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DISSOLUTION KINETICS OF PHLOGOPITE. II. OPEN SYSTEM USING AN ION-EXCHANGE RESIN

CHARLES V. CLEMENCY AND FENG-CHIH LIN

Department of Geological Sciences, State University of New York at Buffalo
4240 Ridge Lea Road, Amherst, New York 14226

Abstract—The rate of dissolution of phlogopite in an open system was measured at low temperature and pressure and at pH 3–5. The maximum dissolution rate was achieved by maintaining extremely low ionic concentrations in the solution using a cation-exchange resin (hydrogen form) as a trap for released cations. The resin also served as a source of hydrogen ions and acted as a buffer. The concentrations of ions adsorbed on the resin and remaining in solution were measured, along with surface area and cation-exchange capacity. The amount of phlogopite dissolved after 1010 hr was 67 times that dissolved using a CO_2-buffered, closed-system method. During the first hour of the experiment, dissolution was incongruent, but later became congruent from 1 to 1010 hr. From 1 to 200 hr the reaction had linear kinetics. The dissolution rate for the first 200 hr of the reaction was 2.0×10^{-14} mole $KMg_3AlSi_3O_{10}(OH)_2/cm^2/sec$. Since no evidence of parabolic kinetics was found, there is no reason to postulate the formation of a "protective layer."

Key Words—Dissolution, Ion-exchange resin, Kinetics, Open system, Mica, Phlogopite.

INTRODUCTION

Part I of this study showed that little phlogopite dissolves under simulated weathering conditions in a closed system. Scott and Smith (1966) pointed out that a very small concentration (a few ppm) of K^+ in solution exerts a repressive effect on the further dissolution of micas, and Hanway *et al.* (1957) showed that small amounts of K^+ or NH_4^+ in the solution prevented the release of NH_4^+ from clay minerals. Removal of such "repressive" ions should presumably enhance the dissolution reaction. A strong acid (H^+-form) cation-exchange resin was used to extract fixed ammonium from layer silicates and soils by Arnold (1958), Scott *et al.* (1960), Haagsma and Miller (1963), Barber and Matthews (1962), and Salomon and Smith (1957). Similar materials have also been used to regulate the ionic composition of clay systems (La Iglesia and Martin-Vivaldi, 1975; Bolt and Frissel, 1960; Lahav *et al.*, 1976). The present study examined the dissolution of phlogopite in open-system conditions where products were continually removed from the system by entrapment in a cation-exchange resin. The resin also acted as a source of hydrogen ions and served as a buffer.

EXPERIMENTAL PROCEDURE

A portion of the phlogopite described by Lin and Clemency (1981) was dry ground to −400 mesh. Using the techniques described earlier, the surface area was determined to be 4.01 m^2/g and the cation-exchange capacity to be 3.5 meq/100 g. The chemical composition was assumed to be the same as listed in Table 1 of Lin and Clemency (1981). One gram of cleaned Amberlite IR-120 cation-exchange resin (hydrogen form, 20–50 mesh), 0.25 g of −400-mesh phlogopite, and 10 ml of deionized water were placed into twenty 15-ml plastic test tubes. The test tubes were capped and mounted on a Roto-Torque Heavy Duty Rotator (Cole-Palmer Instrument Company). Starting at 3 min, and at each desired time interval thereafter, one test tube was removed from the rotator, the pH was measured, and the contents were separated for analysis.

Immediately upon uncapping the test tube, the pH was measured using an Orion Model 901 Ionalyzer equipped with a Sensorex solid state combination pH electrode. The contents of the test tube were then separated into solution, resin, and mica fractions as follows: The contents of the test tube were shaken, the larger resin particles were allowed to settle, and the phlogopite suspension was decanted into a 50-ml plastic filtering syringe and filtered twice through separate 0.1-μm Millipore filters. The filtrate was acidified with one drop of concentrated HNO_3, capped tightly, and stored. When all filtrates had been accumulated, they were analyzed at the same time using the modified methods of Brown *et al.* (1970) for Si, Al, Fe, Mg, Na, and K. Fluorine was determined with a selective-ion electrode using the method described in the Orion Company manual supplied with the electrode. These portions are referred to as the "10 ml of solution" fractions (Table 1).

The resin in the bottom of the test tube was transferred to a 120-mesh stainless steel sieve with distilled water. Adhering phlogopite was removed by washing with a minimum of distilled water. The resin was then transferred to a quartz column. This column was tapered at the bottom so that the resin particles did not pass through. The cations were stripped from the resin by passing 50 ml of 4 N HNO_3 slowly through the resin column. The leachate was caught in a polyethylene bot-

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Table 1. Concentrations in mmole/liter of K, Mg, Al, F, Si, Na, and Fe and the pH of the "10 ml of solution."

Time (hr)	pH	K	Mg	Al	F	Si	Na	Fe
0.05	4.6	0.0342	0.0775	0.0218	0.0489	0.170	0.0133	0.0056
0.17	4.03	0.0328	0.0559	0.0266	0.0134	0.493	0.0081	0.0037
0.5	3.62	0.0097	0.0225	0.0209	0.0327	0.800	0.0096	0.0045
1	3.47	0.0085	0.0200	0.0285	0.161	1.15	0.0123	0.0017
3	3.35	0.0062	0.0112	0.0129	0.356	1.96	0.0112	0.0011
7	3.24	0.0047	0.0085	0.0095	0.662	3.52	0.0123	0.0017
15	3.15	0.0097	0.0070	0.0152	1.13	4.76	0.0156	0.0967
24	3.09	0.0135	0.0041	0.0212	1.49	4.89	0.0107	0.135
48	3.04	0.0328	0.0223	0.0323	2.01	4.94	0.0223	0.0680
72	3.05	0.0809	0.0972	0.0718	2.59	4.75	0.0276	0.0262
120	2.94	0.117	0.126	0.103	3.17	4.43	0.0244	0.0207
168	2.98	0.142	0.130	0.121	2.98	3.95	0.0324	0.0262
240	3.07	0.140	0.0274	0.140	2.32	3.62	0.0313	0.0017
336	3.15	0.195	0.0497	0.225	1.89	3.33	0.0439	0.0045
432	3.14	0.212	0.0340	0.250	1.72	3.36	0.0414	0.0011
504	3.20	0.249	0.0156	0.273	1.53	3.36	0.0398	0.0006
672	3.23	0.282	0.0131	0.296	1.46	3.28	0.0451	0
840	3.36	0.333	0.0120	0.324	1.37	3.22	0.0531	0
1010	3.56	0.416	0.0099	0.355	1.19	3.31	0.0613	0

tle, capped tightly, and stored. These portions are referred to as the "50 ml from resin" fractions (Table 2).

The phlogopite residue on the Millipore filters was air-dried and examined by X-ray powder diffraction and infrared spectroscopy. No changes were detectable between the fresh material and the material leached for 1010 hr. The computer program WATEQF (Plummer *et al.*, 1976) was used for the equilibrium calculations.

EXPERIMENTAL RESULTS

Si and most of the Al are located in the tetrahedral sheets of phlogopite. Their appearance in solution reflects the rate of attack on the tetrahedral part of the mica structure. Al in the pH range of this experiment (3–5) exists primarily as the cationic form Al^{3+}; thus, any Al released into solution should be picked up by the cation-exchange resin before the solubility product of gibbsite is exceeded. Si, on the other hand, exists in this pH range as neutral undissociated H_4SiO_4 or as $(H_3SiO_4)^-$. Neither form should be picked up by the cation-exchange resin, and Si should accumulate in the solution. Mg, K, Na, and Fe exist as cations at these pHs and should also be picked up by the resin. K is located both on the outer surfaces and in the interlayers of phlogopite; thus, its early detection in solution reflects rapid removal from outer surfaces, and its later

Table 2. Concentrations in mmole/liter of K, Mg, Al, F, Fe, and Na in the "50 ml from resin" fraction.

Time (hr)	K	Mg	Al	F	Fe	Na
0.05	0.183	0.110	0.0163	0.0078	0.0076	0.0217
0.17	0.223	0.200	0.0204	0.0204	0.0134	0.0230
0.5	0.300	0.296	0.0428	0.0219	0.0223	0.0268
1	0.362	0.375	0.0897	0.0156	0.0346	0.0293
3	0.437	0.516	0.149	0.0127	0.0417	0.0331
7	0.532	0.790	0.282	0.0135	0.0690	0.0368
15	0.645	1.25	0.452	0.0209	0.0981	0.0418
24	0.753	1.70	0.714	0.0335	0.121	0.0444
48	1.01	2.52	1.28	0.0877	0.201	0.0544
72	1.25	3.72	1.96	0.178	0.295	0.0718
120	1.82	5.32	2.66	0.335	0.416	0.0970
168	2.36	6.89	3.63	0.609	0.551	0.123
240	2.85	8.20	4.60	0.876	0.669	0.141
336	3.15	9.25	5.19	1.09	0.752	0.157
432	3.38	9.87	5.40	1.18	0.788	0.163
504	3.50	10.0	5.83	1.21	0.879	0.176
672	3.59	10.3	5.98	1.28	0.811	0.173
840	3.62	10.6	6.19	1.31	0.884	0.182
1010	3.63	10.6	6.14	1.37	0.865	0.181

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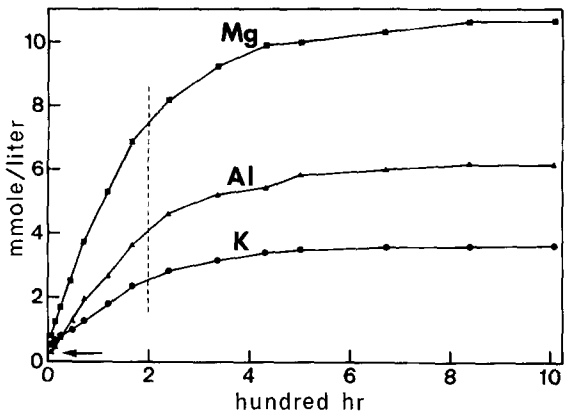


Figure 1. Concentrations in mmole/liter of Mg, Al, and K from the "50 ml from resin" fraction plotted as a function of time. The arrow indicates the amount of phlogopite dissolved after 1010 hr using the CO_2 method described by Lin and Clemency (1981).

detection reflects a slower attack on the deeper interlayers. The rate of release of Mg should be related to the rate of decomposition of the octahedral sheets. Fe and Na are present in very small amounts in the phlogopite under investigation. Their release patterns are not particularly illuminating, except that iron was apparently adsorbed on the resin before it was oxidized and precipitated, in contrast to its behavior noted in Part I. Fluoride ions were mostly adsorbed on the resin, probably as positively charged complexes of $(MgF)^+$, $(AlF_2)^+$, or $(AlF)^{2+}$. Thus, two reservoirs for the ions released from phlogopite can be distinguished: the 10 ml of solution in the test tube, and the resin. The sum of these ions, plus any ions precipitated as insoluble phases will equal the total number of ions released from the phlogopite.

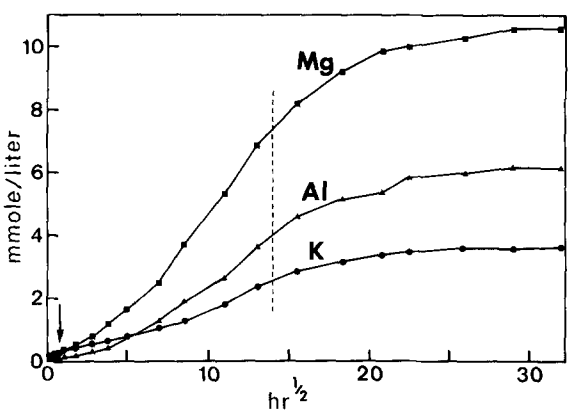


Figure 2. Concentrations in mmole/liter of Mg, Al, and K from the "50 ml from resin" fraction plotted as a function of the square root of time. The dashed line signifies 200 hr.

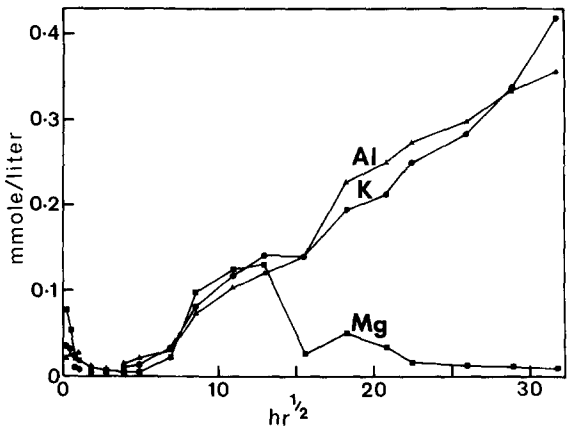


Figure 3. Concentrations in mmole/liter of Al, K, and Mg in the "10 ml of solution" fraction plotted as a function of the square root of time.

The resin fraction

Figure 1 shows the concentrations (in mmole/liter) of K, Al, and Mg on the resin listed in Table 2 vs. time from 0 to 1010 hr. The arrow in the lower left-hand corner of the figure indicates for comparison the small amount of these same ions released in the CO_2 experiment described in Part I. The dashed line signifies 200 hr. In the present experiment, the low ion activities of the solution maintained by the resin permitted continued dissolution of the phlogopite and also prevented the precipitation of insoluble products, specifically gibbsite and ferric hydroxide. Silicic acid, however, accumulated in the solution and precipitated when it exceeded the solubility product of amorphous silica. This material had a very high surface area and could not be separated from the mica. The 82 m^2/g surface area of the phlogopite after 840 hr reaction, a large increase from 4.01 m^2/g for the fresh material, is probably due to precipitated silica gel.

The initial portion of the curves in Figure 1 are approximately linear and are consistent with the linear kinetics reported by Gastuche (1963). Near the origin, the K curve crosses the Al curve because of the rapid initial exchange of surface K ions as discussed in Part I. Figure 2 shows the concentrations of K, Al, and Mg vs. the square root of time. The curves are not linear and indicate that the dissolution is not diffusion controlled by a "protective layer" that formed on the surface of the mica.

The 10-ml solution fraction

Table 1 lists the pH values and the concentrations of K, Mg, Al, F, Si, Na, and Fe in the 10 ml of solution. The cation activities were very low. The computer program WATEQF showed that, except for amorphous silica, no other precipitates formed in the 10 ml of solution because all ionic activity products were below

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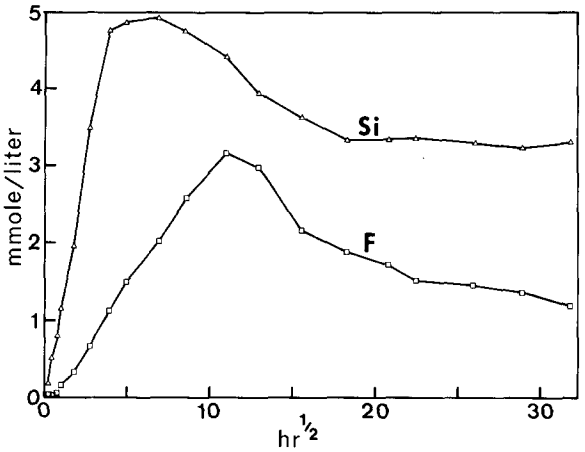


Figure 4. Concentrations in mmole/liter of Si and F in the "10 ml of solution" fraction plotted as a function of the square root of time.

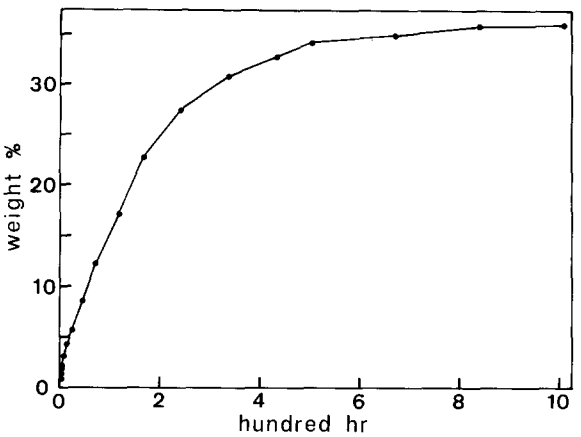


Figure 5. The average weight percentage of phlogopite dissolved plotted as a function of time.

their respective solubility products. The presence of small amounts of Al and K in the 10 ml of solution arises from a distribution coefficient between the solution and the resin for each ion.

The starting pH of 10 ml of deionized water containing 1 g of resin was 3.6. Upon addition of 0.25 g of phlogopite, the pH rose to 4.6 within 3 min, dropped back to 4.0 in 10 min, then to 3.6 after 30 min, and to 3.0 after 50 hr. The sudden increase in pH to 4.6 upon addition of the phlogopite was due to the rapid exchange of cations, such as K and Na, on the outer surfaces of the mineral particles for hydrogen ions in solution as described in Part I. As the flood of K ions released into the solution was adsorbed by the resin, H was released from the resin and the pH decreased. Over the 1010 hr, the pH was buffered between 3 and 5 by the resin.

The decrease of the Mg curve (Figure 3) after 150 hours ($t^{\frac{1}{2}} = 12$) can be explained by the formation of a positively charged $(MgF)^+$ complex that was adsorbed on the resin. In Figure 4, the concentration of F is seen to decrease at about the same rate as Mg decreases in Figure 3, reflecting the formation of a $(MgF)^+$ complex. The Si curve in Figure 4 also reaches a maximum, then decreases, in a manner similar to the F curve. The breaks appear, however, at different times, and the Si and F curves are therefore independent of each other. Analysis of the resin extracts showed more fluoride on the resin than in the 10 ml of solution in the later stages, in accord with the formation and adsorption of cationic complexes. If the total fluoride released (fluorine on resin + fluorine in solution) is plotted against the square root of time, the total F curve is not linear between 0 and 14 $hr^{\frac{1}{2}}$. Therefore, like the release of the cations, the release of F was not parabolic in the early stages. Again, no evidence for postulating the formation of a "protective layer" exists.

DISCUSSION

The present data show that dissolution of phlogopite during the first hour is incongruent and is caused by rapid hydrogen-ion exchange on the surface of phlogopite, in agreement with the results of Part I, and with the results of Arshad *et al.* (1972) and Huang and Keller (1973). After the first hour, however, the dissolution becomes congruent, in agreement with Schnitzer and Kodama (1976) and t'Serstevens *et al.* (1978). Because silica showed the slowest release rate of all the ions in Part I, the rate-controlling "factor" in the later dissolution is probably the destruction of the tetrahedral sheets; therefore, the dissolution changes from incongruent to congruent after the first hour, in keeping with linear kinetics.

The average total percentage of phlogopite dissolved as a function of time is shown in Figure 5. A total of 36% of the phlogopite had dissolved by the end of the experiment at 1010 hr. From the eight data points between 2 and 200 hr in Figure 5 a phlogopite dissolution rate of 0.12%/hr can be calculated, equal to 2.0×10^{-14} mole of $KMg_3AlSi_3O_{10}(OH)_2/cm^2/sec$.

After 200 hr, the dissolution rate decreased (Figure 5) because (1) the resin may have approached saturation; (2) the total surface area may have decreased as the finer particles were dissolved, thus reducing the amount of surface exposed to dissolution; (3) the outer surface disrupted by grinding may have been more soluble; (4) a "protective layer" or residue formed or (5) the increasing concentration of ions in solution may have created a "mass action effect" that retarded the dissolution rate of the phlogopite (Scott and Smith, 1966; Hanway *et al.*, 1957). Although the difficulty of maintaining the same rate of total dissolution as total surface area decreased is recognized, the last possibility is thought to be the most important.

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Резюме—Скорость растворения флогопита измерялась в открытой системе при низких температуре и давлении, и при pH от 3 до 5. Максимальная скорость растворения достигалась путем поддерживания очень низкой концунтрации ионов в растворе при использовании катионообменной смолы (водородная форма) для подхвата освобождающихся катионов. Смола использовалась также, как источник водородных ионов и действовала как буферный раствор. Измерялись концентрации ионов, которые были адсорбированы смолой и ионов, которые оставались в растворе, а также площадь поверхности и катионообменная емкость. Количество флогопита, растворенного после истечения 1010 часов, было в 67 раз больше, чем количество флогопита, растворенного с помощью буферного раствора CO_2 методом замкнутой системы. Во время первого часа эксперимента растворение являлось инконгруэнтным, но потом, от 1 до 1010 часов становилось конгруэнтным. От 1 до 200 часов кинетика реакции была линейная. Скорость растворения во время начальных 200 часов реакции была $2{,}0 \times 10^{-4}$ моль $KMg_3AlSi_3O_{10}(OH)_2/cm^2/$сек. Так как никакой параболической кинетеки не наблюдалось, нет оснований для предположения о формировании "защитного слоя." [E.C.]

Resümee—Die Lösungsgeschwindigkeit von Phlogopit in einem offenen System wurde bei niedriger Temperatur und niedrigem Druck bei pH-Werten von 3–5 gemessen. Die größte Lösungsgeschwindigkeit erhielt man, wenn die Ionenkonzentrationen in der Lösung extrem niedrig gehalten wurden, indem ein Ionenaustauschharz (Wasserstoff-Form) als Falle für die in Lösung gegangenen Kationen verwendet wurde. Das Austauschharz diente auch als Wasserstoffionenquelle und als Puffer. Es wurden die am Austauschharz adsorbierten Ionenkonzentrationen und die in Lösung verbleibenden Ionenkonzentrationen gemessen sowie die Oberfläche und die Ionenaustauschkapazität. Die nach 1010 Stunden gelöste Phlogopitmenge war 67 × so hoch wie die, die im geschlossenen System mit CO_2-Pufferung gelöst wurde. Während der ersten Stunde des Experimentes war die Lösung inkongruent, wurde aber später im Zeitraum von 1–1010 Stunden kongruent. Im Zeitraum von 1–200 Stunden hatte die Reaktion eine lineare Kinetik. Die Lösungsgeschwindigkeit für die ersten 200 Stunden der Reaktion betrug $2{,}0 \times 10^{-14}$ Mol $KMg_3AlSi_3O_{10}(OH)_2/cm^2/$sec. Da kein Hinweis für eine parabolische Kinetik gefunden wurde, gibt es keinen Grund, die Bildung einer Schutzschicht anzunehmen. [U.W.]

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Résumé—Le taux de dissolution de la phlogopite dans un système ouvert a été mesuré à température et pression basses, et à un pH de 3–5. Le taux de dissolution maximum a été atteint en maintenant des concentrations ioniques extrèmement basses dans le système, utilisant une résine à échange de cations (forme hydrogène) comme piège pour les cations relâchés. La résine a aussi servi de source pour les ions hydrogène et s'est comportée comme tampon. Les concentrations des ions adsorbés sur la résine et de ceux restant en solution ont été mesurées, ainsi que l'aire de surface et la capacité d'échange de cations. La quantité de phlogopite dissoute après 1010 heures était 67 fois plus grande que celle dissoute utilisant une méthode tamponée au CO_2, à système fermé. Pendant la première heure de l'expérience, la dissolution était inconforme mais elle est devenue conforme plus tard, de 1 à 1010 heures. D'une à 200 heures, la réaction avait une kinétique linéaire. Le taux de dissolution pour les 200 premières heures de la réaction était $2{,}0 \times 10^{-14}$ mole $KMg_3AlSi_3O_{10}(OH)_2/cm^2/sec$. Puisqu'il n'a été trouvé aucune évidence de kinétique parabolique, il n'y a pas de raison pour postuler la formation d'une "couche protectrice." [D.J.]

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