancy must be attributed either to differences in the experimental design, or to inherent differences in the reactivities of the two albites. Note, however, that the results of Knauss and Wolery (1986) compare well with the rate estimate for the Keystone albite. Stoichiometric dissolution was not achieved in this batch experiment.

The nonstoichiometric dissolution arises because Al, Na, and Ca dissolve more rapidly from the plagioclase structure than Si in the early stages of an experiment. The difference in rate disappears with time as a leached layer of constant thickness develops on the mineral surface. At this stage, the diffusive flux of Al through the leached layer is constant and proportional to the rate of destruction of the residual silicate framework (Chou and Wollast, 1984).

There have been no studies to date documenting the time required to reach a leached layer of constant thickness for plagioclase minerals at pH = 2. The ratio of dissolved substances released from the mineral cannot be trusted, since these fluxes may reflect the dissolution of trace impurities and exsolved phases. The ultimate thick-

ness of the leached layer is controlled by the solution and mineral compositions. In any case, the overall rate of dissolution is controlled by the rate of destruction of the silicate framework, and these kinetics can be described with an approximately zero-order rate law. Thus rates of dissolution become nearly constant with time after the early stages of an experiment.

Mineralogic heterogeneities, however, influence considerably the measured rate of dissolution. Ca-rich plagioclase dissolves many times more rapidly than either Na- or K-rich feldspar (compare the rates compiled in Figure 3 with that reported for potassium feldspar by Holdren and Speyer, 1985). Most plagioclase samples used in this study contain fine-grained intergrowths of two feldspar minerals, or are zoned in composition. The Bancroft albite, for example, is antiperthitic (Appendix). Likewise, the Mitchell County oligoclase contains an exsolved K-rich feldspar and exhibits a wide range in composition (Fig. 1). The net dissolution rate is different than would be measured on homogeneous material with the same nominal composition.

Regular variations in the dissolution rate with time can also lead to uncertainties in the rate estimate. Rates decrease with time in the early stages of an experiment by as much as a factor of ten as the particularly reactive sites dissolve (e.g., Holdren and Berner, 1979; Holdren and Speyer, 1985; Knauss and Wolery, 1986). Such a period of enhanced reactivity is apparent in Figure 2 as anomalously rapid increases in Si concentration in the first  $0.5 \times 10^6$  s of each experiment. Subsequent changes in concentration are approximately constant (Fig. 2), and it is these data that are used to calculate the dissolution rate. Holdren and Speyer (1985), however, also show that the rates decrease slowly with time over many hundreds of hours of reaction. All of the data compiled in Figure 3 are from experiments that lasted several hundred hours.

Subtleties of sample preparation can also cause rates to vary by factors of between two and five. Eggleston et al. (1989), for example, found that diopside dissolution rates decreased for several months after the mineral powder was initially prepared. They attributed the decrease in rate with time to slow recrystallization of the damaged mineral surfaces to a relatively undamaged state. A similar mechanism may explain the duplicate experiments on separately prepared samples of Saranac Lake andesine and the Mitchell County oligoclase (Table 3). The dissolution rates of the duplicates vary by factors of approximately two in each case. One clear distinction between these materials is the time that elapsed since preparation. The slowly dissolving material was prepared 4–5 yr earlier than the more rapidly dissolving material.

The essential point is, however, that the variation in rate for any single plagioclase sample is small relative to the entire variation in rate with composition. Many potential factors can cause rates to vary by a factor of between two and five besides those listed above. Thus the relation between the plagioclase dissolution rates and

mineral composition derived above is meaningful. This relation will be improved, of course, as additional data are acquired.

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