

SERPENTINITE ROCK DISSOLUTION AS A FUNCTION OF  
CARBON DIOXIDE PRESSURE IN AQUEOUS SOLUTION

W. E. WILDMAN,<sup>1</sup> M. L. JACKSON, *Department of Soil Science,  
University of Wisconsin, Madison, Wisconsin*

AND

L. D. WHITTIG, *Department of Soils and Plant Nutrition, University  
of California, Davis, California.*

ABSTRACT

Serpentine rock in four California locations under soils high in iron-rich montmorillonite was ground to a powder and suspended in water in which the partial pressure of CO<sub>2</sub> was varied by bubbling N<sub>2</sub> or various air-CO<sub>2</sub> mixtures through the suspension. Analyses for Mg and Si were made after four hours, and 1, 8, 15, 22, and 29 days. In the high-CO<sub>2</sub> solutions (10–100% CO<sub>2</sub> gas) both Mg and Si dissolved more rapidly and reached higher concentrations than in the low CO<sub>2</sub> solutions (N<sub>2</sub>, air, and 1% CO<sub>2</sub> gas). But the Mg:Si ratio was also higher in the high CO<sub>2</sub> solutions, suggesting that soil water, enriched in CO<sub>2</sub>, removes Mg from the system. Fe and Al, present as impurities in the serpentine, presumably rearrange to form the octahedral layer of the soil montmorillonite.

INTRODUCTION

Soils developing on serpentine rock in the Sierra Nevada and Coast Range of California have been found to contain large quantities of iron-rich montmorillonite (Wildman *et al.*, 1966). This clay is low in Mg relative to Fe, in contrast to the parent serpentine, which is high in Mg relative to Fe. A small percentage of Al in the parent rock also appears to have been concentrated into a larger percentage in the clay. Calculation from chemical analyses of the clays gave formulas for the iron-rich montmorillonite in which the octahedral layer composition, based on a total of four octahedral positions per unit cell, ranged as follows: Fe<sub>1.8–2.7</sub>Al<sub>0.2–1.8</sub>Mg<sub>0–1.1</sub>. In most samples SiO<sub>2</sub>, up to as much as 17 percent, was left over after allocating all Fe, Al, and Mg to montmorillonite and to a small amount of residual serpentine. Evidence for quartz was negative in these fine clays and it was postulated that the dissolution of serpentine minerals, under the influence of CO<sub>2</sub>-containing ground waters has proceeded incongruently, with Mg dissolving more rapidly than Si. The remaining amorphous silica relics slowly dissolve and keep the soil matrix solutions sufficiently high (Haung and Jackson, 1968) in soluble silica to crystallize out iron-rich montmorillonite. The Mg is apparently so soluble in the CO<sub>2</sub>-enriched soil matrix water that much of the Mg leaches out of the soil, a fact which is readily apparent when one observes the

<sup>1</sup> Present address: Department of Soils and Plant Nutrition, University of California, Davis, California 95616.

white encrustations of Mg salts on stones in dry streambeds in lower-lying positions in the serpentinite areas. Small amounts of Fe and Al, which are presumed to occupy structural positions in serpentine minerals and thus would be released by the dissolution, evidently remain in the soil and become incorporated in the montmorillonitic clay which forms.

The purpose of the present experiment was to examine the dissolution characteristics, as a function of  $\text{CO}_2$  pressure in aqueous solution, of four samples of serpentinite rock from the areas in which the montmorillonitic soils are found. Observations of the rates of dissolution and the quantities of Mg and Si dissolved in waters in equilibrium with  $\text{CO}_2$  at several different partial pressures when the total pressure was 1 atmosphere and the temperature  $25^\circ\text{C}$  were carried out as a means of interpreting the ionic factors controlling the genesis of the expansible layer silicate clays formed in these soils. A high ratio of Mg to Si in these solutions would help explain the apparent  $\text{SiO}_2$  excess in the iron-rich clays, and the solubility characteristics of Mg, in comparison with those of Fe and Al, should clarify the question of why iron-rich rather than saponitic montmorillonites were formed in these high Mg soils. The latter question is the subject of a forthcoming paper in which the apparent standard free energy of formation of these serpentinites is calculated, and the stability of the serpentine-brucite system is compared with that of the kaolinite-gibbsite system, and with  $\text{Fe}(\text{OH})_3$ .

### MATERIALS

Serpentinite rock was obtained from four locations in California, two in the Coast Range (Colusa and San Benito Counties) and two in the Sierra Nevada (El Dorado and Fresno Counties). At each of these locations, soil containing a high proportion of montmorillonite in the B horizon was developed over the serpentinite. The soils occurring on these rocks are classified as Henneke, Dubakella, and Fancher gravelly loams, with the fourth soil in the New Idria area unclassified. Since the rock under the soil profile has been subject to varying degrees of weathering, care was taken to select samples for the dissolution experiment which were free from the influence of surface weathering.

### METHODS

The serpentinite samples were ground by hand in an agate mortar until a smooth powder was obtained. No attempt was made to obtain fractions of uniform size from the different rocks, since this would involve sedimentation procedures which would affect the dissolution behavior of the rocks. Five series of dissolution experiments were carried out using  $p_{\text{CO}_2}$  levels of  $0(\text{N}_2)$ ,  $10^{-3.5}$  (air),  $10^{-2}$ ,  $10^{-1}$  and 1. Mixtures of air and  $\text{CO}_2$  were obtained in cylinders for the  $10^{-2}$  and  $10^{-1}$   $p_{\text{CO}_2}$  levels. For each experiment the gas from the cylinder was first bubbled through water in a plastic container in order to saturate the gas with

water vapor and eliminate evaporation of water in the dissolution containers. From these containers the gas continued through a manifold made of rigid polyacrylic tubing to a series of 1.5 pint (approximately 700 ml) capacity square polyethylene containers. These were the dissolution containers and their pressure fitting lids were sealed in addition with plastic electrician's tape. Gas inlet tubes of rigid polyacrylic tubing were introduced into the containers through tightly fitted rubber stoppers. The rate of gas flow was adjusted for each container by means of a screw clamp on the flexible plastic tubing connecting the gas inlet tube to the manifold. Gas flow rates were in the range of 25 to 50 ml per minute per container. Gas outlet tubes with restricted openings to prevent possible diffusion of air into the container were brought out through a second rubber stopper fitted in the lid. Solution samples were withdrawn for analysis and pH determinations were made through this hole in the lid.

At the beginning of each experiment, 5 g of ground rock sample were placed in a dissolution container and 200 ml of distilled water, previously saturated with the gas being used, were placed in the container and mixed with the ground rock. A dialysis bag containing 50 ml of distilled water was also placed in the container in order to capture Fe and Al which might be released from the serpentinite in the ionic state. Since such Fe or Al would tend to oxidize or polymerize after being released, its presence in the dialysis bag would show that it had been released and remained for at least a short time in the ionic or unpolymerized state. These solutions were analyzed at the end of the experiment. After placement of the dialysis bag in the container, containers were sealed and the gas flow was started. Samples were withdrawn for analysis for Mg and Si and pH values were measured in the containers after four hours, 1, 8, 15, 22, and 29 days. The experiment was set up in a constant temperature room at  $25 \pm 1^\circ\text{C}$ . Duplicate samples of the four serpentinites were used throughout the air and  $\text{CO}_2$  experiments and through the 8 day sampling in the  $10^{-1}$  and  $10^{-2}p_{\text{CO}_2}$  experiments. After this sampling one of each pair ( $10^{-2}$  and  $10^{-1}p_{\text{CO}_2}$  experiment) was discontinued in order to preserve the small supply of these special gas mixtures. Single samples of the ground rocks were used in the  $\text{N}_2$  experiment, using a high gas flow rate in order to prevent contamination from atmospheric  $\text{CO}_2$ . In addition it was found necessary to place an ascarite tube in the supply line from the  $\text{N}_2$  cylinder to absorb  $\text{CO}_2$  which was present in significant quantity in the  $\text{N}_2$ .

Si was determined by the heteropoly blue method (Blotz and Mellon, 1947), Mg by an adaptation of the EDTA method (Jackson, 1958), Fe by the orthophenanthroline method (Jackson, 1958), and Al by the aluminon method (Hsu, 1963).

## RESULTS

The rate of Mg dissolution from serpentinite, as well as the quantity of Mg in solution after a steady state had been reached (Fig. 1, Dubakella rock was typical of all samples) was markedly increased by an increase in the  $\text{CO}_2$  content of the solution. Mg concentrations in the solutions in which  $p_{\text{CO}_2}=1$  atmosphere (54 to 100 ppm) were 25 to 50 times those under the  $\text{N}_2$  atmosphere (1.8 to 3.5 ppm) at the 29-day sampling time. The dissolution of Mg is directly related to the  $\text{CO}_2$  content, and thus the pH of solutions with which the rock comes into contact. The higher the  $\text{CO}_2$  content in equilibrium with the solution, the lower the pH and the more Mg dissolved. The  $\text{CO}_2$ -water system is represented (Garrels and Christ, 1965) by the equations

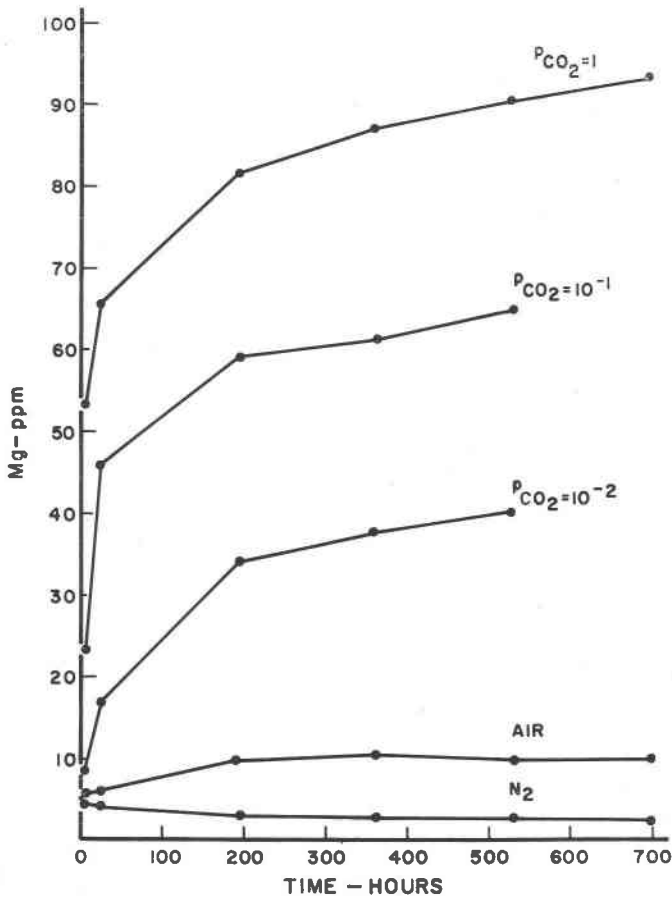
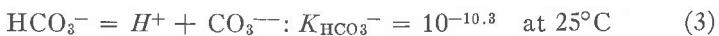
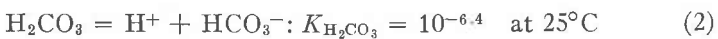


FIG. 1. Mg dissolved from ground Dubakella parent rock by solutions containing different levels of  $CO_2$ .



The concentration of  $H_2CO_3$ , as expressed by equation (1), depends on the  $p_{CO_2}$ . Since the dissociation of carbonic acid is four magnitudes larger than that of bicarbonate ion, the pH of  $CO_2$ -water systems is largely expressed by equations (1) and (2). The theoretical pH of water in equilibrium with gas mixtures containing different  $CO_2$  levels at  $25^\circ C$  is shown

TABLE 1. THEORETICAL AND ACTUAL pH VALUES OF WATER SOLUTIONS AT DIFFERENT VALUES OF  $p_{\text{CO}_2}$  at 25°C AND 1 ATMOSPHERE TOTAL PRESSURE; ACTUAL pH VALUES IN DISSOLUTION CONTAINERS FOR DUBAKELLA ROCK AT DIFFERENT SAMPLING TIMES

$p_{\text{CO}_2}$	pH of water solutions		pH in dissolution containers sampling time—hours					
	Theoretical	Actual	4	24	192	360	528	696
1	3.91	4.2	5.5	5.5	5.7	5.6	5.7	5.7
$10^{-1}$	4.41	4.5	6.1	6.3	6.5	6.5	6.5	—
$10^{-2}$	4.91	4.9	6.9	7.0	7.4	7.3	7.4	—
$10^{-3.5}$ (air)	5.66	5.3	9.3	9.1	8.7	8.6	8.8	8.8
0 (N <sub>2</sub> )	7.00	6.7	9.5	9.5	9.2	9.2	9.0	9.2

in Table 1 compared to the pH values obtained using CO<sub>2</sub>-air mixtures in the dissolution experiment.

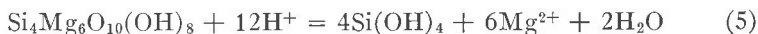
In a solution containing no CO<sub>2</sub>, the dissolution of a serpentine mineral is purely hydrolytic and is represented by the equation



If the Mg<sup>2+</sup> in solution from this reaction were controlled by the solubility product of Mg(OH)<sub>2</sub> its concentration would be about 5 ppm and the pH would be about 10.3 at 25°C and 1 atmosphere.

The actual pH values (Table 1, Dubakella rock) did not reach 10.3 but were 0.5 to 1.5 pH units lower for all of the rock samples. Mg<sup>2+</sup> in solution did not reach the theoretical 5 ppm either. In fact, the highest Mg<sup>2+</sup> concentrations (Fig. 1, Dubakella rock) and pH values (Table 1) were usually found at the 4 hour or 1 day analyses, and then both declined slowly during the remainder of the 29 day experiment. Mg<sup>2+</sup> concentrations at 29 days were from 1.7 to 3.5 ppm. This behavior suggests that the serpentine minerals present controlled Mg<sup>2+</sup> and OH<sup>-</sup> at concentrations below those predicted by the solubility product of Mg(OH)<sub>2</sub>. The higher initial solubility may have been due to the disordering of crystal surfaces by grinding.

In the CO<sub>2</sub>-water solutions H<sup>+</sup> from the dissociation of dissolved H<sub>2</sub>CO<sub>3</sub> attacked serpentinite more vigorously according to the equation



The pH rose rapidly from the initial pH (Table 1) of the CO<sub>2</sub>-water solutions and leveled off 1.5 to 3 pH units above these values, due to buffering by HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.

In contrast to the N<sub>2</sub> treatment, dissolved Mg<sup>2+</sup> rose steadily through-

out the experiment in the three solutions containing the highest  $\text{CO}_2$  levels. The rate of increase in  $\text{Mg}^{2+}$  concentration was greatest during the first day and diminished with the succeeding weekly samplings. The final concentration of  $\text{Mg}^{2+}$  in solution was thus a function of the  $\text{H}^+$  which could be sustained by the amount of  $\text{CO}_2$  which was added to the solutions in the different cases.

Si also dissolved more rapidly and reached higher concentrations (Fig. 2, Dubakella rock) in solutions containing higher levels of dissolved  $\text{CO}_2$ .

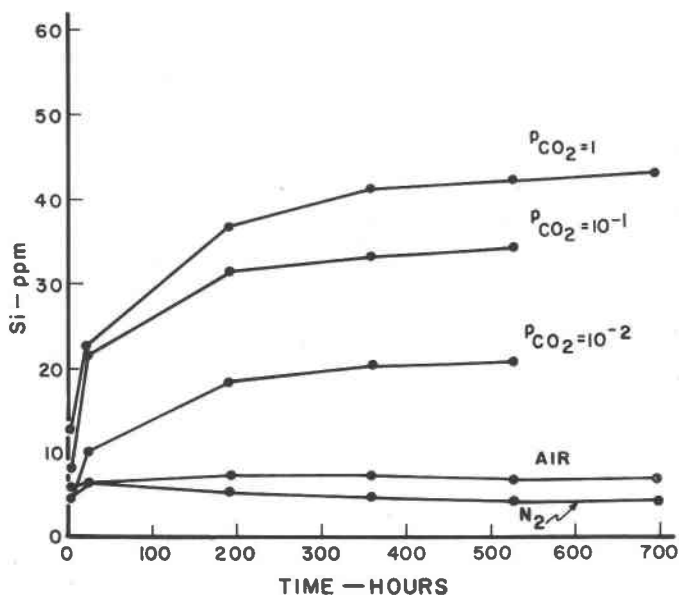


FIG. 2. Si dissolved from ground Dubakella parent rock by solutions containing different levels of  $\text{CO}_2$ .

The Si concentration of the 100 percent  $\text{CO}_2$  treatment solutions (37 to 59 ppm for the different rocks) was 2 to 10 times that of the  $\text{N}_2$  treatment solutions (4.5 to 27 ppm) at the 29 day sampling time. Unlike Mg, the behavior of Si is not thought to be directly due to a pH effect, since the solubility of monosilicic acid is fairly constant at pH values below 9 (Krauskopf, 1959). The Si measured in the solutions is assumed to be monomeric silicic acid. McKeague and Cline (1963) found that all silica that they were able to extract from soils in dissolution experiments was in the monomeric form. There is no reason to think that the present experiment would differ. The increased rate of Si dissolution is probably due to the fact that the increased Mg dissolution at higher  $P_{\text{CO}_2}$  levels

leaves silica relics which, once Mg-silica bonds have been broken, become subject to hydrolytic attack and dissolution. This model can reasonably explain the rapid initial dissolution of Mg in the first 4-hour interval by the solutions in which the  $P_{CO_2}$  was 1 or  $10^{-1}$ , which caused the Mg:Si ratio to be high at first, then to drop to an approximately constant level as Si began to dissolve more rapidly.

The Mg:Si ratio in the experimental solutions increased with increase

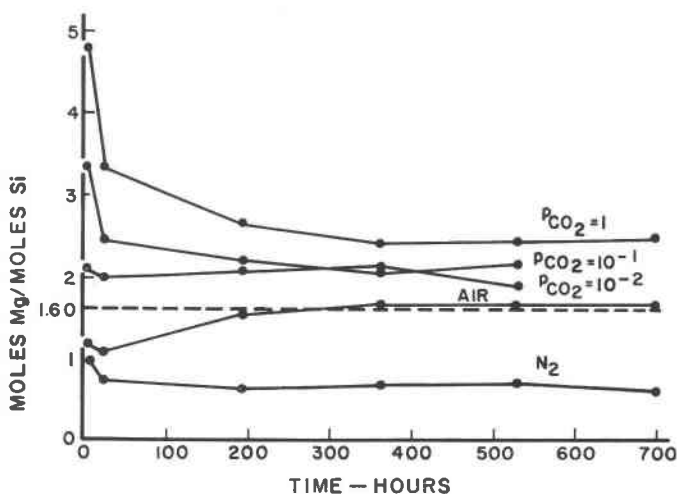


FIG. 3. Molar ratio of Mg to Si dissolved from ground Dubakella parent rock by solutions containing different levels of  $CO_2$ . Dashed line is Mg:Si ratio in parent rock itself.

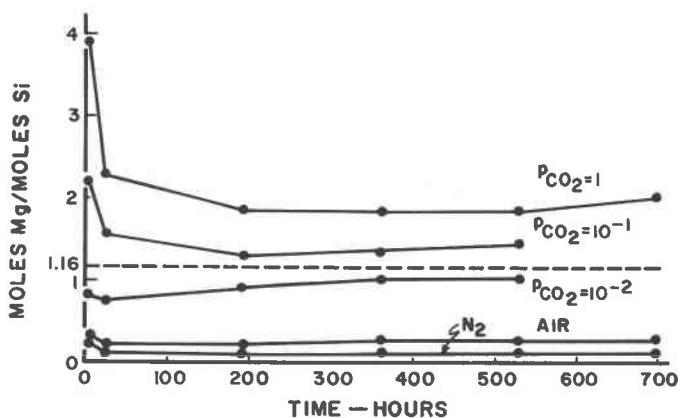


FIG. 4. Molar ratio of Mg to Si dissolved from ground Henneke parent rock by solutions containing different levels of  $CO_2$ . Dashed line is Mg:Si ratio in parent rock itself.

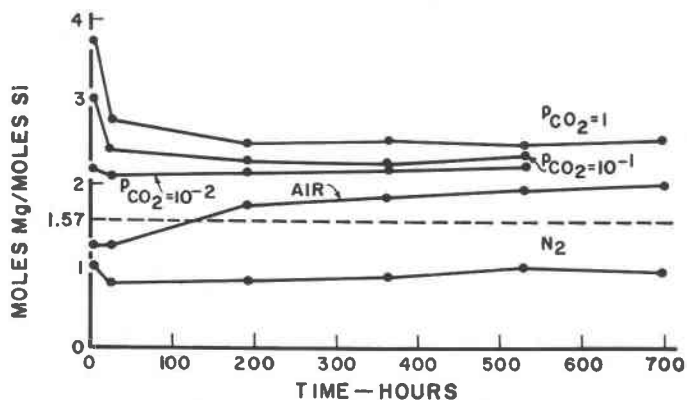


FIG. 5. Molar ratio of Mg to Si dissolved from ground Fancher parent rock by solutions containing different levels of  $CO_2$ . Dashed line is Mg:Si ratio in parent rock itself.

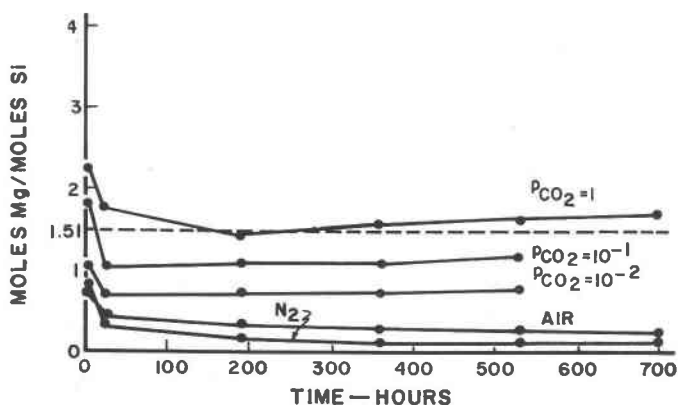


FIG. 6. Molar ratio of Mg to Si dissolved from ground New Idria parent rock by solutions containing different levels of  $CO_2$ . Dashed line is Mg:Si ratio in parent rock itself.

in the  $CO_2$  content of the solution (Figs. 3, 4, 5, 6). The dashed line in these figures indicates the Mg:Si ratio in the rock itself. While all the rocks gave a Mg:Si ratio in solution above that in the rock for the highest  $CO_2$  treatment, there was no consistent relationship between the Mg:Si ratio in the rock and that in the solution at the lower  $CO_2$  levels. The low values of Mg:Si ratio in the  $N_2$  and air treatments of the Henneke and New Idria rocks are due in large part to a considerably larger Si dissolution than was true for the Dubakella and Fancher rocks. This very low Mg:Si ratio (0.1 and 0.2 in  $N_2$  treatments of Henneke and New Idria rocks) could come from the Si-favored incongruent dissolution of the



serpentine mineral, or a small amount of amorphous  $\text{SiO}_2$  present as an impurity in these rocks could account for this behavior. It is evident that there has been no separation of solid  $\text{Mg}(\text{OH})_2$  with attendant incongruent dissolution of Si. Had this been the case, pH and  $\text{Mg}^{2+}$  would have been maintained at a higher level by the  $\text{Mg}(\text{OH})_2$ . If Si did indeed dissolve incongruently, it must have done so by preferential dissolution of Si directly from the serpentine lattice.

On the other hand, there is good evidence for Mg-favored incongruent dissolution at the higher levels of  $\text{CO}_2$ . The Mg:Si ratio in solution rose well above that in the rocks in most treatments in which  $\text{CO}_2$  content was greater than that of air, and most of this Mg is presumed to have come from the serpentine mineral, since there was no evidence for brucite or other Mg minerals from X-ray or differential thermal analyses of the rocks.

When more Mg was dissolved with increased  $\text{CO}_2$  level, Si was able to dissolve to a considerably greater extent, up to 94 ppm as  $\text{SiO}_2$  for the Dubakella rock (Fig. 2) and 125 ppm for the Henneke rock (not shown). These values approach saturation (100 to 140 ppm as amorphous  $\text{SiO}_2$  at  $25^\circ\text{C}$ , Krauskopf, 1959). This suggests that there was an initial rapid attack by the acidic solutions on the exposed side of the crystal plate containing the octahedral layers. After these layers had dissolved off, the remaining silica relics were exposed to hydrolytic dissolution and rapidly dissolved. The fact that the Mg:Si ratio remained above that of the rock itself in most cases in which  $p_{\text{CO}_2}$  was greater than that of air, suggests that there was plucking out of Mg from the edges of the crystals by the acidic solutions, which continued at a higher rate for Mg than for Si.

Fe and Al were not detected in the solutions contained in the dialysis bags by the analytical methods used. These solutions were treated with HCl and analyzed at the end of the experiment. Mg and Si levels in the dialysis bag solutions were the same as in the external solution, showing that equilibration between the external and internal solution was complete with respect to these ions. Fe and Al, though present in much smaller quantities (Table 2) in the serpentine minerals than Si or Mg, could be released in measureable quantities in the solutions under the influence of the higher  $\text{CO}_2$  levels, providing the Fe and Al so released would remain in soluble form long enough to enter the dialysis bag. In the pH range of the dissolution samples (5 to 9), however, Al would precipitate as hydroxide as soon as it was released. Even if Fe were released in the more soluble ferrous state it would be oxidized immediately to insoluble  $\text{Fe}(\text{OH})_3$  in the three treatments containing air. One might expect that ferrous iron released in the  $\text{N}_2$  treatment would remain soluble since Fe in equilibrium with solid  $\text{Fe}(\text{OH})_2$  is soluble to the extent of

TABLE 2. CHEMICAL ANALYSIS OF GROUND SERPENTINITE PARENT ROCK SIMILAR<sup>a</sup> TO THAT USED IN THE DISSOLUTION EXPERIMENT

	Henneke	Dubakella	Fancher	New Idria
SiO <sub>2</sub>	43.3	38.1	40.0	39.8
Al <sub>2</sub> O <sub>3</sub>	0.4	2.4	1.5	0.7
Fe <sub>2</sub> O <sub>3</sub>	6.6	3.6	8.9	3.1
MgO	33.7	41.0	42.2	40.3
CaO	0.0	0.0	1.0	0.3
TiO <sub>2</sub>	0.2	0.1	0.1	0.1
Na <sub>2</sub> O	0.1	0.1	0.1	0.1
K <sub>2</sub> O	0.1	0.1	0.2	0.1
H <sub>2</sub> O <sup>b</sup>	13.4	13.9	4.2 <sup>c</sup>	13.4
Total	97.8	99.3	98.2	97.9

<sup>a</sup> For this analysis, magnetite was removed with a hand magnet; in the dissolution experiment, magnetite was not removed.

<sup>b</sup> 110°C weight basis.

<sup>c</sup> The low H<sub>2</sub>O content is due to the fact that Fancher parent rock is largely olivine, formed by metamorphic upgrading of the original serpentinite.

about 9 ppm at pH 9. However, in the N<sub>2</sub> treatments the amount of Mg dissolved was only 2 to 3 ppm, so Fe released by this dissolution, even if soluble, would be so small that it would be undetectable by wet chemical methods.

### CONCLUSIONS

The fact that dissolution of Mg and Si from serpentinite increases so rapidly with an increase in the  $p_{\text{CO}_2}$  of the atmosphere suggests that this mechanism is of importance in the breakdown of serpentine minerals in soils. Keller *et al.* (1963) have shown the same behavior to be true for several primary mafic minerals. Soil air contains more CO<sub>2</sub> and less O<sub>2</sub> than the atmosphere and the  $p_{\text{CO}_2}$  of soil air increases with depth, with compactness of the soil, and with plant root and microbial respiration occurring in the soil. Boynton and Reuther (1938) measured up to 3.7 percent CO<sub>2</sub> ( $p_{\text{CO}_2} = 10^{-1.43}$ ) in soil air at a 1-foot depth and up to 12 percent CO<sub>2</sub> ( $p_{\text{CO}_2} = 10^{-0.92}$ ) at a five foot depth in a Dunkirk silty clay loam with a dense subsoil. Although plant growth is only moderate and organic matter not high in the serpentinite soils studied, it would not seem unreasonable to expect that the CO<sub>2</sub> content of the serpentinite soil atmosphere below 1 foot is several times greater than in air. The increased CO<sub>2</sub> content of the soil atmosphere would increase the mobility of Mg ions, and possibly explain the apparent excess of SiO<sub>2</sub> in the soil clays.

It is also noteworthy that, while the dissolution experiments were carried out at 25°C, the opportunity for leaching of these serpentinites under natural conditions occurs only with the winter rainfall, since summers are dry in all these areas. It is probable that the soil temperature is 10°C or less during the times of maximum leaching. At lower soil water temperatures the solubility of  $\text{Si}(\text{OH})_4$  would decrease (about 50–80 ppm at 0°C compared with 100–140 ppm at 25°C, both ranges expressed as  $\text{SiO}_2$ ; Krauskopf, 1959) but the solubility of  $\text{CO}_2$  would increase, and both of these factors would operate to increase the Mg:Si ratio in the soil matrix solutions.

No direct evidence was obtained from the dissolution experiments that Fe and Al from lattice positions of serpentine minerals recombine with  $\text{Si}(\text{OH})_4$  to form the iron-rich montmorillonites found in the soils. However, the fact that Fe and Al are found in small amounts in the serpentinite subordinate to Mg, while the reverse is true of the clays, suggests that there was complete disruption of the serpentine lattice with reconstitution of the dissolution products in quite different proportions to form the iron-rich montmorillonite. The low levels of Mg in the clays was unexpected. Garrels *et al.*, (1960) have remarked on the reluctance of Mg ion to form solid precipitates from supersaturated solutions of  $\text{Mg}^{2+}$  and  $\text{CO}_3^{2-}$ . They attribute this behavior to the firm hydration of  $\text{Mg}^{2+}$ , or to the formation of stable  $(\text{MgCO}_3)^\circ$  ion pairs. It may be that this same behavior is also partially responsible for the virtual absence of saponitic montmorillonite in the weathering products of these serpentines.

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