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SERPENTINE STABILITY IN RELATION TO FORMATION OF IRON-RICH MONTMORILLONITE IN SOME CALIFORNIA SOILS

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Abstract

The apparent standard free energy of formation of several California serpentines was calculated from solubility data at 25°C. Based on the end-member formula, $Si_2Mg_3O_5(OH)_4$, the average value is −962.9 kcal/mole (range, −960.6 to −965.9 kcal/mole). Stability diagrams developed from the free energy value indicate that serpentine is unstable in the range of pH and activities of Mg^{2+} and $Si(OH)_4$ encountered in most soils. The Fe and Al substituting for Mg in the serpentines is released during weathering and becomes incorporated with silica in the clay formed. Stability diagrams for brucite, gibbsite, and amorphous $Fe(OH)_3$ indicate that the (Fe, Al)-octahedral sheet is more stable than the brucite sheet when in contact with serpentinite soil matrix solutions. The greater stability of the dioctahedral sheet provides a thermodynamic explanation for nucleation of Fe-rich montmorillonite rather than saponite in soils forming on serpentine rocks. The octahedral sheet formed as serpentine weathers is silicated to expansible phyllosilicate layers in the presence of sufficiently high $Si(OH)_4$ concentration also maintained by serpentine.

Introduction

Stability diagrams such as those utilized by Garrels and Christ (1965) can be useful in predicting the secondary minerals that would form in equilibrium with solutions in contact with weathering primary minerals in soils. Reliable free energy data are not available for many of the more complex secondary soil minerals, for example, the layer silicates of the montmorillonite, vermiculite, and chlorite groups, because of the ubiquitous presence of impurities and uncertainty as to the exact composition of expansible layer silicate minerals in soils. King *et al.* (1967) have reported free energy values for near end-member chrysotile and antigorite samples. Transformation of serpentine to Fe-rich montmorillonite in serpentinite-derived soils of California (Wildman *et al.*, 1968a) affords the opportunity to apply thermodynamic data in predicting why these particular mineralogical transformations took place in these specific soil environments.

In trying to determine the thermodynamic reasons for the formation of montmorillonite rather than saponite in high Mg, serpentinite-derived soils, we have used the indirect approach of examining the stability of the weathering serpentine forming the clay. Dissolution data from a previous experiment (Wildman *et al.*, 1968b) have been used to calculate the apparent standard free energy of formation of serpentine in these rocks. The stability diagrams were developed from the free energy values for serpentine and from known values for brucite, ferric hydroxide, and gibbsite (Garrels and Christ, 1965; Kittrick, 1966). Tests were then made of the hypotheses (a) that the stability diagram of serpentine provides a thermodynamic explanation for the maintenance of sufficiently high $Si(OH)_4$ concentration to form the silica sheets of expansible phyllosilicate clays, and (b) that the stability diagrams for the metal hydroxides that form octahedral sheets likewise provide the key to nucleation of the respective expansible phyllosilicate clay.

EXPERIMENTAL AND RESULTS

Serpentinite rocks used in the dissolution experiments included those under Henneke, Dubakella, and Fancher soils, and under an unnamed soil of the New Idria area. Our approach was similar to that of Keller *et al.* (1963) and Reesman and Keller (1965), but the treatment of the samples was somewhat different. A smaller sample size (5 g versus 10 g) and a larger aqueous solution volume (250 ml versus 100 ml) were used in this study. The rock was ground by hand in an agate mortar, but only enough to make a smooth powder. The powder and water were placed in a polyethylene container and closed to the atmosphere. Gas (N_2 in one series, air in another) was gently bubbled through the liquid for 29 days at room temperature of $25 \pm 1°C$. Attainment of equilibrium between the solutes and the serpentine mineral proper was facilitated by avoidance of continued high energy surface formation, such as would be encountered by grinding of the rock slurry during the dissolution. The pH values and the concentrations of Mg^{2+} and $Si(OH)_4$ were determined for each solution after 4 hours and after 1, 8, 15, 22, and 29 days. Details of the procedure are reported in a previous paper (Wildman *et al.*, 1968b). Chemical analyses of the rocks, necessary for evaluation of effects of elemental composition on free energy of the serpentine, were also reported by Wildman *et al.* (1968b, Table 2).

With the N_2 treatments of all four rocks, the concentration of Mg^{2+} rose rapidly at first, peaked at the 4-hour or 1-day sampling (Wildman *et al.*, 1968b, Fig. 1) then declined slowly to a near-constant level at the 29th day. The concentrations of $Si(OH)_4$ from Dubakella and Fancher rocks declined slightly after 1 day (Wildman *et al.*, 1968b, Fig. 2), reaching a steady state by 29 days. With Henneke and New Idria rocks, the concentrations of $Si(OH)_4$ continued to rise after 1 day. By 29 days, the concentration with Hennecke rock leveled off, while that with New Idria

TABLE 1. SOLUBILITY DATA FOR GROUND SERPENTINITE ROCKS AFTER 29 DAYS EQUILIBRATION WITH WATER UNDER NITROGEN OR AIR

Parent rock for	Gas	$[Mg^{2+}]$ moles/liter	$\log[Mg^{2+}]$	$[Si(OH)_4]$ moles/liter	$\log [Si(OH)_4]$	pH
Henneke soil	N_2	9.0×10^{-5}	-4.05	9.6×10^{-4}	-3.02	8.6
	Air	2.8×10^{-4}	-3.55	1.0×10^{-3}	-3.00	8.4
Dubakella soil	N_2	1.0×10^{-4}	-4.00	1.7×10^{-4}	-3.77	9.2
	Air	4.2×10^{-4}	-3.38	2.5×10^{-4}	-3.60	8.8
Fancher soil	N_2	1.4×10^{-4}	-3.85	1.5×10^{-4}	-3.82	9.4
	Air	5.7×10^{-4}	-3.24	2.9×10^{-4}	-3.54	8.8
Soil from New Idria	N_2	7.0×10^{-5}	-4.15	5.1×10^{-4}	-3.29	8.8
	Air	1.5×10^{-4}	-3.82	5.5×10^{-4}	-3.26	8.3

rock was still increasing. The pH values of all solutions leveled off at 29 days. With the air treatments, the concentrations of Mg^{2+} and $Si(OH)_4$ were nearly constant at 29 days. The fact that the experimental values essentially reached a steady state within 29 days lends confidence that the results will be useful in predicting what may happen in actual soil solutions. Data for dissolution of the ground serpentinite rocks is given in Table 1.

CALCULATION OF APPARENT STANDARD FREE ENERGY OF FORMATION OF SERPENTINE

The standard free energies of formation used in the various calculations are listed in Table 2. For these calculations, molalities were assumed equal to activities. Since pH was measured to the nearest 0.1 unit and since solutions in this experiment were very dilute, error introduced by using molalities rather than activities would be insignificant. Fe and Al released by dissolution of the serpentine were not present in detectable quantities and were not considered in the calculations.

The dissolution of end-member serpentine may be represented as a hydrolysis equation,

$$Si_2Mg_3O_5(OH)_4 + 5H_2O = 2Si(OH)_4 + 3Mg^{2+} + 6OH^- \qquad (1)$$

It is more convenient, however, to use this equation in the form

$$Si_2Mg_3O_5(OH)_4 + 6H^+ = 2Si(OH)_4 + 3Mg^{2+} + H_2O \qquad (2)$$

The apparent equilibrium expression obtained from this equation is

$$aK = \frac{[Si(OH)_4]^2[Mg^{2+}]^3}{[H^+]^6} \qquad (3)$$

TABLE 2. STANDARD FREE ENERGIES OF FORMATION USED IN CALCULATING THE STABILITY FIELDS

Substance	ΔG°_{f}	Source
	kcal/mole	
$Si(OH)_4$	−312.8	Reesman and Keller, 1965
H_2O (liquid)	−56.690	Garrels and Christ, 1965
OH^-	−37.595	Garrels and Christ, 1965
Mg^{2+}	−108.99	Garrels and Christ, 1965
Al^{3+}	−115.0	Garrels and Christ, 1965
Fe^{3+}	−2.52	Garrels and Christ, 1965
AlO_2^-	−200.7	Garrels and Christ, 1965
H^+	0	Garrels and Christ, 1965
$Mg(OH)_2$ brucite	−199.27	Garrels and Christ, 1965
$Fe(OH)_3$ amorphous	−166.0	Garrels and Christ, 1965
$Al(OH)_3$ gibbsite	−277.3	Garrels and Christ, 1965
$Al(OH)_3$ gibbsite	−274.2	Kittrick, 1966

By taking logs, this expression may be written

$$\log aK = 2 \log [Si(OH)_4] + 3 \log [Mg^{2+}] + 6\text{pH} \qquad (4)$$

Solubility and pH data (Table 1) were used in this equation to find values for log aK (Table 3) for the several serpentines. The apparent *equilbrium* constant aK is related to the apparent standard free energy change of the reaction $a\Delta G^{\circ}_{R}$ by the expression

$$a\Delta G^{\circ}_{R} = -\ \mathrm{RT} \ln aK = -\ 1.364 \log aK \qquad (5)$$

$a\Delta G^{\circ}_{R}$ is calculated by subtracting the total standard free energy of formation of the reactants from that of the products. Thus,

$$a\Delta G^{\circ}_{R} = \Sigma \Delta G_{f}^{\circ}\text{products} - \Sigma a\Delta_{f}G^{\circ}\text{reactants} \qquad (6)$$

The standard free energies of formation of all species in equation (6), applied to equation (2), are known except that of the serpentine mineral itself; and this may be calculated from the value of $a\Delta G^{\circ}_{R}$ obtained. The value for the standard free energy of formation of silicic acid (−312.8 kcal/mole) was taken from the calculation made by Reesman and Keller (1965).

The values of log aK, $a\Delta G^{\circ}_{R}$, and $a\Delta G^{\circ}_{f}$ for serpentine (Table 3) are in good agreement for the air and N_2 treatments, and in fairly good agreement among the different rock samples. The agreement is better when the Fancher rock, which is largely forsterite rather than serpentine, is

TABLE 3. CALCULATED FREE ENERGY VALUES FOR GROUND SERPENTINITE ROCK

Parent rock for	Gas Treatment	log aK[a]	$a\Delta G^{\circ}_R$	$a\Delta G^{\circ}_f$[a]
			kcal/mole	kcal/mole
Henneke soil	N_2	33.4	−45.6	−963.7
	Air	33.7	−46.0	−963.3
Dubakella soil	N_2	35.7	−48.7	−960.6
	Air	35.5	−48.5	−960.8
Soil from New Idria	N_2	33.8	−46.1	−963.2
	Air	31.8	−43.4	−965.9
Average		34.0		−962.9
Fancher soil as serpentine	N_2	37.2	−50.8	−958.5
	Air	36.0	−49.1	−960.2
as forsterite	N_2	26.1	−35.6	−495.2
	Air	25.2	−34.4	−496.4

[a] Following Reesman and Keller (1965), the prefix "*a*" refers to "apparent" values calculated from concentrations obtained from the undersaturation side.

removed from consideration. The average ΔG°_f value for serpentine excluding the Fancher rock, is −962.9 kcal/mole. There was close agreement between values obtained for Henneke and New Idria rocks. The value for the Dubakella rock was low (−960.6 and −960.8 kcal/mole, under N_2 and air, respectively). Though not substantiated, the lower value for Dubakella rock may be related to Al substituted in the serpentine. The Fe_2O_3 contents of the Henneke and New Idria rocks (6.6 and 3.1 percent, respectively) fall above and below that (3.6 percent) of the Dubakella rock, yet the $a\Delta G^{\circ}_f$ values for the Henneke and New Idria rocks (Table 3) are in close agreement. On the other hand, the Al_2O_3 content of the Henneke and New Idria rocks is similar (0.4 and 0.7 percent, respectively) whereas that of the Dubakella rock is considerably higher (2.4 percent).

The average ΔG°_f value of −962.9 kcal/mole is in very good agreement with the value of −963 kcal/mole obtained by Luce (unpublished report, 1966; 1969) on a carefully separated sample of New Idria chrysotile serpentine. Luce conducted the dissolution with magnetic stirring at 25°C for a period of 12 months in containers purged with N_2 gas. King *et al.* (1967) obtained a higher value, −964.75 kcal/mole for a New Idria clinochrysotile, using a calorimetric determination at 298.15°K. Hostetler and Christ (1968) obtained values in good agreement with King *et al.*, using identical chrysotile but working at 90°C. The latter two results suggest that chrysotile serpentine is somewhat more stable than suggested in this article. The present authors do not offer their values as standard free energies of formation for pure serpentine mineral species, but rather for field run serpentinite rocks, whose weathering has a bearing on the nature of the soils formed from them.

When the Fancher rock is used to calculate the apparent standard free energy of formation of forsterite, rather than that of serpentine, according to the equation

$$Mg_2SiO_4 + 4H^+ = Si(OH)_4 + 2Mg^{2+} \tag{7}$$

the value obtained is −495.2 kcal/mole in the N_2 treatment and −496.4 kcal/mole in the air treatment. These values compare favorably with the dissolution value for forsterite of −496.9 kcal/mole obtained by Reesman and Keller (1965), values somewhat higher than −490.6 kcal/mole obtained calorimetrically by King *et al.* (1967).

THE STABILITY OF SERPENTINE AND BRUCITE

The stability relations of serpentine at 25°C and 1 atmosphere may be examined graphically by the approach of Garrels and Christ (1965). Taking the average value of log aK (Table 3), equation (4) can be written as

$$2 \log [Si(OH)_4] + 3 \log [Mg^{2+}] + 6pH = 34.0 \tag{8}$$

Setting log $[Si(OH)_4] = -2.6$, which is the saturation solubility value of monomeric silicic acid at 25°C and 1 atmosphere (Garrels and Christ, 1965), the expression

$$3 \log [Mg^{2+}] + 6pH = 39.2 \tag{9}$$

is obtained.

With this expression a stability diagram may be constructed for serpentine at the $Si(OH)_4$ saturation limit by substituting values for either the log $[Mg^{2+}]$ or the pH

at $$\log [Mg^{2+}] = 0, \quad pH = 6.5 \tag{10}$$

at $$pH = 14, \quad \log [Mg^{2+}] = -14.9 \tag{11}$$

The stability diagram (Figure 1) shows that at the saturation solubility of $Si(OH)_4$ ($10^{-2.6}$ moles/liter) a serpentine mineral is not stable below a pH of about 7.0 in a 0.1–M Mg^{2+} solution. As the Mg^{2+} concentration is lowered, the pH below which serpentine is unstable rises one pH unit for each hundred-fold decrease. Thus, in a 1-mM Mg^{2+} solution, serpentine is not stable below pH 8. If now a lower fixed value of $Si(OH)_4$ is considered, for example 10^{-12} moles/liter, equation (9) becomes

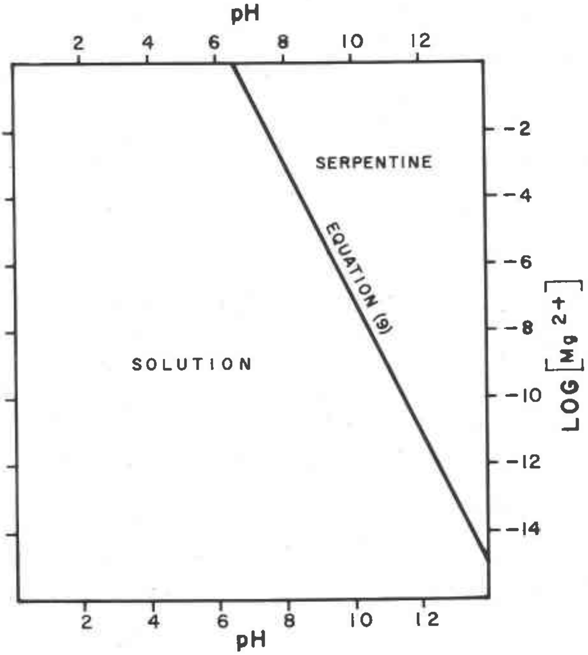

FIG. 1. Stability of serpentine expressed in terms of pH and activity of Mg^{2+} at 25°C and 1 atmosphere. Activity of $Si(OH)_4$ is $10^{-2.6}$ moles/liter.

$$3 \log [Mg^{2+}] + 6pH = 58.0 \tag{12}$$

Substituting values for log $[Mg^{2+}]$ or pH

at $$\log [Mg^{2+}] = 0, \quad pH = 9.7 \tag{13}$$

at $$pH = 14, \quad \log [Mg^{2+}] = -8.7 \tag{14}$$

The stability field of serpentine (Figure 2) has now been decreased by the lowering of the $Si(OH)_4$ concentration. These two-dimensional diagrams can now be used to construct a three-dimensional stability diagram showing the stability of serpentine as a function of all three variables. Figure 2, with $\log [Si(OH)_4] = -12$, is used as the front face of a block; and Figure 1, with $\log [Si(OH)_4] = -2.6$, is used as the rear face. The stability boundaries are connected across the top and side of the block to give a three-dimensional stability field (Figure 3).

Although brucite associated with serpentine can form a carbonate-containing mineral such as coalingite (Mumpton and Thompson, 1966) in surficial weathering zones, the brucite-serpentine join in the stability diagram is of interest here. The brucite phase, in the presence of sufficient

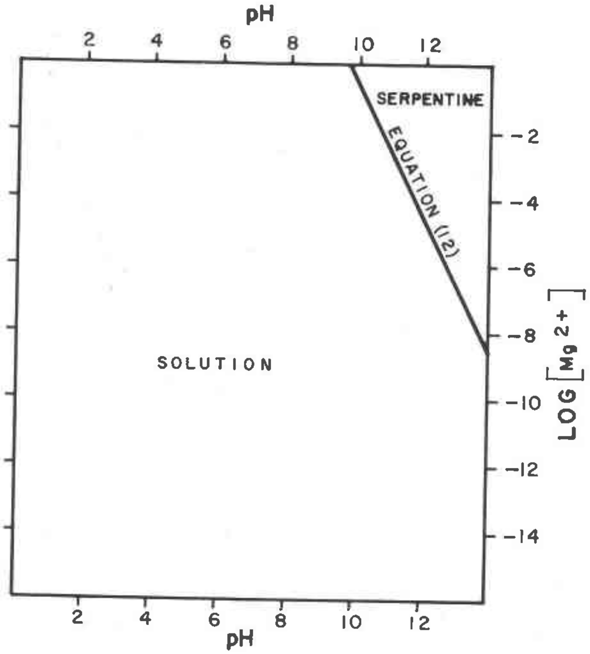

FIG. 2. Stability of serpentine expressed in terms of pH and activity of Mg^{2+} at 25°C and 1 atmosphere. Activity of $Si(OH)_4$ is 10^{-12} moles/liter.

concentration of $Si(OH)_4$ might be silicated to saponite. The equation for the dissociation of brucite is

$$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O \tag{15}$$

$$K = \frac{[Mg^{2+}]}{[H^+]^2} \tag{16}$$

$$\log K = \log [Mg^{2+}] + 2pH \tag{17}$$

From equation (5) and the standard free energies (Table 2) as applied to equation (15),

$$\log K = \frac{\Delta G^\circ_R}{-1.364} = \frac{-23.1}{-1.364} = 16.9 \tag{18}$$

$$\log [Mg^{2+}] + 2pH = 16.9 \tag{19}$$

$$\text{at } \log [Mg^{2+}] = 0, \qquad pH = 8.4 \tag{20}$$

$$\text{at } pH = 14, \qquad \log [Mg^{2+}] = -11.1 \tag{21}$$

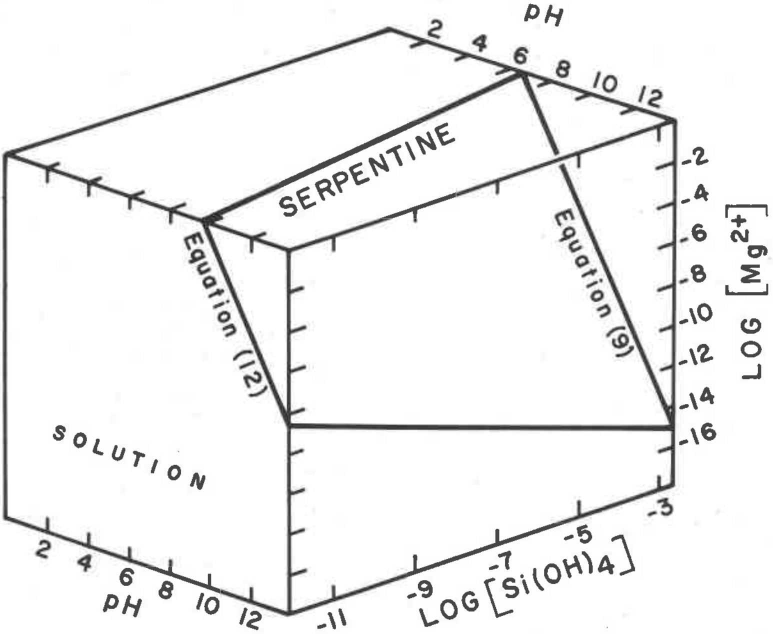

FIG. 3. Stability field of serpentine as defined by its dissociation into Mg^{2+} and $Si(OH)_4$ as a function of pH at 25°C and 1 atmosphere.

Plotted in two dimensions (Figure 4), the stability field of brucite is shown to be similar to that of serpentine, except that it does not vary with the concentration of $Si(OH)_4$. To construct a three-dimensional diagram including both serpentine and brucite, the boundary between these two minerals must be determined. This is obtained by use of the equation

$$Si_2Mg_3O_5(OH)_4 + 5H_2O = 3Mg(OH)_2 + 2Si(OH)_4 \qquad (22)$$

In this equation, the solid phases and H_2O are taken to have activities of unity, and the equilibrium expression is

$$K = [Si(OH)_4]^2 \qquad (23)$$

$$\log K = 2 \log [Si(OH)_4] \qquad (24)$$

Use of the standard free energies (Table 2) and the average free energy for serpentine (Table 3) in equations (5) and (22), gives

$$\log K = \frac{\Delta G_R^\circ}{-1.364} = \frac{2.30}{-1.364} = -16.86 \qquad (25)$$

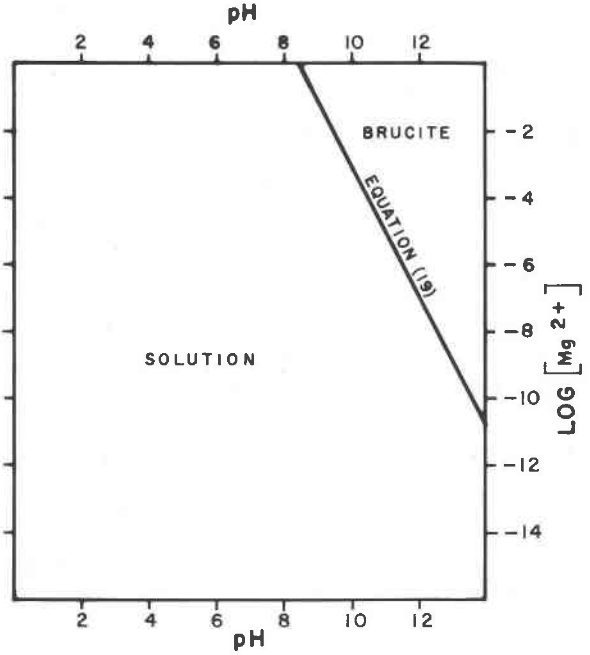

FIG. 4. Stability of brucite expressed in terms of pH and activity of Mg^{2+} at 25°C and 1 atmosphere.

$$\log\,[Si(OH)_4] = -\,8.4 \qquad (26)$$

Since the stability of brucite is independent of $Si(OH)_4$ concentrations below $10^{-8.4}$ moles/liter, a three-dimensional diagram may be constructed with the two-dimensional brucite stability diagram (Figure 4) as the front face at some $Si(OH)_4$ concentration below $10^{-8.4}$. The plane delineating brucite stability is parallel to the log $[Si(OH)_4]$ axis until the plane meets the serpentine boundary, a plane with log $[Si(OH)_4]$ fixed at -8.4. At the the three corners of this plane, straight lines are drawn to meet the two-dimensional serpentine stability diagram (Figure 1) on the rear face of the block, at the saturation concentration of $Si(OH)_4$ ($10^{-2.6}$ moles/liter). Connecting all the lines gives the completed three-dimensional stability diagram for brucite and serpentine at 25°C and 1 atmosphere (Figure 5).

It is apparent from this combination diagram that serpentine and brucite are unstable over a large portion of the pH range in these soils at which the formation of expansible clay took place. Serpentine is not stable in acid soils, except in those corresponding to a small corner of the stability field (Figure 5) which extends to pH 6.5 with Mg and Si present in very high concentrations. Soils with dissolving serpentine are

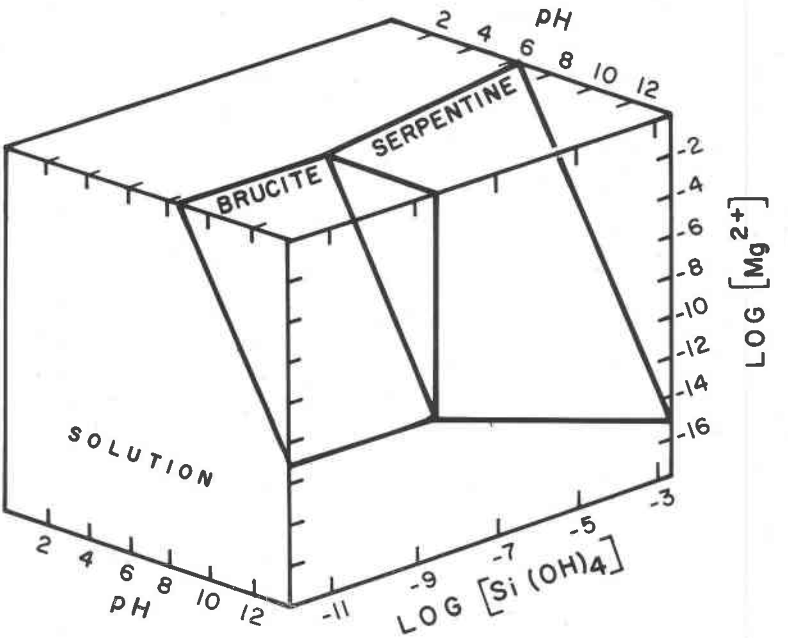

FIG. 5. Stability fields of serpentine and brucite expressed in terms of pH and activities of Mg^{2+} and $Si(OH)_4$ at 25°C and 1 atmosphere.

buffered at a pH greater than 7 by mineral dissolution (equation 2). As the Mg^{2+} concentration decreases, an increasingly higher pH (Figure 5, equation 9) is required for serpentine stability in contact with aqueous solutions. At log $[Mg^{2+}] = -11$ to -15, depending on the Si concentration (Figure 5), serpentine is not stable at any pH. Also, as the Si concentration decreases, serpentine becomes unstable at increasingly higher pH but not as rapidly as with the lowering of Mg^{2+} concentration. At log $[Si(OH)_4] = -8.4$, serpentine becomes unstable relative to brucite.

RELATIVE STABILITIES OF Fe, Al, AND Mg HYDROXIDES

It is worthwhile to compare the stabilities of the hydroxides of Fe, Al, and Mg, the cations of which commonly occupy the octahedral sheet of expansible phyllosilicate clays. Insight thus may be gained into the pedogenesis of Fe-rich montmorillonite (Wildman *et al.*, 1968a) rather than saponite in serpentinite-derived soils even though most parent serpentinite rock contains over 40 percent MgO. The stability of the ferric hydroxide component of the octahedral sheet can be derived as for that of brucite (Figure 4) by the equation

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O \tag{27}$$

$$K = \frac{[Fe^{3+}]}{[H^+]^3} \tag{28}$$

$$\log K = \log [Fe^{3+}] + 3pH \tag{29}$$

From the free energies (Table 2) substituted in equation (5) for equation (27), log K = 4.83, then

at $\log [Fe^{3+}] = 0, \quad pH = 1.6$ (30)

at $pH = 6, \quad \log [Fe^{3+}] = -13.17$ (31)

Equation (29) is plotted in Figure 6.

Al(OH)₃ requires two equations to define its stability, one for the acid

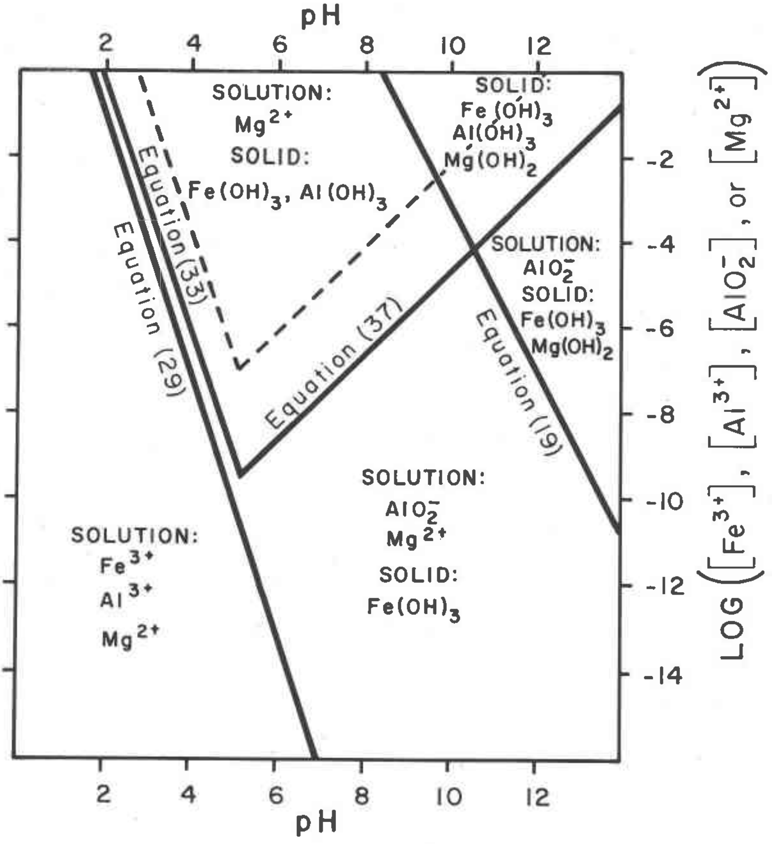

FIG. 6. Stabilities of amorphous ferric hydroxide, gibbsite, and brucite expressed in terms of pH and activities of Fe^{3+}, Al^{3+}, AlO_2^-, and Mg^{2+} at 25°C and 1 atmosphere.

dissolution boundary and the other for the alkaline dissolution boundary. The former is

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \quad (32)$$

$$\log K = 5.7 = \log [Al^{3+}] + 3pH \quad (33)$$

at $$\log [Al^{3+}] = 0, \quad pH = 1.9 \quad (34)$$

at $$pH = 6, \quad \log [Al^{3+}] = -12.3 \quad (35)$$

The alkaline dissolution boundary is represented by the equation

$$Al(OH)_3 = AlO_2^- + H^+ + H_2O \quad (36)$$

$$\log K = -14.6 = \log [AlO_2^-] - pH \quad (37)$$

at $$\log [AlO_2^-] = -2, \quad pH = 12.6 \quad (38)$$

at $$pH = 2, \quad \log [AlO_2^-] = -12.6 \quad (39)$$

Calculations of the $Al(OH)_3$ stabilities were made using the $\Delta G^\circ{}_f$ value for gibbsite (−277.3 kcal/mole as $Al(OH)_3$) given by Garrels and Christ (1965). Use of the value for gibbsite (−274.2 kcal/mole) obtained by Kittrick (1966) would reduce its stability field somewhat, as indicated by the dashed line in Figure 6. Use of free energy values for gibbsite rather than those for amorphous $Al(OH)_3$ is justified by the consideration that the stability conditions necessary for the formation of an aluminous octahedral sheet in a montmorillonite would be more like those of gibbsite than those of amorphous $Al(OH)_3$, even though gibbsite itself would not be expected to form in a soil actively forming montmorillonite.

The stabilities of amorphous ferric hydroxide, gibbsite, and brucite, expressed in terms of pH and activities of Fe^{3+}, Al^{3+}, AlO_2^-, and Mg^{2+} at 25°C and 1 atmosphere (Figure 6) indicate that $Fe(OH)_3$ and $Al(OH)_3$ in the octahedral sheet would be stable in the range of pH and in the low concentrations of Fe^{3+} and Al^{3+} normally found in soil matrix solutions. This indication corresponds to the common observation that these hydroxides, or their dehydration products, are among the materials in soils formed under most intense weathering. In contrast, brucite is unstable over essentially the whole pH range commonly occurring in soils. The only matrix solutions in which brucite could possibly exist without dissolving would have to contain a high Mg^{2+} concentration; for example, 25,000 ppm at pH 8.5, 2,500 ppm at pH 9, or 250 ppm at pH 9.5. Even under these conditions, carbonation to coalingite, pyroaurite or hydromagnesite would be likely to occur (Mumpton and Thompson, 1966).

If one assumes that the free energy relations required to construct the octahedral sheet of a layer silicate in the soil at 25°C and 1 atmosphere are similar to those required for the formation of the above metal hydroxides, it is apparent that hydroxides of Fe and Al are much more likely to nucleate the layer silicate than is $Mg(OH)_2$. The stability diagrams indicate that solid Fe and Al hydroxides are always in contact with matrix solutions of soils in which mafic minerals are weathering. While sparingly soluble near a neutral pH, these hydroxides support small concentrations of $Fe(OH)_2^+$, $Fe(OH)^{2+}$, Fe^{3+}, $Al(OH)_2^+$ and Al^{3+}. Various ferrous ion species may also be present, depending on the Eh. When $Si(OH)_4$ is present in sufficient concentration in the matrix solution, the formation of a layer silicate must provide a lower energy state for Fe or Al ions than is provided by their hydroxides; *i.e.*, the solubility product of the layer silicate must entail an equilibrium state in which Fe or Al ions are at a lower activity than they are when in equilibrium with their hydroxides. Otherwise there would be no thermodynamic driving force to hold Fe or Al ions in the octahedral sheet while $Si(OH)_4$ is being removed from the matrix solution to a silicate layer. Weaver *et al.* (1968) have shown an increase in $Si(OH)_4$ concentration in water extracts of soils after removal of the most active Fe and Al oxides by citrate-bicarbonate-dithionite treatment. This indicates an association of hydrous oxides of Fe and Al with silicon and is in keeping with the consideration that concentrations of $Si(OH)_4$ of soil matrix solutions is a key factor in formation of montmorillonite in soils (Jackson, 1965). Garrels and Christ (1965) have shown that gibbsite becomes unstable with respect to kaolinite as $Si(OH)_4$ activity becomes greater than $10^{-4.7}$ moles/liter. Depending on the magnitude of $Si(OH)_4$ activity above this concentration, a 1:1 or 2:1 layer silicate may be formed. For example, Huang and Jackson (1965) found that aluminous soil montmorillonites, when exposed to water, sustained a characteristic $Si(OH)_4$ concentration of 10 to 100 ppm, depending on the matrix solution pH. In contrast, the range of $Si(OH)_4$ concentration sustained by soil kaolinites under the same conditions was 2 to 15 ppm. These $Si(OH)_4$ solubility functions for montmorillonite and kaolinite define stability fields at log $[Si(OH)_4]$ between -4.7 and -2.6 in the stability diagram for gibbsite-kaolinite (Garrels and Christ, 1965, Fig. 10.3, page 357; Kittrick, 1969), while $Al(OH)_3$ is stable at values more negative than -4.7.

In contrast to the stability fields for Fe and Al hydroxides, that for $Mg(OH)_2$ is very limited (Figure 6); solid $Mg(OH)_2$ would not be expected to be found in soils, as discussed above. The stability of serpentine equals that of brucite at $[Si(OH_4]=10^{-8.4}$ moles/liter, and increases only slightly over that of brucite as $[Si(OH)_4]$ increases to its saturation solubility. Serpentine would not be expected to form in soils from weathering of primary minerals such as olivine or enstatite, except possibly under conditions of unusually high pH and high activities of Mg^{2+} and $Si(OH)_4$. No free energy data are available for saponite, but data are available for montmorillonite and hectorite. Weaver, *et al.* (1970), summarizing data of various investigators, cite standard free energy of formation values ranging from −1253.7 to −1275.4 kcal/mole for montmorillonites and −1340 kcal/mole for hectorite. It seems reasonable from the trends toward greater stability with increased $Si(OH)_4$ activity indicated by these 2:1 minerals as well as by 1:1 mineral formation (gibbsite→kaolinite and brucite→serpentine), that the 2:1 mineral, saponite, should be somewhat more stable than serpentine at some increased $Si(OH)_4$ activity. Even with this increased stability, however, the formation of saponite seems unlikely except in unusual soil environments.

The buildup of high pH and high concentrations of Mg^{2+} and $Si(OH)_4$ in poorly drained basins might conceivably allow formation of saponite, particularly when Al were mobilized by a high pH and Fe by reducing conditions. But in any well-drained soil, the ionic composition would be within the stability fields of Fe or Al montmorillonite long before the composition approached the stability field of saponite. The ionic conditions for saponite formation would occur with dessication and attendant concentration of Mg^{2+} and $Si(OH)_4$. Such an occurrence is rare, and these theoretical considerations are supported by the almost complete lack of reference in the literature to pedogenic saponite. Saponite in tuffaceous rock was partially replaced by montmorillonite (dioctahedral smectite) in the still calcareous surface of Mount Carmel, Israel (Singer, 1968). Several occurrences of saponite in association with weathered serpentinite are reported in the literature (Alietti, 1956; Mazzi, 1952; Malquori and Cecconi, 1956; Minguzzi, 1948). Veniale and van der Marel (1963) describe an interstratified, saponite-swelling chlorite mineral as a weathering product of lizardite rock in Italy. In view of the present findings, however, we feel that a new look at these soils should be taken in order to determine whether the expansible clay component is saponite and whether lithogenesis or authigenesis is involved. The MgO in the chemical analyses by Veniale and van der Marel could be largely allocated to the residual serpentine and mafic chlorite left in these soils, with the result that Fe and Al could be the primary constituents of the octahedral layer of a montmorillonitic component. Furthermore, the interstratified, saponite-swelling chlorite might have been inherited from the parent material in which it may have formed by hydrothermal alteration.

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