SYNTHESIS AND PROPERTIES OF HEAT-STABLE EXPANDED SMECTITE AND VERMICULITE[1]

R. H. LOEPPERT, JR., M. M. MORTLAND, AND T. J. PINNAVAIA

Departments of Crop and Soil Sciences and Chemistry
Michigan State University, East Lansing, Michigan 48824

Abstract—When aqueous dispersions of Na^+-smectite or n-butylammonium-vermiculite react with sulfate salts of Fe(II), Co(II), or Ni(II) bipyridyl or 1,10-phenanthroline complexes in excess of the cation-exchange capacities, intersalated phases with spacings of about 29.5 Å are obtained. Thermal decomposition of the intersalated complex cations affords expanded phases with a d(001) spacing near 18 Å for the smectites and near 28 Å for the vermiculites. These phases are stable to temperatures of at least 550°C. Nitrogen surface areas of the fired products are as high as 400 m^2/g.

Key Words—Expanded Clays, Heat-Stable Clays, Hectorite, Intercalation, Intersalation, Phenanthroline, Smectite, Vermiculite.

INTRODUCTION

One difficulty in the use of smectites and vermiculites as catalysts and molecular sieves at elevated temperatures (400–500°C) has been the collapse of the silicate sheets upon one another as solvent is removed from the interlamellar regions. This collapse results in low surface area since the internal surfaces are no longer available for adsorption. Many attempts have been made to introduce props or columns of material to hold the silicate sheets apart thus permitting internal adsorption. A number of organic materials have been used successfully (Barrer and MacLeod, 1951; Knudson and McAtee, 1973; Clementz and Mortland, 1974; Mortland and Berkheiser, 1976; Shabtai *et al.*, 1976; Berkheiser and Mortland, 1977; and Traynor *et al.*, 1978) to keep the layers apart at low to moderate temperatures, but fail in the temperature range of 250–500°C. Some success has been reported by Lahav *et al.* (1978) and in work reviewed by Barnhisel (1977) in introducing interlamellar structures of aluminum, iron, and nickel hydroxides which are relatively heat stable. Yamanaka and Brindley (1979) have had success in producing thermally stable expanded smectite by reaction with zirconyl chloride.

Work reported by Berkheiser and Mortland (1977) on 1,10-phenanthroline (phen) metal complexes and by Traynor *et al.* (1978) on bipyridyl (bp) metal complexes with smectite shows that once the exchange complex is occupied by the complex cation, additional amounts of the complex salt are adsorbed. It is believed that the intercalation of the complex salt results from a screening of the electrostatic charge of the clay by the complex cation permitting the penetration of more of the complex cation and its *anion* into the interlamellar re-

gions of the clay. Apparently the large ligands are responsible for this screening effect since inorganic salts do not behave in this way. When the anion of the complex is sulfate, superstructures within the interlamellar regions are formed with a d(001) spacing of about 29.5 Å (Traynor *et al.*, 1978). The work reported here describes the formation of these superstructures and, more particularly, demonstrates expanded structures having a d(001) spacing of about 18 Å for the smectites and 28 Å for vermiculite upon firing up to 550°C. In addition, the properties of these expanded smectites and vermiculites and their possible use as catalysts and molecular sieves are discussed.

EXPERIMENTAL

Preparation of clay

Hectorite was obtained from the Baroid Division of NL Industries as a centrifuged and air-dried powder. Montmorillonite (Upton, Wyoming), Ward's standard #25, was Na^+ saturated and the <2-μm fraction obtained. Vermiculite (Libby, Montana) was Na^+ saturated and the <2-μm fraction obtained. Some of the vermiculite was then saturated with n-butylammonium cation by ion exchange with the chloride salt. As the excess salt was removed, the vermiculite expanded to very high spacings in accordance with the observations of Walker (1960). The cation-exchange capacities (CEC) of hectorite, Upton montmorillonite, and Libby vermiculite were found to be 84 (Berkheiser and Mortland, 1977), 92 (Ross and Mortland, 1966), and 160 meq/100 g, respectively.

Preparation of complexes

Sulfate salts of *tris* bipyridyl or *tris* 1,10-phenanthroline metal complexes, $M(bp)_3^{2+}$ or $M(phen)_3^{2+}$, respectively, were obtained by adding free ligand to aqueous solutions of the metal sulfate at twice the stoichiometric ratio. Excess ligand was removed from the

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aqueous solution of complex salt by liquid-liquid extraction with benzene. The complex salts were recrystallized, freeze-dried, and stored in a desiccator over P_2O_5.

Metal complex exchange forms of clays

Exchange complexes of the complex salt with the various clay minerals were prepared by suspending 200 mg of the freeze-dried clay in 50 ml of deionized water and then adding 50 ml of water containing the appropriate quantity of dissolved complex salt. The suspensions were allowed to stand for 24 hr and were centrifuged to remove as much supernatant liquid as possible before being freeze-dried. The quantity of complex salt allowed to equilibrate with the clay was 0.5, 1, 2, 5, 10, or 20 times the exchange capacity of the clay, expressed as CEC-equivalents. The quantity of metal complex bound to the clay was determined by difference following analysis of the complex salt remaining in solution.

As will be discussed later, the intersalation of complex salt by the clay mineral is highly dependent on the dispersion and initial swelling of the clay; therefore, in all cases, it was necessary to disperse the clay before addition of the complex salt.

X-ray powder diffraction measurements

A Philips X-ray diffractometer with Ni-filtered CuKα radiation was used to measure basal spacings. Diffractograms were usually recorded to three orders of d(001) reflections. Powder samples of the clay complexes were prepared by placing aqueous suspensions from the equilibrium mixtures or pastes of the centrifuged mixtures onto glass microscope slides and drying them at 60°C. The samples were fired successively in a muffle furnace for 4 hr at 450°C and 550°C. Samples to be fired to 650°C were sedimented onto ceramic tiles instead of glass slides.

Surface area measurements

Surface areas were determined with a Perkin-Elmer Shell model 212-B sorptometer at liquid nitrogen temperature using N_2 as the adsorbate and He as the carrier gas. All samples were degassed by heating at 160°C under flowing helium. The adsorption data were plotted according to the BET equation (Berkheiser and Mortland, 1977; Traynor *et al.*, 1978).

Scanning electron microscopy

Samples were mounted on Al stubs with double stick tape and sputter coated with 200–300 Å of Au with a Film-Vac sputter coater. Electron micrographs were obtained with an ISI Super III Scanning Electron Microscope at 2000 to 30,000× magnification.

Elemental analyses

Suspensions of the clay complex were pipetted onto glass microscope slides, air-dried, and fired at 550°C for

Table 1. Adsorption of complex salt by Na^+-saturated hectorite, Na^+-saturated Upton montmorillonite, and n-butylammonium-saturated vermiculite in a 0.2% clay suspension.

| Clay | Complex salt | CEC-equivalents of complex salt added to clay | | | |
| | | 0.5 | 1.0 | 2.0 | 5.0 |
		(CEC-equivalents adsorbed by clay)			
Na^+-Hectorite	$Fe(phen)_3SO_4$	0.50	1.00	1.98	2.77
	$Fe(bp)_3SO_4$	0.50	1.00	1.90	2.68
	$Ni(phen)_3SO_4$	0.50	1.00	1.99	2.78
	$Co(phen)_3SO_4$	0.50	1.00	1.98	2.76
Na^+-Upton Montmorillonite	$Fe(phen)_3SO_4$	0.50	1.00	1.98	2.54
	$Fe(bp)_3SO_4$	0.50	1.00	1.94	2.47
n-butyl-NH_3^+-Vermiculite	$Fe(phen)_3SO_4$	0.50	1.00	1.82	1.99
	$Ni(phen)_3SO_4$	0.50	1.00	1.88	2.08
	$Co(phen)_3SO_4$	0.50	0.98	1.85	2.06

5 hr. Samples for analysis were scraped from the slides and were analyzed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

RESULTS AND DISCUSSION

Adsorption of complex salt on the clay

Analysis of the supernatant solutions, following centrifugation of the equilibrium clay complexes, indicated that Fe^{2+}, Ni^{2+}, and Co^{2+} complexes of phen and bp, when present as the sulfate salt, were readily exchanged onto the surface of Na^+-saturated hectorite and Upton montmorillonite (Table 1). In all cases, exchange of 0.5 or 1.0 CEC equivalent of complex cation onto the clay surface was essentially complete, indicating the exchange equilibrium proceeded completely in the direction of the metal-clay complex. Previous studies by Berkheiser and Mortland (1977) and Traynor *et al.* (1978) demonstrated the quantitative exchange of $Fe(phen)_3^{2+}$ and $Fe(bp)_3^{2+}$, respectively, on Na^+-hectorite. This study demonstrates the formation of Fe^{2+}-, Ni^{2+}-, and Co^{2+}-bp or phen complexes with Upton montmorillonite and Libby vermiculite as well as with hectorite.

At higher CEC equivalents of complex salt in solution, the amount of metal complex adsorbed exceeded the exchange capacity of the mineral, indicating that once the exchange sites were occupied by the complex cation, additional amounts of complex salt were adsorbed, which is in accordance with the findings of Berkheiser and Mortland (1977) and Traynor *et al.* (1978).

It was observed that the intercalation of excess complex salt was highly dependent on the exchange cation, conditions of solvation, and swelling of the clay at the time of addition of excess salt (Table 2). For example, dispersed Na^+-hectorite was able to intercalate a total of 2.68 CEC equivalents of complex cation and salt when equilibrated with 5.0 CEC equivalents of
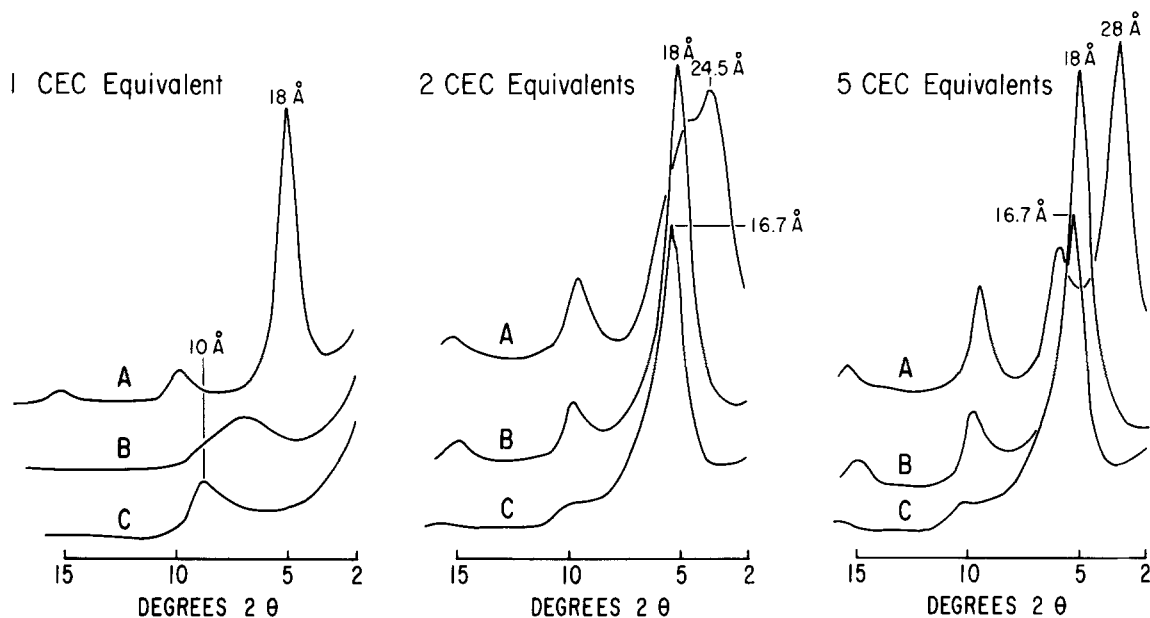
Figure 1.   X-ray powder diffraction patterns of clay complexes produced from reaction of 0.2% Na$^+$-hectorite suspensions with three different levels of Ni(phen)$_3$SO$_4$ and following heat treatment in air to: (A) 60°C, (B) 450°C, and (C) 550°C.

Fe(phen)$_3$SO$_4$ in solution, compared to Ca^{2+}- and Fe(phen)$_3^{2+}$-hectorite which were able to intercalate 1.05 and an additional 0.3 CEC equivalents, respectively. Upon addition of the complex salt to Na$^+$-, Fe(phen)$_3^{2+}$-, and Ca^{2+}-hectorite, d(001) spacings of 29, 18, and 18 Å were obtained, respectively. These results indicate that large quantities of complex salt were intercalated into a second layer in the interlamellar region of the clay only in the highly expanded Na$^+$-hectorite system. Even though exchangeable Ca^{2+} was displaced from the hectorite surface by Fe(phen)$_3^{2+}$, the driving force for intercalation of excess salt in a second layer was not sufficiently great to force the layers of clay open beyond the ~20 Å of hydrated Ca^{2+}-hectorite.

Table 2.   Adsorption of Fe(phen)$_3$SO$_4$ by hectorite and Libby vermiculite and d(001) reflections of the clay complex as affected by the initial saturating cation.

Clay	Saturating cation	Complex added	Total complex adsorbed	d(001)Å	
		(CEC-equivalents)		60°C	550°C
Hectorite	Na$^+$	1.00	1.00	17.9	10.2
	Na$^+$	5.00	2.68	28.7	16.7
	Ca^{2+}	5.00	1.05	17.9	10.3
	Fe(phen)$_3^{2+}$	4.00	1.30	17.9	11.4
Vermiculite	n-butyl NH$_3^+$	1.00	1.00	28.6	17.6
	Na$^+$	3.00	0.00	14.0	9.4
	Ca^{2+}	3.00	0.00	14.0	9.4
	n-butyl NH$_3^+$	3.00	1.82	29.7	28.9
	Fe(phen)$_3^{2+}$	2.00	1.78	29.5	28.9

Further expansion would be required for intercalation of additional large quantities of excess salt.

Fe(phen)$_3^{2+}$ was not exchanged onto the interlamellar surfaces of Na$^+$- and Ca^{2+}-vermiculite (d ~ 14 Å). However, Fe(phen)$_3^{2+}$ and excess Fe(phen)$_3$SO$_4$ were readily intercalated by the highly expanded n-butylammonium-vermiculite. Both the 1.0 CEC-equivalent complex and the intercalated systems containing excess complex salt gave basal spacings of approximately 29 Å. Obviously, the energy of exchange and adsorption was not sufficiently great to separate the vermiculite layers beyond their normal 14 Å position in the Na$^+$- and Ca^{2+}-exchange forms. It thus appears that intercalation of large quantities of excess salt was only possible in a highly expanded clay which allowed free movement of complex salt into the interlamellar region, and that normally hydrated vermiculite (d ~ 14 Å) will not expand to permit exchange of its interlamellar cations with the complex cations.

X-ray powder diffraction of clay complexes

The effects of complex salt on the d(001) spacings of swelling clays are shown in Figures 1 and 2. Exchange complexes of Upton montmorillonite or hectorite with 1.0 CEC equivalent of Fe(phen)$_3^{2+}$-, Ni(phen)$_3^{2+}$-, or Co(phen)$_3^{2+}$-sulfates resulted in 18 Å basal spacings, while 29.5 Å basal spacings were obtained for clay complexes prepared in the presence of high concentrations of excess complex salt (Figure 1). Intermediate loadings of complex salt resulted in randomly interstratified systems with d(001) values between 18 and 29.5 Å. The 1.0 CEC-equivalent complexes of Libby vermiculite
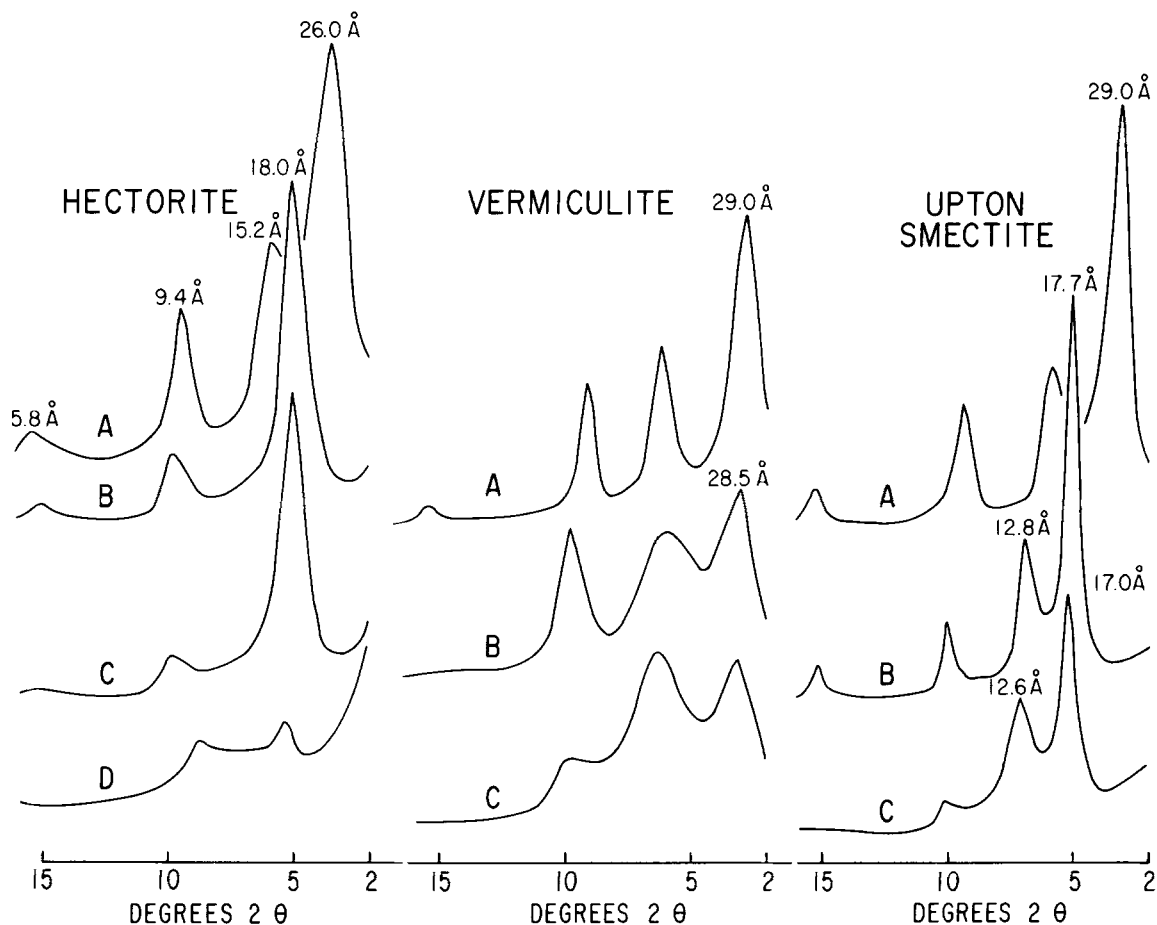
Figure 2. X-ray powder diffraction patterns of 5.0 CEC-equivalent Fe(phen)$_3$SO$_4$-hectorite, 3.0 CEC-equivalent Fe(phen)$_3$SO$_4$-vermiculite, and 5.0 CEC-equivalent Fe(phen)$_3$SO$_4$-Upton montmorillonite following heat treatment in air to: (A) 60°C, (B) 450°C, (C) 550°C, and (D) 650°C. (CuKα radiation.)

with Fe(phen)$_3$SO$_4$ or Ni(phen)$_3$SO$_4$ resulted in basal spacings of approximately 28.5 Å compared to 29.5 Å at the highest loadings of salt.

The differences in expansion properties of 1.0 CEC-equivalent smectite and vermiculite samples may be attributed to differences in charge characteristics of the minerals. Consideration of the size of M(phen)$_3^{2+}$ and M(bp)$_3^{2+}$ complexes shows that approximately 102 meq of complex cation per 100 g of clay would be required to form a complete monolayer in the interlayer of an expanding clay. Since the CEC of hectorite (84 meq/100 g) and Upton montmorillonite (92 meq/100 g) are less than the concentration of complex cation needed for monolayer coverage, the 18 Å spacing is sufficient to accommodate all the exchanged complex cations. However, the CEC of Libby vermiculite (160 meq/100 g) exceeds the concentration of cation needed for monolayer coverage; therefore, we would expect at least a partial two-layer coverage, resulting in higher

spacings, if all the exchange sites are occupied by complex cation. X-ray powder diffraction analysis does show a one-layer interlamellar complex, d(001) ≈ 18 Å, in hectorite and Upton montmorillonite and a two-layer complex in Libby vermiculite.

At the highest loadings of complex salt, basal spacings of clays dried at 60°C did not exceed 29.5 Å, which is indicative of a two-layer interlamellar complex made up of the exchanged complex cations and excess complex salt. Therefore, where larger quantities of excess complex salt were intersalated by the highly expanded Na$^+$-smectite or n-butylammonium-vermiculite in water, salt in excess of that required to produce the two-layer complex was evidently expelled from the interlayers upon air drying.

X-ray powder diffraction of fired complexes

The X-ray powder diffraction properties of clay complexes prepared in solutions of from 1.0 to 5.0 CEC

Table 3. Surface areas of clay complexes as measured by nitrogen adsorption.

| Clay | Complex salt | CEC-equiva-lents added[1] | N_2 surface area, m^2/g Heat treatment | | |
			160°C	450°C	550°C
Hectorite	$Fe(phen)_3SO_4$	1	166	151	143
		2	63	65	114
		5	7	19	50
		10	3	4	18
	$Co(phen)_3SO_4$	5	10	13	46
	$Ni(phen)^3SO_4$	5	2	4	29
Upton	$Fe(phen)_3SO_4$	1	122	116	115
Montmorillonite		2	13	14	56
		5	7	9	50
		10	5	5	19
Vermiculite	$Fe(phen)_3SO_4$	1	178	162	121
		3	13	46	236
		5	11	19	102
	$Co(phen)_3SO_4$	3	9	18	217
	$Ni(phen)_3SO_4$	3	7	31	220

[1] The CEC-equivalents term refers to the quantity of complex salt in solution at the time of preparation of the clay complex. The actual quantity of complex adsorbed by the clay in aqueous suspension is shown in Table 1.

equivalents of complex salt were investigated to see what their response would be to heat treatments up to 650°C.

One CEC-equivalent complexes with Upton montmorillonite and hectorite which showed 18-Å basal spacings before heating, collapsed to approximately 12.6 Å following heating to 450°C and to approximately 10.3 Å following heating to 550°C (Figure 1). The 1.0 CEC-equivalent vermiculite complexes collapsed from near 28 Å on drying at 60°C to approximately 17.6 Å upon heating to temperatures up to 550°C. With the 1.0 CEC-equivalent samples, the cation-exchange sites of the mineral are occupied by the complex cation, but there is no excess complex salt in the interlamellar region. However, it is possible that some of the Na+ and the counter ion SO_4^{2-} could remain in the interlayer of an unwashed clay.

X-ray powder diffraction patterns showing heat treatment effects for the $Fe(phen)_3SO_4$ complexes with Na+-hectorite, Na+-Upton montmorillonite, and n-butylammonium-vermiculite prepared at the 5.0 CEC-equivalent level appear in Figure 2. The diffraction patterns (A) show the superstructure obtained (~29 Å) upon reaction of these expanded clays with 5.0 CEC equivalents of the complex salt and drying at 60°C. Patterns B and C show the results of firing these systems at 450° and 550°C, respectively. The development of an 18 Å spacing concomitant with the loss of the 29 Å system in the hectorite and Upton montmorillonite is quite evident. On the other hand, the vermiculite complexes retain d(001) reflections near 28.5 Å although they are obviously highly interstratified systems. One difference

between the hectorite and Upton-montmorillonite complexes is the appearance of a peak near 12.8 Å in the latter upon firing at elevated temperatures. The intensity of this peak varied greatly in different samples, being quite evident in some but appearing only as a shoulder to the 18 Å peak in others. Results similar to those exhibited in Figure 2 were found for $Ni(phen)_3SO_4$ complexes as shown in Figure 1 and for $Co(phen)_3SO_4$ complexes as well. Also, when a bipyridyl (bp) ligand was substituted for the o-phenanthroline (phen), very similar data were obtained. When the above complexes were heated to 650°C, loss of the expanded structures occurred as indicated by the disappearance of the 18 and 28 Å peaks and the appearance of a peak near 10 Å.

The heat-stable 18 Å phases for the smectite and 28 Å phases for the vermiculite arise from the presence of intercalated complex salt which was not present in the 1.0 CEC-equivalent complex clays. The structures formed from the intercalated complex salt following firing to 450°C or 550°C hold the silicate sheets of the clay apart and result in d(001) reflections of approximately 18 Å and 28 Å for the smectites and vermiculite, respectively.

Surface area analyses

Surface areas, as determined by N_2 adsorption at liquid nitrogen temperatures and application of the BET equation, are summarized in Table 3. In all cases, the surface areas of unfired samples were greatest for the 1.0 and 2.0 CEC-equivalent complexes. In the 1.0 CEC-equivalent samples, voids would exist between adsorbed complex cations within the interlayer. However, at the higher loadings these interstitial voids would be filled with intercalated salt. Also, at higher loadings, complex salt at the external surfaces of clay particles may present a physical barrier to diffusion of N_2 into the interlamellar regions of the clay (Traynor *et al.*, 1978).

Surface areas of 1.0 CEC-equivalent samples were decreased slightly upon firing, whereas surface areas of samples with higher loadings were increased following firing. For example, surface areas of the 3.0 CEC-equivalent vermiculite complex increased from approximately 10 m^2/g for the samples dried at 160°C to approximately 220 m^2/g for samples fired to 550°C.

The slightly decreased surface areas of 1.0 CEC-equivalent samples following firing may have been due to partial collapse of the clay. Collapse was not complete as evidenced by the surface areas of approximately 100–150 m^2/g and the broad X-ray bands indicative of interstratification. Clay layers may have been partially propped apart by metal oxide, residual carbon, and/or residual Na_2SO_4 in the smectites and n-butylammonium sulfate in vermiculite.

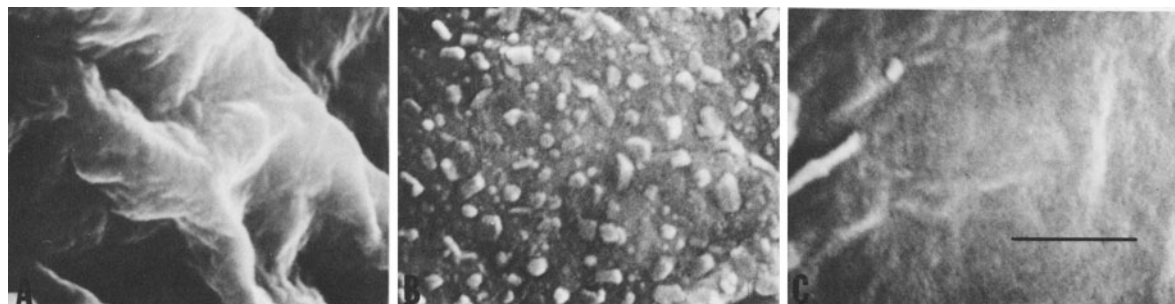The effect of firing on increasing surface areas of 2.0

Figure 3.   Electron micrographs of 5.0 CEC-equivalent $Fe(phen)_3SO_4$-hectorite complexes following (A) air drying, (B) heat treatment at 550°C for 5 hr, and (C) heat treatment at 550°C and washing with 2.5 N HCl. The line in the micrograph represents 1 μm.

to 5.0 CEC-equivalent samples was due to thermal decomposition of both the interlayer complex and complex salts coating the surfaces of clay mineral particles. Surface areas of fired clay complexes were not noticeably affected by thorough washing with water (Table 4); however, surface areas were noticeably increased following a washing with 2.5 N HCl. This is quite likely because of the removal of material at the mineral edges which would prevent access of nitrogen to internal surfaces.

Electron microscopy

Electron micrographs (Figure 3) show some interesting differences in morphology following firing and washing of the 5.0 CEC-equivalent $Fe(phen)_3SO_4$-hectorite complex. Unfired samples have a smooth, wavy, folded appearance (Figure 3A). Upon firing, the surfaces of the clay particles appear to be coated with rectangular and slightly rounded aggregates (Figure 3B). The aggregates apparently resulted from decomposition of complex salts which were adsorbed on the external surfaces of clay particles. Aggregates were not affected by washing with water but were dissolved and almost entirely removed by treatment with 2.5 N HCl (Figure 3C). The general appearance of the aggregates, along with their solubility characteristics, suggest an iron oxide structure.

Elemental analyses

Elemental analyses of 2.0 CEC-equivalent complexes (Table 5) indicated that large quantities of carbon remained after heating and that only 10% of the original carbon and 15% of the original nitrogen was removed by firing to 550°C; however, approximately 60% of the original carbon and nitrogen was removed on similarly treated 5.0 CEC-equivalent complexes. In both cases the clay complexes maintained 18 Å basal spacings. Apparently, complex cation and complex salt on the interlayer of the clay were less subject to complete thermal decomposition than complex salt on the

external surfaces of the particles. Infrared spectra indicated that the original organic species were decomposed at these heat treatments and no specific new bands appeared. Upon firing above 600°C the carbon contents are greatly reduced. It appears that the silicate layers finally collapse at a temperature near the temperature at which the last quantities of carbon are lost. Therefore, it is likely that the decomposition products of the complex cation and intersalated complex salt play an important role in stabilizing the structure of the expanded clay.

DISCUSSION

Assuming a theoretical surface area of 800 m²/g for an expanded clay and a surface area of 130 Å² in the *ab* plane occupied by a single $Fe(phen)_3^{2+}$ ion, the calculated monolayer coverage by complex cations is approximately 102 meq $Fe(phen)_3^{2+}$ per 100 grams of clay. Since cation-exchange capacities of Upton montmorillonite, hectorite, and Libby vermiculite are 92, 84, and

Table 4.   Surface areas of fired clay complexes following washing with H_2O or 2.5 N HCl.

Clay	Complex salt	CEC-equivalents added[1]	Chemical treatment	N₂ surface area, m²/g	
				Heat treatment	
				450°C	550°C
Hectorite	$Fe(phen)_3SO_4$	1	H_2O	147	108
		2	H_2O	67	111
		5	H_2O	31	51
	$Fe(phen)_3SO_4$	1	HCl	202	358
		2	HCl	166	263
		5	HCl	108	159
Vermiculite	$Fe(phen)_3SO_4$	3	H_2O	54	224
		3	HCl	208	406

[1] The CEC-equivalent term refers to the quantity of complex salt in solution at the time of preparation of the clay complex. The actual quantity of complex adsorbed by the clay from aqueous suspension is shown in Table 1.

Table 5. Chemical analyses of Fe(phen)$_3$SO$_4$- and Ni(phen)$_3$SO$_4$-hectorite complexes following firing to 550°C.

Complex	CEC-equivalents added	Composition, percentage by weight						% of original remaining	
		Si	Fe	Ni	C	N	S	C	S
Fe(phen)$_3$SO$_4$	2.0	19.85	2.59	—	17.35	3.40	1.37	86.5	91.9
	5.0	19.02	6.16	—	18.02	3.52	1.81	37.8	51.1
Ni(phen)$_3$SO$_4$	2.0	18.05	—	2.81	19.44	4.10	1.32	94.0	86.3
	5.0	17.69	—	6.32	19.51	4.09	2.86	38.0	82.9

160 meq/100 g, respectively, the amount of material required for a single layer interlayer coverage for these clays is approximately 1.11, 1.21, and 0.64 CEC equivalents of the complex cations. Likewise, the two-layer interlamellar complexes of these clays theoretically contain approximately 2.22, 2.42, and 1.28 CEC equivalents of complex cation, respectively. The adsorption data (Table 1) indicate that 2.47, 2.76, and 1.99 CEC equivalents of complex, respectively, were actually adsorbed by the clay from a 5.0 CEC-equivalent solution of complex salt. Therefore, it is possible that in an aqueous suspension a quantity of complex salt in excess of that required to produce a complete two-layer complex may be intercalated by the expanded clay. This is corroborated by isotherms obtained for adsorption of Fe(bp)$_3$SO$_4$ on Na$^+$-hectorite (Traynor et al., 1978).

The 29.5 Å d(001) reflection of air-dried Fe(phen)$_3$SO$_4$-clays is attributed to two layers of the complex cation which has a cross-sectional thickness of approximately 8 Å along the C$_3$ axis (Berkheiser and Mortland, 1978) and the associated counter anion SO$_4^{2-}$ which has a cross-sectional diameter of approximately 4 Å. Since no more than a 29.5 Å d(001) spacing was observed for air-dried clay complexes, it is likely that any salt in excess of that required for a complete two-layer complex was expelled from the interlayer upon air drying and coated external surfaces of the clay particles. Also any unintercalated salt used in preparation of the clay complex would exist on the external surfaces of the clay particles upon air drying. This excess salt may prevent diffusion of nitrogen into the interlamellar regions of the clay and therefore result in very low experimentally determined surface areas. Low surface areas were observed for samples prepared in the presence of high concentrations of excess complex salt and dried at 160°C.

In this study, it was observed that firing generally had the effect of reducing surface areas of samples containing 1.0 CEC equivalent of complex cation. This was probably due to partial collapse of the clay structure. The increased surface areas obtained upon firing of the samples more highly loaded with complex salt were likely due to partial decomposition of the interlamellar complex, resulting in voids within the matrix, and to the decomposition of the surface coating. In order to produce a high surface area, heat-stable structure, it is essential to produce a two-layer complex but to avoid large excesses of salt which would coat the surfaces of clay particles. However, the data in Table 4 show that surface areas can be greatly improved by washing the samples in HCl which apparently removes occluding material and opens up additional surface for nitrogen adsorption.

Smectites and vermiculites which contained 1.0 CEC equivalent of complex cation collapsed to approximately 10 Å upon firing to 550°C, whereas clays which contained an excess of intercalated complex remained expanded to 18 Å (smectites) and 29 Å (vermiculite). It appears that the decomposition products of the excess salt served as a prop to hold layers of the silicate structure apart.

The carbon contents of 2.0 CEC-equivalent hectorite complexes fired to 550°C (greater than 80% of the original carbon content) indicate that thermal decomposition products of complex cation and intersalated complex salt play an important role in the maintenance of the expanded structure. Upon firing to 650°C, less than 1% of the original carbon remains. It appears that the silicate layers finally collapse at a temperature near that at which the last quantities of carbon are lost.

Extensive washing of the fired complexes with water did not appreciably affect the d(001) spacings of the clays or the surface areas. Since the metal sulfate salts of Fe^{2+}, Ni^{2+}, and Co^{2+} would be quite soluble in water, these data provide evidence that inorganic sulfate salts were not responsible for propping apart layers of the fired clay systems. Likewise, H$_2$S was not detected following treatment of the fired clay complex with 2.5 N HCl, providing evidence that sulfide salts were not responsible for holding clay layers apart.

The characteristic infrared absorption bands attributed to M(phen)$^{2+}$ or M(bp)$^{2+}$ in the clay complexes are no longer observed following firing to 550°C. The only major absorption bands in the fired system are very broad ones centering at approximately 1600, 1580, 1520, 1420, and 1390 cm^{-1} which may be attributed to C–C multiple bond stretching vibrations of the aromatic matrix and possibly to C–H bending vibrations of aliphatic constituents. The basic structures of o-phenanthroline and bipyridyl were destroyed or drastically altered during the heat treatment.

Studies are currently underway to investigate the chemical and physical properties of the interlamellar material more thoroughly. The heat stability of the expanded clays, the high surface areas, and the presence of metal ions in the interlayer suggest the potential usefulness of these materials as catalytic supports and molecular sieves.

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Резюме—Когда водные дисперсии Na⁺-смектита или n-бутил-аммониевого вермикулита реагируют с сульфатными солями Fe(II), Co(II), или Ni(II)-бипиридиловыми, или 1,10-фенантролиновыми комплексами сверх катионных обменных способностей, образуются межсолевые фазы с промежутками около 29,5 Å. В результате термальной декомпозиции катионов межсолевого комплекса образуются расширенные фазы с промежутками d (001) около 18 Å для смектитов и около 28 Å для вермикулитов. Эти фазы стабильны к температуре по крайней мере до 550°C. Азотные поверхностные площади прокаленных продуктов достигают 400 м²/г.

Resümee—Wenn wäßrige Dispersionen von Na⁺-Smektit oder n-Butylammonium-Vermiculit mit Sulfaten von Fe(II), Co(II), oder Ni(II) bipyridyl oder 1,10-Phenanthrolinkomplexen über die Kationenaustauschkapazitäten hinaus reagieren, werden intersalierte Phasen mit Netzabständen von 29,5 Å erhalten. Thermischer Abbau der intersalierten komplexen Kationen ergibt ausgedehnte Phasen mit einem d(001) Abstand von fast 18 Å für die Smektiten und fast 28 Å für die Vermiculite. Diese Phasen sind bis auf Temperaturen von mindestens 550°C stabil. Stickstoff-Oberflächen der gefeuerten Produkte gehen bis auf 400 m²/g hinauf.

Résumé—Lorsque des dispersions aqueuses de smectite-Na⁺ ou de n-butylammonium-vermiculite réagissent avec des complexes de sels de sulfate de Fe(II), Co(II), ou Ni(II) bipyridyl ou de 1,10-phenanthroline en excès des capacités d'échange de cations, des phases intersalatées avec des espacements d'environ 29,5 Å sont obtenues. La décomposition thermale des cations du complexe intersalaté permet des phases dilatées avec un espacement d(001) près de 18 Å pour les smectites et près de 28 Å pour les vermiculites. Les phases sont stables jusqu'à des températures d'au moins 550°C. Les régions superficielles de nitrogène des produits calcinés sont aussi élevées que 400 m²/g.