

SOLUBILITY OF TWO HIGH-Mg AND TWO HIGH-Fe CHLORITES USING MULTIPLE EQUILIBRIA¹

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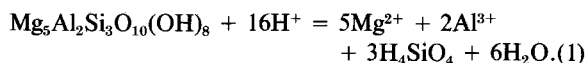
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Abstract—High-Mg chlorites from Vermont and Quebec and high-Fe chlorites from Michigan and New Mexico were equilibrated at room temperature in the near-neutral pH range. Gibbsite, kaolinite, and hematite of known stability were added to the samples to control unmeasurable variables at calculable levels. Equilibrium solution compositions were obtained from undersaturation and from supersaturation. Other indicators of equilibrium were good agreement between successive analyses over a long period of time, between duplicate samples, between independent systems, and between independent measures of equilibrium. All four chlorites were stable relative to brucite and, with a few exceptions, relative to talc under the conditions of study. When in equilibrium with gibbsite, the $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ value of the chlorites ranged from 6.3 to 6.5, at a pH_4SiO_4 value of 4.0. These values are in good agreement with prior estimates of chlorite stability. The calculated standard free energy of formation of the chlorites is dependent upon solution Fe^{2+} calculated from the sample Eh and assumed equilibrium with hematite, with the assumption that the Fe^{2+} - Fe^{3+} couple is at the same Eh as the sample.

Key Words—Chlorite, Free energy of formation, Iron, Magnesium, Solubility, Stability.

INTRODUCTION AND EXPERIMENTAL DESIGN

No actual calorimetric or solubility determinations of the standard free energy of formation (ΔG^0_f) of chlorite have been made, but several investigators have indirectly estimated ΔG^0_f of the magnesium end member (clinochlore), $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$, as shown in Table 1. These ΔG^0_f values can be better understood in terms of solution compositions by considering the dissolution of clinochlore as follows (all equations herein involve crystalline mineral phases, aqueous ions, and liquid water):



Defining K_1 as the equilibrium constant for Eq. (1), assuming the activity of mineral phases and liquid water to be unity, and taking negative logarithms:

$$\text{p}K_1 = 5\text{pMg}^{2+} + 2\text{pAl}^{3+} + 3\text{pH}_4\text{SiO}_4 - 16\text{pH}. \quad (2)$$

Hence, if Al^{3+} and H_4SiO_4 are held constant, the stability of clinochlore can be expressed in terms of pMg^{2+} and pH. If $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ is controlled by gibbsite and pH_4SiO_4 is maintained at 4.0, for example, it can be seen from the last column in Table 1 that the estimated values of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ in equilibrium with clinochlore range from 5.4 to 7.0. If $\frac{1}{2}\text{pMg}^{2+}$ in experimental samples were furthermore held to approximately 1.0 by addi-

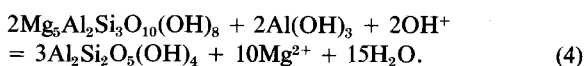
tion of appropriate salts, the anticipated equilibrium pH of the clinocllore-gibbsite system would range from 6.4 to 8.0. It seems likely that chlorite could reach stable equilibrium in this pH range, considering that Rich and Bonnet (1975) found a swelling chlorite that appeared to form in a soil whose pH ranged from 7.6 to 8.1.

An Al-containing mineral in the soil system must maintain Al^{3+} at the same low level as other minerals if it is to be stable (Kittrick, 1969). It is instructive, therefore, to isolate the Al^{3+} variable in Eq. (2):

$$\text{pAl}^{3+} = 8\text{pH} - \frac{5}{2}\text{pMg}^{2+} - \frac{3}{2}\text{pH}_4\text{SiO}_4 + \text{p}K_1/2. \quad (3)$$

It is evident from Eq. (3) that for clinocllore to keep Al^{3+} low (high pAl^{3+}), the pH must be high and pMg^{2+} and pH_4SiO_4 must be low. To determine $\text{p}K_1$ by solubility methods, all common ion activities must be known. Unfortunately, relatively high pH values (near neutrality) are likely to present analysis problems for Al with regard to both the amount and the nature of ion species. To circumvent this problem, gibbsite of known stability (Kittrick, 1966a) can be added to the system to control $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ at constant values. Thus, at equilibrium, pAl^{3+} can be calculated from the measured pH.

If kaolinite is also added to the system, gibbsite-kaolinite equilibria should control pH_4SiO_4 (Kittrick, 1967). Measurements of pH_4SiO_4 can then be compared with predicted equilibria to provide an independent indicator of equilibrium. For the clinocllore-gibbsite-kaolinite system:



¹ Scientific Paper No. SP5881. College of Agriculture Research Center, Washington State University, Pullman, Washington. Project 1885.

Table 1. Chlorite ΔG_f^0 values and the level of pH - $\frac{1}{2}$ pMg²⁺ in equilibrium with chlorite and gibbsite at pH₄SiO₄ of 4.0.

Chlorite	Source	ΔG_f^0 , kJ/mole ¹	Estimated from	pH - $\frac{1}{2}$ pMg ²⁺
Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	Zen (1972)		High-temperature, high pressure data of Fawcett and Yoder (1966)	5.4
	Bird and Anderson (1973)	-8268		
Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	Nriagu (1975)	-8190	Thermochemical model	6.8
Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	Helgeson (1969)	-8187	Seawater solubility data of MacKenzie and Garrels (1965)	6.8
Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	Tardy and Garrels (1974)	-8174	Thermochemical model	7.0
(Si _{2.97} Al _{1.03})(Al _{1.44} Fe ³⁺ _{0.07} Fe ²⁺ _{0.99} Mg _{3.24})O ₁₀ (OH) ₈	Vermont ²	-7793	Solubility measurements	6.5
(Si _{2.99} Al _{1.01})(Al _{1.39} Fe ³⁺ _{0.21} Fe ²⁺ _{0.57} Mg _{3.52})O ₁₀ (OH) ₈	Quebec ²	-7869	Solubility measurements	6.4
(Si _{2.47} Al _{1.53})(Al _{1.60} Fe ²⁺ _{3.29} Mg _{1.05})O ₁₀ (OH) ₈	Michigan ²	-7290	Solubility measurements	6.3
(Si _{2.84} Al _{1.16})(Al _{1.75} Fe ²⁺ _{2.61} Mg _{1.16} Fe ³⁺ _{0.12})O ₁₀ (OH) ₈	New Mexico ²	-7319	Solubility measurements	6.5

¹ Literature ΔG_f^0 values recalculated using $\Delta G_{f, Al^{3+}}^0 = -489,400$ J/mole.

² Present paper.

$$pK_4 = 10pMg^{2+} - 20pH. \quad (5)$$

Thus, the system is defined by measurements of pMg²⁺ and pH.

The unfortunate reality of obtaining chlorite samples suitable in amount and purity for solubility studies is that none match the simple formula used for clinocllore. Chlorites contain both Fe²⁺ and Fe³⁺, which makes the situation much more complicated. Following the strategy of multiple equilibria introduced by the gibbsite-kaolinite additions described above, one can add hematite to control Fe³⁺ at calculable levels. For hematite (Kittrick, 1971):

$$pFe^{3+} = 0.96 + 3pH. \quad (6)$$

From Garrels and Christ (1965, p. 196), pFe²⁺ can be calculated from pFe³⁺ and a measurement of Eh as follows:

$$pFe^{2+} = (Eh_{Fe^{2+}/Fe^{3+}} - 0.771)/0.0592 + pFe^{3+}. \quad (7)$$

At the extremely low levels of Fe³⁺ and Fe²⁺ anticipated in these experiments, the Fe³⁺-Fe²⁺ couple will not control sample Eh. Unfortunately, the sample and the Fe³⁺-Fe²⁺ couple may not even be at the same Eh (Bohn, 1968). To avoid this possibility, it was anticipated that quinhydrone could be added to the samples as an Eh buffer, to bring all portions of the sample system to the same Eh.

MATERIALS AND METHODS

Materials

Gibbsite. Commercial Alcoa hydrated alumina C-730 was obtained from the Aluminum Company of Ameri-

ca. X-ray powder diffraction (XRD), differential thermal (DTA), and other characteristics of this material, including solubility measurements, were described by Kittrick (1966a).

Hematite. Mapico 347 was obtained from Columbia Carbon Co. The particle size range is given as 0.06 to 0.8 μ m. Chemical, DTA, and XRD analyses (not reported) show this material to be very pure hematite.

Kaolinite. The English kaolinite was obtained from Hammill and Gillespie, Inc. and the "Georgia 2" kaolinite was obtained from Southern Clays, Inc. XRD and other characteristics of these kaolinites, including solubility measurements, were described by Kittrick (1966b).

Chlorite. Massive chlorites from Ward's Natural Science Establishment, Rochester, New York, were ground with an impact grinder to pass a 150 mesh sieve (<104 μ m). XRD analyses of oriented samples, including various combinations of Mg and K saturation, heating, and glycerol solvation, detected no phases other than chlorite. XRD patterns before and after solution equilibria were indistinguishable. Portions of the oriented patterns are shown in Figure 1 and illustrate the characteristic relative peak intensities of high-Mg chlorites (Vermont and Quebec) and high-Fe chlorites (Michigan and New Mexico), their good crystallinity, and the lack of impurities. Random powder XRD peaks necessary for polytype identification were relatively weak, but appeared to be adequate for the task of polytype identification when compared with the data of Bailey (1975, p. 242). The Vermont, Quebec, and Ishpe-

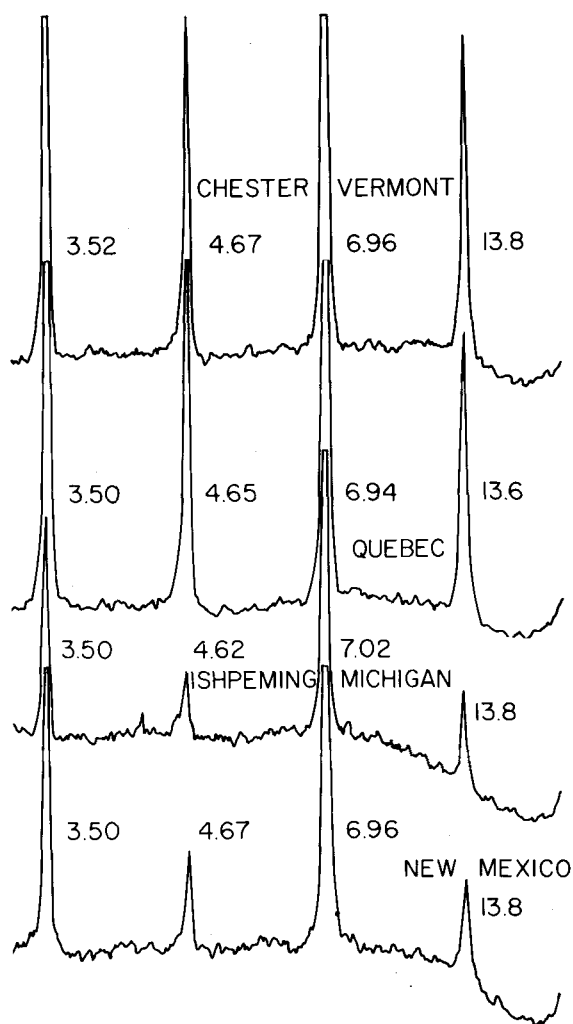


Figure 1. A portion of the chlorite X-ray diffraction patterns. Glycerated, oriented samples; Ni-filtered $\text{CuK}\alpha$ radiation; $1^\circ/2\theta/\text{min}$.

Michigan, chlorites can be classified as Ib(97), whereas the chlorite from New Mexico is Ia(97).

Methods

Total chemical analysis of chlorites. Analyses for Si, Al, Ti, Fe, Mn, Ca, Mg, K, Na, and P were made by X-ray spectroscopy. Fe^{2+} and Fe^{3+} were independently determined with orthophenanthroline after HF decomposition (Roth *et al.*, 1968). Cation-exchange capacities were negligible. The unit-cell formulae were calculated according to an 18 oxygen unit cell (Jackson, 1969).

Sample preparation and equilibration. To 10.0 g of chlorite was added 10.0 g of hematite, plus 10.0 g of kaolinite or 40.0 g of gibbsite, or both. Following treatment with hot 0.50 M NaOH to remove soluble substances (after Foster, 1953), each sample was washed

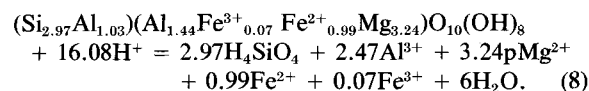
on a Buchner funnel with 1% NaOH, then with pH 5.0 NaOAc, and then with 0.010 M MgCl_2 . The sample was then placed in a 250-ml polycarbonate centrifuge bottle, given several centrifuge washes, and equilibrated with 50 ml of 0.0080 M to 0.0100 M MgCl_2 solution. In some samples the initial pH and H_4SiO_4 levels were adjusted with NaOH and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ so as to permit equilibration of the sample from both undersaturation and supersaturation with respect to variables of interest. After equilibration, the pH_4SiO_4 ranged from 3.66 to 4.40, pMg^{2+} ranged from 2.02 to 2.39, and pH ranged from 7.04 to 7.89. For some samples, a portion of the solution was removed by centrifuging for analysis after a close approach to equilibrium was indicated by successive pH measurements (a few days to a few months). For other samples, portions of the solution were removed for analysis until successive analysis indicated a close approach to equilibrium (a year or two). Equilibrated samples were sometimes centrifuge washed and equilibrated with another solution whose composition permitted a different approach to equilibrium. Quinhydrone at a concentration of 0.10 g/liter was added to some samples. Samples were agitated almost continuously in a constant temperature room at 25°C and were centrifuged in a temperature-controlled centrifuge. Room temperature during analysis was $23\text{--}25^\circ\text{C}$.

Chemical analysis of solutions. Prior to analysis, all samples were centrifuged, and an aliquot of the supernatant was further centrifuged until clear to a Tyndall beam. Si was determined colorimetrically with molybdate (APHA, 1960), Mg with an atomic absorption spectrometer, and K and Na with a flame photometer. Ion activities were computed from the extended Debye-Hückel equation. All pH measurements were with a glass combination electrode and a Corning Model 12 meter calibrated to ± 0.02 units with 2 buffers. Equilibrium pH was determined with the aid of a slow-speed, strip-chart recorder. Analysis precision estimated from duplicate determinations for all analyses is approximately ± 0.02 p units. Eh measurements, ranging from 0.347 to 0.388 V, were to the nearest millivolt, using a bright platinum foil electrode and a calomel reference electrode. ZoBell solution (ZoBell, 1946) was used as a standard.

EXPERIMENTAL RESULTS

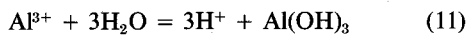
Chlorite from Chester, Vermont

Chlorite-gibbsite-kaolinite-hematite system. The equilibrium of the chlorite from Vermont with its constituent ions can be depicted as follows:



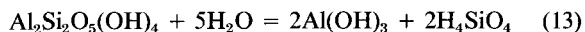
$$\begin{aligned}
 \text{p}K_8 &= 2.97\text{pH}_4\text{SiO}_4 + 2.47\text{pAl}^{3+} + 3.24\text{pMg}^{2+} \\
 &+ 0.07\text{pFe}^{3+} + 0.99\text{pFe}^{2+} - 16.08\text{pH} \quad (9) \\
 &= 2.97\text{pH}_4\text{SiO}_4 - 7.41(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\
 &- 6.48(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) \\
 &- 0.21(\text{pH} - \frac{1}{3}\text{pFe}^{3+}) \\
 &- 1.98(\text{pH} - \frac{1}{2}\text{pFe}^{2+}). \quad (10)
 \end{aligned}$$

If gibbsite is in equilibrium with the chlorite, $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ should be constant (Kittrick, 1980) as follows:



$$\begin{aligned}
 \frac{1}{3}\text{p}K_{11} &= \text{pH} - \frac{1}{3}\text{pAl}^{3+} \\
 &= 2.68 \pm 0.07. \quad (12)
 \end{aligned}$$

If gibbsite and the English kaolinite are in equilibrium with the chlorite, the pH_4SiO_4 should be constant (Kittrick, 1980) as follows:



$$\frac{1}{2}\text{p}K_{13} = \text{pH}_4\text{SiO}_4 = 4.5. \quad (14)$$

According to Eq. (6), $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ is a constant if the chlorite is in equilibrium with hematite, and $\text{pH} - \text{pFe}^{2+}$ can then be calculated from the Eh and Eq. (7).

Initial experiments involved attempts to obtain $\text{p}K_8$ by measuring pH_4SiO_4 , pMg^{2+} , and pH, controlling Eh with quinhydrone and calculating pFe^{2+} from Eqs. (6) and (7). For eight identical samples that had been equilibrated over a period of 479 days, however, $\text{p}K$ values varied by 5 units or more. Furthermore, this amount of variation did not significantly diminish over time, as indicated by analyses at ten intervals during the equilibration period. The results could not be explained by analytical errors, which at most would contribute approximately ± 0.5 units of variation. After much experimentation, it was discovered that the variation in $\text{p}K$ was due to the presence of quinhydrone. Changes in pH, probably resulting from quinhydrone breakdown, prevented attainment of equilibrium. Quinhydrone was thereafter omitted from the experiments.

To determine sample equilibrium in this investigation, the three measured variables from Table 2 (pH_4SiO_4 , pMg^{2+} , pH) were combined into two parameters (pH_4SiO_4 and $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$) so that sample equilibrium could be approached from supersaturation and undersaturation with respect to each. This permits equilibrium to be approached from four different directions on a plot of pH_4SiO_4 vs. $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ (Figure 2). The convergence of the data for chlorite-gibbsite-kaolinite-hematite samples equilibrated for 7 to 30 days (Figure 2, triangles) indicates that a real equilibrium point was being approached, as opposed to fortuitous agreement between samples of similar composition subjected to processes having similar kinetics.

Chlorite-gibbsite-hematite system. Decreasing the number of phases by one increases the degrees of freedom of the system by one. Specifically, when this sys-

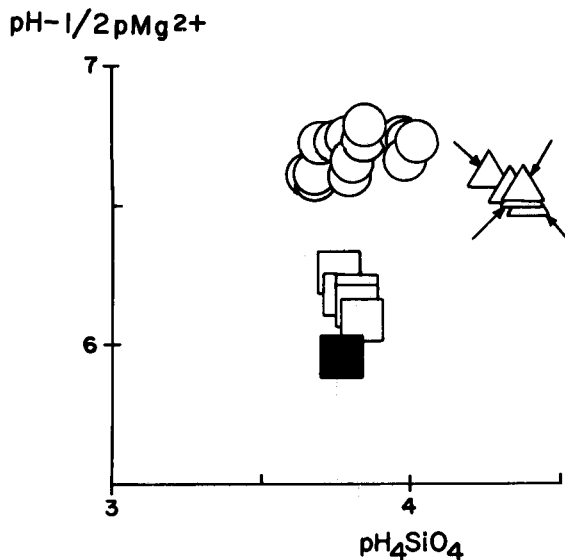


Figure 2. Solution compositions of several systems containing Vermont chlorite. Chlorite-gibbsite-kaolinite-hematite samples (Δ) were equilibrated for 7 to 30 days from four different directions of supersaturation and undersaturation as indicated by the arrows. Duplicates of the chlorite-gibbsite-hematite system (\square) were sampled repeatedly from 98 to 534 days, with one solution obtained by immiscible displacement (\blacksquare). Duplicates of the chlorite-kaolinite-hematite system (\circ) were sampled repeatedly from 37 to 793 days. Symbol size represents the deviations in $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ that could be engendered by the known variation in the gibbsite stability determination.

tem is in equilibrium, pH_4SiO_4 should not be controlled at the fixed value of Eq. (14), as when kaolinite is also present. However, the $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ should still be controlled by gibbsite. In Figure 2, analyses from Table 2 for duplicate samples are plotted (as squares) after equilibrating from 90 to 543 days, where there were no apparent differences due to equilibration time. Earlier analyses were undersaturated with respect to those shown. After 543 days of equilibration, the Eh of the two samples was 0.347 V and 0.355 V, respectively. Insufficient liquid remained for further analyses after regular centrifugation, so an additional set of analyses on one sample was made after immiscible displacement (Kittrick, 1980). All analyses plotted appear to be in reasonably good agreement.

Chlorite-kaolinite-hematite system. When this system is in equilibrium, the $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ value should be controlled by kaolinite (Georgia 2 in this case) and should depend upon pH_4SiO_4 (Kittrick, 1980). As can be seen in Figure 2 (circles), analyses from Table 2 at 37 to 793 days for duplicate samples were all in reasonably good agreement. Earlier analyses were undersaturated with respect to those shown. After 793 days, the Eh of the two samples was 0.368 V and 0.377 V, respectively.

Table 2. Solution compositions of chlorite samples.

Days	pH ₄ SiO ₄	pH	pMg ²⁺	Days	pH ₄ SiO ₄	pH	pMg ²⁺	Days	pH ₄ SiO ₄	pH	pMg ²⁺
Vermont chlorite, gibbsite kaolinite, hematite ¹				Vermont, chlorite, kaolinite hematite, Eh = 0.377 V				Michigan chlorite, gibbsite hematite, Eh = 0.384 V			
19	4.40	7.67	2.31	37	3.99	7.76	2.20	6	4.11	7.26	2.24
30	4.39	7.74	2.39	63	4.03	7.84	2.20	28	4.09	7.33	2.22
20	4.34	7.68	2.24	113	3.98	7.85	2.20	90	4.03	7.38	2.22
7	4.27	7.74	2.24	215	3.85	7.89	2.20	172	3.95	7.39	2.22
13	4.39	7.70	2.27	349	3.79	7.84	2.20	327	3.88	7.39	2.22
				506	3.76	7.80	2.14	544	3.82	7.38	2.20
				678	3.69	7.66	2.10	ID ²	3.77	7.11	2.18
				793	3.70	7.76	2.08				
Vermont chlorite, gibbsite hematite, Eh = 0.347 V				Quebec chlorite, gibbsite kaolinite, hematite ¹				Michigan chlorite, gibbsite hematite, Eh = 0.387 V			
90	3.82	7.25	2.22	8	4.47	7.53	2.34	21	4.09	7.32	2.22
172	3.82	7.30	2.20	1	4.40	7.52	2.36	54	4.04	7.41	2.24
327	3.82	7.30	2.20	9	4.45	7.74	2.26	98	4.02	7.38	2.26
543	3.75	7.35	2.18	4	4.43	7.65	2.31	174	3.95	7.37	2.24
								328	3.90	7.27	2.20
								545	3.82	7.31	2.18
Vermont chlorite, gibbsite hematite, Eh = 0.355 V				Quebec chlorite, gibbsite hematite, Eh = 0.388 V				New Mexico chlorite, gibbsite, hematite, Eh = 0.382 V			
98	3.85	7.22	2.26	28	3.71	7.36	2.22	6	4.05	7.22	2.24
174	3.84	7.22	2.22	90	3.73	7.47	2.22	28	3.97	7.29	2.22
328	3.82	7.27	2.20	172	3.72	7.54	2.22	90	3.90	7.49	2.24
543	3.77	7.28	2.24	327	3.69	7.50	2.20	172	3.89	7.49	2.24
ID ²	3.77	7.04	2.16	544	3.70	7.47	2.18	327	3.87	7.43	2.20
				ID ²	3.66	7.23	2.18	545	3.78	7.41	2.22
								ID ²	3.77	7.20	2.20
Vermont chlorite, gibbsite hematite, Eh = 0.368 V				Quebec chlorite, gibbsite hematite, Eh = 0.378 V				New Mexico chlorite, gibbsite, hematite, Eh = 0.384 V			
37	3.99	7.81	2.22	54	3.73	7.51	2.24	21	4.01	7.32	2.24
63	4.02	7.82	2.20	98	3.71	7.44	2.22	54	3.96	7.43	2.24
113	3.98	7.84	2.24	174	3.71	7.52	2.22	98	3.92	7.34	2.26
215	3.85	7.82	2.20	328	3.71	7.48	2.20	174	3.90	7.34	2.22
349	3.82	7.73	2.18	544	3.70	7.53	2.18	328	3.82	7.47	2.20
506	3.80	7.67	2.12					545	3.78	7.47	2.20
678	3.69	7.64	2.10								
793	3.66	7.62	2.02								

¹ Separate individual samples.

² ID = immiscible displacement after last analysis.

Agreement between systems. The experimental values for the three systems displayed in Figure 2 tend to lie in three separate groups. To compare them directly, it is necessary to ensure that they are displayed at the same constant values of all parameters that do not appear on the coordinates of Figure 2. Thus Eq. (10) should be solved for $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ as follows:

$$\begin{aligned} \text{pH} - \frac{1}{2}\text{pMg}^{2+} = & 0.46\text{pH}_4\text{SiO}_4 - 1.14(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\ & - 0.31(\text{pH} - \frac{1}{2}\text{pFe}^{2+}) \\ & - 0.03(\text{pH} - \frac{1}{3}\text{pFe}^{3+}) \\ & - 0.15\text{pK}_s. \end{aligned} \quad (16)$$

It can be seen from Eq. (16) that if $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ is plotted against pH_4SiO_4 (as in Figure 2), equilibrium solution analyses for Vermont chlorite should lie along

a line of slope 0.46 if $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$, and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ are held constant. From Eq. (6), hematite should control $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ in all samples at -0.32 . Where gibbsite is present, $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ should be constant at 2.68 (Kittrick, 1980). Where no gibbsite is present, the values of $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ can be obtained from the pH_4SiO_4 of the samples and the known stability of Georgia 2 kaolinite (Kittrick, 1980). From these values of $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, the experimental values of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ can be converted to calculated values of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ appropriate to a $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ value of 2.68 (Eq. 27, Appendix).

The calculated $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of each sample varies with the pH and Eh of the sample (Eq. 6 and 7). The measured Eh was used in this calculation for all systems except for the chlorite-gibbsite-kaolinite-hematite sys-

tem where no Eh measurements were made. The Eh of this system was assumed to be the same as that of the chlorite-gibbsite-hematite system. Values of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ appropriate to a constant $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of -1.0 could then be calculated from Eq. (27) in the Appendix.

Because the Fe content of the Vermont chlorite is small, the coefficient of the $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ term in Eq. (16) is small. The range in measured Eh values of about ± 0.01 volt between systems therefore had only a small impact on adjustment of experimental $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ values to a common $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of -1.0 . When adjustments for constant $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ and $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ are made, it can be seen from Figure 3 that the three independent systems agreed with each other and with a line of slope 0.46, as predicted in Eq. (16).

Calculated ΔG value. In Figure 3, the solubility of Vermont chlorite is displayed at a $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ of 2.7, a $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ of -0.3 and a $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of -1.0 . At a pH_4SiO_4 of 4.0, this chlorite can be seen to support a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ of 6.5. From Eq. (10):

$$\begin{aligned} \text{pK}_8 &= 2.97(4.0) - 7.41(2.7) - 6.48(6.5) \\ &\quad - 0.21(-0.3) - 1.98(-1.0) \\ &= -48.2 \pm 0.5, \end{aligned}$$

where the error estimate is derived from the known variation in the gibbsite solubility determination, because it is the only term in Eq. (10) where the error is accurately known. It is thought to represent a rough estimate of *minimum* analytical error. Furthermore, from the Nernst equation, where ΔG_r is the standard free energy of reaction, and ΔG_f^0 values are taken from Robie *et al.* (1978):

$$\begin{aligned} \Delta G_r &= 5.71\text{pK} = -292 \pm 3 \text{ kJ} \\ &= 2.97\Delta G_{f, \text{H}_4\text{SiO}_4}^0 + 2.47\Delta G_{f, \text{Al}^{3+}}^0 \\ &\quad + 3.24\Delta G_{f, \text{Mg}^{2+}}^0 + 0.07\Delta G_{f, \text{Fe}^{3+}}^0 \\ &\quad + 0.99\Delta G_{f, \text{Fe}^{2+}}^0 + 6\Delta G_{f, \text{H}_2\text{O}}^0 - \Delta G_{f, \text{chlorite}}^0 \\ \Delta G_{f, \text{chlorite}}^0 &= 275.2 + 2.97(-1308.0) \\ &\quad + 2.47(-489.4) + 3.24(-454.8) \\ &\quad + 0.07(-4.6) + 0.99(-78.9) \\ &\quad + 6(-237.1) \\ &= -7793 \pm 3 \text{ kJ/mole}, \end{aligned}$$

where the error estimate is the minimum due to analytical error.

Chlorite from Quebec

Chlorite-gibbsite-kaolinite-hematite system. The equilibrium of the chlorite from Quebec with its constituent ions can be given as follows:

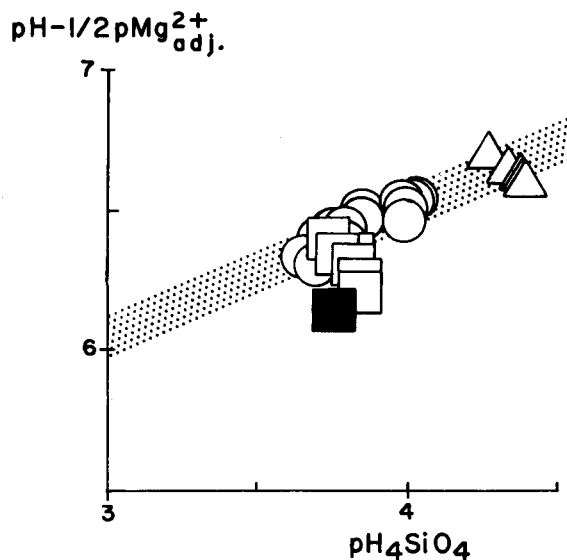
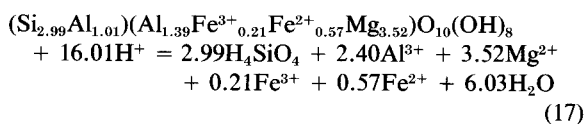


Figure 3. Adjusted solution compositions of several systems containing Vermont chlorite. Using Eq. (27), the experimental $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ values of the chlorite-kaolinite-hematite samples (O) of Figure 2 were adjusted to a $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ of 2.68. The chlorite-gibbsite-kaolinite-hematite (Δ) and chlorite-gibbsite-hematite (\square and \blacksquare) systems were also adjusted to a $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of -1.0 with Eq. (27). The shaded line has a slope of 0.46. Line width and symbol size represent the deviations in $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ that could be engendered by the known variation in the gibbsite stability determination.

$$\begin{aligned} \text{pK}_{17} &= 2.99\text{pH}_4\text{SiO}_4 + 2.40\text{pAl}^{3+} + 3.52\text{pMg}^{2+} \\ &\quad + 0.57\text{pFe}^{2+} + 0.21\text{pFe}^{3+} - 16.01\text{pH} \\ &= 2.99\text{pH}_4\text{SiO}_4 - 7.20(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\ &\quad - 7.04(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) \\ &\quad - 0.63(\text{pH} - \frac{1}{3}\text{pFe}^{3+}) \\ &\quad - 1.14(\text{pH} - \frac{1}{2}\text{pFe}^{2+}). \end{aligned} \quad (18)$$

As indicated previously for this system, both $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ should be constant, controlled by gibbsite and hematite, respectively. The $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ will not necessarily be constant, but will depend upon the pH and Eh.

As for the chlorite from Vermont, the chlorite (Quebec) gibbsite-kaolinite-hematite system (Table 2) was equilibrated with solutions whose initial composition was such that the equilibrium was approached from four different directions on a plot of pH_4SiO_4 vs. $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ (Figure 4). The convergence of the samples about a line of slope 0.42 again indicates that a real equilibrium was being approached.

Chlorite-gibbsite-hematite system. Plotted in Figure 4 are analyses from Table 2 for duplicate samples equilibrated for 28 to 544 days. Earlier analyses were undersaturated with respect to those shown. After 544 days of equilibration, the Eh of the two samples was 0.388 V and 0.378 V, respectively. Insufficient liquid

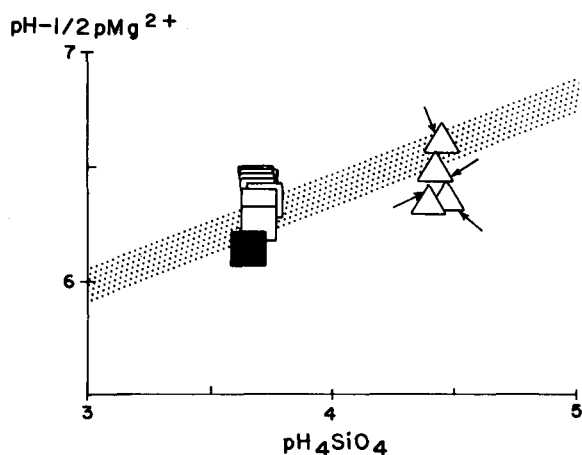


Figure 4. Solution compositions of several systems containing Quebec chlorite. The chlorite-gibbsite-kaolinite-hematite system (Δ) were equilibrated for 1 to 9 days from four different types of supersaturation and undersaturation as indicated by the arrows. Samples of the chlorite-gibbsite-hematite system (\square) were equilibrated for 28 to 544 days, with one solution obtained by immiscible displacement (\blacksquare). The shaded line has a slope of 0.42. Line width and symbol size represent the deviations in $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ that could be engendered by the known variation in the gibbsite stability determination.

remained for further analyses after regular centrifugation, so an additional set of analyses was made on one of the samples after immiscible displacement. All analyses plotted in Figure 4 for this system were very close.

Agreement between systems. To determine the theoretical slope of the chlorite solubility line on the coordinates of Figure 4, Eq. (18) must be rearranged as follows:

$$\begin{aligned} \text{pH} - \frac{1}{2}\text{pMg}^{2+} &= 0.42\text{pH}_4\text{SiO}_4 - 1.02(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\ &\quad - 0.16(\text{pH} - \frac{1}{2}\text{pFe}^{2+}) \\ &\quad - 0.09(\text{pH} - \frac{1}{3}\text{pFe}^{3+}) \\ &\quad - 0.14\text{pK}_{17}. \end{aligned} \quad (19)$$

It can be seen from Eq. (19) that, if $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ is plotted against pH_4SiO_4 (as in Figure 4), equilibrium solution analyses for Quebec chlorite should lie along a line of slope 0.42 if $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ are held constant. All samples contained both gibbsite and hematite, so $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ should have remained constant. Eh was measured only for the chlorite-gibbsite-hematite system, however, so one cannot be sure that both systems had the same $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ values.

The most reasonable assumption concerning the Eh of the samples in Figure 4 is probably that all samples had an Eh of about 0.380 V (see preceding section). This would mean that all samples had essentially the same $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ value of -1.0, and no adjustment of data points would be necessary for direct comparisons. Fortunately the coefficient of the $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ term in Eq.

(19) is small, so only large variations in $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ would have appreciable effect. Large variations in $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$, at least due to the pH term, are unlikely because most samples were within 0.1 unit of pH 7.50. With no appreciable variations anticipated in $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$, or $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ among samples in Figure 4, they may be directly compared. As can be seen in Figure 4, the two independent systems agree well with each other and with a line of slope 0.42 as predicted in Eq. (19).

Calculated ΔG_f^0 value. In Figure 4, the Quebec chlorite has a $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ of 2.7, a $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ value of -0.3, and a $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ value of -1.0. At a pH_4SiO_4 of 4.0, this chlorite can be seen to support a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ value of 6.4. From Eq. (18):

$$\begin{aligned} \text{pK}_{17} &= 2.99(4.0) - 7.20(2.7) - 7.04(6.4) \\ &\quad - 0.63(-0.3) - 1.14(-1.0) \\ &= -51.2 \pm 0.5, \end{aligned}$$

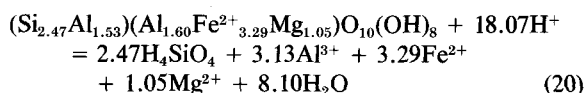
where the error estimate is derived from the known variation in the gibbsite solubility determination and is thought to represent a rough estimate of minimum analytical error. Then from the Nernst equation, where ΔG_f^0 values are taken from Robie *et al.* (1978):

$$\begin{aligned} \Delta G_r &= 5.71\text{pK} = -292 \pm 3\text{kJ} \\ &= 2.99\Delta G_{f, \text{H}_4\text{SiO}_4}^0 + 2.40\Delta G_{f, \text{Al}^{3+}}^0 + 3.52\Delta G_{f, \text{Mg}^{2+}}^0 \\ &\quad + 0.21\Delta G_{f, \text{Fe}^{3+}}^0 + 0.57\Delta G_{f, \text{Fe}^{2+}}^0 \\ &\quad + 6.03\Delta G_{f, \text{H}_2\text{O}}^0 - \Delta G_{f, \text{chlorite}}^0 \\ \Delta G_{f, \text{chlorite}}^0 &= 292.4 + 2.99(-1308.0) + 2.40(-489.4) \\ &\quad + 3.52(-454.8) + 0.21(-4.6) \\ &\quad + 0.57(-78.9) + 6.03(-237.1) \\ &= -7869 \pm 3\text{kJ/mole}, \end{aligned}$$

where the error estimate is the minimum due to analytical error.

Chlorite from Ishpeming, Michigan

Chlorite-gibbsite-hematite system. Equilibrium of chlorite from Michigan with its constituent ions can be depicted as follows:



$$\begin{aligned} \text{pK}_{20} &= 2.47\text{pH}_4\text{SiO}_4 + 3.13\text{pAl}^{3+} + 3.29\text{pFe}^{2+} \\ &\quad + 1.05\text{pMg}^{2+} - 18.07\text{pH} \end{aligned} \quad (21)$$

$$\begin{aligned} \text{pK}_{20} &= 2.47\text{pH}_4\text{SiO}_4 - 9.39(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\ &\quad - 6.58(\text{pH} - \frac{1}{2}\text{pFe}^{2+}) \\ &\quad - 2.10(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) \end{aligned} \quad (22)$$

In Figure 5, analyses for duplicate samples (Table 2) are plotted after equilibrating from 6 to 545 days. Earlier analyses were undersaturated with respect to those shown. After 545 days of equilibration, the Eh of the two samples was 0.384 V and 0.387 V, respectively.

Insufficient liquid remained for further analyses after regular centrifugation, so an additional set of analyses on one sample was made using an immiscible displacement technique (Kittrick, 1980).

Calculated ΔG. If the analyses of Figure 5 represent equilibrium, then $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ is 2.7 and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ is -0.3. From pH and Eh measurements on the 544 and 545 day samples and Eqs. (6) and (7), $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ is calculated to be -0.9. From Eq. (22) we see that, if $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ and $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ are constant, then

$$2.10(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) = 2.47\text{pH}_4\text{SiO}_4 + K, \text{ and}$$

$$\text{pH} - \frac{1}{2}\text{pMg}^{2+} = 1.18\text{pH}_4\text{SiO}_4 + K^1.$$

Thus the slope of the line in Figure 5 is 1.18. All analyses plotted in Figure 5 are in good agreement with this theoretical relationship. At a pH_4SiO_4 of 4.0 in Figure 5, the line indicates a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ of 6.3. Thus, from Eq. (22),

$$\begin{aligned} \text{pK}_{20} &= 2.47(4.0) - 9.39(2.7) \\ &\quad - 6.58(-0.9) - 2.10(6.3) \\ &= -22.8 \pm 0.5 \end{aligned}$$

where the error estimate is derived from the known variation in the gibbsite solubility determination and is thought to represent a rough estimate of minimum analytical error. Then, from the Nernst equation,

$$\Delta G_r = 5.71\text{pK}_{20} = -130 \pm 3 \text{ kJ}.$$

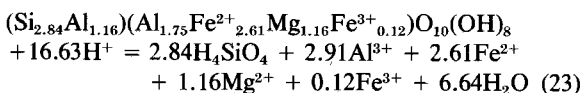
From Eq. (20) and using ΔG_f^0 values from Robie *et al.* (1978):

$$\begin{aligned} \Delta G_r &= 2.47\Delta G_{f, \text{H}_4\text{SiO}_4}^0 + 3.13\Delta G_{f, \text{Al}^{3+}}^0 \\ &\quad + 3.29\Delta G_{f, \text{Fe}^{2+}}^0 + 1.05\Delta G_{f, \text{Mg}^{2+}}^0 \\ &\quad + 8.10\Delta G_{f, \text{H}_2\text{O}}^0 - \Delta G_{f, \text{chlorite}}^0 \\ \Delta G_{f, \text{chlorite}}^0 &= 130 + 2.47(-1308.0) + 3.13(-489.4) \\ &\quad + 3.29(-78.9) + 1.05(-454.8) \\ &\quad + 8.10(-237.1) = -7290 \pm 3 \text{ kJ/mole}, \end{aligned}$$

where the error estimate is the minimum due to analytical error.

Chlorite from New Mexico

Chlorite-gibbsite-hematite system. Equilibrium of the chlorite from New Mexico with its constituent ions can be depicted as follows:



$$\begin{aligned} \text{pK}_{23} &= 2.84\text{pH}_4\text{SiO}_4 + 2.91\text{pAl}^{3+} \\ &\quad + 2.61\text{pFe}^{2+} + 1.16\text{pMg}^{2+} \\ &\quad + 0.12\text{pFe}^{3+} - 16.63\text{pH} \end{aligned} \quad (24)$$

$$\begin{aligned} \text{pK}_{23} &= 2.84\text{pH}_4\text{SiO}_4 - 8.73(\text{pH} - \frac{1}{3}\text{pAl}^{3+}) \\ &\quad - 5.22(\text{pH} - \frac{1}{2}\text{pFe}^{2+}) \\ &\quad - 2.32(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) \\ &\quad - 0.36(\text{pH} - \frac{1}{3}\text{pFe}^{3+}). \end{aligned} \quad (25)$$

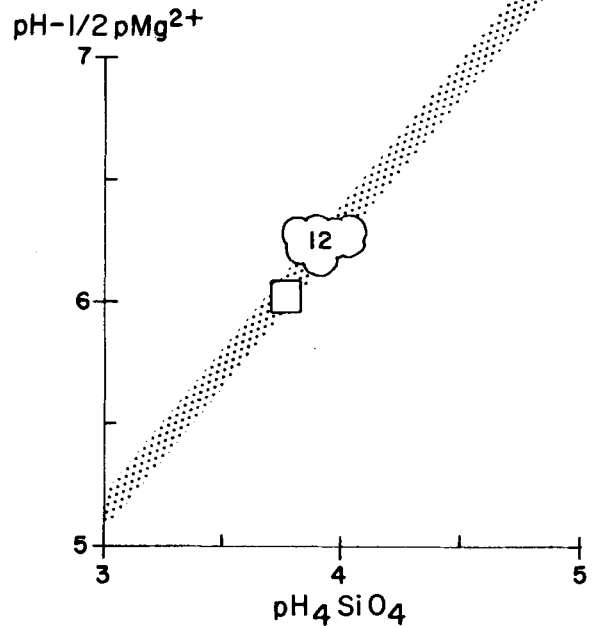


Figure 5. Solution compositions of two samples containing chlorite from Michigan, plus gibbsite and hematite (○). Duplicates were sampled repeatedly from 6 to 545 days, with one solution obtained by immiscible displacement (□). The group contains 12 analysis points. The shaded line has a slope of 1.18. Symbol size and line width represent the deviation in $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ that could be engendered by the known variation in the gibbsite stability determination.

As before, with $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ held constant according to Eq. (12), $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ held constant according to Eq. (6), and pFe^{2+} calculated from Eq. (7), pK_{23} is defined by measurements of equilibrium pH_4SiO_4 , pMg^{2+} , pH, and Eh (Table 2). In Figure 6, three of these variables are plotted for duplicate samples after equilibrating for 6 to 545 days. Earlier analyses were undersaturated with respect to those shown. After 545 days of equilibration, the Eh of the two samples was 0.382 V and 0.384 V, respectively. Insufficient liquid remained for further analysis after regular centrifugation, so an additional set of analyses was made on one sample using an immiscible displacement technique.

Calculated ΔG value. If the analyses of Figure 6 represent equilibrium, then $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ is 2.7 and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ is -0.3. From pH and Eh measurements on the 545 day samples and Eqs. (6) and (7), $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ is calculated to be -0.9. From Eq. (25), if $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$, and $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ are constant,

$$2.32(\text{pH} - \frac{1}{2}\text{pMg}^{2+}) = 2.84\text{pH}_4\text{SiO}_4 + K, \text{ and}$$

$$\text{pH} - \frac{1}{2}\text{pMg}^{2+} = 1.22\text{pH}_4\text{SiO}_4 + K^1.$$

Thus the slope of the line in Figure 6 is 1.22. All analyses plotted in Figure 6 are in good agreement with this

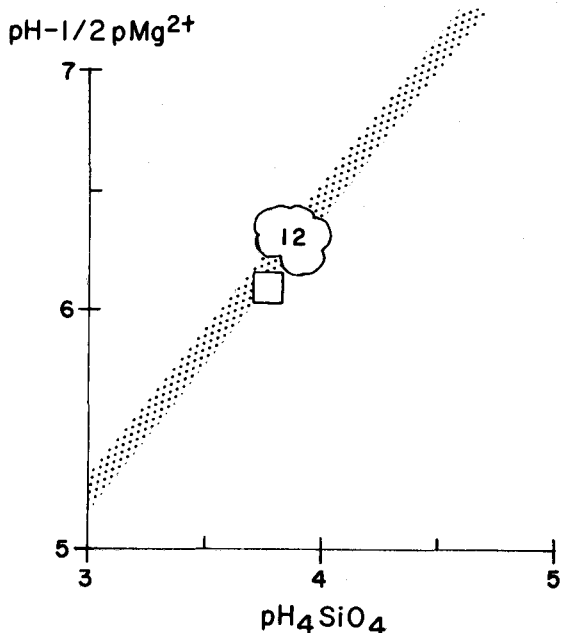


Figure 6. Solution compositions of two samples containing chlorite from New Mexico, plus gibbsite and hematite (O). Duplicates were sampled repeatedly from 6 to 545 days with one solution obtained by immiscible displacement (□). The group contains 12 analysis points. The shaded line has a slope of 1.22. Line width and symbol size represent the deviations in $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ that could be engendered by the known variation in the gibbsite stability determination.

relationship. At a pH_4SiO_4 of 4.0, the line indicates a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ value of 6.5. Thus, from Eq. (25),

$$\begin{aligned} \text{pK}_{23} &= 2.84(4.0) - 8.73(2.7) - 5.22(-0.9) \\ &\quad - 2.32(6.5) - 0.36(-0.3) \\ &= 22.5 \pm 0.5, \end{aligned}$$

where the estimate of minimum analytical error is again derived from the known variation in the gibbsite solubility determination. Similarly

$$\Delta G_r = 5.71\text{pK}_8 = 128 \pm 3 \text{ kJ.}$$

and from Eq. (23)

$$\begin{aligned} \Delta G_r &= 2.84\Delta G_{f, \text{H}_4\text{SiO}_4}^0 + 2.91\Delta G_{f, \text{Al}^{3+}}^0 \\ &\quad + 2.61\Delta G_{f, \text{Fe}^{2+}}^0 + 1.16\Delta G_{f, \text{Mg}^{2+}}^0 \\ &\quad + 0.12\Delta G_{f, \text{Fe}^{3+}}^0 + 6.64\Delta G_{f, \text{H}_2\text{O}}^0 \\ &\quad - \Delta G_{f, \text{chlorite}}^0 \\ \Delta G_{f, \text{chlorite}}^0 &= 128 + 2.84(-1308.0) + 2.91(-489.4) \\ &\quad + 2.61(-78.9) + 1.16(-454.8) \\ &\quad + 0.12(-4.6) + 6.64(-237.1) \\ &= -7319 \pm 3 \text{ kJ/mole.} \end{aligned}$$

DISCUSSION AND CONCLUSIONS

Sample equilibrium

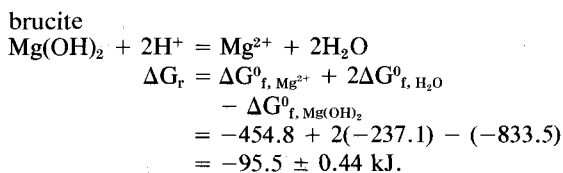
The most common flaw in mineral stability determinations by the solubility method is the lack of demon-

strated sample equilibrium. In the present experiments there were five indicators of sample equilibrium for the high-Mg chlorites (Vermont and Quebec). First, good agreement was achieved between successive analyses of single samples over a long period of time. Second, there was good agreement between duplicate samples. Third, the same values were obtained for samples equilibrated from both undersaturation and supersaturation. Fourth, an independent measure of equilibrium was made involving the measured pH_4SiO_4 levels of samples containing both gibbsite and kaolinite. The pH_4SiO_4 of such samples in Figures 2 and 4 ranges from 4.3 to 4.5. These values are in good agreement with Eq. (14) and with the stability of gibbsite and kaolinite as determined by long-term solubility methods and by immiscible displacement of solutions following short-term equilibration (Kittrick, 1980). A fifth check on sample equilibrium involved a comparison of three independent systems containing chlorite, i.e., chlorite-gibbsite-kaolinite-hematite, chlorite-gibbsite-hematite, and chlorite-kaolinite-hematite. Agreement between these systems with regard to directly measured variables was good, and could be made essentially perfect, depending upon assumptions relative to sample Eh values.

The same five indicators of sample equilibrium were also applied to the high-Fe chlorites (Michigan and New Mexico), but data supporting equilibrium checks three and five are not shown. A lack of Eh measurements on the chlorite-gibbsite-kaolinite-hematite system made these data marginally useful for equilibrium constant calculations where high-Fe chlorites are involved, so they were omitted. The three equilibrium indicators shown are sufficient to indicate that the likelihood of sample equilibrium is good.

Interstratification and solid solution

A gradation exists in the brucitic layers of natural chlorites with regard to both layer completeness and the binding of adjacent smectitic units. It is, therefore, uncertain as to whether the brucitic and smectitic layers should be considered units within a single-phase mineral, or independent, regularly interstratified components. Separate brucite and talc components, for example, controlling their individual solubilities should generate solution analyses that cluster at the intersection of the brucite and talc stability lines. The $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ supported by brucite can be determined as follows:



There is good agreement among recent compilations (Sadiq and Lindsay, 1979; Robie *et al.*, 1978; Parker *et*

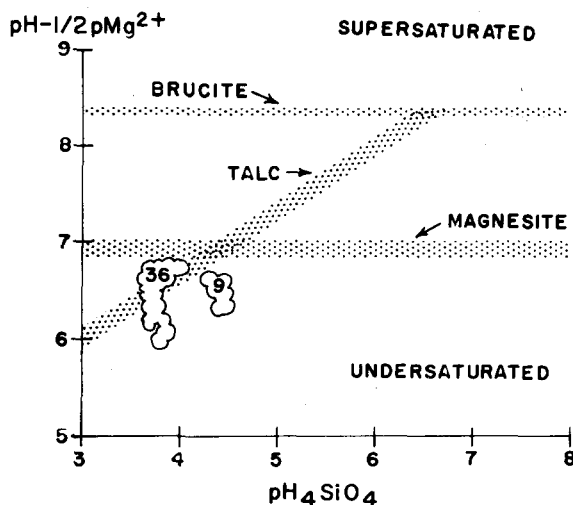


Figure 7. Solution compositions of Vermont and Quebec chlorites (from Figures 2 and 4) in relation to stability lines of brucite, talc, and magnesite. Line widths and symbol size represent estimates of experimental error. There are 36 points in one cluster and 9 in the other. The intersection of the brucite and talc lines is derived from Eq. (26).

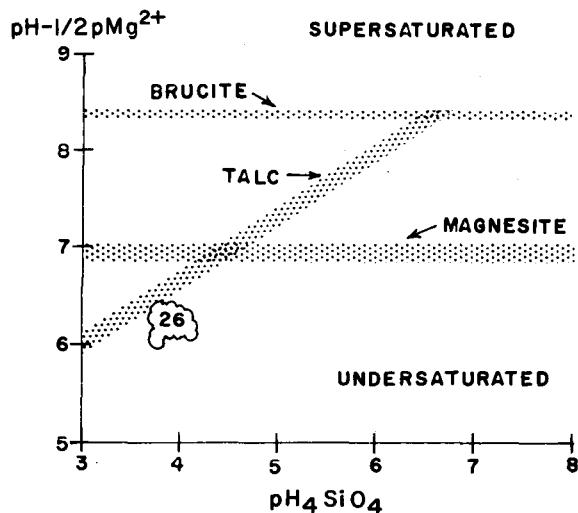


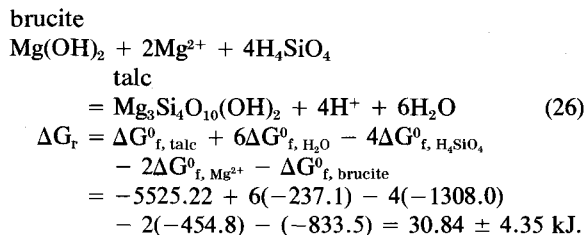
Figure 8. Solution compositions of Michigan and New Mexico chlorites (from Figures 5 and 6) in relation to stability lines for brucite, talc, and magnesite. Line widths and symbol size represent estimates of experimental error. The group contains 26 analysis points.

al., 1971) for the ΔG_f^0 of brucite. The value given by Robie *et al.* (1978) for brucite is used above, where the error in the ΔG_f^0 of brucite is assigned to the error in ΔG_r . Furthermore,

$$\begin{aligned} pK &= \Delta G_r / 5.707 = -16.73 \pm 0.08 \\ pK &= 2pMg^{2+} - 2pH \\ pH - \frac{1}{2}pMg^{2+} &= -pK/2 = 8.37 \pm 0.04. \end{aligned}$$

Thus, the stability line for brucite (as shown in Figures 7 and 8) is parallel to the pH_4SiO_4 axis, intersecting the $pH - \frac{1}{2}pMg^{2+}$ axis at 8.37.

If the brucitic and talcitic components of chlorite were to control solution equilibria, solution analyses should occur at the intersection of the brucite and talc stability lines. This intersection can be determined as follows:



The $\Delta G_{f, talc}^0$ selected is from Sadiq and Lindsay (1979), with the error in the $\Delta G_{f, talc}^0$ assigned to the error in ΔG_r . Then, from Eq. (26),

$$\begin{aligned} pK &= 4pH^+ - 4pH_4SiO_4 - 2pMg^{2+} \\ &= 30.84/5.707 = 5.40 \pm 0.76. \end{aligned}$$

$$\begin{aligned} 4pH_4SiO_4 &= 4pH - 2pMg^{2+} - pK \\ pH_4SiO_4 &= pH - \frac{1}{2}pMg - pK/4 = 8.37 - 1.84 \\ &= 6.53 \pm 0.19. \end{aligned}$$

The intersection of the brucite and talc lines is shown in Figures 7 and 8, where it can be seen that the solution analyses are not clustered about the intersection, but rather, occur over a range in $pH - \frac{1}{2}pMg^{2+}$ and pH_4SiO_4 values. In particular, none lie close to the intersection of brucite and talc lines. None of the solution analyses parallel or lie close to the brucite line although some coincide with the talc stability line. It therefore appears that neither brucite individually, nor brucite and talc collectively, control solution equilibria as solid solution components. Control of solution equilibria by a talc component appears doubtful, but perhaps cannot be entirely eliminated.

When conducting mineral solubility determinations, it is always necessary to consider the possible precipitation of other mineral phases which may then control solution ion levels. Magnesite can be readily precipitated in room temperature solutions in contact with the CO_2 of the atmosphere. The shaded line in Figures 7 and 8 (Kittrick, 1973) is based upon the $\Delta G_{f, magnesite}^0$ selected from Robie *et al.* (1978). Because all solution analyses are undersaturated with respect to magnesite, magnesite does not appear to be controlling samples in Figures 7 and 8. Chrysotile does not ordinarily precipitate in solutions at room temperature, but again using ΔG_f^0 values from Robie *et al.* (1978), it can be calculated that chrysotile supports a $pH - \frac{1}{2}pMg^{2+}$ value of 6.7 ± 0.1 at a pH_4SiO_4 of 4.0. This is somewhat more

soluble than the four chlorites which range from $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ values 6.3 to 6.5 under those conditions (Table 1), thus chrysotile does not appear to be controlling sample solubilities either.

There seems little doubt that chlorite, with its wide and essentially continuous variation in chemical composition, is a solid solution. However, distribution of the solution analyses along lines of theoretical slope (Figures 3-6) indicate control by a single phase of bulk chlorite composition rather than control by solid solution components. The solid solution components appear to be "frozen in." The fact that the slope of solubility lines are compatible with the bulk chemical composition of the chlorites indicates that the proportion of their solid solution components does not change appreciably during the course of the equilibration. If these chlorites formed under equilibrium conditions of low temperature metamorphism, their proportion of various solid solution components would be expected to be that which is most stable for those particular conditions. That is not likely to be the same proportion of components that is most stable during room temperature solubility experiments. Because the chlorite composition showed no appreciable change during the course of those experiments, the system should be considered to be at a metastable equilibrium.

Chlorite stabilities compared

Because ΔG_f^0 is an extensive variable, ΔG_f^0 values of minerals of variable composition are strongly dependent upon the exact chemical composition of the individual minerals. Thus, a comparison of stabilities of minerals of variable composition cannot be obtained by comparing ΔG_f^0 values (Table 1). However, their stabilities can be compared by considering their level of control of some constituent at fixed levels of other constituents. For example, at a pH_4SiO_4 of 4.0 under identical conditions of $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$, $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$, and $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$, the chlorite from Michigan supports a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ of 6.3 compared to 6.4 for the chlorite from Quebec and 6.5 for the chlorites from Vermont and New Mexico. This can be directly compared with the estimates for clinocllore stability in Table 1, which range from 5.4 to 7.0. The estimate of 6.8 for $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$, as calculated from Helgeson (1969) and Nriagu (1975), is particularly close to the experimental values.

The chlorite from Michigan is the more stable (least soluble) of the four under the conditions of comparison, but one must note that the difference between the four in terms of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ is approximately the width of the estimated error band for the talc stability line in Figures 7 and 8. Thus, in terms of the uncertainties involved in determining mineral stabilities, the stabilities of the Vermont, Quebec, Michigan, and New Mexico chlorites must be considered to be quite similar. They probably serve as a useable estimate of the high pH-

high Mg limit in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MgO-H}_2\text{O-H}^+$ system and of the general stability of chlorites formed under low-temperature metamorphism. As a first approximation, a $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ of 6.4 at a pH_4SiO_4 of 4.0 may be used to represent a wide range of chlorites formed under low-temperature metamorphism if Al control is close to that of gibbsite. Chlorites that are formed at room temperature are presumably more stable at room temperature than those investigated here. Whether this is reflected in a measurable difference in equilibrium levels of constituents remains to be determined.

The values of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ and pH_4SiO_4 in equilibrium with the four chlorites are directly determined with good accuracy and dependable precision. The values of $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ and $\text{pH} - \frac{1}{3}\text{pFe}^{3+}$ depend upon equilibrium with gibbsite and hematite respectively, which appear to be good assumptions. The values of pK_8 , pK_{17} , pK_{20} , and pK_{23} and their corresponding ΔG_f^0 , $\Delta G_{f, \text{chlorite}}$ are less certain because in addition to the aforementioned parameters, they also depend upon the assumption that the measured Eh of the samples is the same as that of the $\text{Fe}^{2+}\text{-Fe}^{3+}$ couple in the samples. This assumption is important for the high-Fe chlorites. For example, for every 10 mV change in Eh, the ΔG_f^0 of the Michigan chlorite changes 3.2 kJ (0.76 kcal) and the ΔG_f^0 of the New Mexico chlorite changes 2.5 kJ (0.60 kcal).

The Eh of the chlorite samples is not controlled by the chlorite-hematite pair, because they support such low levels of Fe^{2+} and Fe^{3+} in solution. Quinhydrone additions controlled the Eh and probably would have ensured that the $\text{Fe}^{2+}\text{-Fe}^{3+}$ couple was at the measured Eh. When quinhydrone was eliminated for other reasons, the Eh of the chlorite systems was left to be controlled by dissolved oxygen. This Eh was measured, but one cannot be sure that the $\text{Fe}^{2+}\text{-Fe}^{3+}$ couple is at that Eh (Bohn, 1968). Thus, the determination of high-Fe chlorite stabilities by solubility methods can be accomplished only within the constraints of whatever uncertainty exists as to the actual Eh of the $\text{Fe}^{3+}\text{-Fe}^{2+}$ couple.

ACKNOWLEDGMENTS

This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, under Grant PRF5872-AC2. Appreciation is expressed to Mr. E. W. Hope and Mr. W. L. Moore who performed the solution analyses and to Dr. P. R. Hooper who analyzed the chlorites.

APPENDIX

Based upon Eq. (16), the analytically determined $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ for Vermont chlorite may be adjusted to a $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ of 2.68 and a $\text{pH} - \frac{1}{2}\text{pFe}^{2+}$ of -1.0

as follows: $\text{pH} - \frac{1}{2}\text{pMg}^{2+}_{\text{adjusted}} = \text{pH} - \frac{1}{2}\text{pMg}^{2+}_{\text{analysis}} + 1.14(\text{pH} - \frac{1}{3}\text{pAl}^{3+}_{\text{analysis}} - 2.68) + 0.31(\text{pH} - \frac{1}{2}\text{pFe}^{2+}_{\text{analysis}} + 1.0)$. (27)

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(Received 16 April 1981; accepted 17 September 1981)

Резюме—Высоко-Mg хлориты из Вермонта и Квебека и высоко-Fe хлориты из Мичигана и Новой Мексики уравнивались при комнатной температуре в почти нейтральном диапазоне pH. Гиббсит, каолинит и гематит о известной стабильности были добавлены к образцам, чтобы контролировать неизмеряемые переменные на уровнях, поддающихся исчислению. Составы равновесного раствора определялись путем ненасыщения и перенасыщения. Другие индикаторы равновесия были в хорошем согласии между последующими анализами в течение длинного времени, между спаренными образцами, между независимыми системами и между независимыми измерениями равновесия. Все четыре хлориты были стабильны по отношению к бруциту и, за несколькими исключениями, по отношению к тальку в условиях проведения исследования. В случае равновесия с гиббситом величина $\text{pH} - 1/2\text{Mg}^{2+}$ хлоритов изменялась от 6,3 до 6,5 при величине pH_4SiO_4 равной 4,0. Эти величины хорошо согласуются с прежними оценками стабильности хлоритов. Рассчитанная стандартная свободная энергия образования хлоритов зависит от растворения Fe^{2+} , вычисленного для Eh образца при предположении равновесия с гематитом, а также при допущении, что пара $\text{Fe}^{2+}\text{-Fe}^{3+}$ имеет такое Eh как образец. [E.C.]

Resümee—Mg-reiche Chlorite von Vermont und Quebec und Fe-reiche Chlorite von Michigan und New Mexico wurden bei Raumtemperatur im neutralen pH-Bereich ins Gleichgewicht gebracht. Den Proben wurden Gibbsit, Kaolinit, und Haematit mit bekannter Stabilität hinzugefügt, um den Einfluß unmeßbarer Variablen unter Kontrolle zu halten. Die Gleichgewichtszusammensetzungen der Lösungen wurden aus der Untersättigung und Übersättigung ermittelt. Weitere Hinweise für Gleichgewicht waren eine gute Übereinstimmung von aufeinanderfolgenden Analysen übereinen langen Zeitraum zwischen Parallelproben, zwischen unabhängigen Systemen und zwischen unabhängigen Gleichgewichtsmessungen. Alle vier Chlorite waren unter den untersuchten Bedingungen in Bezug auf Brucit und—mit wenigen Ausnahmen—auch in Bezug auf Talk stabil. Im Gleichgewicht mit Gibbsit lag bei einem pH_4SiO_4 von 0,4 der $\text{pH} - 1/2\text{Mg}^{2+}$ der Chlorite zwischen 6,3 und 6,5. Diese Werte stimmen gut mit früheren Schätzungen der Chloritstabilität überein. Die berechnete Freie Standardbildungsentnergie der Chlorite hängt vom Fe^{2+} -Gehalt der Lösung ab, wie aus dem Eh der Probe berechnet wurde und sich auch aus dem Gleichgewicht mit Haematit ergab. Voraussetzung dafür ist, daß das $\text{Fe}^{2+}\text{-Fe}^{3+}$ Paar den gleichen Eh wie die Probe hat. [U.W.]

Résumé—Des chlorites à contenu élevé en Mg du Vermont et du Québec, et des chlorites à contenu élevé en Fe de Michigan et de New Mexico ont été équilibrées à température ambiante à un pH quasiment neutre. De la gibbsite, de la kaolinite et de l'hématite de stabilité connue ont été ajoutées aux échantillons pour contrôler des variables non-mesurables à des niveaux calculables. Des compositions de solution équilibrée ont été obtenues par sousaturation et supersaturation. D'autres indicateurs d'équilibre étaient la correspondance d'analyses successives pendant une longue durée, d'échantillons répétées, de systèmes indépendants, et de mesures indépendantes d'équilibre. Les quatre chlorites étaient stables relatives à la brucite, et, avec quelques exceptions, au talc sous les conditions de l'étude. Lorsque les chlorites étaient en équilibre avec la gibbsite, leurs $\text{pH} - 1/2\text{Mg}^{2+}$ s'étagaient de 6,3 à 6,5, à une valeur pour pH_4SiO_4 de 4,0. Ces valeurs s'accordent bien avec des estimations précédentes de stabilité pour les chlorites. L'énergie libre standard calculée pour la formation des chlorites dépend de la solution Fe^{2+} calculée à partir de l'échantillon Eh et de l'équilibre supposé avec l'hématite, en supposant que le couple $\text{Fe}^{2+}\text{-Fe}^{3+}$ a le même Eh que l'échantillon. [D.J.]