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Swinefordite, A Dioctahedral-Trioctahedral Li-Rich Member of the Smectite Group from Kings Mountain, North Carolina

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Abstract

A clay resembling petroleum jelly occurs in an open pit mine, as coatings along the walls of the fracture zones and as small patches along the fissures or as pseudomorphs after spodumene crystals in the pegmatites. Field evidence indicates that the clay is an alteration product associated with spodumene and other lithium-rich aluminum silicates in the pegmatites. The fully hydrated clay has large basal *d* values. It dehydrates within hours in the laboratory atmosphere through transitional phases into a stable phase, the first basal reflection of which occurs at 13 Å when the relative humidity is under 60 percent. This stable phase has a *C*-centered cell with considerable stacking disorder and has approximately five cations in the octahedral positions, indicating solid solution between dioctahedral and trioctahedral composition. The approximate structural formula for this stable phase is $(Si_{7.66}Al_{0.34})(Al_{1.87}Fe^{3+}{}_{0.15}Fe^{2+}{}_{0.09}Mg_{1.31}Li_{1.76})O_{20}(F_{0.65}OH_{3.35})\cdot Ca_{0.23}Mg_{0.05}Na_{0.11}Li_{0.72}K_{0.04}$. The data obtained from X-ray diffraction, differential thermal, and infrared analyses are comparable with those for smectites. The stable phase of this clay differs, however, from the known smectites by high lithium content and high degree of crystallinity. The presence of a moderate quantity of Al, and of even a relatively small amount of Mg, rules out the possibility of hectorite. The stable phase of this clay has been named swinefordite in honor of Dr. Ada Swineford.

Introduction

A lithium-rich clay resembling petroleum jelly occurs as coatings on the quarry walls, as thin films or small patches along fissures, or as pseudomorphs after spodumene in the open pit mine of the Foote Mineral Company at Kings Mountain, Cleveland County, North Carolina. The clay is an alteration product associated with spodumene and other lithium-rich silicates in the tin- and lithium-enriched pegmatites of the Carolina tin-spodumene belt (Kesler, 1942). Some of the clay is associated with switzerite and vivianite; some covers fine drusy crystals of quartz, albite, and apatite. The clay appears to be most abundant on the west side of the quarry, where fractures are pronounced and ground water is abundant. The moving ground water deposits the fully hydrated clay along the fracture zones, in voids, and on the bottoms of the depressions in the mine floor. Then the clay transforms to various unstable and stable phases upon dehydration.

X-ray diffraction reveals the clay to have large basal *d* spacings; under laboratory conditions it dehydrates through transitional phases into a phase which by X-ray diffraction, DTA, and infrared analysis resembles smectite (Tien, 1972). Chemical analysis and cation-exchange capacity determination show there are approximately five cations in the octahedral positions, indicating solid solution between dioctahedral and trioctahedral composition.

The name swinefordite ('swainfədait) has been proposed for this new smectite. The name and the mineral have been approved by the Commission of New Minerals and Mineral Names, International Mineralogical Association, in honor of Dr. Ada

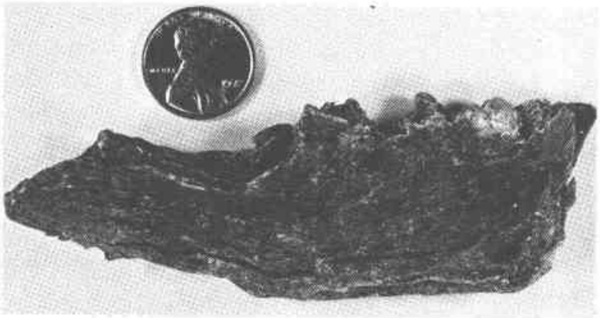

FIG. 1. Photograph showing swinefordite.

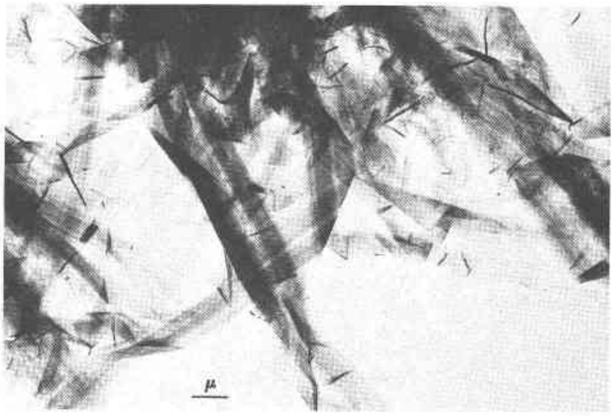

FIG. 3. Transmission electron photomicrograph of swinefordite.

Swineford, dedicated clay mineralogist and Professor of Geology at Western Washington State College. The type specimens are preserved in the collections of the Department of Geology, East Carolina University, Greenville, North Carolina; the Irenee duPont Mineral Collection, University of Delaware, Newark, Delaware; The National Museum of Natural History, Smithsonian Institution, Washington, D. C.; and Musée de Minéralogie, Ecole Nationale Superieure des Mines, Paris.

Physical Properties

The hydrated clay is moderate greenish yellow (10Y 7/4) to light olive (10Y 5/4) of the Munsell system. It looks like petroleum jelly and feels like heavy-equipment grease. It absorbs water and dehydrates within hours through transitional phases into swinefordite.

Swinefordite is light greenish gray (5GY 8/1) to grayish olive (10Y 4/2). The mineral changes its color upon heat treatment. It is light brown when heated to 450°C, silver gray when heated to 650°C, and white when heated to 900°C.

The mineral has a white streak, a dull-to-glistening luster, and a Mohs' hardness of about 1. It is very tough, and almost impossible to disaggregate and disperse completely in water. It feels greasy and resembles "mountain leather" with fibrous habit (Fig. 1). The specific gravity of the stable phase could not be determined because of the porous character of the aggregates.

Under a polarizing microscope, the smeared film of the fully hydrated clay shows fine-particle aggregates which rapidly dehydrate and become fibrous (Fig. 2). The measured indices of refraction of swinefordite are: $\beta = 1.524 \pm 0.002$, and $\gamma = 1.526 \pm 0.002$. The optical angle varies from 29° to 45° determined by Tobi's method (Tobi, 1956) with an average of 37°. A value of α equal to 1.492 is obtained from the Mertie nomogram (Mertie, 1942) by using $2V = 37°$. Y equals a, and X is near c. It is pleochroic with Y nearly colorless, and Z = pale yellow brown.

Under the transmission electron microscope, the particles of swinefordite seem to be thin ribbons, some of which are folded and twisted (Fig. 3), whereas under a scanning electron microscope, swinefordite (Fig. 4) shows curled sheets as a result of

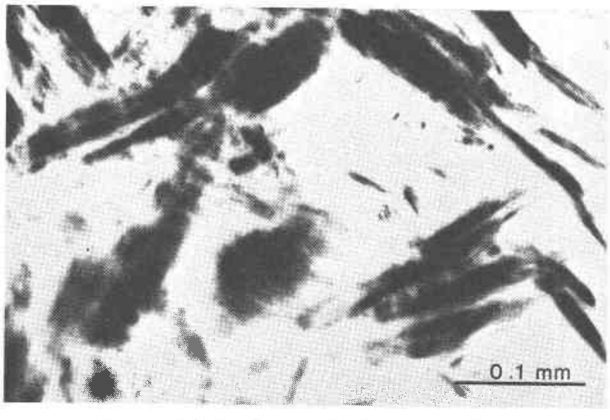

FIG. 2. Photomicrograph of swinefordite.

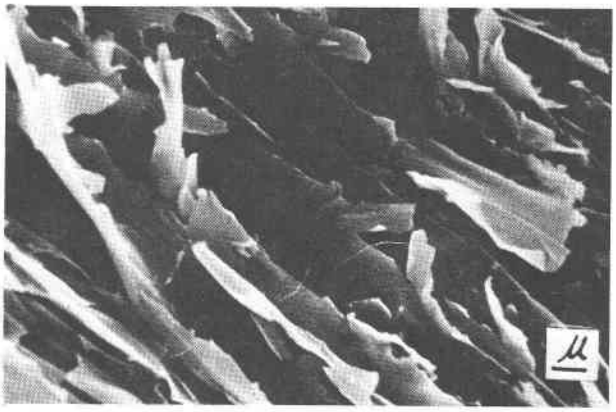

FIG. 4. Scanning electron photomicrograph of swinefordite.

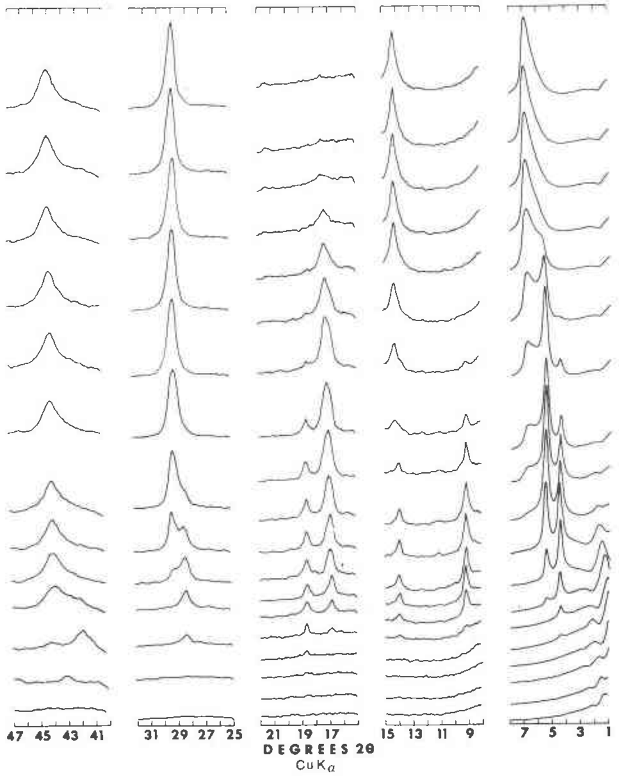

FIG. 5. X-ray diffraction patterns showing the structural changes of hydrated clay upon dehydration.

the aggregation of the individual ribbon-like particles.

X-Ray Diffraction Analyses

Untreated smear slides of the fully hydrated clay and smear slides of swinefordite treated with glycerol and others heated to various temperatures were analyzed by X-ray diffractometry. A powdered sample of swinefordite was analyzed by use of a film. The fine powder sample was packed in a 0.2 mm diameter quartz-glass capillary. The photograph was taken with a 114.6 mm Debye-Scherrer camera using nickel filtered Cu-radiation. A General Electric XRD-6 diffractometer using LiF monochromatized Cu*K*α radiation was operated at 45 kV and 20 mA.

The wet smear slides of hydrated clay were run separately at predetermined 2*θ* intervals in order to detect any structural changes upon dehydration. The time for each run was 3.5 minutes (2° 2*θ* per minute), plus a minute for changing the settings. Because the thickness of the clay film could not be standardized, the time required for complete dehydration of each slide varies accordingly. Figure 5 shows the structural changes of the hydrated clay upon dehydration in the laboratory atmosphere. The patterns in each column are continuously repeated. In the first column, the time from the beginning of the bottom pattern to the ending of the top pattern was 84.5 minutes. Six states can be recognized from totally hydrated clay to swinefordite:

1. The totally hydrated clay shows no reflections within detectable range, but under a polarizing microscope the clay is anisotropic, indicating that the fully hydrated clay has large *d* values.
2. A transitional phase shows a reflection that gradually shifts from large *d* values to 40 Å.
3. A second transitional or intermediate phase has the first-order basal reflection at 19.6 Å.
4. A third transitional or intermediate phase has the first-order basal reflection at 16 Å.
5. A fourth transitional or intermediate phase has the first-order basal reflection at 14.5 Å, and is stable under laboratory atmosphere with relative humidity above 60 percent.
6. Swinefordite, the stable phase under laboratory atmosphere with relative humidity below 60 percent.

X-ray powder data for swinefordite are listed in Table 1. It is noteworthy that the *33,06* reflections occur at 1.508 Å, a spacing similar to that for dioctahedral smectite (MacEwan, 1961). The basal reflections of the treated and untreated swinefordite are shown in Figure 6. X-ray diffraction patterns of untreated sample slides show the first basal reflection of swinefordite at 13 Å. If the sample is saturated with glycerol, at least 10 orders of basal reflections (Table 2) can be obtained, with the first-order at 18 Å. If the sample is heated to 450°C and X rayed immediately, the first-order basal reflection occurs at 9.8 Å and then shifts to 11.3 Å within hours upon hydration in the laboratory atmosphere (Fig. 7). Further hydration to 13 Å has also been detected within months. If the sample is heated to 575°C for one-half hour, the first-order basal reflection occurs at 9.8 Å and no hydration has been observed within 2 months; however, 6 months later it shifts to 11.3 Å and a year later to 13 Å.

X-ray diffraction data of samples heated above

TABLE 1. X-ray Powder Diffraction Data of Swinefordite

	d(obs) Å	I		d(obs) Å	I		d(obs) Å	I
001	12.96	vvs	005	2.51	vw	26,40	1.304	m
002	6.27	w	22,04	2.27	2	35,17,42	1.256	w
11,02	4.53	vs	006	2.14	vvw	08,44	1.127	vvw
004	3.09	s	31,15,24	1.713	m	19,35,46	0.984	vvw
13,20	2.62	m	33,06	1.508	vs	39,60	0.8715	vvw

550°C were obtained by back-loading the sample powder in a modified Philips aluminum holder. The sample heated to 550°C shows an anhydrous smectite pattern. Above 650°C, reflections of unidentified phases are noted (Fig. 8).

The X-ray diffraction data for swinefordite have been compared with those of API reference smectites. Generally, they agree in *d* values; however, the basal reflections for swinefordite are much sharper and more intense.

Single-crystal precession photographs were made by one of the authors (P.B.L.) from flakes of swinefordite trimmed with a razor blade. The *hk*0 level shows a *C*- centered cell with blurred reflections indicating considerable stacking disorder. The *h*0*l* level (Fig. 9) shows 00*l* spots and 0*k* bands. The presence of 00*l* reflections with *l* odd is incompatible with a *C* glide; the diffraction symbol is thus *C*2/*m*.

Thermal Analyses

Powdered samples of swinefordite were analyzed by a Stanton Redcroft Differential Thermal Analysis (DTA) and HT-D Thermobalance simultaneous system. The weight of sample was 100 mg, with an equal weight of Al_2O_3 used as reference. The heating rate was 8°C per minute. The furnace was preheated. The input for the DTA was 50 mμV.

TABLE 2. Basal Spacings of Glycerated Swinefordite

	d(obs) Å	I/I_o		d(obs) Å	I/I_o
001	18.033	1000	006	2.9785	61
002	9.025	123	007	2.5495	3.5
003	5.985	61	008	2.2299	11.5
004	4.483	84	009	1.9795	11.5
005	3.561	86	0010	1.7859	2.5

The DTA curve for swinefordite (Fig. 10) shows three endothermic reactions at 125°, 200°, and 625°C, and an exothermic reaction at 680°C. The endothermic reactions at 125° and 200°C are related to the loss of sorbed water. The presence of these double reactions in the low temperature region has been attributed to the fact that smectite had been saturated with divalent cations or monovalent Li ions in the interlayers. Smectite saturated with monovalent cations other than Li ions does not show double reactions (Hendricks, Nelson, and Alexander, 1940). According to the cation exchange capacity determination, only small amounts of divalent cations are exchangeable; the double endothermic reactions in the low temperature region, therefore, may be related to the saturation of Li ions in the interlayers. The third

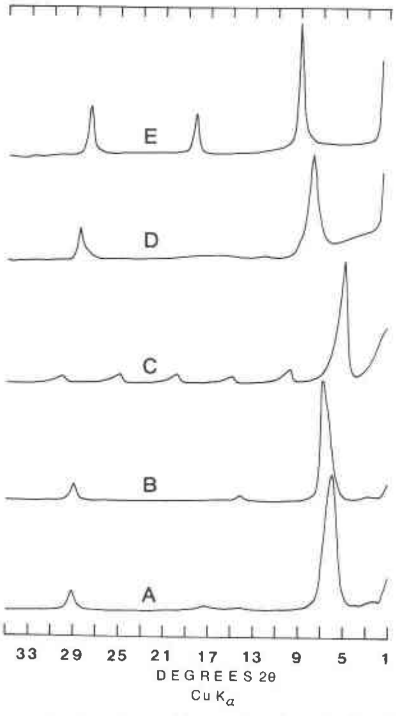

FIG. 6. X-ray diffraction patterns showing the basal reflections of swinefordite and that of various treatments. A. R.H. 65 percent; B. R.H. 45 percent; C. glycerated; D. heated to 450°C; E. heated to 575°C for ½ hour.

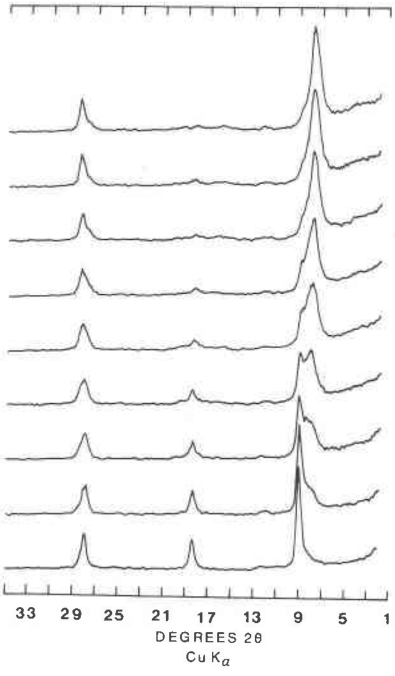

FIG. 7. X-ray diffraction patterns of swinefordite heated to 450°C showing the changes of basal reflections from 9.8 Å (bottom) to 11.3 Å (top) upon hydration. The time for each run was 10 minutes.

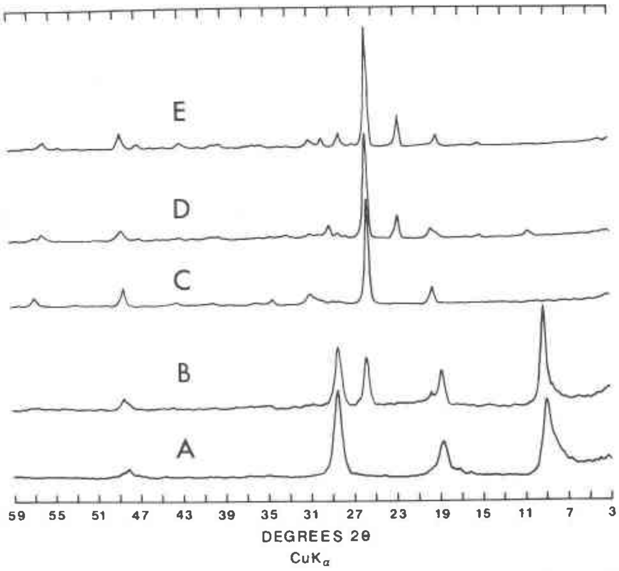

FIG. 8. X-ray diffraction patterns of the thermal products of swinefordite. A. heated to 550°C; B. heated to 650°C; C. heated to 750°C; D. heated to 950°C; E. heated to 1150°C.

endothermic reaction, which shows a poorly resolved doublet at 620° and 630°C, accompanies the loss of hydroxyl groups. The exothermic reaction at 680°C is related to a phase change which is also indicated by the X-ray diffraction analysis.

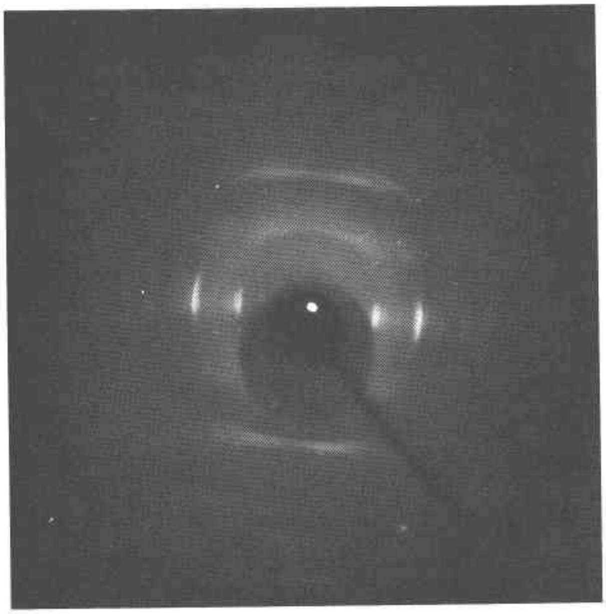

FIG. 9. Single-crystal precession photograph for swinefordite.

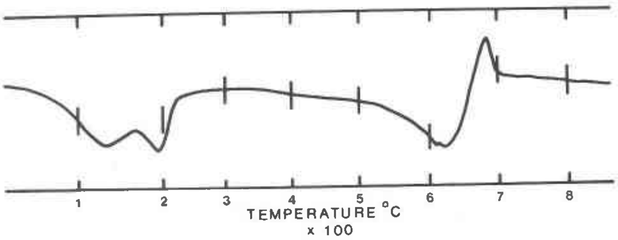

FIG. 10. Differential thermal analysis curve of swinefordite. Sample size: 100 mg; heating rate 8°C/min.

A sample has also been prepared for DTA following the method of Tien and Bauleke (1970), using 10 mg of sample and 8 mg of Al_2O_3 as reference. The number of reactions is comparable with that using larger samples, but the reaction temperature maxima are different owing to the sample size, heating rate, and type of equipment (Fig. 11). There are two well-defined endothermic reactions at 140° and 650°C and one weak endothermic reaction as a shoulder at 195°C; the exothermic reaction takes place at 790°C.

The DTA curves for swinefordite, when compared with those for smectites in the literature, resemble in general appearance those of Li-saturated smectites (Greene-Kelly, 1957).

Thermogravimetric analysis (Fig. 12) indicates two stages of weight loss, corresponding to dehydration and dehydroxylation respectively. The sample loses 11.0 percent of its original weight between room temperature and 340°C, 0.7 percent between 340° and 665°C, and 2.4 percent between 665° and 780°C. Additional 0.2 percent weight loss was recorded between 780° and 1000°C. A 5.1 percent weight loss occurred during the cooling of the sample in the furnace from 1000°C to room temperature. The total weight loss is 19.4 percent.

Infrared Absorption Spectral Analyses

Infrared absorption spectra (Fig. 13) of swinefordite were obtained from a Beckman IR-12 spectrophotometer and KBr pellet method. Swinefordite shows absorption bands at 3620, 3435, 1635,

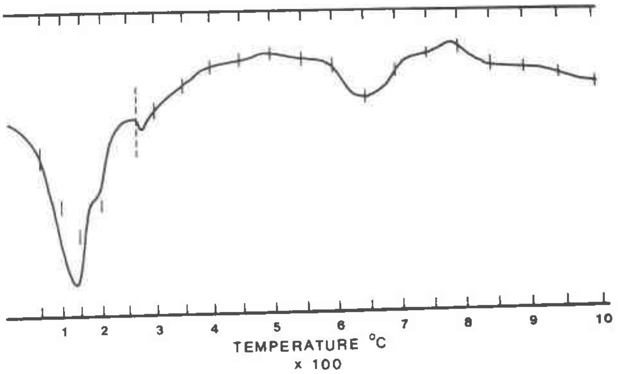

FIG. 11. Differential thermal analysis curve of swinefordite. Sample size: 10 mg; heating rate 25°C/min.

1095, 1020, 810, 780, 510, 470, and 420 cm^{-1}, similar to those for smectites given by Roy and Roy (1957), Stubičan and Roy (1961), Tettenhorst (1962), and Farmer and Russell (1964).

Chemical Analyses

Five chemical analyses of swinefordite (Table 3) were made in three different laboratories. Samples for analyses nos. 1, 3, and 4 were purified by dispersing the hydrated clay with distilled water. Sample no. 1 was dried at room temperature, samples nos. 3 and 4 at 150°C, and samples for analyses nos. 2 and 5 were naturally dried in the pit without purifications. Materials for chemical analysis were prechecked by a polarizing microscope and by X-ray diffraction. No impurities were detected.

Sample no. 1 is the only one analyzed for fluorine and for semi-quantitative spectrographic analysis. The others are assumed to contain the same amounts.

The cation exchange capacity (Cec) has been determined for samples 1 and 3. The total values of Cec in the two analyzed samples are 102 and 92.67 meq/100 g respectively, which are in the normal range for smectites (Ross and Hendricks, 1945; Weaver and Pollard, 1973). The individual values of exchangeable Ca, Na, and K agree well with the amounts of these elements found in the chemical analyses, and, therefore, they are considered as completely exchangeable. The value of exchangeable Li in analysis no. 3 probably resulted because the heat in the drying process caused Li to migrate out from interlayer positions (Hofmann and Klemen, 1950; Greene-Kelly, 1955; Tettenhorst, 1962). The exchange capacity for Li in the unheated sample may be considerably high. In analysis no. 1, it appears that there was sample dissolution by NH_4Cl, because the sum of cations is higher than the determined capacity. It is difficult to tell whether the excess is in the Li or in the Ca and Na figures (personal communications with Mr. Harry C. Starkey, USGS). If the value of exchangeable Li is correct, 28.67 percent of the Li_2O in this sample is exchangeable. The value of Cec for analysis 3 indicates a trioctahedral smectite with most Li in octahedral coordination; that of analysis 1, a smectite with about 5 cations in the octahedral position and a large amount of Li in the interlayers. Judging by the doublets of endothermic reactions in the low-temperature region of the stable phase, and the large *d* value of the basal reflections of the hydrated clay, it

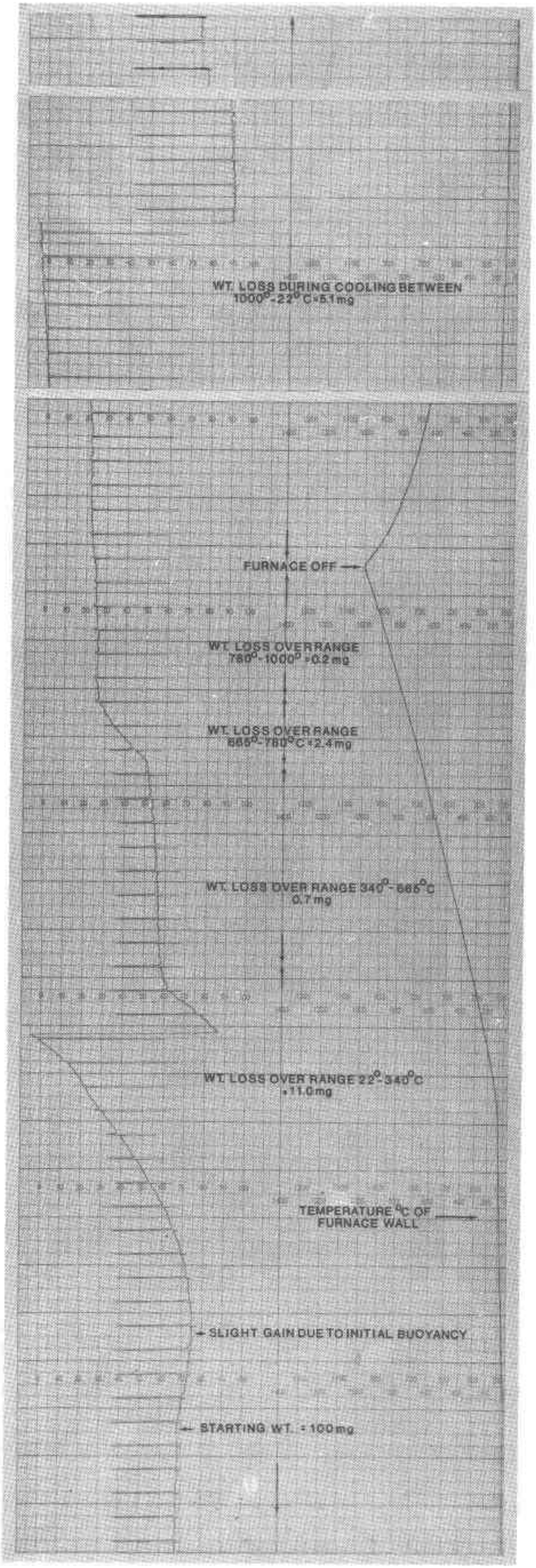

Fig. 12. Thermobalance record for swinefordite.

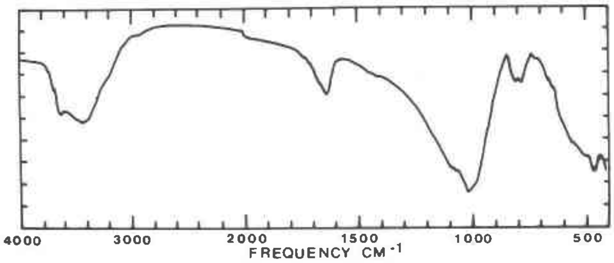

FIG. 13. Infrared spectra for swinefordite.

is likely that fairly high amounts of Li are in the interlayer positions. Accordingly, the structural formulae for each sample of swinefordite are calculated on the basis of 22 oxygen equivalents (Deer, Howie, and Zussman, 1962, p. 235), and on the assumption that 28.67 percent of the total Li_2O per formula is in interlayer positions. The structural formula for swinefordite, therefore, can be expressed approximately as $(Si_{7.66}Al_{0.34})$ $(Al_{1.87}Fe^{3+}{}_{0.15}Fe^{2+}{}_{0.09}Mg_{1.31}Li_{1.76})O_{20}$ $(F_{0.65}OH_{3.35}) \cdot Ca_{0.23}Mg_{0.05}Na_{0.11}Li_{0.72}K_{0.04}$. The composition of swinefordite in the smectite group is thus similar to that of lepidolite in the mica group (Deer, Howie, and Zussman, 1962).

Semi-quantitative spectrographic analysis for sample no. 1 gives, in parts per million: Mn, 1250; Ti, 50; Ba, 30; Be, 15; Cr, 5; Cu, 7; Sn, 15; Sr, 30; V, 15; Ga, 10.

Swinefordite does contain more Li than any other known smectite. The presence of a moderate quantity of Al, and of even a relatively small amount of Mg, rules out the possibility of hectorite $(Si_8)(Mg_{5.34}Li_{0.66})O_{20}(OH)_4$, which is a trioctahedral smectite. Because chemical analyses for swinefordite show only a limited chemical variation, and in the absence of compositions intermediate to hectorite, beidellite, or montmorillonite, the authors do not wish to propose compositional limits for the name swinefordite.

Acknowledgments

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TABLE 3. Chemical Analyses of Swinefordite

	1.	2.	3.	4.	5.
SiO_2	54.1	56.73	59.46	60.59	60.54
Al_2O_3	13.1	13.87	14.68	14.13	15.75
Fe_2O_3	1.9	1.97	1.79	1.98	-
FeO	-	-	-	0.57	3.67
MgO	6.8	6.43	7.38	7.12	6.52
CaO	0.8	0.47	1.71	2.58	2.59
Na_2O	0.63	0.53	0.27	0.59	0.10
K_2O	-	0.11	0.14	0.48	0.03
Li_2O	4.7	4.29	4.58	5.66	4.43
TiO_2	-	-	-	0.04	-
MnO	-	-	0.07	0.29	-
H_2O^+	15.6	8.17	9.94	5.64	6.04
H_2O^-		-	-	-	-
F	1.49	-	-	-	-
Total	99.12	99.21	100.02	99.67	99.67
Cation exchange capacity (meq/100g)					
Mg	7.0		10.43		
Ca	38.6		47.47		
Na	20.4		10.67		
Li	91.0		7.85		
K	-		1.42		

	1.	2.	3.	4.	5.
Tetrahedral					
Si	7.47	7.82	7.72	7.62	7.67
Al	0.53	0.18	0.28	0.38	0.33
Octahedral					
Al	1.60	2.07	1.97	1.71	2.02
Fe^{+3}	0.19	0.20	0.17	0.19	-
Fe^{+2}	-	-	-	0.06	0.39
Mg	1.37	1.29	1.39	1.31	1.21
Li	1.86	1.62	1.70	2.04	1.60
Interlayer charge					
Ca/2	0.12	0.07	0.24	0.35	0.35
Mg/2	0.03	0.03	0.04	0.03	0.03
Na	0.17	0.14	0.07	0.14	0.02
Li	0.75	0.68	0.69	0.82	0.65
K	-	0.03	0.03	0.11	0.01
Total charge					
	42.59	43.88	43.95	43.93	43.97

Analysts: 1. Harry C. Starkey, U.S. Geological Survey.
2. and 3. O. Karmie Galle, Kansas Geological Survey.
4. and 5. Joseph A. Nelen, Smithsonian Institution.

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