The dissolution kinetics of brucite, antigorite, talc, and phlogopite at room temperature and pressure

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Abstract

Dissolution experiments were done on a series of layer-type Mg minerals (brucite, antigorite, talc, and phlogopite) of progressively more complex structure and chemical composition. Twenty-five gram portions of these minerals were dry-ground to <400 mesh and then subjected to controlled dissolution in distilled water at 25°C and 1 atm CO_2 partial pressure. For antigorite, talc, and phlogopite, Mg from the octahedral sheets was released more rapidly than was Si from the tetrahedral sheets, *i.e.*, the dissolution was incongruent. It appears that the solubility of these layer-type minerals is related to the relative number of octahedral to tetrahedral sheets present in the structure, *i.e.*, the dissolution kinetics of layer-type silicate minerals is controlled by the rate of destruction of the tetrahedral silica sheets of the mineral.

Introduction

The present experiments were designed to test the hypothesis that the dissolution kinetics of layer-type magnesium silicate minerals are controlled by the rate of destruction of the tetrahedral silica sheets of the mineral. The rate of release of Mg and Si were used to follow the destruction of the octahedral and tetrahedral sheets, respectively. The layer-type magnesium mineral series brucite, antigorite, talc, and phlogopite were chosen for study. This series shows increasing chemical and structural complexity. Originally, it was also planned to study the analogous series of aluminum layer-type minerals gibbsite, kaolinite, pyrophyllite, and muscovite for comparison, but this study was precluded because gibbsite precipitates immediately upon release of Al from these minerals because of its great insolubility (Hem and Roberson, 1967). Since the precipitated gibbsite cannot be separated from the mineral suspension, the rate of release of Al cannot be followed, and this aspect of the study had to be abandoned.

In earlier studies by the present authors, the dissolution in closed systems of phlogopite (Lin and Clemency, 1981a) and of two muscovites (Lin and Clemency, 1981b) was found to be incongruent. In these experiments the release rate of silicon was the slowest of all the ions and appeared to be the rate controlling "factor". Other workers, such as Luce *et al.*, (1972) found serpentine to dissolve incongruently, whereas Hostetler and Christ (1968) found chrysotile to dissolve congruently in water. In our present study, we found antigorite and also talc to dissolve incongruently.

Sample characterization and preparation

Clear white platy transparent brucite (Madoc, Ontario) was obtained from Ward's Natural Science Establishment Inc. Greenish-yellow massive antigorite-serpentine (Warren County, New York) and pale green talc (Chester, Vermont) were from the collections of the Department of Geological Sciences, State University of New York at Buffalo. The phlogopite (Madagascar) was the same material as used by Lin and Clemency (1981a). Antigorite was reduced to <400 mesh by means of a Spex Industries Model 8500 "Shatterbox"; brucite and talc were reduced to <400 (<38 μ) mesh by dry grinding in a Waring blender, with frequent intermittent sieving to remove the <400 mesh fraction so as to prevent excessive surface disruption. The average of duplicate wet chemical analyses of <400 mesh brucite, antigorite, and talc using the methods of Shapiro (1975), are shown in Table 1. The calculated crystallochemical compositions are based on the total cation valence. The Stokes equivalent size distributions of the <400 mesh material was determined by the pipet method

Table 1. The chemical compositions of brucite, antigorite, and talc used in the experiments

	Brucite	Antigorite	Talc
SiO_2	0.12	42.78	62.03
Al_2O_3	0.05	0.13	0.13
Fe_2O_3	0.17	0.72	0.23
FeO	0.57	0.06	3.21
MgO	68.78	42.47	29.54
CaO	0.44	0.47	0.00
Na_2O	0.01	0.01	0.06
K_2O	0.02	0.05	0.00
TiO_2	0.00	0.01	0.00
MnO	0.16	0.04	0.00
H_2O+	30.49	13.44	4.81
Total	100.81	100.18	100.01

Numbers of ions

	Brucite		Antigorite		Talc	
Si	0.007		3.939	3.95	7.954	7.97
Al	---		0.011		0.015	
Fe^{3+}	0.007		0.055		0.015	
Fe^{2+}	0.028		0.006		0.347	
Mn	0.007	6.06	0.006		---	
Mg	5.978		5.826	5.95	5.649	6.03
Ca	0.028		0.044		---	
Na	---		---		0.015	
K	---		0.011		---	
OH	11.872	11.87	8.266	8.27	4.116	4.12

on separate fractions and are shown in Table 2. The average surface areas of brucite (4.05 m²/g), antigorite (17.0 m²/g), talc (4.90 m²/g), and phlogopite (3.77 m²/g) were measured by analyzing duplicate samples by the single-point BET[1] method using a Quantachrome Monosorb MS-5, with flowing N² gas. Analogous data for phlogopite can be found in Lin and Clemency (1981a).

X-ray diffraction revealed no impurities in any of the samples. Under the binocular microscope at about 15×, neither brucite, antigorite, talc, or phlogopite contained any visible impurities. Under the petrographic microscope at 35×, both the antigorite and the phlogopite contained a small amount of black opaque particles of less than 0.01 mm in size, probably much less than 0.1% by weight. The brucite appeared quite pure at 35×, whereas the talc contained a few scattered grains of a yellow sulfide

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[1]Brunauer *et al.*, 1938.

mineral (pyrite?) and brown mica (phlogopite?), again much less than 0.1% by weight.

Experimental procedure

Twenty-five gram portions of these dry-ground <400 mesh minerals were subjected to controlled dissolution in distilled water at 25°C and 1 atm CO_2 partial pressure. Fines were deliberately not removed from the samples, even though their presence affects the early dissolution rates. This aspect is discussed by Lin and Clemency (1981a; 1981b). After various reaction times ranging from 3 minutes to 1180 hours, the pH of the solution was measured using a standardized Orion Model 901 Ionalyzer with a Sensorex solid state combination electrode. Then, 30 ml aliquots were withdrawn, filtered twice through a 0.1 μm Millipore filter. The concentration of Mg was measured by atomic absorption and that of Si colorimetrically by the modified molybdate blue method. Details of the apparatus and experimental procedure used were the same as described by Busenberg and Clemency (1976).

Results and discussion

The pH

Grandstaff (1980) evaluated the complexing effects of various organic ions and of commercial buffers on the solubility of the magnesium silicate olivine and found their effects to be of large magnitude when compared with pure water. In order to represent more natural weathering conditions, the pH buffer used in our experiments was one atm CO_2, and the H_2CO_3 formed provided the buffering action. Such a condition might be approached in a carbonate rock environment or in CO_2-charged spring waters.

The initial pH of the CO_2-saturated water was about 4. Upon adding 25 g of mineral to one liter of

Table 2. The size distribution of brucite, antigorite, and talc used in the experiments

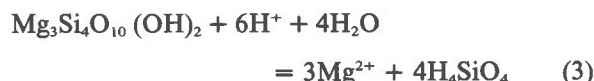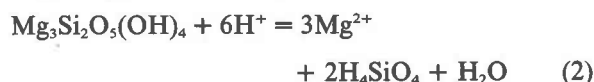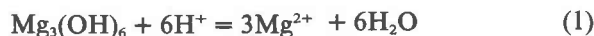| Size(μm)	Brucite	Antigorite	Talc
37–25	16.2	5.3	10.9
25–20	11.4	1.9	12.7
20–15.6	13.7	24.4	20.0
15.6–7.8	22.7	23.2	24.8
7.8–3.9	11.2	12.8	12.0
3.9–1.95	11.1	3.6	6.0
1.95–0.98	3.9	1.6	6.4
0.98–0.49	5.8	2.8	4.0
0.49–0.00	4.0	14.4	3.2

Table 3. The pH and the concentrations in mmole/liter of Mg and/or Si for brucite, antigorite, and talc in solution at various times

	Brucite		Antigorite			Talc		
Hour	pH	Mg	pH	Mg	Si	pH	Mg	Si
0.05			6.04	2.52	0.516			
0.17	9.25	13.7	6.59	3.22	0.782	4.85	0.511	0.0366
0.5	9.22	13.9	6.95	3.78	1.27	4.98	0.549	0.0466
1	9.06	16.3	6.84	4.21	1.59	5.04	0.580	0.0617
3	8.77	24.8	6.31	5.11	2.18	4.85	0.623	0.0873
7	8.49	41.1	6.27	6.08	2.63	4.87	0.694	0.117
15	8.53	47.2	6.24	7.06	2.76	4.91	0.733	0.163
24	8.31	54.1	6.40	7.26	2.52	4.92	0.745	0.201
48	8.35	66.5	6.62	7.39	2.36	4.95	0.784	0.275
72	7.48	127	6.96	7.79	2.35	4.98	0.822	0.330
120	7.17	204	6.15	9.75	2.22	5.06	0.842	0.424
168	7.21	196	6.16	11.0	2.86	5.02	0.900	0.498
240	7.26	188	6.25	12.3	3.03	5.08	0.926	0.595
340	7.22	192	6.27	13.4	2.83	5.10	0.984	0.700
409	7.23	206	6.28	13.9	2.76	5.09	1.02	0.762
509	7.20	201	6.25	15.0	2.76	5.12	1.05	0.836
682	7.20	211	6.28	16.3	2.65	5.12	1.08	0.942
845	7.16	192	6.50	16.3	2.52	5.11	1.12	1.01
1013	7.17	222	6.30	15.9	2.50	5.19	1.16	1.07
1182	7.17	214	6.60	15.9	2.29	5.25	1.17	1.11

water, the pH rose rapidly at first, then more slowly, finally to reach values of 4.8–5.2 for talc (Table 3), 5.1–5.4 for phlogopite (Lin and Clemency, 1981a), 6–7 for antigorite, and 7–9 for brucite. Since the hydrolysis of the mineral consumes H^+ ions, the more mineral that dissolves, the higher is the final pH.

Reactions

The reactions of brucite (equation 1), antigorite (equation 2), and talc (equation 3) are as follows:

$$Mg_3(OH)_6 + 6H^+ = 3Mg^{2+} + 6H_2O \qquad (1)$$

$$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+}$$
$$+ 2H_4SiO_4 + H_2O \qquad (2)$$

$$Mg_3Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O$$
$$= 3Mg^{2+} + 4H_4SiO_4 \qquad (3)$$

If the concentration of silicic acid exceeds the saturation point of amorphous silica, then amorphous silica may precipitate as a solid phase. If the size of the silica particles exceeds 0.1 μm, they will be filtered out along with the mineral particles. The silicon measured in the solution then was the sum of the silicic acid in true solution plus amorphous silica particles smaller than 0.1 μm which dissolved during the analytical procedures. Krauskopf (1956) gives the silica saturation value at 25°C as somewhere between 100–140 ppm (~2.0 mmoles/l). Robie *et al.* (1978) give thermodynamic data from which the silica saturation value can be calculated as 0.97 mmole/l, about half the Krauskopf value. Because of the range in Kraus-

kopf's values and other uncertainties in the analysis involving monomeric *vs.* polymerized forms of silica, we will use the Robie *et al.* (1978) calculated value as the saturation value of silica at 25°C.

A computer program WATEQF (Plummer *et al.*, 1976) was used to calculate the chemical equilibria. In the brucite experiment, only the ionic activity products of magnesite and hydromagnesite were oversaturated with respect to their equilibrium constants and the ionic activity product of brucite was always undersaturated. Although magnesite is oversaturated, it is unlikely to precipitate according to the work of Lippmann (1973, p. 71). The Mg will be precipitated out as hydromagnesite before reaching the equilibrium concentration of brucite (equation 1). The brucite therefore will continue to dissolve, and hydromagnesite will continue to precipitate. The reaction for brucite (equation 1) is therefore irreversible. X-ray diffraction data showed that brucite completely disappeared after three days of reaction time and only hydromagnesite was found in the suspension.

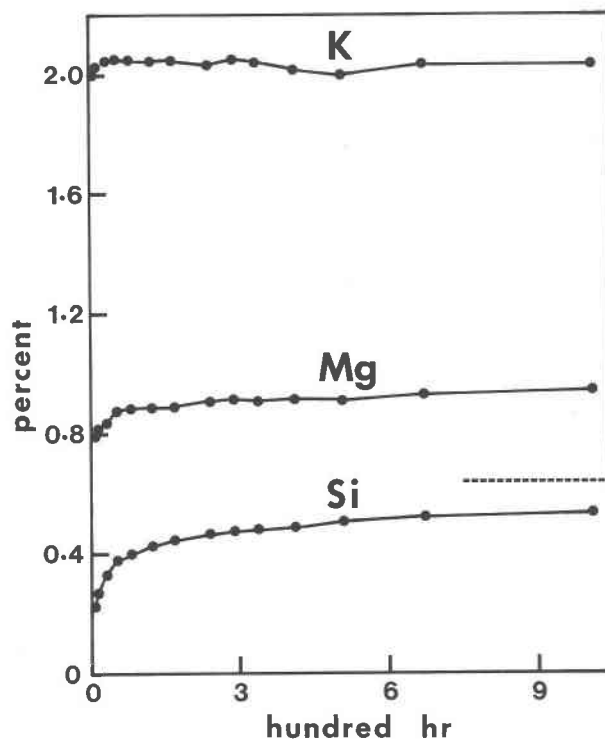In the antigorite experiment, only the ionic activity

Fig. 1. The weight percentages of K, Mg, and Si released from phlogopite plotted as a function of time. The dotted line represents the weight percentage of the phlogopite in the reaction cell that would have to be dissolved to saturate the solution with silica gel.

product of magnesite is oversaturated with respect to the equilibrium constant; however, no magnesite was detected in the suspensions by X-ray diffraction. The antigorite reaction is therefore also irreversible (equation 2). In the talc experiment the solution was undersaturated with respect to all Mg minerals, and Mg released to the solution was not conserved by any other solid phase. In addition, the ionic activity product of talc is far below the equilibrium constant, and therefore equation 3 does not reach equilibrium and talc will continue to dissolve.

Incongruent dissolution

The weight percentages of Mg and Si released are plotted in Figure 1 for phlogopite, in Figure 2 for talc, and in Figure 3 for antigorite. In all cases under these conditions of pH, T, P_{CO_2} octahedral sheets containing Mg are about twice as soluble as tetrahedral sheets containing Si, and the dissolutions were incongruent. Since brucite does not contain any silicon, it cannot be used to decide the incongruency. In the phlogopite dissolution experiment (Fig. 1) the con-

Fig. 3. The weight percentages of Mg and Si released from antigorite plotted as a function of time. The dotted line represents the weight percentage of the antigorite in the reaction cell that would have to be dissolved to saturate the solution with silica gel.

centration of silicic acid released into solution never exceeded the saturation level of amorphous silica (dotted line). In the talc and antigorite experiments the saturation level of amorphous silica was reached after about 740 hours and 30 minutes respectively (dotted lines in Figures 2 and 3).

Comparison of behavior

The concentrations of Mg in the bulk solution (Table 3, and Lin and Clemency, 1981a) are in the decreasing order brucite > antigorite > phlogopite > talc, *i.e.*, proportional to the number of octahedral to tetrahedral sheets in the layer structures. If the weight percentages of Mg released to the solution are compared (Figure 4), they are in the same order. The flattened curve of brucite is caused by the precipitation of hydromagnesite. For antigorite, the ionic activity product for hydromagnesite is below the equilibrium constant, and hydromagnesite will not precipitate; therefore the precipitation of magnesite is possibly responsible for the flattened curve of antigorite. Since no magnesite was detected by X-ray diffraction of the suspension, perhaps the amount of magnesite present is below the limit of detection (5–
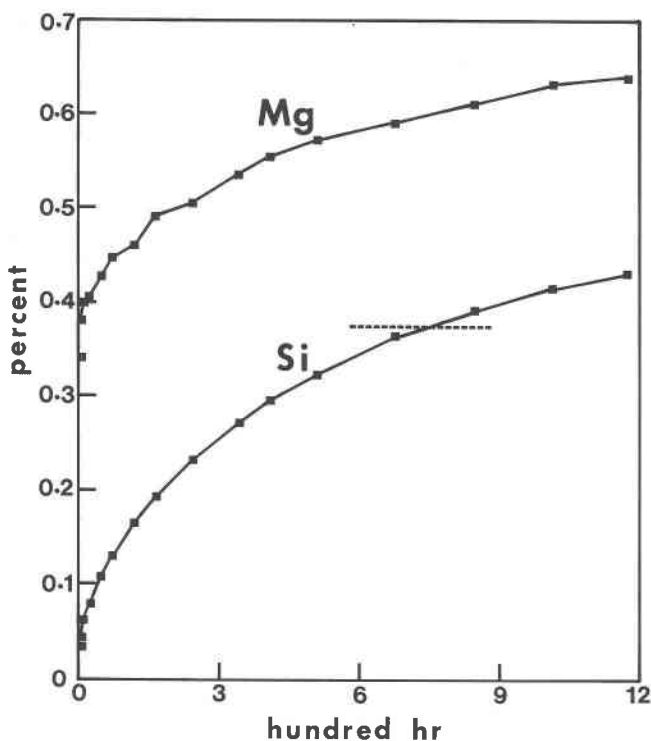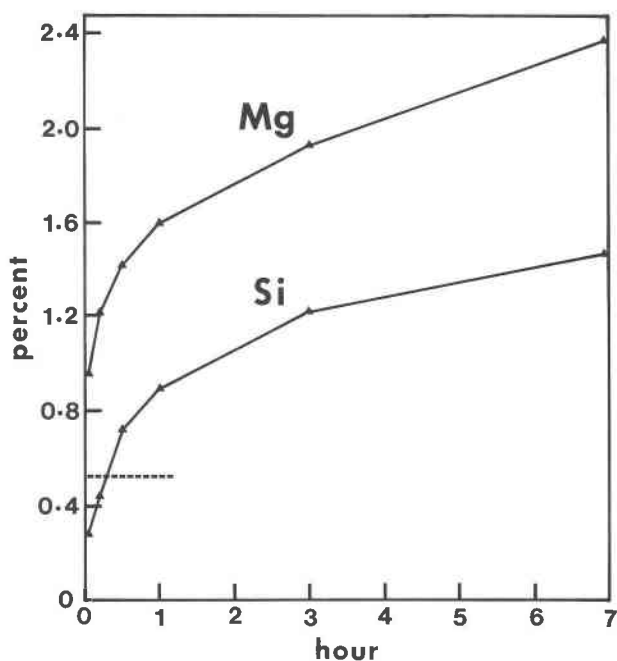
Fig. 2. The weight percentages of Mg and Si released from talc plotted as a function of time. The dotted line represents the weight percentage of the talc in the reaction cell that would have to be dissolved to saturate the solution with silica gel.
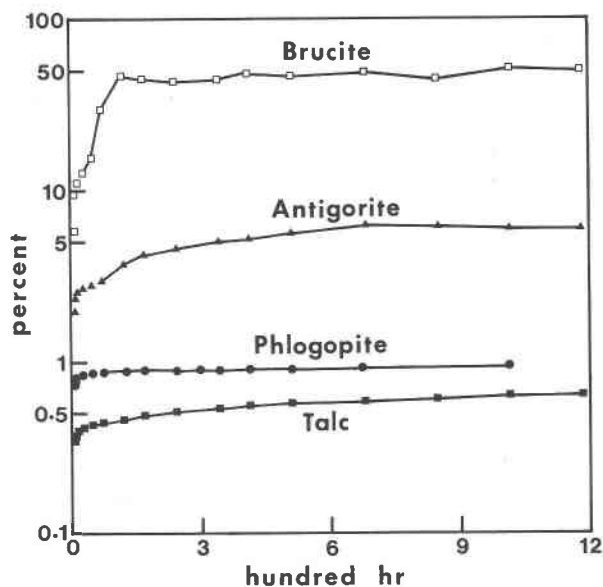
Fig. 4. The weight percentages of Mg released from brucite, antigorite, phlogopite, and talc plotted as a function of time.

10%?). Otherwise, higher Mg curves would be seen in the brucite and antigorite experiments.

The amount of the mineral dissolved is also a function of the total surface area exposed to contact with the water. The more surface area exposed, the more mineral dissolves in a given time. If the comparison of the weight percentages of Mg released to

the solution is based on equal surface area (Fig. 5), the minerals are still in the order brucite > antigorite > phlogopite > talc, except phlogopite showed a higher amount of Mg release than antigorite in the early stages. This is probably due to the fact that phlogopite has interlayer cations which are easily and rapidly replaced by hydrogen ions. In addition, since the comparison is based on the same surface area, but not on the same pH value, the comparison should be modified according to the respective pH's developed. The solution pH's are in the order talc < antigorite < brucite. The lower the pH, the more mineral will dissolve (Luce, et al., 1972; Grandstaff, 1980). If the pH of the antigorite solution were lowered to the same range as the phlogopite solution, more antigorite would have dissolved, and the antigorite curve of Figure 5 would have been displaced upward. The phlogopite curve would then be below the antigorite curve in the early stages. Finally, if the experimental conditions were adjusted so that each sample had equal surface area, and if each were then exposed to solutions with the same pH, the amounts of Mg released would be in the decreasing order: brucite > antigorite > phlogopite > talc. From the experimental data, we conclude that the dissolution kinetics of layer-type silicate minerals are controlled by the rate of destruction of the tetrahedral silica sheets of the mineral.

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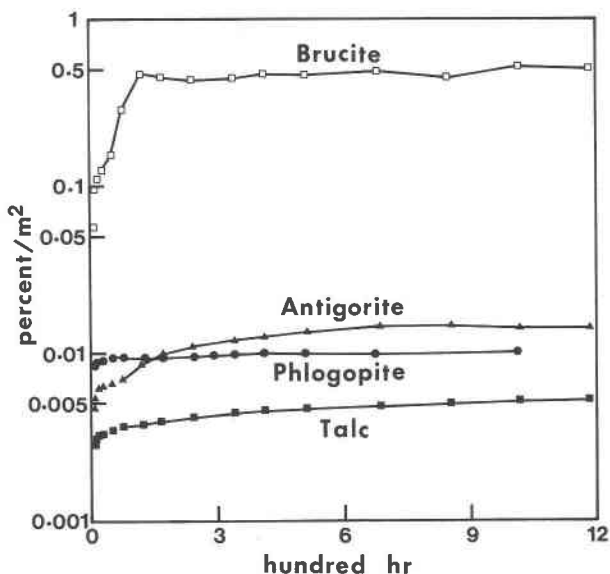

Fig. 5. The weight percentages of Mg released from brucite, antigorite, phlogopite, and talc based on the same surface area plotted as a function of time.

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