Clays and Clay Minerals, Vol. 29, No. 2, 101–106, 1981.

DISSOLUTION KINETICS OF PHLOGOPITE. I. CLOSED SYSTEM

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Abstract—Dry ground phlogopite was placed in deionized water saturated with CO_2 at room temperature and pressure. The bulk solution was buffered between a pH of 5 and 6 which is close to the pH of natural weathering systems. The conditions simulated a closed system. After 1010 hr, 2.0% of the total K, 0.95% of the Mg, 0.54% of the Si, and 0.74% of the F had been released, indicating that the dissolution was incongruent. Most of the K was released within 3 min, apparently by a rapid surface exchange with hydrogen ion. One-third of the cation-exchange capacity of this phlogopite arises from cations released from the outer surfaces, while two-thirds arises from the release of more deeply seated cations. All cations exhibited decreasing release with time, the slowest being Si. The rate-controlling "factor" in the later stages is related to the release of Si. It is difficult to distinguish linear from parabolic kinetics in the later stages because of the slow rate of dissolution; however, linear kinetics is most likely. If linear kinetics is applicable, the dissolution rate of Si was 3.8×10^{-17} mole/cm²/sec. Conclusions may be affected by the length of the experimental run.

Key Words—Closed system, Dissolution, Kinetics, Mica, Phlogopite.

INTRODUCTION

The study of mineral dissolution and the rate of release of ions into solution provides insight into natural weathering processes, the evolution of groundwater composition, and the genesis of clay minerals. The results of such studies, however, are often ambiguous; some workers, for example, have reported that the dissolution of mica is congruent (Schnitzer and Kodama, 1976; t'Serstevens *et al.*, 1978), while others found the reaction to be incongruent (Arshad *et al.*, 1972; Huang and Keller, 1973). Because the rate of these reactions at room temperature is very slow, much of the work has been carried out at elevated temperatures and pressures. Unfortunately, extrapolation of the results to surface conditions may or may not be valid. Other studies have utilized strong chemical reagents to accelerate the dissolution process, but conclusions made regarding weathering phenomena from such experiments may be of questionable validity.

The use of buffers in dissolution studies poses special problems. Some workers either were unaware or unconcerned by the fact that commercial buffers contain reagents whose effect on the dissolution is not known. For example, the common buffer for pH 4.01 is a 0.05 M solution of potassium acid phthalate. What is the effect of such a solution already 0.05 M in potassium on the dissolution rate of potassium-rich feldspars or mica? Scott and Smith (1966) showed that very small quantitites of K (a few ppm) greatly retard the rate of release of K from mica. Grandstaff (1980) found large complexing effects for phthalate and other organic anions, compared with pure water. Thus, the validity of such "natural weathering" experiments must be questioned.

In many previous dissolution studies, the mineral sample was usually wet-ground, wet-screened and washed to remove fines, or etched to remove disrupted outer surfaces. Wet-grinding and washing procedures can give rise to large losses of cations, even if organic solvents such as alcohol or acetone are used. The effect of such losses on subsequent results has almost always been ignored. Berner *et al.* (1980) showed that the removal of fines by ultrasonic cleaning or removal of disrupted surfaces by etching with HF-H_2SO_4 resulted in more linear kinetics than if the untreated material had been used. Grandstaff (1980) also obtained more linear kinetics by using mineral grains whose surfaces had been "cleaned" of disrupted material by water washing. Although such treatments have certain advantages, e.g., the elimination of surface ion-exchange effects, does the treated product have the same composition as the untreated material, or is it now coated by a "depleted" layer (e.g., a "hydrogen" surface rather than a "potassium" surface) whose dissolution behavior may be different than that of the unleached material?

To avoid the problems associated with the above treatments and to keep conditions as close as possible to those of natural weathering, the fines were not removed by washing in the present experiments, nor were the grains etched with HF. In addition, CO_2 was used to form carbonic acid with water which acted as a buffer and as a source of hydrogen ions. Each choice, of course, will have its own effect on the results.

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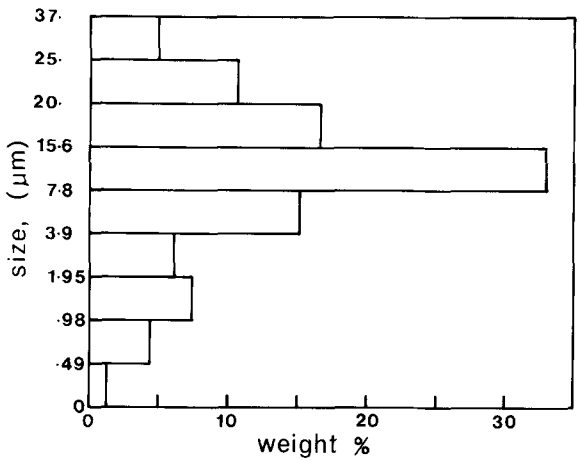


Figure 1. Particle size distribution of −400-mesh phlogopite.

Table 1. The chemical composition and structural distribution of ions in phlogopite.

Chemical composition		Crystallochemical composition based on method used by Deet *et al.* (1962) assuming (O, OH, F) = 24		
SiO_2	39.17	Si	5.573	8.00
Al_2O_3	16.80	Al	2.427	
Fe_2O_3	1.29	Al	0.390	6.02
FeO	2.04	Fe^{3+}	0.138	
MgO	24.28	Ti^{4+}	0.082	
CaO	0.07	Fe^{2+}	0.243	
Na_2O	0.37	Mg	5.148	
K_2O	9.97	Mn	0.015	
TiO_2	0.77	Ca	0.010	1.92
MnO	0.12	Na	0.103	
H_2O+	3.01	K	1.809	
F	2.03	OH	2.859	3.77
		F	0.913	
Total	99.92			
F≡O	0.85			
Total	99.07			

EXPERIMENTAL PROCEDURES

Sample preparation and characterization

Large, clear sheets of electronic grade #4 phlogopite (Madagascar) were obtained from the Spruce Pine Mica Company, Spruce Pine, North Carolina. Using a razor blade, the sheets were peeled as thinly as possibly by hand and reduced to −400 mesh by dry grinding in a Waring Blendor. Although fine grinding may disrupt surfaces, a large surface area is necessary to obtain measurable amounts of ions in solution. The −400-mesh fraction was removed frequently by sieving to prevent excessive surface disruption. The Stokes equivalent size distribution of the −400-mesh material was determined by the pipet method and is shown in Figure 1. A surface area of 3.77 m^2/g was measured on duplicate samples by the single-point BET method using a Quantachrome Monosorb Model MS-5 with flowing N_2 gas. The cation-exchange capacity of duplicate portions was 4.11 meq/100 g as determined by the method of Busenberg and Clemency (1973). The average wet chemical analyses of duplicate −400-mesh samples, using the methods of Shapiro (1975), is shown in Table 1. X-ray examination using the Buerger precession technique showed a 1*M* polytype with cell dimensions a = 5.22 Å, b = 9.21 Å, c = 10.08 Å, and β = 100°0′. X-ray powder diffraction (XRD) patterns of the −400-mesh material showed extremely sharp basal peaks with no evidence of line broadening. A pattern of the material after leaching for 1010 hr was indistinguishable from that of the fresh material.

Reaction conditions

Details of the apparatus and experimental procedure are described in Busenberg and Clemency (1976). Briefly, 25 g of −400-mesh phlogopite was placed in a polyethylene reaction cell with 1 liter of deionized water. The cell was mechanically stirred in a thermostated water bath at 25° ± 2°C. CO_2 saturated with water vapor was bubbled gently through the cell at 1 atm pressure. As noted above, CO_2 was preferred to commercial buffers which may contribute various organic and inorganic ions to the solution whose ionic strength and complexing effects might seriously affect the dissolution rate of mica.

The pH of the CO_2-saturated deionized water was 3.78. Beginning at 3 min after adding the phlogopite, 30-ml aliquots were periodically withdrawn from the cell, filtered through a 0.1-μm Millipore filter into small polyethylene bottles, acidified with 3 drops of concentrated HCl, and tightly stoppered. Eighteen aliquots were taken over the 1010-hr reaction time and analyzed together at the end of the experiment for Si, Al, Fe, Mg, Ca, Na, and K using modified standard procedures described by Brown *et al.* (1970). When the aliquots were taken, the pH of the suspension was measured using a standardized Orion Model 901 Ionalyzer with a Sensorex solid state combination electrode to minimize contamination of the solution by the electrolyte from the electrodes. Fluorine was determined using an Orion fluoride selective-ion electrode and an Orion Model 901 Ionalyzer. A computer program WATEQF (Plummer *et al.*, 1976) was used to calculate the chemical equilibria.

RESULTS AND DISCUSSION

The pH changes and the chemical data are presented in Table 2 and are plotted as mmole/liter vs. time in Figure 2. The rate of release of ions during dissolution may indicate the way the mineral is attacked. Thus, Brindley and Youell (1951), by acid dissolution of chlorite in warm dilute HCl, distinguished between Al lo-

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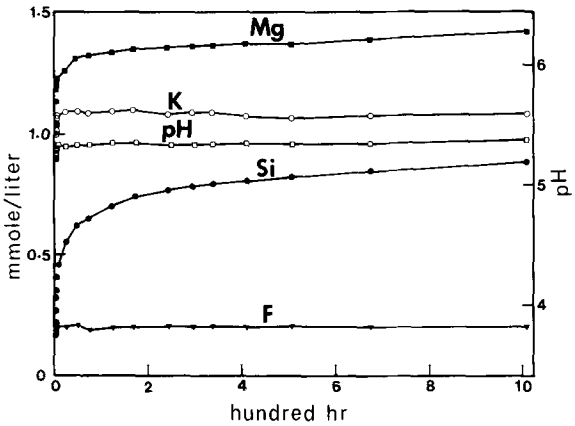


Figure 2. Concentrations of K, Mg, Si, and F and pH plotted against time.

cated in tetrahedral and octahedral sheets. Not every ion is equally useful in following the dissolution. During dissolution of the mica, for example, the solubility product of gibbsite, which is very insoluble at pH 5–6, is quickly exceeded, and Al precipitates as fast as it is dissolved, keeping the amount of Al in solution at a low and constant value. Because precipitated gibbsite cannot be recovered from the suspension, the attack on the tetrahedral sheet cannot be followed by studying the Al concentration of the solution. Likewise, Fe^{2+} oxidizes after release from the mica and precipitates as ferric hydroxide, rendering it useless for studying attack on the octahedral sheet. Fortunately, phlogopite contains about 2% fluorine proxying for hydroxyl in the octahedral sheet. Although it is not possible to measure the release of hydroxyl ions to the solution, fluoride can be measured easily with a fluoride selective-ion electrode, and useful information may thus be obtained on the destruction of the octahedral sheets.

Potassium release and pH

In Figure 2, pH and K concentration are plotted against time from 0 to 1010 hr. Upon addition of the phlogopite, the pH of the CO_2-saturated solution rose rapidly from 3.78 to 5.11 within 3 min, then increased more slowly to about 5.25 within 1 hr, and remained near 5.3 for the remainder of the experiment. About 1.0 mmole of K was released within 3 min, 1.06 mmole after 1 hr, and 1.08 mmole after 1010 hr. In addition, 0.10 mmole of Na was released. The pH and K-concentration curves follow each other closely and suggest an ion-exchange reaction between surface potassium and hydrogen ions in solution (see Garrels and Howard, 1959). This hypothesis can be checked as follows: If the entire surface area can be accounted for by the area of basal planes, and one K ion is associated with each 48.1 $Å^2$ of basal plane, a total surface area of 3.77 m^2/g should yield 0.325 mmole of K (and Na) exposed on the total surface. However, three times this amount of K and Na was exchanged into solution. Re-measurement of the surface area after a 10-min reaction time showed no significant change. The "extra" K and Na ions, (1.18 − 0.32 = 0.86 mmole "extra") then, undoubtedly came from deeper interlayers. Since the amount of K and Na in solution after 3 min (1.08 mmole/25 g) was nearly equal to the cation-exchange capacity (1.03 meq/25 g) about ⅓ of the cation-exchange capacity of this particular phlogopite must arise from surface cations and ⅔ from more deeply seated cations, or from cations associated with edges.

Table 2. pH and concentration in mmole/liter of Mg, K, Si, F, Na, Al, Fe, and Ca in solution at various times.

Time (hr)	pH	Mg	K	Si	F	Na	Al	Fe	Ca
0.050	5.11	0.897	1.00	0.211	0.157	0.0802	0.0705	0.0146	0.0067
0.167	5.19	1.04	1.02	0.264	0.153	0.0833	0.0821	0.0196	0.0086
0.5	5.23	1.14	1.04	0.314	0.181	0.0885	0.0862	0.0225	0.0107
1	5.25	1.18	1.06	0.345	0.171	0.0885	0.0887	0.0235	0.0122
3	5.28	1.20	1.06	0.402	0.199	0.0866	0.0858	0.0235	0.0125
7	5.32	1.23	1.08	0.457	0.207	0.0874	0.0849	0.0235	0.0133
24	5.31	1.26	1.09	0.554	0.199	0.0897	0.0862	0.0229	0.0135
50	5.32	1.32	1.09	0.621	0.203	0.0917	0.0854	0.0221	0.0146
74	5.33	1.33	1.09	0.652	0.186	0.0919	0.0842	0.0209	0.0154
124	5.34	1.34	1.09	0.703	0.196	0.0924	0.0859	0.0203	0.0156
170	5.34	1.35	1.10	0.739	0.198	0.0929	0.0860	0.0194	0.0158
243	5.33	1.36	1.08	0.766	0.203	0.0914	0.0831	0.0174	0.0154
294	5.32	1.37	1.09	0.784	0.197	0.0923	0.0847	0.0184	0.0160
338	5.33	1.36	1.09	0.794	0.201	0.0939	0.0860	0.0172	0.0164
409	5.34	1.37	1.07	0.803	0.199	0.0915	0.0839	—	0.0156
506	5.33	1.37	1.06	0.821	0.198	0.0940	0.0852	0.0136	0.0162
673	5.34	1.39	1.08	0.849	0.196	0.0953	0.0857	0.0124	0.0185
1010	5.38	1.42	1.08	0.877	0.200	0.0969	0.0837	0.0079	0.0185

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The surface area of the solid product after 1010 hr of reaction time was 5.78 m^2/g in contrast to that of the fresh material, 3.77 m^2/g. This increase is probably due to the presence of precipitated gibbsite rather than to an actual increase in surface area of the phlogopite. Nevertheless, the concentration of K increased very little during the 1010 hr, and it may be concluded that the basal surface area did not change during this period. The release of interlayer K by exfoliation and cleavage into separate flakes suggested by Scott and Smith (1967) was not observed.

Magnesium and silicon release

Mg and Si are present in the mineral in approximately equal ionic proportions (Table 1). The solution is undersaturated with respect to silica gel and magnesium minerals even after 1010 hr of reaction. Figure 2 shows that magnesium is released from the mica at about twice the rate of silicon. Since the final solution shows a large increase in the activities of Mg and Si, this environmental change will slow the rate of the forward reaction. A second possibility for the slowdown in release rate is that a "protective layer, residue, or coating" may have developed around particles of the mica. This material could be composed of a collapsed aluminosilicate residue remaining after removal of potassium and magnesium, or of precipitated $Al(OH)_3$ or $Fe(OH)_3$. The term "residue" implies that the ingredients were never in solution, while the ingredients of a "precipitate" were previously in ionic form in the solution. Both Al and Fe apparently precipitated from the solutions and were probably filtered off along with the mica on the 0.1-μm filter. When $Al(OH)_3$ precipitates from solution, it quickly exceeds a particle size of 0.1 μm and is filtered off (Smith and Hem, 1972; Busenberg and Clemency, 1976). In Table 2 the Fe concentration decreases with time, possibly due to a growth of $Fe(OH)_3$ to a size large enough to be filtered off on the 0.1-μm filter. Thus, it is unlikely that $Al(OH)_3$ and $Fe(OH)_3$ formed a precipitated protective coating on the mica particles. Petrovic *et al.* (1976), Berner and Holdren (1977, 1979), and Holdren and Berner (1979) in experiments on feldspar dissolution found no evidence of a protective layer, either residual or precipitated.

Incongruent dissolution

After 1010 hr, 0.95% Mg, 0.74% F, and 0.54% Si are present in the solution; therefore the dissolution is incongruent. The release of Si, being the slowest, is the rate-determining "factor," and the rate of dissolution of phlogopite will thus be affected by the rate of release of Si in the final stages, i.e., the rate of destruction of the tetrahedral sheets. This should not be construed as the rate-determining "step" of a sequential series of reactions in which the product of one becomes the reactant of the following steps.

Kinetics

The dissolution kinetics of micas has been found to be both linear (Gastuche, 1963) and parabolic (Cabrera and Talibudeen, 1978; Huang and Keller, 1973; Newman and Brown, 1969). Huang and Keller (1973) also found that Si had the slowest release rate from illite. The concentrations of Mg and Si are plotted against time in Figure 2. The curve has an almost zero slope after 300 hr, however, the curve appears to be a straight line, suggesting linear kinetics. The same kind of low slope is found when Mg and Si are plotted against the square root of time, suggesting parabolic kinetics after 300 hr. This in turn suggests diffusion through a protective layer, in contrast to the linear kinetics found by plotting concentration against time. Because both curves have very low slopes, it is difficult to tell which type of kinetics is applicable. If the last 6 points (294–1010 hr) of Si-release are considered on the basis of linear kinetics, the release of Si will be 3.8×10^{-17} mole/cm^2/sec (after 294 hr). On the basis of parabolic kinetics, the release rate of Si will be 1.1×10^{-13} mole/$cm^2/sec^{\frac{1}{2}}$ after 294 hr. Linear kinetics appears to be most likely.

Interpretations are complicated by: precipitation of released ions as their solubility products are exceeded, possible effects of a "protective layer or residue" on the mineral particles formed by collapse of leached surface layers or precipitation on mineral surfaces, the effect on the dissolution rate of increasing activities of ions in the solution, and the difficulty of distinguishing between linear and parabolic kinetics. If the ion activities of the solution could be reduced, for example, more of the mineral might dissolve, possibly clarifying the kinetics picture. An attempt to reduce the ionic activities by means of a cation-exchange resin acting as a trap for dissolved ions is described in Part II of this study.

ACKNOWLEDGMENTS

This study was carried out under the support of Army Research Office Grant DAAG29-77-G-0199. The authors thank Dr. George W. Brindley for valuable advice and suggestions.

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(Received 22 February 1980; accepted 23 August 1980)

Резюме—Сухой, перемеленый флогопит был помещен в деионизированную воду, насыщенную CO_2 при комнатной температуре и давлении. Основной раствор был буферован между pH 5 и 6, эти величины близки к pH в системе природной эрозии. Условия симулировали замкнутую систему. После 1010 часов 2% из всего K, 0,95% из Mg, 0,54% из Si и 0,74% из F были освобождены, что указывает на инконгруэнтное растворение. Большая часть K была освобождена во время 3 минут, очевидно, при помощи быстрого поверхностного обмена с водородными ионами. Одна треть катионообменной емкости этого флогопвта является результатом освобождения катионов из внешних поверхностей, а две трети—резюльтатом освобождения катионов, находящихся внутри. Для всех катионов наблюдалась уменьшающаяся способность освобождения со временем, самая медленная для Si. "Фактор," регулирующий скорость обмена на более поздних этапах реакции, связан с освобождением Si. На этих поздних этапах трудно отличить линейную кинетику от параболической вследствие медленной скорости растворения. Тем не менее, линейная кинетика является более вероятной. При предположении линейной кинетики, скорость растворения Si была 3, 8×10^{-17} моль/см^2/сек. Время проведения экспериментов может влиять на эти выводы. [E.C.]

https://doi.org/10.1346/CCMN.1981.0290203 Published online by Cambridge University Press

Resümee—Trocken gemahlener Phlogopit wurde in deionisiertes Wasser gegeben, das bei Zimmertemperatur und Atmosphärendruck mit CO_2 gesättigt war. Die Gesamtlösung wurde auf pH 5–6 gepuffert, was dem pH-Wert der natürlichen Verwitterung nahekommt. Die Bedingungen simulierten ein geschlossenes System. Nach 1010 Stunden Reaktionszeit waren 2,0% des Gesamt-Kalium, 0,95% des Mg, 0,54% des Si, und 0,74% des F in Lösung gegangen. Das deutet darauf hin, daß die Auflösung inkongruent verlief. Das meiste Kalium ging innerhalb von 3 Minuten in Lösung, offensichtlich durch einen schnellen Austausch gegen Wasserstoffionen an den Oberflächen. Ein Drittel der Ionenaustauschkapazität dieses Phlogopit rührt von den Kationen her, die von den äußeren Oberflächen in Lösung gehen, während zwei Drittel von tiefer gelegenen Kationen herrühren. Alle Kationen gingen mit zunehmender Zeit in abnehmenden Mengen in Lösung, wobei Silicium am langsamsten in Lösung ging. Der geschwindigkeitsbestimmende Faktor in den letzten Stadien hängt mit dem Inlösunggehen des Siliciums zusammen. In den späten Stadien ist, wegen der geringen Lösungsgeschwindigkeit, schwer zwischen linearer und parabolischer Kinetik zu unterscheiden; jedoch ist eine lineare Kinetik am wahrscheinlichsten. Wenn eine lineare Kinetik angewendet werden kann, dann betrug die Lösungsgeschwindigkeit für Silicium $3{,}8 \times 10^{-17}$ Mol/cm²/sec. Diese Schlußfolgerungen könnten durch die Länge der Versuchszeit beeinflußt sein. [U.W.]

Résumé—De la phlogopite sèche moulue a été placée dans de l'eau déionisée saturée de CO_2 à température et pression ambiantes. La solution en masse a été tamponée entre un pH de 5 et de 6, ce qui est proche du pH de systèmes d'altération naturels. Après 1010 heures, 2,0% du K total, 0,95% du Mg, 0,54% du Si, et 0,74% du F avaient été relâchés, indiquant que la dissolution était inconforme. La plupart du K a été relâché endéans 3 min, apparemment par un échange de surface rapide avec l'ion hydrogène. Un tiers de la capacité d'échange de cations de cette phlogopite provient de cations relâchés des surfaces externes, tandis que deux tiers proviennent du relâchement de cations situés plus profondément. Tous les cations ont exhibé un relâchement décroissant à mesure que le temps augmentait, le plus lent étant Si. Le "facteur" contrôllant l'allure dans les derniers stages est apparenté au relâchement de Si. Il est difficile de différencier la kinétique linéaire de la kinétique parabolique dans les derniers stages à cause du taux de dissolution lent, cependant, la kinétique linéaire est la plus probable. Si la kinétique linéaire peut être appliquée, le taux de dissolution de Si était $3{,}8 \times 10^{-17}$ mole/cm²/sec. Les conclusions peuvent être affectées par la longueur de l'expérience. [D.J.]

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