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A SURVEY STUDY OF THE KINETICS OF WOLLASTONITE DISSOLUTION IN H_2O–CO_2 AND BUFFERED SYSTEMS AT 25°C

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ABSTRACT. The aqueous dissolution of wollastonite was examined at 25°C in two types of systems: (1) systems of approximately constant pH, and (2) systems evolving under different partial pressures of carbon dioxide. In all cases calcium, silica, and pH were determined as a function of time.

Results indicate that the decomposition is by hydrogen ion attack. Rates of appearance of calcium, and perhaps silica, in the bulk solution may be governed by diffusion through an aqueous surface film. The calcium gradient through the film is a function of the pH of the system and is larger for lower pH values.

In solutions under different partial pressures of carbon dioxide, the overall reaction appears to be one of decreasing rate of calcium release with increasing pH and a corresponding decrease in calcium gradient in the surface film. Eventually, a state is reached at which the pH and rate of calcium release become approximately constant.

INTRODUCTION

One of the more important mechanisms of silicate weathering in nature is attack by carbon dioxide-bearing solutions. An understanding of such reactions is therefore important for an understanding of the weathering process. The relatively simple system wollastonite–water–carbon dioxide was selected for this study because the system illustrates features that are useful for understanding decomposition of silicates occurring in natural systems.

Since the decomposition reaction between the carbon dioxide-bearing solutions and mineral may be through hydrogen ions from the carbonic acid, solutions of constant pH were used to single out the importance of hydrogen ions during mineral attack.

Relatively little work has been done specifically on decomposition of inosilicates under mild acid conditions. Previous work by Correns (1963) indicates that the general dissolution of silicates is incongruent and perhaps controlled by diffusion through a residual layer. Wollast (1967), Helgeson (1971), and others indicate the important role of hydrogen ions in the decomposition process.

EXPERIMENTAL PROCEDURE

Material

Wollastonite from Willsboro, New York, was broken in an iron mortar, and the minor amounts of garnet and diopside, present as impurities, were picked out by hand. Following this, the material was ground in an iron mortar, the 100 to 150 mesh fraction separated by sieving, and the resulting material purified by running it through a Frantz magnetic separator. The resulting wollastonite was verified by optical examination and X-ray diffraction. Microscopic examination also indicated that most of the grains were prismatic cleavage fragments with average long and short dimensions of 0.535 and 0.0796 mm, respectively. Using the approximation that the solid is made up of square

prisms of dimensions 0.535 × 0.0796 × 0.0796 mm, the specific surface is about 1.885×10^{-2} M^2/g.

Systems

Essentially, two different types of systems were examined: systems at approximately constant pH, and systems evolving under different partial pressures of carbon dioxide. All the systems at constant pH were examined in stirred and unstirred states. Of the systems evolving under different partial pressures of carbon dioxide, only the 5 percent carbon dioxide system was examined in a stirred state. All experiments were carried out at about 25°C.

Systems at constant pH.—Systems at constant pH were set up by placing 0.5000 g of the mineral in 500 ml of solution in a 1 liter, polyethylene container. Systems buffered at pH values of 2.85 (0.1 N HOAc) and 4.01 (K biphthalate) were used. The pH values rose slightly during the first 140 hours so that the pH values of these solutions are taken to be about 3 and 4, respectively. To obtain systems at a pH of about 6, the pH of the system was readjusted five times daily with a drop or two of weak HCl. The pH, calcium, and silica were monitored over a period of about 10 days. Silica was determined by the silicomolybdate blue method, calcium by EDTA titration, and the pH with a pH meter. For calcium and silica analyses 10-ml samples were withdrawn, and the original buffer solution used to replace the sample aliquot. The pH was measured in the sample container.

Systems evolving under different partial pressures of carbon dioxide.—These systems were set up by placing 0.5000 g of the mineral in 500 ml of deionized water which had been saturated with the gas to be used in the particular experiment. The experiments were carried out in 1 liter, polyethylene containers, the gas passing into the covered container through tygon tubing and out through a piece of slit tubing so that the total pressure in the container was maintained at about 1 atm. The gas was not run continuously, but rather the system was reequilibrated, and gas in the space above the solution renewed five times daily. Hence, the gas produced little agitation. A schematic of the apparatus is shown

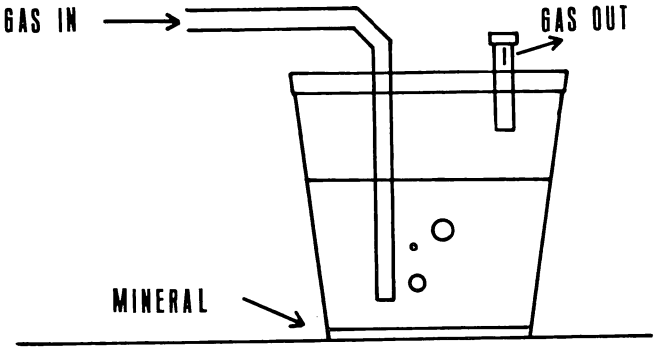

Fig. 1. Schematic of the apparatus used in the experiments done under different partial pressures of carbon dioxide.

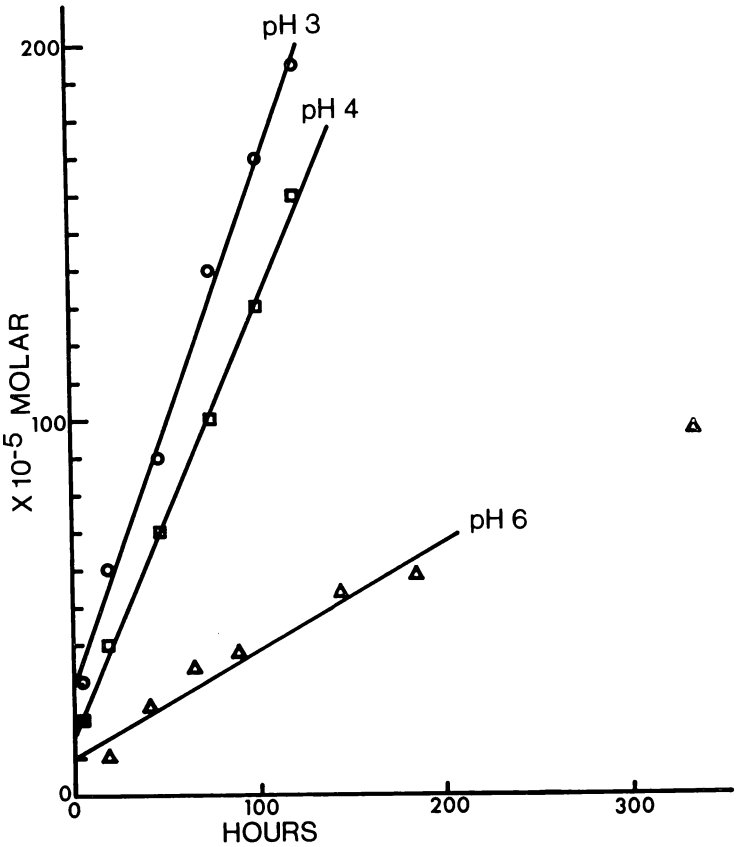

Fig. 2. Plots of molar concentrations of calcium as a function of time for stirred systems held at approximately constant pH. The last point of the pH 6 curve was added after the least-squares line was drawn.

in figure 1. Runs were made using N_2, air, and 5 percent CO_2-95 percent O_2 atm and lasted approximately 20 days. One run was made under the 5 percent carbon dioxide gas using a magnetic stirrer to agitate the solution. During the runs the pH, calcium, and silica were monitored in the manner previously indicated. Replacement of the sample aliquots was with deionized water.

RESULTS

Systems at constant pH.—From the concentration-time measurements, plots of molar concentrations of calcium were constructed for experiments carried out at pH values of 3, 4, and 6 and in stirred versus unstirred states. The two sets of curves are shown in figures 2 and 3. The slopes of straight lines, as determined by the method of least squares, are given in table 1.

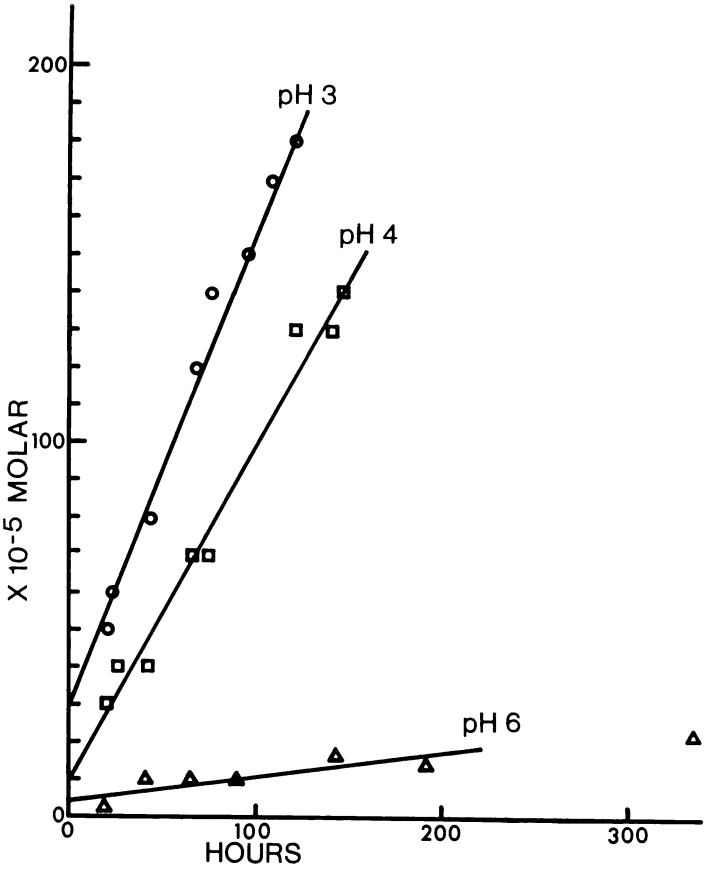

Fig. 3. Plots of molar concentrations of calcium as a function of time for unstirred systems held at approximately constant pH. The last point on the pH 6 curve was added after the least-squares line was drawn.

TABLE 1

Rate constants in stirred and unstirred solutions as a function of pH (in units of molar concentration per hour per gram of mineral)

pH	Unstirred	Stirred
3	2.52×10^{-5}	2.80×10^{-5}
4	1.79×10^{-5}	2.32×10^{-5}
6	0.13×10^{-5}	0.55×10^{-5}

The silica release was not followed as closely as the calcium release. Those values determined during the pH 3 and pH 4 runs indicate that the silica was released incongruently early in the experiments, being about 6. $\times 10^{-5}$ molar in both the stirred and unstirred solutions. After approximately 100 hours the concentrations were about 27. $\times 10^{-5}$ molar in the unstirred cases and about 42. $\times 10^{-5}$ molar in the stirred cases. No silica determinations were made in the pH 6 runs.

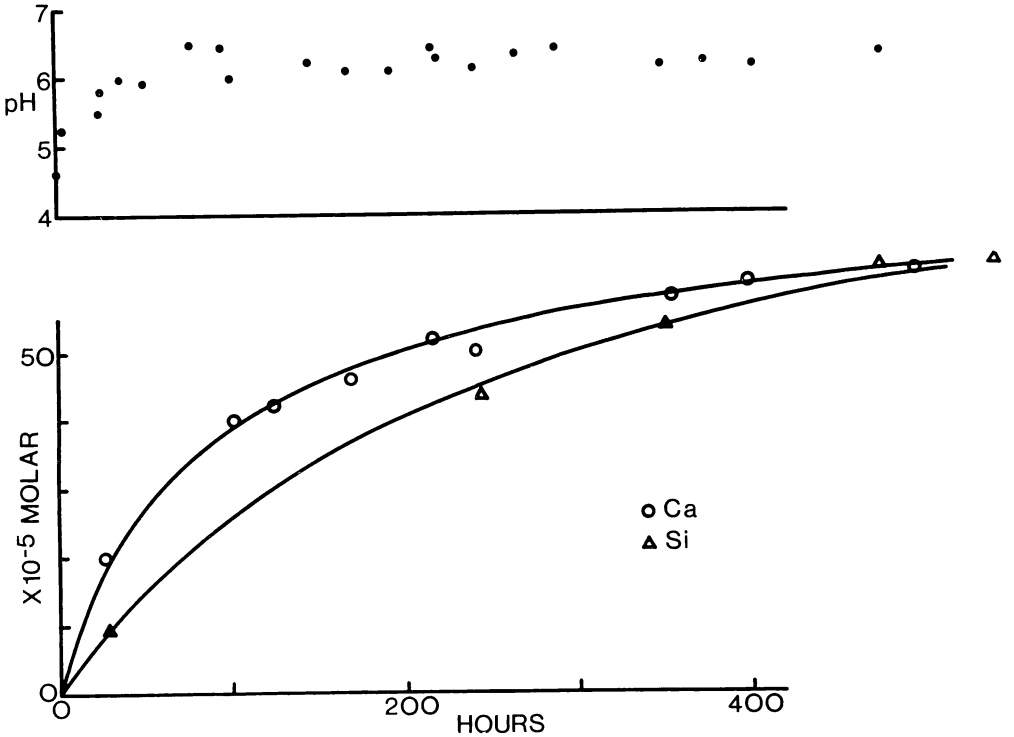

Fig. 4. Plots of molar concentrations of calcium and silica and pH as functions of time for the unstirred system under 1 atm of 5 percent CO_2-95 percent O_2 gas.

Systems evolving under different partial pressures of carbon dioxide.—From the concentration-time measurements, plots of molar concentrations of calcium, silica, and pH were constructed as a function of time for each of the partial pressures of carbon dioxide. These are shown in figures 4, 5, and 6. A stirred run was also carried out with the 5 percent CO_2-95 percent O_2 gas. The results of this run are shown in figure 7.

DISCUSSION AND CONCLUSIONS

The results previously enumerated indicate that the decomposition of wollastonite in aqueous carbon-dioxide solutions is essentially by acid attack. This is indicated by the initial decrease in the hydrogen ion activity with increasing calcium concentration in the solution, by the initial incongruency in the dissolution process and by the rates of calcium release at various pH values during the evolution of the system. The decreasing rates of calcium release for those solutions with increasing pH are near the values that would be predicted by considering the rate of calcium release as a function of the pH.

The process of hydrogen ion attack is visualized as a rapid transfer (almost instantaneous) of hydrogen ions between the bulk solution and

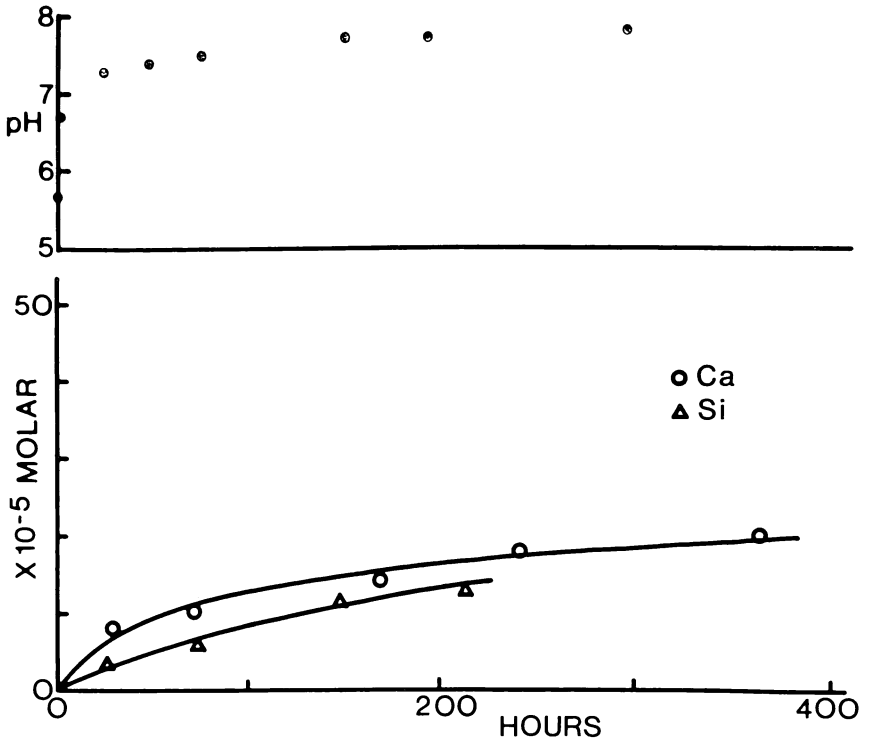

Fig. 5. Plots of molar concentrations of calcium and silica and pH as functions of time for the unstirred system under 1 atm of air.

the surface. The surface concentration of hydrogen ions is a strong function of the bulk concentration. The rate of calcium release from the surface is then proportional to the surface hydrogen ion concentration. However, the rate of appearance of calcium in the solution is determined by diffusion from the surface. Evidence suggesting these processes can be found in the series of constant-pH experiments. The variation in rate of calcium release with changing pH, the constant rate of calcium release at constant pH, and enhanced release of calcium by stirring suggest a diffusion-controlled process of the Nernst-Brunner type (Moelwyn-Hughes, 1933, p 274-278). Two basic steps are involved in the reaction in addition to the actual exchange: movement of the hydrogen ion to the surface and movement of the calcium away from the surface. Since proton charge transfer in hydrogen-bonded systems is extremely rapid, it is difficult to imagine that movement of hydrogen ions is a slow step. Yet the rate of calcium release is dependent on pH. Thus, the rate equation may be of the following type:

$$\text{Rate of change of bulk calcium concentration} = \frac{A\, D_{Ca}\, (a_{Ca,S} - a_{Ca,B})}{V\, \delta} \qquad (1)$$

where

A = surface area,
D_{Ca} = diffusion coefficient for calcium in the surface film,
δ = thickness of the surface film,
V = volume of solution,
$a_{Ca,S}$ = activity of unbonded calcium at the surface,

and

$a_{Ca,B}$ = bulk activity of calcium (essentially constant with respect to the surface concentrations in these experiments).

The rate of silica release may also be governed by similar diffusion away from the surface. Being uncharged, it could be expected to diffuse more slowly, giving the appearance of incongruent decomposition. For the initial stage of the reactions, it is difficult to determine between slow diffusion due to lack of charge or retarded release due to polymerization originally present in the mineral (that is, silica gel rind). In either case, the silica remaining behind does not appear to form a barrier of increasing thickness to the release of calcium even though it may be involved in the surface film.

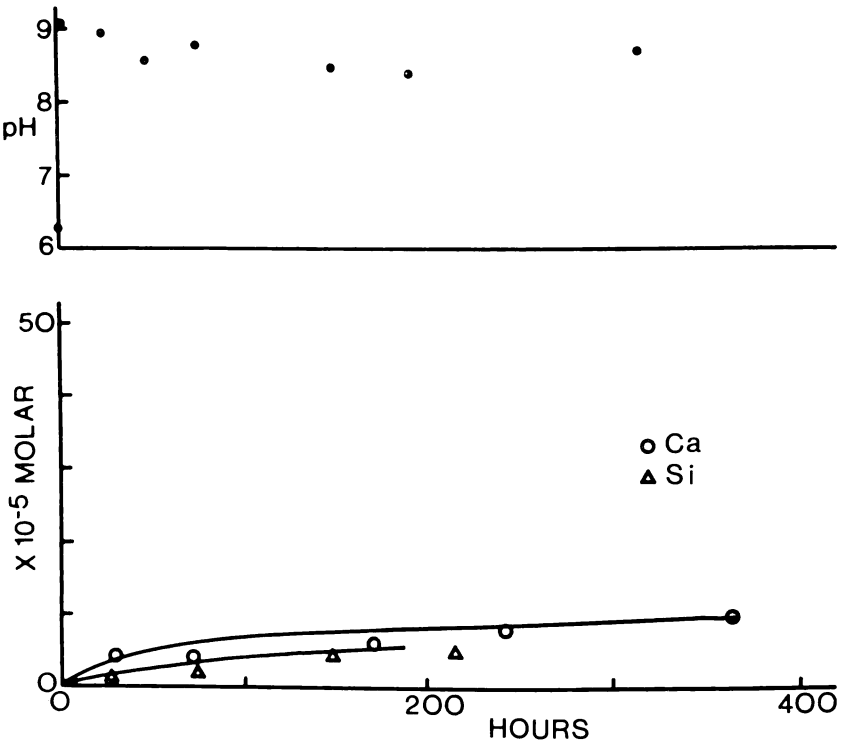

Fig. 6. Plots of molar concentrations of calcium and silica and pH as functions of time for the system under 1 atm of nitrogen.

The experiments with systems under different partial pressures of carbon dioxide can be related to equation (1). When the mineral is placed in the solution it rapidly reacts with the reservoir of hydrogen ions, decreasing ($a_{Ca,S}$ — $a_{Ca,B}$), thereby slowing the reaction. Eventually, a situation is reached where the pH becomes effectively constant and the rate of dissolution becomes approximately constant. If the process continued long enough, calcite and amorphous silica would probably form. Data cited by Langmuir (1968) on the solubility of calcite and Alexander, Heston, and Iler (1954) on the solubility of amorphous silica indicate that the solubility of neither of these was exceeded in the experiments described in this paper.

SUMMARY

The following points are demonstrated by the study:

1. Dissolution of the wollastonite in the systems described in this paper appears to be hydrogen ion attack with dissolution being incongruent initially on the megascopic scale.
2. The slowest step in the release of calcium appears to be diffusion of calcium through an aqueous surface film of effectively constant

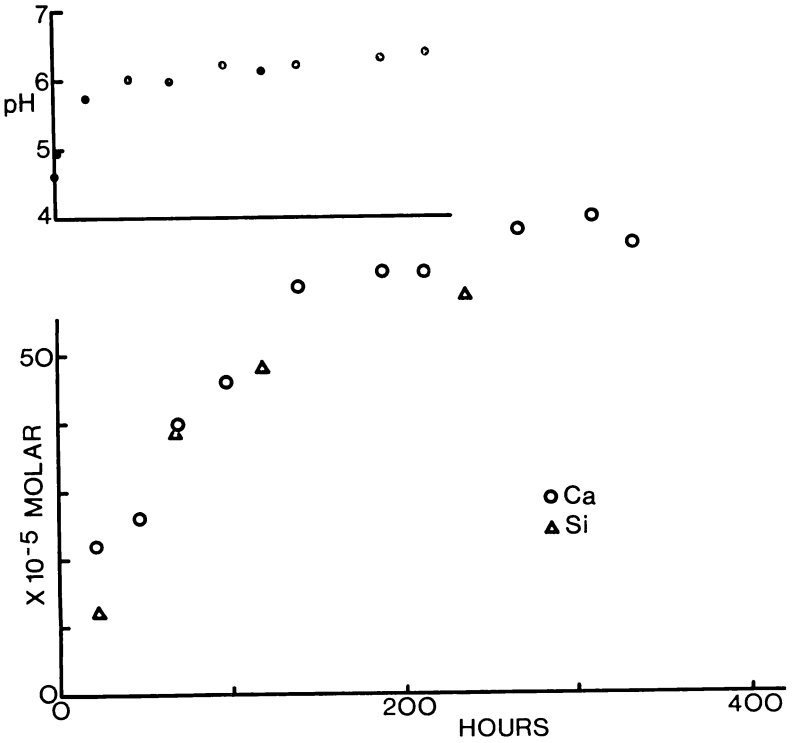

Fig. 7. Plots of molar concentrations of calcium and silica and pH as functions of time for the stirred system under 1 atm of 5 percent CO_2-95 percent O_2 gas.

thickness. The effect of pH appears to be to determine the unbonded calcium concentration near the surface, thereby controlling the activity gradient away from the mineral and the diffusion rate of calcium. Silica release may also be diffusion controlled.

3. In the carbon dioxide-water systems the rate of calcium release appears to decrease as the pH increases and ($a_{Ca,S} - a_{Ca,B}$) decreases. Eventually, a state is reached at which the pH and rate become approximately constant.

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