X-RAY AND INFRARED DATA ON HECTORITE–GUANIDINES AND MONTMORILLONITE–GUANIDINES[1]

by

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ABSTRACT

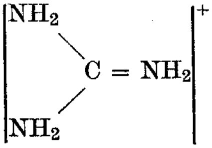
Clay–organic complexes of the clay minerals sodium hectorite and sodium montmorillonite with the hydrochlorides of guanidine, amino-guanidine, methylguanidine, and triamino-guanidine were examined for thermal stability by the oscillating-heating x-ray technique. Completely exchanged complexes increase the thermal stability of these two clays by as much as 275°C.

Infrared analyses were also made on these same clay–organic complexes. There is a marked difference between the infrared patterns of the clay–organic complexes and the patterns of the clays or the organic salts alone. More experimental work must be done before it will be possible to interpret completely the clay–organic infrared patterns.

INTRODUCTION

The apparatus used in the oscillating-heating x-ray studies of this paper was adapted from a furnace used by Birks and Friedman (1917) and described more completely by Weiss and Rowland (1956) and Rowland, Weiss, and Lewis (1959). Applications of the oscillating-heating technique to studies of clay minerals are given by Weiss and Rowland (1956) and Rowland, Weiss, and Bradley (1956). Some of the original clay–organic oscillating-heating research has been done by Rowland and Weiss (unpublished work) on complexes of clay with simple amines.

The crystal structures of clay minerals have been determined by many investigators. Hectorite and montmorillonite are sheet structures of the three-layer type with exchange cations between the sheets. These lattices expand when treated with water, alcohols, amines, and other organic liquids. An organic compound having a planar structure and a resonating charge should fit easily into the clay structure and be strongly bound. The guanidinium ion



is promising for an initial investigation. The crystal structure has not been

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determined for guanidine, but it has been for guanidinium bromate (Drenth *et al.*, 1953), methylguanidinium nitrate (Curtis and Pasternak, 1955), aminoguanidine hydrochloride (Bryden, 1957), and triaminoguanidinium chloride (Okaya and Pepinsky, 1957). In each compound the CN_3 group is approximately trigonal and the structure is planar, a typical layer structure.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental clay materials were hectorite (Hector, California) and Wyoming bentonite (Upton, Wyoming) both of which were run through a sodium exchange column. The experimental amines were the hydrochlorides of guanidine, aminoguanidine, methylguanidine, and triaminoguanidine, abbreviated as G, AG, MG, and TAG. One hundred fifteen milliequivalents per hundred grams was taken as the cation exchange capacity of hectorite (Ames, Sand and Goldich, 1958); ninety milliequivalents as that of Wyoming bentonite, an average for this material.

The dilute clay suspension of montmorillonite contained 15.0 g per 1000 ml (a 1.5 percent suspension); of hectorite, 10.0 g per 1000 ml (a 1 percent suspension). Two concentration levels of the hydrochlorides of G, AG, MG, and TAG were used: 0.01 meq per ml, and 0.1 meq per ml. Organic–clay complexes of each clay with G, AG, MG, and TAG were prepared for 25 percent, 200 percent, and 1000 percent of the amount needed for complete exchange reaction with the clay.

The preparation of material for examination by the oscillating-heating method was made by putting 5 ml of clay suspension into a glass vial, adding the calculated amount of amine, and shaking vigorously. The clay flocculated readily. The mixture stood a minimum of 24 hr and was occasionally shaken vigorously. One ml of flocculated clay was pipetted on to a platinum plate, air dried, and examined by the oscillating-heating technique. In all x-ray traces of this study, oscillation was over the first order basal maximum (001). The ordinates in Figs. 1–8 are in arbitrary units.

The initial and final decomposition temperatures in Table 1 are picked from Figs. 1–8. The temperatures in the figures were recorded by the operators (from potentiometric measurements of thermocouple voltages) as the runs were being made. The initial decomposition temperature was chosen as the temperature at which the diffraction peak began to decrease rapidly both in intensity and spacing. The final decomposition temperature is that at which a sharp 10Å peak is formed and the peak intensity does not increase appreciably.

DISCUSSION

The subject of clay mineral organic reactions is summarized in Grim (1953, pp. 250–277). Gieseking (1939), Gieseking and Jenny (1936), Ensminger and Gieseking (1939, 1941), Hendricks (1941), Bradley (1945a, 1945b), and

MacEwan (1944, 1946) discuss extensively the kinds of organic molecules which can be adsorbed in the cation exchange position on silicate sheet structures. Organic ions are held more firmly by three-layer clays than are inorganic positive ions (Hendricks, 1941). In addition, these authors and

TABLE 1.—TEMPERATURES OF INITIAL DECOMPOSITION AND DEVELOPMENT OF GOOD 10 Å MATERIAL

	Initial Decomposition Temperature, C°	Final Decomposition Temperature, C° Good 10 Å Material
Na–Hectorite	38	79
Na–Montmorillonite	36	68
Hectorite–G, 25%	25	110
Montmorillonite–G, 25%	40	75–80
Hectorite–G, 200%	220	385
Montmorillonite–G, 200%	240	320
Hectorite–G, 1000%	315	600
Montmorillonite–G, 1000%	310	530
Hectorite–AG, 25%	38	265
Montmorillonite–AG, 25%	36	95
Hectorite–AG, 200%	260	360
Montmorillonite–AG, 200%	185	420
Hectorite–AG, 1000%	285	570
Montmorillonite–AG, 1000%	225	505
Hectorite–MG, 25%	30	355
Montmorillonite–MG, 25%	35	220
Hectorite–MG, 200%	250	500
Montmorillonite–MG, 200%	235	460
Hectorite–MG, 1000%	290	580
Montmorillonite–MG, 1000%	280	420
Hectorite–TAG, 25%	35	265
Montmorillonite–TAG, 25%	38	165
Hectorite–TAG, 200%	220	420
Montmorillonite–TAG, 200%	200	420
Hectorite–TAG, 1000%	230	480
Montmorillonite–TAG, 1000%	220	480

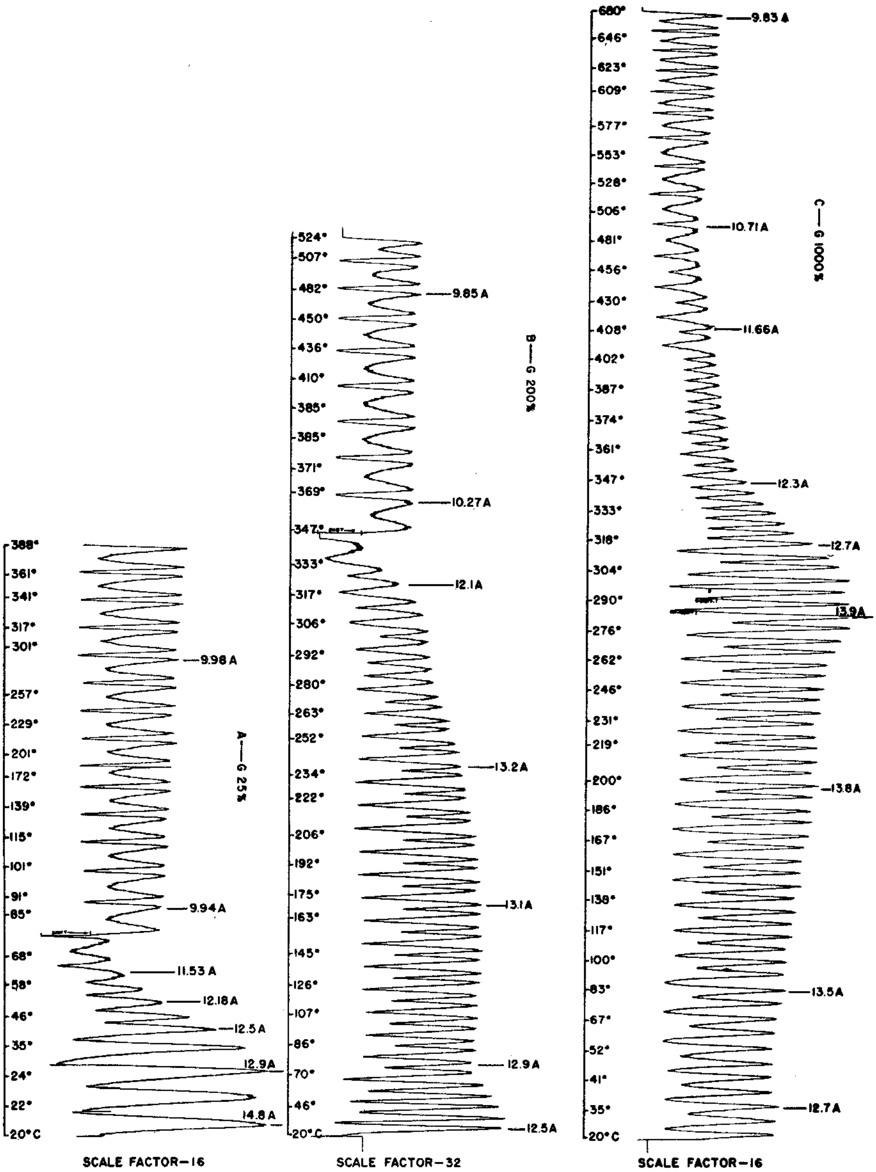

FIGURE 1.—Oscillating-heating x-ray diffraction patterns, 001, hectorite-guanidine.

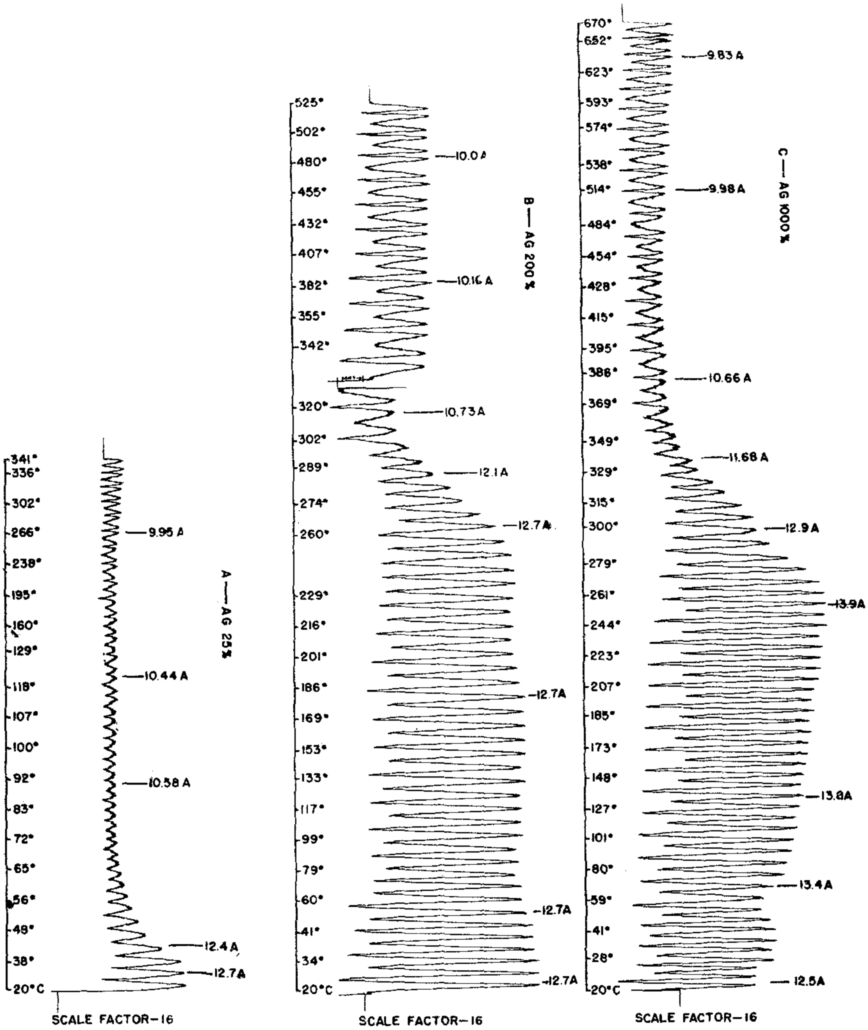

Figure 2.—Oscillating-heating x-ray diffraction patterns, 001, hectorite–aminoguanidine.

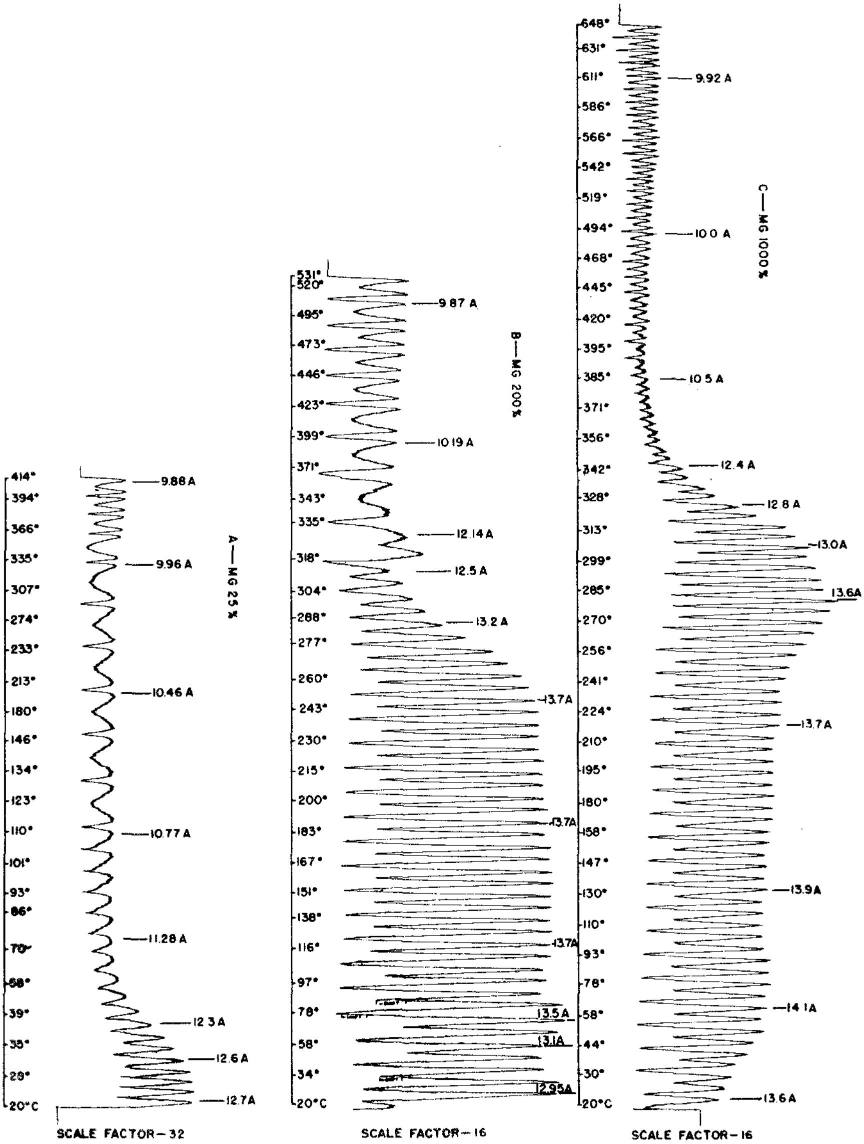

FIGURE 3.—Oscillating-heating x-ray diffraction patterns, 001, hectorite–methylguanidine.

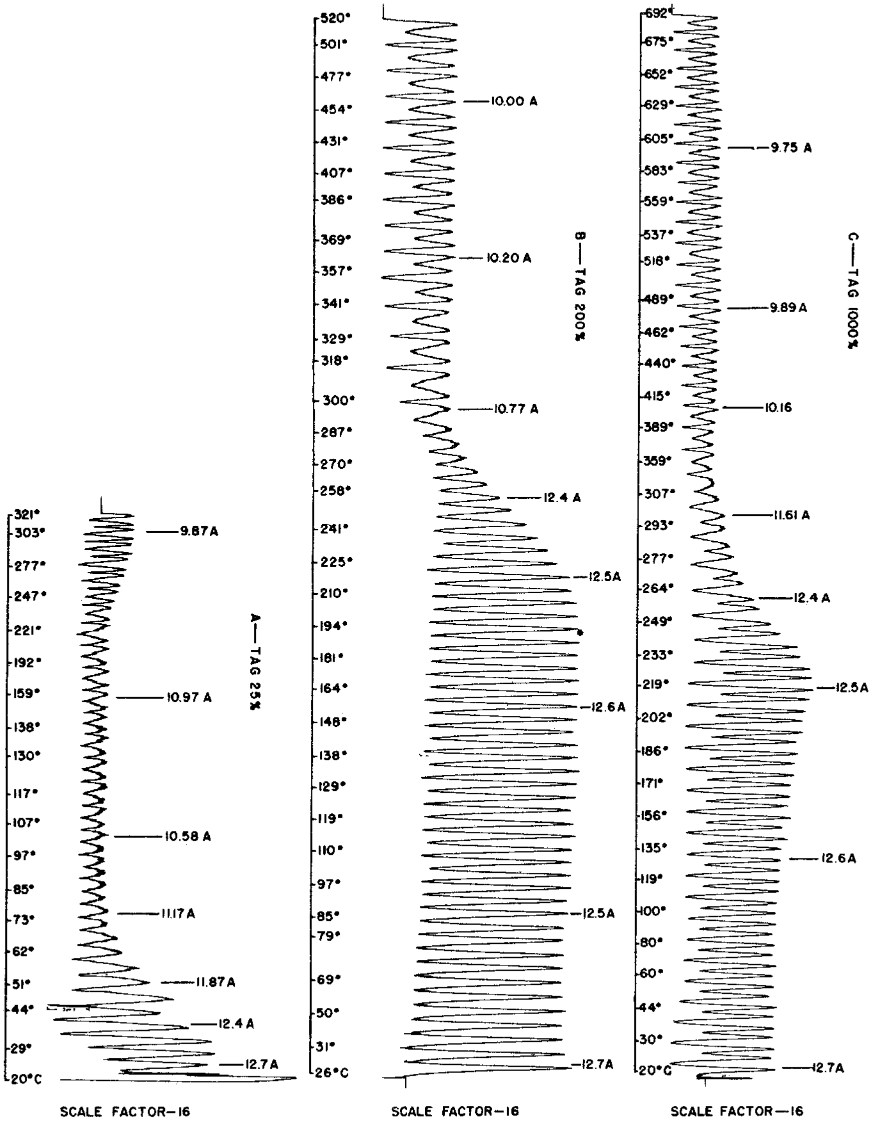

FIGURE 4.—Oscillating-heating x-ray diffraction patterns, 001, hectorite–triaminoguanidine.

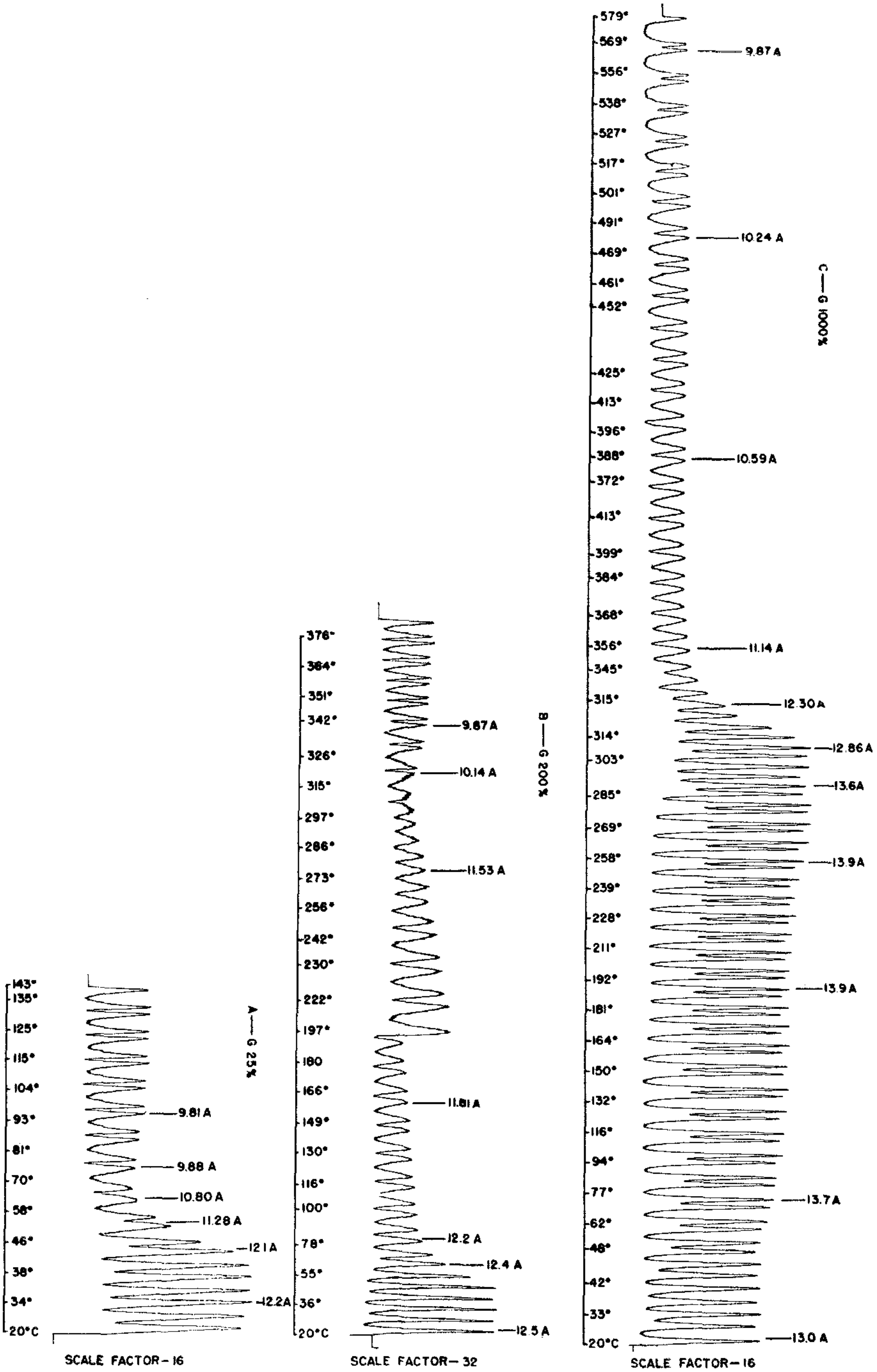

FIGURE 5.—Oscillating-heating x-ray diffraction patterns, 001, montmorillonite–guanidine.

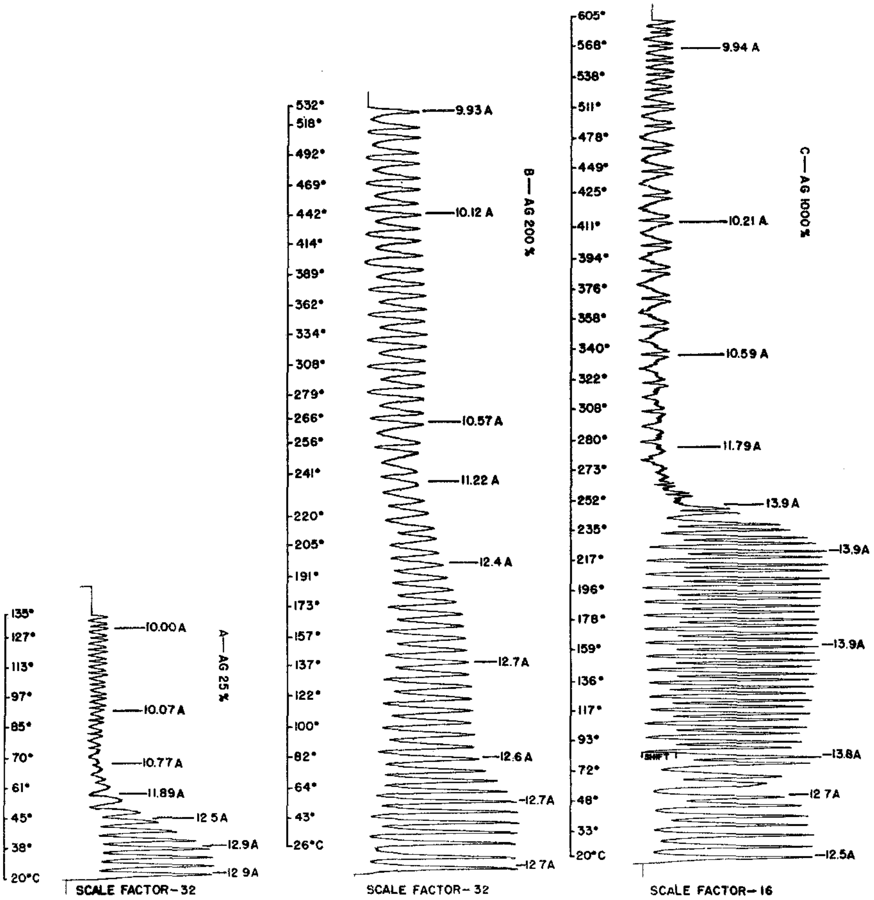

Figure 6.—Oscillating-heating x-ray diffraction patterns, 001, montmorillonite–aminoguanidine.

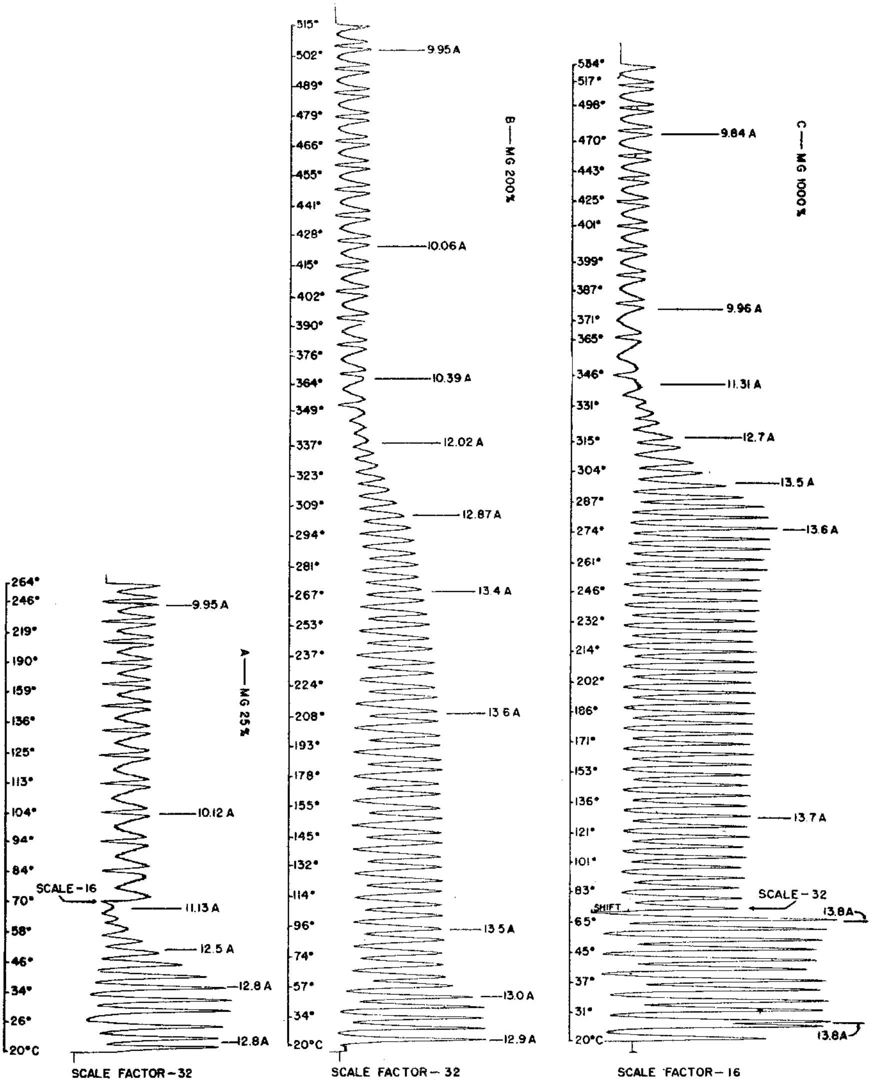

FIGURE 7.—Oscillating-heating x-ray diffraction patterns, 001, montmorillonite–methylguanidine.

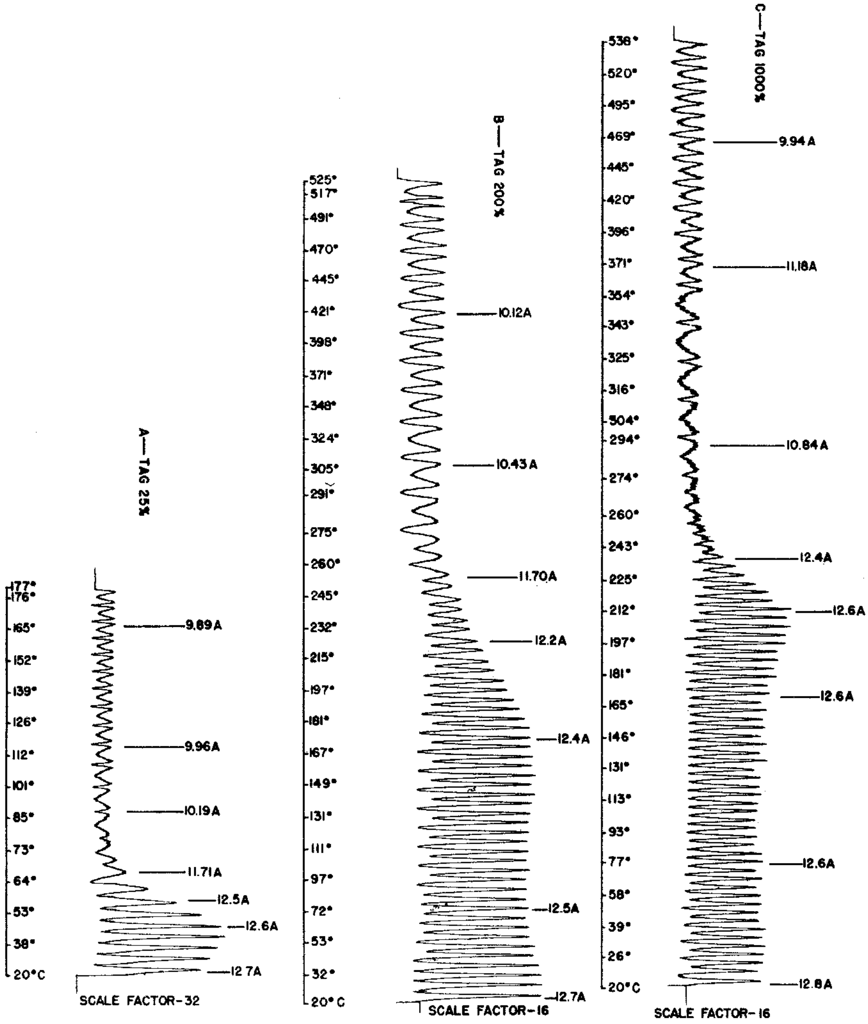

FIGURE 8.—Oscillating-heating x-ray diffraction patterns, 001, montmorillonite–triaminoguanidine.

Greene-Kelly (1955a, 1955b) discuss the number of layers of organic molecules which are adsorbed as well as their orientation on the silicate sheet structure. Hendricks (1941), Bradley (1945a) and others believe that the adsorbed organic molecule is oriented so that its smallest dimension is perpendicular to the sheet surface. The basal (001) spacing of the talc and pyrophyllite structures is a 9.6 Å. The observed increase in the 001 dimension of expandable clay minerals over the ideal dimension of 9.6 Å represents the thickness of the adsorbed layer. Some organic molecules with non-coplanar atoms are distorted into planar arrangements when adsorbed on a clay sheet. The basal (001) spacing of montmorillonite having one molecule of interlayer water is 12.3–12.4 Å. Most of the published values for the 001 spacing of montmorillonite having one layer of an adsorbed organic molecule range from 12.7 Å for methylamine to 13.2–13.4 Å for other polyamines (MacEwan, 1944, 1946; Bradley, 1945a, 1945b). Values exceeding 13.5 Å for the 001 spacing of montmorillonite are explained by Hendricks (1941) as an average value for 1–2 layers of organic molecules, but are explained by Greene-Kelly (1955a, 1955b) in elaborate detail as orientations which present dimensions of the organic molecule other than its shortest one perpendicular to the 001 dimension of the clay mineral.

G, AG, MG, and TAG are cation exchanged in the interlayer position of hectorite and montmorillonite and the succeeding discussion refers to both of these clays. The results of the oscillating-heating for each clay–organic complex are illustrated in Figs. 1–8. The addition of ions of guanidine and guanidine derivatives gives 001 spacing of two ranges: 12.6–12.8 Å and 13.6–13.9 Å. If the CN_3 groups lie parallel to the sheet structure and are hydrogen-bonded to the sheets, spacings of the 12.6–12.8 Å range are to be expected. For example, the interplanar distance of TAG normal to the CN_3 plane (*c*-axis) is 3.1 Å (Okaya and Pepinsky, 1957). Other possibilities of bonding must be considered. Structurally, the guanidine molecule can be cross hydrogen-bonded, or alternate guanidine molecules can form cross hydrogen-bonds to upper and lower sheets. In the latter type, overlap is possible (Hendricks, 1941) and will increase the 001 spacing. With a large excess of guanidines to clay it is possible to have van der Waals bonding between the organic molecules. Finally, the possibility of mixed layering should be considered. Two molecules in the interlayer position would give a spacing of 15.8 Å [$9.6+2\times 3.1$]. In such a case the observed spacing of 13.9 for some 1000 percent guanidines would represent about 43 percent of layers with a spacing of 15.8 Å and 57 percent with a spacing of 12.6 Å.

AG and MG are approximately the same size, but 200 percent AG has a one-layer spacing of 12.7 Å whereas 200 percent MG has a 13.6 Å spacing. The additional amine group of AG lies in the plane of the CN_3 group and does not increase the spacing. The methyl group, however, has a tetrahedral arrangement and, when sufficient thermal energy is supplied, can rotate. The van der Waals radius of the methyl group is 2.0 Å (Pauling, 1930). Consequently, when the methyl group rotates, it will effectively occupy a diameter of 4.0 Å and the predicted *d*-spacing of 13.6 Å (9.6+4.0) is also the observed *d*-spacing for 200 percent MG (Table 2).

TABLE 2.—001 SPACINGS OF COMPLEXES

	Hectorite	Montmorillonite
	d	*d*
G, 25%	12.8	12.6
AG, 25%	12.6	12.8
MG, 25%	12.6	12.8
TAG, 25%	12.7	12.6
G, 200%	13.1	12.4
AG, 200%	12.7	12.6
MG, 200%	13.6	13.6
TAG, 200%	12.7	12.6
G, 1000%	13.9	13.9
AG, 1000%	13.9	13.9
MG, 1000%	13.9	13.8
TAG, 1000%	12.7	12.7

G, AG, and MG have *d*-spacing of 13.9 Å for the 1000 percent equivalencies, but the corresponding TAG has a *d*-spacing of 12.7 Å. These data by the oscillating-heating technique seem to favor Hendricks' (1941) explanation for values exceeding 13.5 Å rather than Greene-Kelly's (1955a, 1955b) varying orientations. Excess amounts of G, AG, and MG could exhibit overlap and still be tightly bound. However, if they were arranged in different orientations it would be expected that with increasing thermal energy the guanidines would orient with the shortest dimension parallel to the (001) sheet structure and a spacing of 12.7 Å would be recorded. 1000 percent TAG does not show the overlap *d*-spacing because of the relatively large molecules.

The thermal stability of each complex increases with increasing percentage of the organic compound (Table 1). With an excess (1000 percent) of complexing agent the thermal stability increases with an increase in the charge/size ratio of the organic molecule. With lesser amounts of complexing agents there is no apparent order to the thermal stability.

INFRARED

The last part of this study is a survey of infrared patterns of the same clay–organic complexes. The patterns from these analyses are in Figs. 9 and 10. The samples were all run either as self-supporting films or as films on AgCl plates.

The absorption peaks of the organic components have been altered in every case by adsorption on the clay, but we cannot unequivocally assign reasons for this alteration from the data at the present time. The greatest change occurs with the guanidinium ion on these clays and this ion is the most basic of the four. There seems to be multiple displacement in wave length and intensity in the C—N asymmetric stretching and NH_2 bending vibrations. It will require a more detailed analysis of the position and kinds of adsorption of clay minerals whose chemical composition and structures are better known before a valid interpretation is possible. The data from this survey merely show that changes do occur and that they are reproducible on any given clay. Our experimental work has shown this to be true regardless of the metallic ions which may be on the clay before treatment with the organic cation. Hydrogen-bonding of the organic cation to the clay is indicated but not proved.

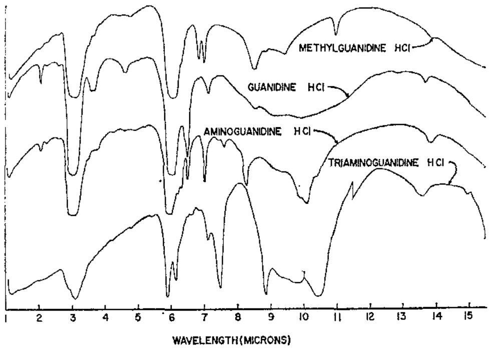

FIGURE 9.—Infrared absorption spectra of guanidinium salts.

CONCLUSIONS

The x-ray results of this investigation are summarized in Tables 1 and 2 and Figs. 1–8. The temperature of initial decomposition of the complexes and the development of good 10Å material, which is the final decomposition product having the same *d*-spacing as illite (10Å), are recorded in Table 1. Generally, the range of temperature between the two recorded temperatures is a transition zone where the organic material is gradually removed from the structure. Water and alcohols, on the other hand, generally are removed rapidly and the collapse of the expanded clay structure is abrupt. The long transition range attests to the tenacity with which guanidine and guanidine derivatives adhere to the interlayer position and keep the three-layer clays expanded. The fact that the decomposition temperature of the complexes is as much as 275°C above the untreated clay is additional evidence of the thermal stability of these complexes. An inspection of Table 1 shows that the

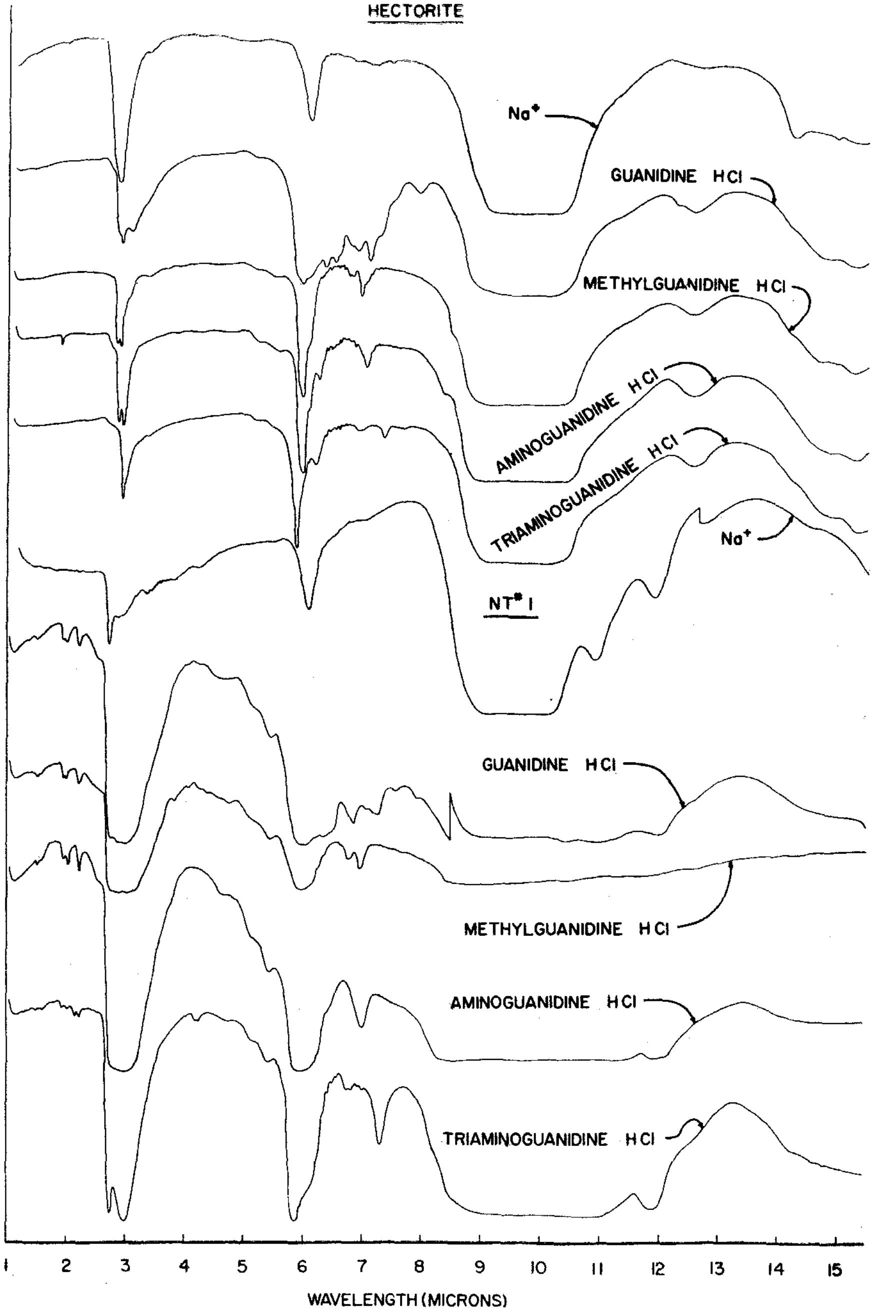

Figure 10.—Infrared absorption spectra of hectorite and montmorillonite with guanidinium ions.

hectorite complexes are slightly more stable thermally than the analogous montmorillonite complexes.

The 001 spacings of the well-organized clay–organic complexes under consideration are recorded in Table 2. Adsorption of guanidinium ion on the clays produces changes in the infrared patterns, but they are not satisfactorily explained (Figs. 9 and 10). The ordinate in the figures is absorbance but the spectra have been offset by arbitrary amounts.

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