

SOLUBILITY MEASUREMENTS OF PHASES IN THREE ILLITES¹

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Abstract—Goose Lake, Beavers Bend, and Fithian illites were equilibrated in the presence of goethite (or hematite) at room temperature for as long as 2.6 yr. Kaolinite of known stability was added to some samples. Samples of solution were obtained after centrifuging with, or without, immiscible displacement or column leaching. Equilibrium was indicated by constant values over a long period of time, with kaolinite solubility as an internal indicator, and most importantly, by the approach to equilibrium from both undersaturation and supersaturation. Data plots indicate that the illites contain two or more phases or components in equilibrium with each other. Statistical and graphical techniques were used to analyze hundreds of equilibrations. The constancy of pK values for various expressions indicates that bulk illite composition and pyrophyllite are likely solution-controlling phases or components, but that muscovite, leucophyllite, phlogopite, and talc are not. A muscovite-like phase, of lower K content than muscovite, fit one pK expression well, but failed on two others.

Key Words—Equilibration, Illite, Kaolinite, Phase analysis, Pyrophyllite, Solubility.

INTRODUCTION

Mixed-layer minerals such as many illites are identified primarily by X-ray powder diffraction, which measures structural, rather than thermodynamic properties. Thus, although the phase status (how many, what kind) of mixed-layer minerals is essential to an understanding of their equilibrium relations (Zen, 1962), it is usually unknown. Investigators have of necessity assumed illite to be (1) a single phase consisting of a single component; (2) a single phase consisting of multiple components; or (3) multiple phases.

For convenience in solubility studies, illite has generally been considered a single-phase, single-component mica. Reesman (1974, 1978) compared illite equilibrium constants calculated on the basis of a single muscovite phase of ideal composition, and Routson and Kittrick (1971) calculated equilibrium constants on the basis of a single K-mica phase. On the other hand, Lippman (1977) and Velde (1977, p. 62) considered illite to be a single solid-solution phase containing multiple components, such as a muscovite component, a leucophyllite component, etc.

In addition to an assumed muscovite-like phase, several *operationally-defined* non-micaceous phases have often been identified in mixed-layer illite samples by standard mineralogical techniques. Chlorite, montmorillonite, and vermiculite have been identified in the Beavers Bend and Fithian illite samples by quan-

titative mineralogical analyses (Raman and Jackson, 1966), and montmorillonite was identified in Fithian material by X-ray powder diffraction (Yoder and Eugster, 1955). The apparent multiphase nature of illite has been strikingly demonstrated by the study of variations in chemical composition between individual mineral flakes (Bodine and Standaert, 1977). The present investigation was undertaken to determine if the phase status of illite could be determined by solubility studies, although multiple phases may make this difficult.

MATERIALS AND METHODS

Minerals

Beavers Bend illite was obtained from the Oklahoma Geological Survey (Mankin and Dodd, 1963). The Fithian illite used was API reference illite H-35, from Ward's Natural Science Establishment, Rochester, New York. Goose Lake illite (gründite) was obtained from the Illinois Clay Products Company, Joliet, Illinois, and was characterized by Grim and Bradley (1939). All three illites were characterized by Routson (1970). They appear to have formed during low-temperature metamorphism. Total chemical analyses of the K-saturated, 0.2–2.0- μm size fractions yield the following formulae: $\text{K}_{0.53}(\text{Al}_{1.66}\text{Fe}_{0.20}\text{Mg}_{0.13})(\text{Si}_{3.62}\text{Al}_{0.39})\text{O}_{10}(\text{OH})_2$ for the Beavers Bend, $\text{K}_{0.64}(\text{Al}_{1.54}\text{Fe}_{0.29}\text{Mg}_{0.19})(\text{Si}_{3.51}\text{Al}_{0.49})\text{O}_{10}(\text{OH})_2$ for the Fithian, and $\text{K}_{0.59}(\text{Al}_{1.58}\text{Fe}_{0.24}\text{Mg}_{0.15})(\text{Si}_{3.65}\text{Al}_{0.35})\text{O}_{10}(\text{OH})_2$ for the Goose Lake illites (Routson and Kittrick, 1971). The samples used in the present study were those used by Routson and Kittrick (1971) who described pretreatments of grinding, par-

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ticle size separation, pyrite removal and K-saturation. The hematite and goethite used to control pH $- \frac{1}{3}p\text{Fe}^{3+}$ at a constant value were the Mapico 347 and Mapico 100 products, respectively. The particle size range is 0.06 to 0.8 μm as reported by the supplier, Columbian Carbon Company, New York, New York. Chemical, differential thermal, and X-ray powder diffraction analyses (not reported here) demonstrated that these materials are essentially pure hematite and goethite. Georgia 2 kaolinite, used in some of the experiments, was obtained from the Georgia Kaolin Company, Elizabeth, New Jersey. X-ray powder diffraction and other characteristics of this kaolinite, including solubility measurements, were reported by Kittrick (1966, 1980).

Illite equilibration

Ten grams of either goethite or hematite was added to 20-g samples of 0.2–2.0- μm illite. Twenty grams of kaolinite was also added to some samples. After mixing, the samples were centrifuge-washed three times with 0.01 M KOAc solution (pH 4.0) and four times with 0.01 M KCl–0.0001 M MgCl_2 solution. They were then quartered and placed in 60-ml polyethylene bottles. The samples were then centrifuge-washed with various equilibration solutions and shaken for varying periods of time up to 2.6 yr, with 35–50 ml of the solution. The equilibration solutions generated final solution compositions ranging from pH_4SiO_4 2.6 to 3.7; pMg^{2+} 2.0 to 3.9; pK^+ 1.5 to 3.2; and pH 3.7 to 7.1. Samples were agitated almost continuously in a constant temperature room at 23–25°C and were centrifuged in a temperature-controlled centrifuge. A few samples were equilibrated for periods of only 5–23 days with a minimum of liquid. Approximately 9 ml of solution was obtained by immiscible displacement with CCl_4 (Kittrick, 1980). A few additional samples were equilibrated by recycling solution flowing at the rate of 1–2 ml/day through 10–20 cm of sample packed in a 0.64-cm ID glass tube. X-ray powder diffraction patterns of all illites before and after equilibration were essentially identical.

For analysis, the samples (except columns) were centrifuged and an aliquot of the supernatant liquid centrifuged further until clear to a Tyndall beam. Si in the equilibrated supernatant liquids was determined colorimetrically with molybdate (APHA, 1960), Al with aluminon (Hsu, 1963), Mg with an atomic absorption spectrophotometer, K with a flame photometer, and Cl^- with a Buchler-Cotlove chloridometer. Ion activities were computed from the extended Debye Hückel equation. The pH measurements were made with a glass combination electrode and a Corning Model 12 meter calibrated to ± 0.02 units. Equilibrium pH was determined with the aid of a slow-speed stripchart recorder. Precision was estimated from duplicate determinations to be approximately ± 0.02 log units.

RESULTS AND DISCUSSION

Multiple phases

The compositions of all solutions equilibrated with illite samples are presented in Table 1. Because illite may be a solid solution, there may be a solution-controlling phase, or a solution-controlling component, or both. Because the proper designation is unknown, the term phase will be used for simplicity in the following discussion. The most common direct approach to solubility determinations is to calculate pK values for the controlling phase as a function of time or some other variable. Because the phase(s) of illite are not known with certainty, a more oblique approach was used. A straight-line fit ($r = 0.97$) was obtained from a plot of $\text{pH} - \frac{1}{2}\text{pMg}^{2+}$ vs. pH_4SiO_4 of the Goose Lake illite (Figure 1, left). The plotted points represent approach from both undersaturation and supersaturation. Beavers Bend and Fithian illites give similar results (not shown), although the data for the Fithian material are more scattered. A single magnesium silicate phase could equilibrate along a line such as in Figure 1. Unfortunately, a talc phase does not fit the data, as will be shown below. There appears to be no other likely magnesium silicate, thus, the possibility of solution control by an aluminum magnesium silicate, with $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ on the vertical axis (perpendicular to the page) must be considered. Solution analysis points in equilibrium with an aluminum magnesium silicate could lie anywhere on the surface of a stability plane in those three dimensions. If so, why should they be constrained to lie along a straight line? One possibility is that the straight line results from systematic kinetics (rather than true equilibrium) as various samples are initially adjusted to a range in pH values. It seems unlikely, however, that samples adjusted to one side of a fortuitous line from oversaturation should approach the same line from undersaturation. More plausibly, the line represents the chemical potential boundary between *two* controlling phases (or components). It is the approach to true equilibrium that would constrain the samples to approach such a boundary from both supersaturation and undersaturation. If the line in Figure 1 represents two phases, the single phase-single component alternative for illite is not possible.

Because the composition of the controlling phases in Figure 1 (left) cannot be explicitly derived from the position of the line, pK values can only be calculated for what may be reasonable phases in equilibrium with the solutions, testing whether or not they become constant over time (or otherwise fit the data). For example, if a muscovite phase controls solution composition, regardless of other phases present, the following equilibrium should prevail:

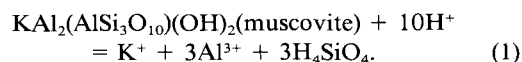


Table 1. Solution composition of illite and illite-kaolinite mixture samples.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ³⁺
Goose Lake illite						
330-21	9	3.62	2.89	2.50	2.30	4.24
330-21	21	3.66	2.81	2.49	2.31	—
330-21	41	3.68	2.79	2.46	2.29	—
330-21	76	3.71	2.79	2.44	2.33	—
330-21	146	3.73	2.76	2.44	2.31	4.45
330-21	244	3.78	2.77	2.38	2.32	—
330-21	387	3.83	2.76	2.40	2.30	—
330-21	559	3.86	2.77	2.33	2.29	4.45
330-22	9	3.71	2.94	2.54	2.29	4.43
330-22	21	3.74	2.82	2.47	2.32	—
330-22	41	3.73	2.82	2.48	2.43	—
330-22	76	3.78	2.80	2.46	2.33	—
330-22	146	3.77	2.76	2.41	2.31	4.55
330-22	244	3.85	2.76	2.37	2.31	—
330-22	387	3.88	2.79	2.44	2.30	—
330-22	559	3.96	2.75	2.30	2.27	4.53
330-23	9	3.71	2.94	2.52	2.29	4.53
330-23	21	3.74	2.85	2.48	2.33	—
330-23	41	3.75	2.83	2.51	2.42	—
330-23	76	3.79	2.82	2.51	2.33	—
330-23	146	3.79	2.77	2.43	2.32	4.54
330-23	244	3.93	2.74	2.36	2.31	—
330-23	387	3.96	2.74	2.46	2.29	—
330-23	559	3.95	2.79	2.33	2.30	4.55
330-24	25	5.47	3.52	2.44	2.31	—
330-24	47	5.53	3.48	—	2.32	—
330-24	150	5.31	3.42	2.47	2.28	—
330-24	311	5.33	3.38	2.44	2.29	—
330-24	485	5.47	3.37	—	2.28	—
330-24	613	5.20	3.33	2.34	2.29	—
330-25	25	6.77	3.79	2.28	2.33	—
330-25	47	6.82	3.72	—	2.34	—
330-25	150	6.51	3.72	2.30	2.31	—
330-25	311	6.16	3.68	2.30	2.31	—
330-25	485	6.44	3.63	—	2.31	—
330-25	613	6.18	3.61	2.22	2.32	—
330-26	5	4.87	3.28	2.91	2.30	—
330-26	12	4.89	3.22	2.88	2.30	—
330-26	28	4.85	3.18	2.92	2.28	—
330-26	88	4.83	3.13	2.84	2.27	—
330-26	217	4.87	3.10	2.80	2.26	—
330-26	426	4.91	3.09	2.76	2.29	—
330-27	5	7.26	3.82	2.32	2.36	—
330-27	12	7.50	3.73	2.32	2.36	—
330-27	28	7.46	3.69	2.39	2.37	—
330-27	88	7.35	3.68	2.32	2.33	—
330-27	217	7.30	3.68	2.30	2.34	—
330-27	426	6.94	3.65	2.27	2.34	—
Goose Lake illite-kaolinite						
337-15	28	2.87	2.47	2.66	1.93	3.71
337-15	49	3.04	2.48	2.62	2.01	3.65
337-15	77	3.12	2.51	2.60	1.99	3.65
337-15	172	3.21	2.55	2.60	1.99	3.69
337-15	320	3.38	2.56	2.57	1.99	3.68
337-15	518	3.45	2.56	2.50	2.01	3.66
337-16	21	2.88	2.56	2.67	2.03	3.65
337-16	42	3.05	2.55	2.62	2.04	3.63
337-16	70	3.13	2.56	2.62	1.96	3.67
337-16	165	3.23	2.57	2.62	2.02	3.67
337-16	313	3.40	2.60	2.55	2.03	3.65

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ³⁺
337-16	511	3.47	2.59	2.51	2.01	3.62
337-25	19	5.53	3.00	2.82	2.11	—
337-25	38	5.66	3.03	2.79	2.12	—
337-25	74	5.77	3.04	2.78	2.10	—
337-25	173	5.74	3.08	2.78	2.10	—
337-25	321	5.69	3.10	2.76	2.10	—
337-25	518	5.50	3.08	2.69	2.11	—
337-26	21	4.89	3.00	2.83	2.04	—
337-26	42	5.01	3.04	2.79	2.05	—
337-26	70	5.05	3.09	2.79	2.06	—
337-26	166	5.47	3.06	2.75	2.05	—
337-26	314	5.59	3.06	2.84	2.04	—
337-26	511	5.32	3.04	2.65	2.02	—
337-35	20	7.49	3.33	2.79	2.11	—
337-35	39	7.52	3.32	2.69	2.12	—
337-35	76	7.49	3.35	2.74	2.12	—
337-35	175	7.47	3.40	2.71	2.10	—
337-35	320	7.42	3.40	2.68	2.11	—
337-35	521	7.23	3.40	2.65	2.11	—
337-36	13	7.60	3.54	3.02	2.12	—
337-36	32	7.66	3.47	2.84	2.13	—
337-36	69	7.67	3.49	2.93	2.14	—
337-36	168	7.67	3.51	2.91	2.12	—
337-36	313	7.62	3.48	2.88	2.13	—
337-36	514	7.48	3.44	2.82	2.12	—
Beavers Bend illite						
330-11	9	3.65	3.03	2.77	2.24	4.49
330-11	21	3.74	2.90	2.74	2.24	—
330-11	41	3.85	2.84	2.72	2.24	—
330-11	76	3.91	2.82	2.69	2.25	—
330-11	146	4.04	2.79	2.62	2.24	5.03
330-11	244	4.15	2.84	2.60	2.25	—
330-11	387	4.19	2.85	2.58	2.22	—
330-11	559	4.23	2.87	2.51	2.21	4.96
330-12	9	3.87	3.17	2.79	2.24	5.12
330-12	21	3.95	2.99	2.78	2.26	—
330-12	41	4.01	2.92	2.74	2.25	—
330-12	76	4.10	2.88	2.70	2.26	—
330-12	146	4.21	2.86	2.65	2.26	5.39
330-12	244	4.34	2.87	2.62	2.26	—
330-12	387	4.51	2.91	2.67	2.22	—
330-12	559	4.54	2.93	2.56	2.21	5.58
330-13	9	3.86	3.12	2.79	2.25	5.12
330-13	21	3.95	2.95	2.74	2.25	—
330-13	41	4.04	2.91	2.70	2.25	—
330-13	76	4.12	2.90	2.70	2.26	—
330-13	146	4.19	2.87	2.65	2.25	5.42
330-13	244	4.27	2.86	2.60	2.25	—
330-13	387	4.28	2.85	2.56	2.20	—
330-13	559	4.29	2.87	2.45	2.16	5.18
330-14	25	5.83	3.34	2.50	2.27	—
330-14	47	6.16	3.26	—	2.28	—
330-14	150	6.00	3.21	2.50	2.25	—
330-14	311	5.87	3.18	2.45	2.23	—
330-14	485	5.91	3.18	—	2.23	—
330-14	613	5.88	3.19	2.40	2.21	—
330-15	25	6.74	3.40	2.50	2.27	—
330-15	47	6.84	3.29	—	2.26	—
330-15	150	6.67	3.28	2.48	2.25	—
330-15	311	6.47	3.24	2.51	2.23	—
330-15	485	6.63	3.26	—	2.22	—
330-15	613	6.48	3.25	2.35	2.23	—

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ²⁺
Beavers Bend illite-kaolinite						
337-11	28	3.00	2.52	2.67	2.05	3.43
337-11	49	3.18	2.53	2.65	2.08	3.38
337-11	77	3.25	2.55	2.65	2.07	3.38
337-11	172	3.37	2.60	2.63	2.07	3.39
337-11	320	3.49	2.60	2.60	2.07	3.38
337-11	517	3.54	2.60	2.53	2.06	3.39
337-12	21	2.94	2.62	2.75	2.08	3.42
337-12	42	3.16	2.60	2.72	2.10	3.33
337-12	70	3.24	2.60	2.74	2.09	3.36
337-12	165	3.36	2.65	2.71	2.07	3.35
337-12	313	3.48	2.64	2.64	2.08	3.36
337-12	510	3.53	2.65	2.60	2.06	3.37
337-21	19	5.36	2.98	2.97	2.10	—
337-21	38	5.71	2.99	2.91	2.11	—
337-21	74	5.83	2.96	2.90	2.11	—
337-21	172	5.61	2.97	2.89	2.10	—
337-21	321	6.02	2.95	2.78	2.10	—
337-21	518	6.18	2.92	2.72	2.09	—
337-22	12	5.55	3.21	3.01	2.16	—
337-22	31	5.93	3.14	2.94	2.16	—
337-22	67	5.92	3.10	2.96	2.16	—
337-22	166	5.79	3.07	2.90	2.15	—
337-22	314	6.06	3.05	2.85	2.16	—
337-22	511	6.08	3.05	2.80	2.16	—
337-31	20	7.28	3.22	2.73	1.89	—
337-31	39	7.37	3.17	2.66	1.96	—
337-31	75	7.44	3.16	2.68	1.96	—
337-31	174	7.50	3.19	2.64	1.95	—
337-31	320	7.30	3.16	2.64	1.94	—
337-31	518	6.99	3.14	2.52	1.94	—
337-32	13	7.44	3.49	3.20	2.19	—
337-32	32	7.53	3.40	3.10	2.19	—
337-32	68	7.57	3.37	3.13	2.19	—
337-32	167	7.61	3.34	3.05	2.20	—
337-32	313	7.42	3.31	3.00	2.20	—
337-32	511	6.98	3.28	2.90	2.20	—
Fithian illite						
311-1	92	4.35	2.76	3.07	2.28	5.65
311-2	92	4.28	2.76	3.29	2.28	5.65
311-3	87	4.30	2.83	1.47	2.17	5.46
311-4	87	4.30	2.83	1.74	2.16	5.46
321-1	34	3.25	2.60	2.59	2.98	4.07
321-1	99	3.45	2.53	2.64	2.95	4.17
321-1	140	3.48	2.56	2.55	2.94	4.35
321-1	176	3.52	2.57	2.60	2.92	4.26
321-1	233	3.56	2.55	2.68	2.92	4.28
321-1	343	3.60	2.57	2.56	2.93	4.35
321-1	469	3.66	2.60	2.65	2.89	4.37
321-1	600	3.67	2.59	2.52	2.89	4.40
321-1	706	3.69	2.56	2.51	2.90	4.43
321-1	840	3.69	2.62	2.45	2.88	4.51
321-2	44	3.45	2.53	2.64	2.95	4.19
321-2	175	3.52	2.54	2.57	2.92	4.35
321-2	233	3.59	2.57	2.60	2.92	4.33
321-2	343	3.61	2.56	2.54	2.93	4.37
321-2	469	3.68	2.60	2.60	2.88	4.44
321-2	600	3.67	2.58	2.59	2.88	4.43
321-2	706	3.70	2.56	2.48	2.88	4.43
321-2	840	3.72	2.57	2.44	2.87	4.55
321-3	34	6.83	3.02	1.97	3.90	—
321-3	99	6.24	2.95	1.99	3.91	—

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ²⁺
321-3	140	6.37	2.96	2.00	3.90	—
321-3	176	6.33	2.96	1.98	3.05	—
321-3	236	6.26	2.95	2.05	3.86	—
321-3	343	6.07	2.94	2.01	3.89	—
321-3	469	6.09	2.93	1.97	3.88	—
321-3	600	6.04	2.93	1.97	3.69	—
321-3	706	6.10	2.90	1.96	3.81	—
321-3	840	6.05	2.89	1.94	3.69	—
321-3	1000	6.22	2.90	1.94	3.70	—
321-3	1167	5.98	2.90	1.89	3.68	—
321-4	44	7.71	3.06	1.98	4.23	—
321-4	175	7.51	3.12	1.96	3.23	—
321-4	236	7.52	3.13	2.02	3.21	—
321-4	343	7.42	3.09	2.01	4.22	—
321-4	469	7.45	3.10	2.03	4.17	—
321-4	600	7.39	2.94	1.94	3.85	—
321-4	706	7.32	3.01	1.98	3.88	—
321-4	840	7.27	3.03	1.95	3.87	—
321-4	1000	7.19	3.05	1.91	4.04	—
321-4	1167	7.13	3.07	1.83	3.97	—
330-34	25	5.87	3.51	2.51	2.30	—
330-34	47	5.96	3.47	—	2.30	—
330-34	150	5.75	3.48	2.47	2.28	—
330-34	311	5.74	3.48	2.50	2.28	—
330-34	485	5.14	3.48	—	2.28	—
330-34	613	5.63	3.49	2.45	2.28	—
330-35	25	6.81	3.75	2.43	2.31	—
330-35	47	6.82	3.72	—	2.32	—
330-35	150	6.51	3.70	2.40	2.29	—
330-35	311	6.33	3.68	2.37	2.28	—
330-35	485	6.57	3.67	—	2.30	—
330-35	613	6.46	3.65	2.40	2.28	—
Fithian illite-kaolinite						
317-1	40	7.59	3.67	2.03	4.70	—
317-1	74	7.63	3.66	1.99	5.06	—
317-1	76	7.50	3.79	2.19	4.62	—
317-1	103	7.53	3.74	2.08	4.67	—
317-1	61	7.73	3.69	1.86	5.00	—
317-1	82	6.29	3.72	1.25	3.14	—
317-1	92	6.30	3.72	1.24	3.36	—
317-2	40	7.50	3.64	2.07	4.64	—
317-2	74	7.64	3.68	1.94	5.14	—
317-2	76	7.64	3.80	2.30	4.32	—
317-2	103	7.72	3.75	2.23	4.90	—
317-2	61	7.76	3.78	2.12	5.27	—
317-2	82	7.65	3.70	2.93	5.26	—
317-2	92	7.58	3.68	2.81	5.28	—
317-3	40	8.27	4.03	2.00	5.05	—
317-3	74	8.39	3.83	1.90	4.94	—
317-3	76	7.97	4.00	2.19	4.39	—
317-3	103	7.99	3.96	2.57	5.37	—
317-3	61	8.12	3.90	2.07	5.29	—
317-3	82	8.02	3.87	2.75	5.29	—
317-3	92	7.89	3.81	2.62	5.20	—
317-4	40	8.10	4.08	2.11	5.11	—
317-4	74	8.28	4.03	2.00	5.29	—
317-4	76	7.88	4.05	2.18	4.62	—
317-4	103	8.01	4.03	2.68	5.35	—
317-4	61	8.17	3.96	2.09	5.35	—
317-4	82	6.87	4.03	1.19	3.33	—
317-4	92	6.87	4.03	1.20	3.47	—
317-12	0	6.67	3.63	—	5.00	—

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ²⁺
317-12	7	7.31	—	—	—	—
317-12	23	7.35	—	—	—	—
317-12	35	7.16	3.67	2.59	4.51	—
317-12	69	7.19	3.68	2.12	4.35	—
317-12	132	7.00	3.72	2.03	4.36	—
317-12	182	6.99	3.71	2.06	4.33	—
317-12	251	6.94	3.70	2.00	4.30	—
317-12	293	6.90	3.73	2.05	4.28	—
317-12	370	6.94	3.72	2.01	4.16	—
317-13	0	6.54	4.26	—	2.60	—
317-13	7	7.02	—	—	—	—
317-13	23	7.25	—	—	—	—
317-13	35	7.32	3.89	2.32	3.47	—
317-13	69	7.42	3.87	2.34	3.41	—
317-13	132	7.44	3.89	2.24	3.39	—
317-13	182	7.55	3.87	2.28	3.35	—
317-13	251	7.41	3.91	2.19	3.31	—
317-13	293	7.39	3.89	2.15	3.28	—
317-13	370	7.28	3.86	2.19	3.24	—
317-14	0	6.86	3.32	—	2.60	—
317-14	7	7.27	—	—	—	—
317-14	23	7.33	—	—	—	—
317-14	35	7.31	3.55	2.24	3.62	—
317-14	69	7.52	3.67	2.20	3.53	—
317-14	132	7.62	3.74	2.19	3.45	—
317-14	182	7.56	3.76	2.08	3.41	—
317-14	251	7.45	3.50	2.11	3.43	—
317-14	293	7.48	3.72	2.04	3.41	—
317-14	370	7.38	3.76	2.07	3.38	—
317-21C	0	6.50	3.70	—	5.00	—
317-21C	14	7.16	3.68	3.09	6.77	—
317-21C	14	7.06	3.53	3.32	6.06	—
317-21C	14	7.24	—	—	—	—
317-21C	13	7.17	3.45	3.40	6.11	—
317-21C	17	7.07	3.41	3.42	5.24	—
317-21C	18	6.31	3.28	2.69	4.91	—
317-21C	48	6.58	3.33	2.93	5.08	—
317-21C	13	6.08	3.18	2.49	4.19	—
317-21	56	6.40	3.36	3.13	4.76	—
317-21	161	6.26	3.45	3.01	3.16	—
317-21	256	5.99	3.45	3.04	4.89	—
317-21	332	6.05	3.47	2.98	4.54	—
317-21	459	6.21	3.42	2.92	4.49	—
317-21	589	6.09	3.38	2.80	4.23	—
317-22C	0	6.50	4.30	—	2.60	—
317-22C	15	6.06	3.85	2.89	2.93	—
317-22C	17	6.86	3.85	3.41	2.84	—
317-22C	28	6.82	3.89	3.81	2.65	—
317-22C	51	7.09	3.98	3.60	2.71	—
317-22C	20	7.06	3.92	3.42	2.71	—
317-22C	22	6.98	3.92	3.04	2.66	—
317-22C	17	7.23	3.89	2.95	2.64	—
317-22C	14	7.04	3.94	2.95	2.65	—
317-22C	22	7.00	3.94	2.97	2.63	—
317-22C	17	6.88	3.92	2.98	2.63	—
317-23C	0	6.50	3.40	—	5.00	—
317-23C	9	7.14	3.56	3.51	2.80	—
317-23C	14	6.92	3.40	3.75	2.73	—
317-23C	7	6.93	3.35	3.40	2.70	—
317-23C	9	6.79	3.35	2.99	2.69	—
317-23C	14	5.57	3.34	3.54	2.66	—
317-23C	10	6.62	3.34	2.21	2.65	—
317-23C	27	6.52	3.34	2.22	2.72	—

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ²⁺
317-23C	24	6.69	3.33	2.21	2.70	—
317-23C	6	6.71	3.33	2.21	2.70	—
317-23C	33	6.65	3.28	2.20	2.61	—
317-23C	25	6.65	3.28	2.10	2.63	—
317-23C	8	6.78	3.24	2.06	2.61	—
317-23C	10	6.71	3.31	2.09	2.59	—
317-23	0	6.88	3.40	—	2.60	—
317-23	82	6.54	3.29	2.75	2.77	—
317-23	155	6.42	3.29	2.73	2.77	—
317-23	282	6.44	3.26	2.73	2.77	—
317-23	414	6.42	3.27	2.75	2.75	—
317-23	516	6.32	3.22	2.69	2.74	—
317-31C	0	6.50	3.70	—	5.00	—
317-31C	14	7.32	3.81	2.94	5.80	—
317-31C	14	7.16	3.66	3.18	5.97	—
317-31C	14	7.34	—	—	—	—
317-31C	13	7.23	3.48	3.19	5.92	—
317-31C	17	7.07	3.43	3.21	5.69	—
317-31C	17	6.81	3.27	2.89	4.76	—
317-31C	36	6.94	3.34	3.00	5.29	—
317-31	10	6.59	3.36	2.92	4.93	—
317-31	50	6.75	3.44	3.04	5.06	—
317-31	52	6.71	3.48	3.13	5.07	—
317-31	79	6.31	3.52	3.04	4.92	—
317-31	140	6.70	3.57	3.14	3.51	—
317-31	235	6.38	3.53	3.04	4.99	—
317-31	311	6.33	3.48	3.09	4.77	—
317-31	438	6.56	3.45	2.94	4.74	—
317-31	568	6.62	3.42	2.92	4.30	—
317-32C	0	6.50	4.30	—	2.60	—
317-32C	16	6.89	3.85	2.86	2.95	—
317-32C	17	7.03	3.83	3.07	2.90	—
317-32C	28	6.97	3.88	3.66	2.69	—
317-32C	65	6.92	3.92	3.25	2.77	—
317-32	10	6.72	3.94	3.47	2.73	—
317-32	50	6.74	3.89	3.56	2.76	—
317-32	52	6.72	3.94	3.86	2.76	—
317-32	79	6.66	3.96	3.71	2.73	—
317-32	141	6.55	4.02	3.50	2.70	—
317-32	238	6.52	3.89	2.58	2.71	—
317-32	312	6.49	3.82	2.97	2.71	—
317-32	441	6.51	3.66	3.37	2.69	—
317-32	568	6.40	3.71	3.25	2.65	—
317-33C	0	6.50	3.40	—	2.60	—
317-33C	9	7.02	3.60	3.45	2.80	—
317-33C	14	7.02	3.52	3.58	2.75	—
317-33C	7	6.94	3.40	3.47	2.68	—
317-33C	13	6.79	3.40	3.55	2.70	—
317-33C	15	6.65	3.36	3.64	2.66	—
317-33C	10	6.66	3.39	3.08	2.70	—
317-33C	27	6.56	3.37	2.75	2.72	—
317-33C	24	6.55	3.36	2.77	2.67	—
317-33C	6	6.63	3.38	2.64	2.66	—
317-33C	17	6.65	3.34	2.52	2.60	—
317-33C	17	6.64	3.36	2.43	2.60	—
317-33	21	6.57	3.34	3.01	2.71	—
317-33	118	6.43	3.33	2.99	2.75	—
317-33	191	6.42	3.33	3.52	2.75	—
317-33	321	6.43	3.28	2.94	2.74	—
317-33	450	6.40	3.29	2.99	2.72	—
317-33	552	6.35	3.24	2.87	2.73	—
323-1	56	4.32	2.96	2.36	2.25	5.44
323-1	129	4.52	3.01	2.32	2.25	5.80

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ³⁺
323-1	254	4.68	3.06	2.36	2.23	—
323-1	386	4.74	3.13	2.33	2.21	—
323-1	491	4.81	3.11	2.45	2.22	—
323-1	623	4.81	3.11	2.31	2.21	5.70
323-1	779	4.86	3.13	2.26	2.16	—
323-11	56	3.50	2.63	2.53	2.13	4.05
323-11	129	3.64	2.69	2.46	2.13	4.07
323-11	254	3.65	2.76	2.45	2.12	4.16
323-11	386	3.69	2.79	2.45	2.10	4.13
323-11	491	3.69	2.78	2.50	2.11	4.20
323-11	623	3.72	2.79	2.42	2.11	4.21
323-11	779	3.75	2.79	2.40	2.08	4.19
323-11	951	3.75	2.79	2.35	2.07	4.19
323-12	56	3.50	2.61	2.48	2.14	4.05
323-12	129	3.62	2.68	2.41	2.12	4.09
323-12	254	3.64	2.73	2.40	2.13	4.10
323-12	386	3.67	2.77	2.40	2.09	4.11
323-12	491	3.67	2.74	2.40	2.12	4.15
323-12	623	3.71	2.76	2.36	2.10	4.16
323-12	779	3.73	2.76	2.30	2.07	4.13
323-12	951	3.71	2.75	2.25	2.00	4.14
323-21	138	5.82	2.78	2.82	2.22	—
323-21	172	5.70	2.80	2.83	2.21	—
323-21	216	5.73	2.77	—	2.20	—
323-21	250	5.70	2.80	—	2.17	—
323-21	294	5.34	2.77	2.67	2.12	—
323-21	328	5.68	2.79	—	2.12	—
323-21	358	5.73	2.78	2.58	2.09	—
323-21	13	5.95	2.67	2.90	2.25	—
323-21	38	5.75	2.68	—	2.26	—
323-21	114	5.70	2.69	2.84	2.26	—
323-21	232	5.50	2.71	2.78	2.24	—
323-21	392	5.92	2.74	2.75	2.23	—
323-31	5	6.10	3.04	3.36	2.25	—
323-31	12	6.05	3.05	—	2.23	—
323-31	26	5.83	3.07	3.34	2.24	—
323-31	54	6.01	3.09	3.25	2.26	—
323-31	146	5.58	3.11	3.17	2.22	—
323-31	266	5.92	3.12	3.11	2.22	—
323-31	357	5.45	3.12	—	2.22	—
323-31	478	5.68	3.13	3.02	2.19	—
323-32	5	5.95	3.02	3.38	2.25	—
323-32	12	5.94	3.05	—	2.24	—
323-32	26	5.88	3.06	3.32	2.24	—
323-32	54	5.88	3.06	3.27	2.25	—
323-32	146	5.45	3.11	3.21	2.22	—
323-32	266	5.83	3.11	3.16	2.22	—
323-32	357	5.67	3.11	—	2.20	—
323-32	478	5.74	3.11	3.02	2.18	—
338-21D	5	3.77	2.85	3.10	2.25	4.35
338-21D	9	3.95	2.88	3.22	2.25	4.73
338-21D	23	3.96	2.92	3.30	2.25	4.97
338-21D	26	4.39	2.93	3.49	2.27	5.42
338-21D	19	5.26	3.01	—	2.22	—
338-21D	10	5.32	2.92	—	2.23	—
338-21D	14	5.12	2.90	—	2.22	—
338-21D	18	5.01	2.90	—	2.24	—
338-21D	9	4.98	2.90	—	2.22	—
338-21D	7	4.92	2.90	—	2.22	—
338-21D	14	4.85	2.91	—	2.23	—
338-21D	13	5.68	2.94	—	2.23	—
338-21D	6	5.77	3.06	—	2.22	—
338-21D	6	5.81	3.17	—	2.23	—
338-21D	6	5.71	3.24	—	2.22	—

Table 1. Continued.

Sample ¹	Days	pH	pH ₄ SiO ₄	pK ⁺	pMg ²⁺	pAl ³⁺
338-22D	24	5.73	2.90	3.60	2.22	—
338-22D	19	6.13	2.91	—	2.22	—
338-22D	6	6.45	3.29	—	2.23	—
338-22D	6	6.51	3.48	—	2.21	—
338-22D	28	6.77	3.47	—	2.20	—

¹ C = column equilibrated. D = liquid removed by immiscible displacement.

K(muscovite) would be the equilibrium constant for Eq. (1). Taking negative logarithms:

$$\text{pK(muscovite)} = \text{pK}^+ + 3\text{pAl}^{3+} + 3\text{pH}_4\text{SiO}_4 - 10\text{pH}. \quad (2)$$

The activity of the muscovite phase must be considered when comparing pK(muscovite) to reported values for pure muscovite. This need not be done until it is determined that the samples indicate the presence of a muscovite phase by generating a constant pK(muscovite).

A common measure of the constancy of any measurement is the standard deviation (σ). For deviations in values of $\text{pH} - 1/3\text{pAl}^{3+}$ for solubility determinations on gibbsite (Kittrick, 1966), σ was ± 0.07 , which generates a σ of ± 0.06 log units for individual pH and pAl^{3+} analyses, but includes deviations due to equilibration and sampling. A σ of ± 0.02 is obtained from analysis alone. Using these results for gibbsite, the anticipated σ for a muscovite phase in Eq. (2) is

$$\begin{aligned} \sigma \text{ pK(muscovite)} &= [(0.06)^2 + 3(0.06)^2 \\ &\quad + 3(0.06)^2 + 10(0.06)^2]^{1/2} \\ &= 0.25. \end{aligned}$$

The σ of ± 0.25 estimated for pK(muscovite) for Eq. (2) is probably a minimum value because illite is apparently a much more complex mineral than gibbsite. For example, 21 solution analyses of the Goose Lake illite (Table 1) had an experimental pK(muscovite) value of -11.9 with a σ of 2.28 (Table 2).

The easiest way to evaluate the constancy of the experimental pK values in Table 2 is to compare the experimental σ values (σ_e in Table 2) with those based upon gibbsite constancy (σ_g). The ratio σ_e/σ_g is denoted by R in Table 2. The approximate R of muscovite for the Goose Lake illite is 9. If a phase was controlling solution composition in an equilibrating illite sample and the errors in analysis, sampling, and equilibration were similar to those found for gibbsite, R should be unity. Apparent pK values for a phase that was not controlling solution composition should vary considerably with changes in one or more solution parameters, resulting in R values much larger than unity. R values close to, but higher than unity might occur when

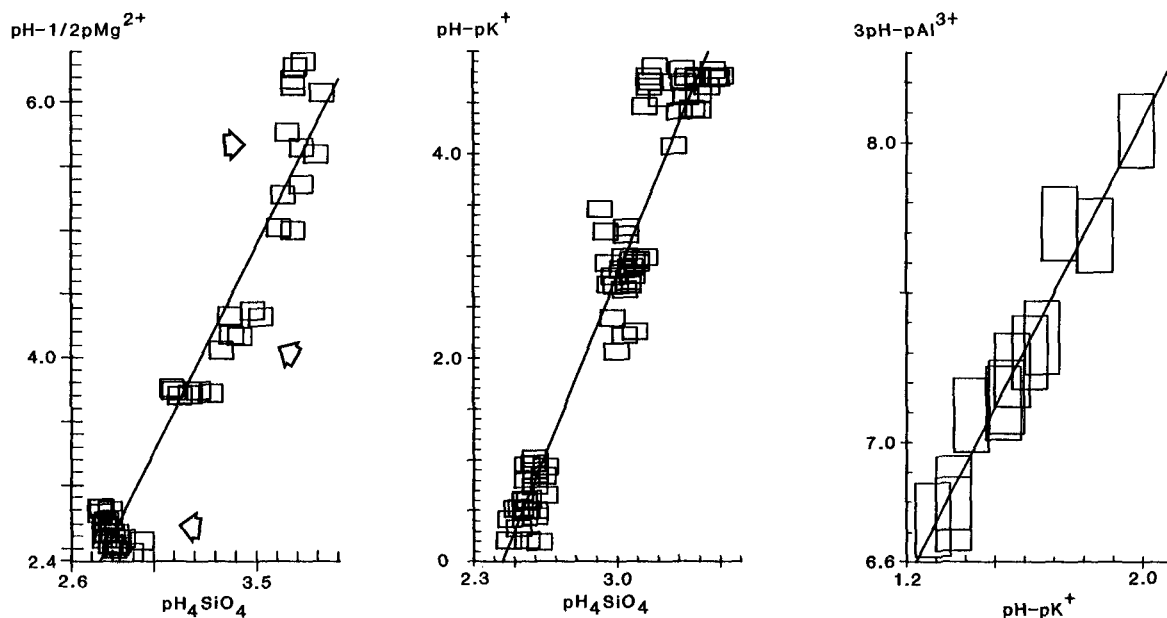
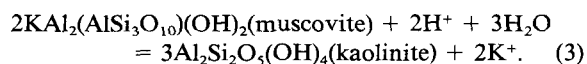


Figure 1. Compositions of solutions equilibrated with illites (plus goethite). Symbol size is anticipated 2σ for each coordinate, based upon solubility results for gibbsite. *Left*. Goose Lake illite. Slope = 3.26, intercept = -6.52, $r = 0.97$, $n = 48$. Arrows indicate the approximate direction of approach to equilibrium. *Middle*. Goose Lake illite plus kaolinite, and Beavers Bend illite plus kaolinite. 12- and 13-day samples omitted. Slope = 4.96, intercept = -12.9, $r = 0.96$, $n = 69$. *Right*. Goose Lake and Beavers Bend illites. 9-day samples omitted. Slope = 1.92, intercept = 4.24, $r = 0.98$, $n = 12$.

the phase is controlling if errors were larger than they were for gibbsite. Alternatively, the phase may not be controlling, but a narrow range in solution parameters may result in relatively constant apparent pK values. All of the R values of Table 2 exceed unity, with those of talc and phlogopite so high as to exclude them immediately from consideration as phases for controlling illite solubility. The lowest R values were obtained for the bulk sample formulae, for pyrophyllite, and for leucophyllite. Muscovite was intermediate.

Again using a muscovite phase as an example, its equilibration with kaolinite can be considered.



$$\text{pK}_{\text{M-K}} = 2\text{pK}^+ - 2\text{pH}. \quad (4)$$

The $\text{pK}_{\text{M-K}}$ in Eq. (4) does not involve an Al^{3+} term, whereas $\text{pK}(\text{muscovite})$ in Eq. (2) does. A large number of samples in Table 1 were equilibrated with kaolinite in order that pK calculations for at least those samples not be limited to conditions where Al^{3+} could be determined. In practical terms, this means that $\text{pK}(\text{muscovite})$ could only be evaluated at low pH, where there is sufficient Al in solution for analysis. By way of contrast, $\text{pK}_{\text{M-K}}$ can be evaluated over a wide range in pH, which constitutes a much more rigorous test of pK constancy. Indeed, R values for muscovite-

kaolinite in Table 2 were much higher than for muscovite alone, because pK values for muscovite-kaolinite changed considerably with pH. If solubility determinations are to be used as a tool for *identifying* unknown phases (instead of only characterizing *known* phases), the constancy of pK values for a phase *both* alone and also with another phase such as kaolinite is a much more demanding test. Certainly a phase that really is present and controlling solution composition should pass both tests. By this criterion only pyrophyllite and the bulk illite compositions still have promise as solution-controlling phases. It can be seen that they have R values approximately the same as kaolinite which, of course, is known to be present in the samples considered, because it was added to them initially.

No doubt some of the values in Table 2 are better than others. For example, values obtained after a long period of equilibration are more likely to be at equilibrium than are those obtained initially from the same sample. For this reason, σ_e values were calculated for the last analysis of long-term equilibrations (not shown). The Goose Lake and Beaver Bend illites were used because they gave the highest correlation coefficients in plots such as Figure 1. It was found that R values for muscovite, leucophyllite, pyrophyllite, and bulk illite phases for these illites were decreased to half or less of the values of Table 2, showing that long-term

Table 2. Equilibrium constant and standard deviation for potential phases in solutions equilibrated with three illites.

Data base ¹	N ²	pK ³	σ_g	σ_e	R
muscovite $pK^+ + 3pAl^{3+} + 3pH_4SiO_4 - 10pH$					
GL	21	-11.9	0.25	2.28	9
BB	21	-13.1	0.25	2.32	9
F	45	-13.6	0.25	1.50	6
muscovite-Kl $2pK^+ - 2pH$					
GL-Kl	36	-5.3	0.12	3.45	27
BB-Kl	36	-5.4	0.12	3.27	29
F-Kl	183	-7.4	0.12	2.71	23
pyrophyllite $2pAl^{3+} + 4pH_4SiO_4 - 6pH$					
GL	21	-2.0	0.21	1.10	5
BB	21	-2.6	0.21	1.32	6
F	45	-2.8	0.21	0.60	3
pyrophyllite-Kl $2pH_4SiO_4$					
GL-Kl	36	6.0	0.08	0.74	9
BB-Kl	36	5.9	0.08	0.59	7
F-Kl	216	6.8	0.08	0.82	10
leucophyllite $pK^+ + pMg^{2+} + pAl^{3+} + 4pH_4SiO_4 - 6pH$					
GL	21	-1.4	0.22	1.34	6
BB	21	-1.9	0.22	1.68	8
F	45	-2.4	0.22	1.21	6
leucophyllite-Kl $2pK^+ + 2pMg^{2+} + 6pH_4SiO_4 - 6pH$					
GL-Kl	36	-4.7	0.24	8.41	35
BB-Kl	36	-5.4	0.24	8.47	35
F-Kl	183	-5.6	0.24	4.48	19
phlogopite $pK^+ + 3pMg^{2+} + pAl^{3+} + 3pH_4SiO_4 - 10pH$					
GL	21	-13.5	0.25	2.55	10
BB	21	-15.0	0.25	3.38	14
F	45	-15.3	0.25	3.03	12
phlogopite-Kl $2pK^+ + 6pMg^{2+} + 4pH_4SiO_4 - 14pH$					
GL	36	-45.5	0.31	23.4	76
BB	36	-47.0	0.31	22.7	73
F	183	-50.2	0.31	12.2	39
talc $3pMg^{2+} + 4pH_4SiO_4 - 6pH$					
GL	84	-11.7	0.22	7.98	36
BB	72	-12.5	0.22	8.02	36
F	272	-15.1	0.22	8.74	40
GL $0.59pK^+ + 1.93pAl^{3+} + 0.15pMg^{2+} + 3.65pH_4SiO_4 - 6.68pH$					
GL	21	-3.7	0.22	1.39	6
GL-Kl $0.59pK^+ + 0.15pMg^{2+} + 1.72pH_4SiO_4 - 0.89pH$					
GL-Kl	36	2.3	0.11	0.93	8
BB $0.53pK^+ + 2.05pAl^{3+} + 0.13pMg^{2+} + 3.62pH_4SiO_4 - 6.94pH$					
BB	21	-5.2	0.22	1.58	7
BB-Kl $0.53pK^+ + 0.13pMg^{2+} + 1.57pH_4SiO_4 - 0.79pH$					
BB-Kl	36	2.1	0.10	0.89	9
F $0.64pK^+ + 2.03pAl^{3+} + 0.19pMg^{2+} + 3.51pH_4SiO_4 - 7.11pH$					
F	41	-8.0	0.22	0.90	4
F-Kl $0.64pK^+ + 0.19pMg^{2+} + 1.48pH_4SiO_4 - 1.02pH$					
F-Kl	183	0.9	0.11	0.77	7

Table 2. Continued.

Data base ¹	N ²	pK ³	σ_g	σ_e	R
Kl $2pAl^{3+} + 2pH_4SiO_4 - 6pH$					
GL-Kl	12	-6.7	0.19	1.21	6
BB-Kl	12	-7.8	0.19	1.19	6
F-Kl	23	-8.5	0.19	0.76	4
GL-Kl; BB-Kl mica $0.29pK^+ + 1.42pH_4SiO_4 - 0.29pH$					
GL-Kl;					
BB-Kl	69	3.5	0.08	0.13	2
GL; BB mica $0.30pK^+ + 2.30pAl^{3+} + 3.70pH_4SiO_4 - 7.20pH$					
GL; BB	42	-5.2	0.21	1.53	7

¹ GL = Goose Lake illite, BB = Beavers Bend illite, F = Fithian illite, Kl = kaolinite. For example, GL refers to all Goose Lake samples producing the necessary analyses, whereas GL-Kl refers only to those GL samples to which kaolinite had been added.

² N = number of observations, σ_g = anticipated standard deviation based upon gibbsite, σ_e = experimental standard deviation, $R = \sigma_e/\sigma_g$.

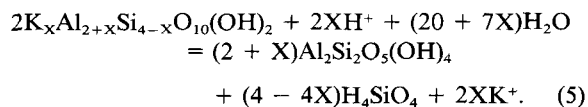
³ pK for the mineral calculated from the indicated formula.

equilibration values were indeed less variable with respect to those phases than were all values taken together. However, when illite-kaolinite samples were similarly selected and recalculated for the same phases, the R values remained essentially unchanged. Apparently most of the variation that caused the high R values for samples containing kaolinite was due to the wide range in pH, not to time. Thus, pyrophyllite and bulk composition phases, which had similar R values with and without kaolinite, again appeared to be the only likely phases. Because R values for kaolinite decreased considerably when last analyses were selected, the presence of pyrophyllite and bulk composition phases was not as likely as kaolinite (in the samples to which it was actually added) on the basis of the last analysis. It is curious that pK values for bulk illite formulae fit the data so well. It has been shown that each illite contains at least two phases or components, yet a bulk formula is best suited to a sample containing only one phase. Perhaps Figure 1 (left) displays equilibria between components, or between two phases, each close to bulk composition.

Evaluating a mica phase

Of the mica phases considered in Table 2, only the bulk illite compositions generated R values close to those of kaolinite. It is possible that a mica phase of appropriate composition would fit the data of Table 1 more closely than any of those tried in Table 2. The problem, of course, is devising some systematic way to obtain the composition of this "appropriate" mica phase, so that it could be evaluated. For an approach

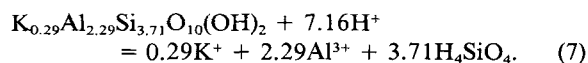
utilizing some assumptions and the data itself, consider Eq. (3). A muscovite-pyrophyllite solid solution resulting in an aluminum silicate can be assumed with a K content of X (where $1 > X > 0$). Such a mica, equilibrated with kaolinite, would generate an equation as follows:



$$pK/2 = XpK^+ + (2 - 2X)pH_4SiO_4 \\ - XpH \\ pH - pK^+ = [(2 - 2X)/X]pH_4SiO_4 \quad (6) \\ - pK/2X.$$

It can be seen from Eq. (6) that if the mica phase of Eq. (5) was controlling solution composition, the equilibrium data should lie along a straight line of slope $(2 - 2X)/X$ on a plot of $pH - pK^+$ vs. pH_4SiO_4 . From Figure 1 (middle), it can be seen that solution analyses for Goose Lake illite-kaolinite and Beavers Bend illite-kaolinite produce a reasonably straight line ($r = 0.96$). These values were united to increase the data base for the calculations because these illites gave similar results in the calculations shown in Table 2 and in various data plots, including Figure 1. The line slope of 4.96 in Figure 1 (middle) is equal to $(2 - 2K)/K$ (from Eq. (6)). This corresponds to a K content of 0.29, which in turn corresponds to a formula of $K_{0.29}Al_{2.29}Si_{4.71}O_{10}(OH)_2$ when Eq. (5) is considered. In Table 2, it can be seen that for Goose Lake illite-kaolinite and Beavers Bend illite-kaolinite mica, the pK values fit the data very well ($R = 2$).

The phase generated from these data should also be in equilibrium with its constituents as follows:



$$pK = 0.29pK^+ + 2.29pAl^{3+} \\ + 3.71pH_4SiO_4 - 7.16pH. \quad (8)$$

As shown at the bottom of Table 2, this second test of the Goose Lake illite and Beavers Bend illite mica formula resulted in a much larger R of 7. Examination of these data (not shown) shows that the inclusion of Al^{3+} in Eq. (8) requires a much larger pH term, which is the main cause of the variability in pK.

A third test of the mica formula in Eq. (7) can be obtained by rearranging Eq. (8):

$$3pH - pAl^{3+} = -0.13(pH - pK^+) \\ + (1.62pH_4SiO_4 - 0.44pK). \quad (9)$$

As a first approximation, pH_4SiO_4 is assumed to be constant. Eq. (9) then indicates that the line slope for

equilibrium data should be -0.13 . For this test it was necessary to exclude some of the Goose Lake and Beavers Bend data of Table 1. The 9-day analyses were excluded because they were probably not at equilibrium. This narrowed the range of pH_4SiO_4 . The Goose Lake illite-kaolinite and Beavers Bend illite-kaolinite samples also were excluded, because at constant pH_4SiO_4 , the $3pH - pAl^{3+}$ parameter was fixed, and thus the system represented by Eq. (9) was invariant. The remaining 12 solution values for the Goose Lake and Beavers Bend illites were plotted in Figure 1 (right), where a straight line was generated ($r = 0.98$), but the slope was 1.92 (not -0.13). The line slope of Eq. (9) is $-(K/2) + K$, so that for a slope of 1.92, K calculates to be -1.3 . This is not only incompatible with the formula in Eq. (7), it is impossible. Thus, the agreement of the first test with the formula of Eq. (7) is diminished by the disagreement of the third test.

The formula of Eq. (7) may have failed because some of the assumptions made in generating it were unwarranted or the data base was too limited in size and range. A promising phase formula should pass more than one reasonable test of pK constancy. It should be noted that bulk illite formulae and pyrophyllite were at least not eliminated in two tests, although R values were not low enough to guarantee their presence. The results of phases tested indicated that it is much easier to eliminate phases as candidates for solution control than it is to confirm their presence.

In summary, it has been demonstrated that multiple phases or components control solution equilibria in three illites, but that the chemical composition of these phases cannot unequivocally be determined from the solubility data. The statistical and graphical techniques applied, however, are promising for evaluation of phase composition formulae derived from other considerations. The solubility data for the three illites provides an extensive data base upon which to test compositions and theories.

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REFERENCES

- APHA. (1960) *Standard Methods for the Examination of Water and Waste-water*: 11th ed., American Public Health Association, New York, 626 pp.
- Bodine, M. W., Jr. and Standaert, R. R. (1977) Chlorite and illite compositions from the upper Silurian rock salts, Retsof, New York. *Clays & Clay Minerals* 26, 327-340.

- Grim, R. E. and Bradley, W. F. (1939) A unique clay from the Goose Lake, Ill. area: *J. Amer. Ceram. Soc.* **22**, 157–164.
- Hsu, P. H. (1963) Effect of initial pH, phosphate, and silicate on the determination of aluminum with aluminon: *Soil Sci.* **96**, 230–235.
- Kittrick, J. A. (1966) Free energy of formation of kaolinite from solubility measurements: *Amer. Mineral.* **51**, 1457–1466.
- Kittrick, J. A. (1980) Gibbsite and kaolinite solubilities by immiscible displacement of equilibrium solutions: *Soil Sci. Soc. Amer. J.* **44**, 139–142.
- Lippmann, F. (1977) The solubility products of complex minerals, mixed crystals, and three-layer clay minerals: *N. Jb. Miner. Abh.* **130**, 243–263.
- Mankin, C. J. and Dodd, C. G. (1963) Proposed reference illite from the Ouachita mountains of Southeastern Oklahoma: in *Clays and Clay Minerals, Proc. 10th Natl. Conf., Austin, Texas, 1961*, Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 372–379.
- Raman, K. V. and Jackson, M. L. (1966). Layer charge relations in clay minerals of micaceous soils and sediments: in *Clays and Clay Minerals, Proc. 14th Natl. Conf., Berkeley, California, 1965*, S. W. Bailey, ed., Pergamon Press, New York, 53–68.
- Reesman, A. L. (1974) Aqueous dissolution studies of illite under ambient conditions: *Clays & Clay Minerals* **22**, 443–454.
- Reesman, A. L. (1978) Extrapolation of aqueous dissolution data to determine comparative free energies of formation (ΔG_f°), and relative mineral stabilities: *Clays & Clay Mineral.* **26**, 217–226.
- Routson, R. C. (1970) *Illite solubility*: Ph.D. Thesis, Washington State University, Pullman, Washington, 123 pp.
- Routson, R. C. and Kittrick, J. A. (1971) Illite solubility: *Soil Sci. Soc. Amer. Proc.* **35**, 714–718.
- Velde, B. (1977) *Clays and Clay Minerals in Natural and Synthetic Systems*: Elsevier, Amsterdam, 218 pp.
- Yoder, H. S. and Eugster, H. P. (1955) Synthetic and natural muscovites: *Geochim. Cosmochim. Acta* **8**, 255–280.
- Zen, E-An (1962) Problem of the thermodynamic status of the mixed-layer minerals: *Geochim. Cosmochim. Acta* **26**, 1055–1067.

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Резюме—Иллиты из Гусевого Озера, Бобрового Изгиба, и Фитиана уравнивались в присутствии гетита (или гематита) при комнатной температуре в течении 2,6 лет. Каолинит с известной стабильностью был добавлен к некоторым образцам. Образцы раствора получались после центрифугирования при или без несмешиваемого перемещения или выщелачивания колонны. Симптомами равновесия были постоянные величины в течение длительного периода времени с использованием растворимости каолинита как внутреннего индикатора. Главным признаком создания равновесия был подход к этому состоянию из обоих, ненасыщенного и перенасыщенного состояния. Графики данных указывают на то, что иллиты содержат две или больше фазы или компоненты в равновесии между собой. Статистические и графические подходы использовались для анализа сотни равновесий. Неизменяемость величин рК для различных выражений указывает на то, что общий состав иллита и пирофиллит являются фазами или компонентами контролирующими растворы. Мусковит, лейкофиллит, флогопит, и тальк не проявляют таких черт. Фаза похожа на мусковит, но с меньшим содержанием К, согласуется хорошо с одним выражением рК, но не согласуется с двумя другими. [E.G.]

Resümee—Illite von Goose Lake, Beaver Bend, und Fithian wurden in der Gegenwart von Goethit (oder Haematit) bei Raumtemperatur und über den Zeitraum von 2,6 Jahren ins Gleichgewicht gebracht. Kaolinit mit bekannter Stabilität wurde zu manchen Proben hinzugegeben. Lösungsproben wurden nach dem Zentrifugieren mit oder ohne nicht mischbaren Ersatz oder mehrmaliger Auslaugung genommen. Das Gleichgewicht wurde durch konstante Werte über eine längere Zeit angezeigt—wobei die Kaolinitlöslichkeit als innerer Standard verwendet wurde—und vor allem auch dadurch, daß das Gleichgewicht von seiten der Untersättigung und der Übersättigung eingestellt wurde. Die Datenplots deuten darauf hin, daß die Illite zwei oder mehr Phasen oder Komponenten im Gleichgewicht miteinander enthalten. Statistische und graphische Methoden wurden angewandt, um hunderte von Gleichgewichte zu analysieren. Die Konstanz der pH-Werte für verschiedene Ausdrücke weist darauf hin, daß die Durchschnittszusammensetzung von Illite und Pyrophyllit wahrscheinlich Lösungs-kontrollierende Phasen oder Komponenten sind, während das für Muskovit, Leukophyllit, Phlogopit, und Talk nicht zutrifft. Eine Muskovit-ähnliche Phase mit niedrigerem K-Gehalt als Muskovit entsprach einem pK-Wert gut, während sie zwei anderen nicht entsprach. (U.W.)

Résumé—Des illites de Goose Lake, Beavers Bend, et Fithian ont été équilibrées en présence de goethite (ou d'hématite) à température ambiante pour aussi longtemps que 2,6 ans. On a ajouté de la kaolinite de stabilité connue à quelques échantillons. Des échantillons de solution ont été obtenus après la centrifugation avec, ou sans déplacement immiscible ou délavement de colonne. L'équilibre était indiquée par des valeurs constantes pendant une longue période de temps, avec la solubilité de la kaolinite comme indicateur interne, et de manière plus importante, par l'approche de l'équilibre à partir d'à la fois la sous saturation et la supersaturation. Des graphes de données indiquent que les illites contiennent deux phases ou composés, ou plus, en équilibre les uns avec les autres. Des techniques statistiques et graphiques ont été employées pour analyser des centaines d'équilibres. La constance des valeurs pK pour des expressions variées indique que la composition d'illite en masse et la pyrophyllite sont de vraisemblables phases ou composés contrôlant la solution, mais que la muscovite, la leukophyllite, et le talc ne le sont pas. Une phase semblable à la muscovite, mais de moindre contenu en K que la muscovite s'est bien associée avec une expression pK, mais pas avec deux autres. [D.J.]