

## GEOCHEMICAL STUDIES OF CLAY MINERALS: II—RELATION BETWEEN IONIC SUBSTITUTION AND SWELLING IN MONTMORILLONITES\*†

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### ABSTRACT

The swelling of Na-saturated montmorillonites from 12 different localities was determined after the clays were separated from associated minerals. The degree of swelling, which ranged between 21 and 66 ml. per gram of sample, showed no correlation with cation-exchange capacity or with tetrahedral charge but did show a correlation with octahedral substitution, in the direction of decrease in swelling with increase in octahedral substitution. Substituted  $\text{Fe}^{+2}$  had a greater depressing effect on swelling than  $\text{Fe}^{+3}$ , which in turn appeared to have about the same depressing effect as  $\text{Mg}^{+2}$ .

Swelling, considered as an osmotic property of montmorillonites, is affected by degree of dissociation. The greater the dissociation the greater the swelling, and vice versa. It is suggested that substitutions in the montmorillonite structure affect the energy relationships of the structural constituents and hence the degree of dissociation of the montmorillonite in water. The decrease in swelling found to accompany increase in octahedral substitution seems to indicate that the effect of substitution of Mg and Fe for Al is in the direction of decrease in the degree of dissociation of the montmorillonite.

### INTRODUCTION

Studies on the swelling of montmorillonite have given much more attention to the effect of the exchangeable cation than to the effect of the composition although Grim (1935) pointed out, some years ago, that the physical properties of clays may be ascribed to the two factors—the character of the exchangeable cation and the composition of the clay mineral. By composition Grim referred to the make-up of the clay mineral, particularly with regard to substitutions within the structure. “Two montmorillonites, identical except for differences in  $\text{Mg}^{+2}$  replacements of  $\text{Al}^{+3}$  in gibbsite positions, may be expected to impart different physical properties to clays containing them. In other words the properties depend not only on the presence of montmorillonite, but on the composition of the particular montmorillonite.”

Differences in the physical properties of two montmorillonites identical in composition except for differences in  $\text{Mg}^{+2}$  replacements of  $\text{Al}^{+3}$  in gibbsite positions might be attributed to differences in cation-exchange capacity. However, Kelley (1943) pointed out that, although swelling of soil colloids seems to increase as the base-exchange capacity increases,

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† The term “montmorillonite” as used in this paper refers specifically to the mineral montmorillonite and not to the group unless so designated.

different soil colloids having equal exchange capacity may swell very differently and that the swelling of Na-saturated montmorillonite samples from different sources is not always proportional to the base-exchange capacity.

The difference in swelling between a montmorillonite and a beidellite (an aluminian montmorillonite) of equal exchange capacity has been attributed by Marshall (1936) to the fact that in the one mineral the seat of the charge is in the Al layer and in the other it is in the Si layers. An excess negative charge originating in the outer Si layers is presumed to be strong enough to hold the units closely together and to prevent the entrance of water and expansion. An excess negative charge originating in the Al layer is, on the other hand, generally thought to have the strength to hold exchangeable cations but not the strength necessary to hold the units closely together and prevent expansion and the entrance of water. Interpreted osmotically, the cations associated with a charged Al layer are presumed to be more easily dissociated than the cations associated with a charge originating in the Si layers, since they are physically separated from the seat of the charge by the Si layers and are consequently less strongly held. The degree of dissociation of a montmorillonite and consequently the swelling would, therefore, be expected to be greater than that of a beidellite having the same charge.

On the presumption that the difference in swelling between a beidellite and a montmorillonite is due to the source of the charge, whether on the Al layer or the Si layers, two montmorillonites of equal exchange capacity but differing in the proportion of the charge originating in the Al and Si layers would also be expected to swell differently. And two montmorillonites with equal exchange capacity originating to the same degree in the Al and Si layers would be expected to swell to the same degree. Thus the composition of a montmorillonite, especially with respect to substitutions in the structure that contribute to total charge and to the relative distribution of the charge between the outer and inner layers, would be expected to have a significant influence on the swelling volume. As  $\text{Fe}^{+3}$  substituted for  $\text{Al}^{+3}$  does not change the charge on the inner layer, it would not be expected to affect the swelling volume.

The purpose of the present study was to determine whether and to what extent the swelling volume of montmorillonite is affected by composition. The 12 samples of montmorillonite used in the study differed considerably in the extent of Fe and Mg substitution in the Al layer, in total exchange capacity, and in the relative distribution of charge between the Al and Si layers. In order to hold constant the second factor mentioned by Grim—character of exchangeable cation—all the specimens were converted to the Na form at the beginning of the investigation.

TABLE 1. ANALYSES OF BENTONITES AND PEGMATITE CLAYS

	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub>	54.58	54.28	53.35	54.07	58.31	52.09	54.28	58.13	57.80	51.50	51.29	51.72
Al <sub>2</sub> O <sub>3</sub>	16.44	22.94	17.53	21.07	20.20	18.98	17.92	15.96	17.06	19.44	15.96	17.24
Fe <sub>2</sub> O <sub>3</sub>	2.59	.24	2.25	2.45	3.26	.06	3.88	.84	1.71	.10	2.46	5.30
FeO	.11	Tr.	—	.74	.55	—	—	—	—	—	.14	.37
TiO <sub>2</sub>	.18	.06	—	.14	.11	none	.20	.07	.15	none	.18	.69
CaO	.72	3.18	.91	.55	.25	3.28	1.80	1.35	1.65	.48	2.21	.72
MgO	4.90	2.92	.354	1.92	2.50	3.80	3.76	3.72	3.01	5.07	3.95	2.50
Na <sub>2</sub> O	3.02	.08	{	2.35	2.35	—	.10	.10	.05	.20	.05	.09
K <sub>2</sub> O	.81	—	—	.40	.15	—	.25	.04	.02	—	.13	1.04
MnO	—	—	—	.01	—	.06	—	—	—	—	.00	—
SO <sub>3</sub>	.03	none	—	.17	.30	none	.01	none	none	—	none	.01
H <sub>2</sub> O <sup>-</sup>	11.10	7.82	—	11.60*	6.65*	14.75	10.84	—	—	14.50	18.00*	15.65*
H <sub>2</sub> O <sup>+</sup>	5.49	8.70	—	4.89	5.15	7.46	7.32	—	—	8.04	5.37	4.66
Total	99.97	100.22	—	100.36	99.78	100.48	100.36	—	—	99.33	99.74	99.99
Total cation ex- change per gram	1.110	1.029	.805	.860	.877	.980	.856	.833	.810	.975	.900	.665
Associated minerals	.50	3.49	1.81	7.33	8.85	.18	.94	8.65	4.41	.22	2.04	7.55
Excess SiO <sub>2</sub>	none	none	2.80	2.18	1.91	none	none	10.85	7.97	none	none	none
Excess Al <sub>2</sub> O <sub>3</sub>	none	2.25	none	none	none	.90	none	none	none	none	.39	—

1. Amargosa Valley, Calif.—J. G. Fairchild<sup>1</sup>2. Greenwood, Maine.—J. G. Fairchild<sup>1</sup>

3. Fort Steel, Wyo.—M. D. Foster

4. Belle Fourche, S. D.—M. D. Foster

5. Upton, Wyo.—M. D. Foster

6. Tatatila, Mex.—K. J. Murata<sup>1</sup>7. Nieder-Bayern, Germany—J. G. Fairchild<sup>1</sup>

8. Rideout, Utah—M. D. Foster

9. San Antonio, Tex.—M. D. Foster

10. Santa Rosa, Mex.—J. G. Fairchild<sup>1</sup>

11. Burns, Miss.—M. D. Foster

12. Aberdeen, Miss.—M. D. Foster

\* H<sub>2</sub>O— at 300° C.<sup>1</sup> Same sample as described by Ross and Hendricks. (1945)

## PREPARATION AND ANALYSES OF SPECIMENS

Many of the specimens of montmorillonite used in this study were used by Ross and Hendricks (1945) in their investigation of the minerals of the montmorillonite group and by the author (1951)\* in her study of exchangeable magnesium and cation-exchange capacity in montmorillonites. For these specimens analyses and cation-exchange data were available. The specimens from Mississippi, South Dakota, and Upton, Wyoming, were collected and analyzed by the author. Analyses of the bentonites and pegmatite clays used in the study are given in Table 1. Also included are data on cation-exchange capacity, associated minerals, and soluble or excess  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Free  $\text{SiO}_2$  and free  $\text{Al}_2\text{O}_3$  were obtained by digesting the clay in 0.5*N* NaOH. The details of this procedure will be described in a forthcoming paper.

TABLE 2. ANALYSES OF CLAY (MONTMORILLONITE) FRACTIONS  
(Sample numbers same as in Table 1)

M. D. Foster, analyst

	1	2	3 <sup>1</sup>	4 <sup>1</sup>	5 <sup>1</sup>	6 <sup>2</sup>	7	8 <sup>1</sup>	9 <sup>1</sup>	10	11	12
$\text{SiO}_2$	56.56	55.56	59.09	54.07	57.50	52.78	57.78	57.44	58.19	56.60	57.74	55.68
$\text{Al}_2\text{O}_3$	17.18	22.48	18.86	21.02	20.59	17.91	18.64	19.40	19.91	21.24	17.38	19.42
$\text{Fe}_2\text{O}_3^3$	2.80	.20	2.08	3.72	3.94	.06	4.18	1.10	2.22	2.0	3.11	6.51
$\text{TiO}_2$	.16	.00	.20	.14	.11	—	.16	.14	.22	.00	—	.80
MgO	4.85	3.30	4.20	2.09	2.45	3.56	3.37	3.85	3.04	3.46	4.25	2.30
$\text{Na}_2\text{O}$	3.58	3.68	3.10	2.84	2.87	3.19	3.03	3.39	3.13	3.71	3.35	2.48
MnO	.02	.08	.00	—	—	—	—	.01	.00	.01	—	.01
Cation ex- change per gram	1.11	1.14	.96	.88	.89	.99	.94	1.05	.97	1.15	1.04	.77
Excess $\text{SiO}_2$	—	—	3.2	2.18	1.91	—	—	7.00	7.10	—	—	—
Excess $\text{Al}_2\text{O}_3$	—	—	—	—	—	1.30	—	—	—	—	—	—

<sup>1</sup> Values adjusted to correct for free  $\text{SiO}_2$ .<sup>2</sup> Values adjusted to correct for free  $\text{Al}_2\text{O}_3$ .<sup>3</sup> Total Fe as  $\text{Fe}_2\text{O}_3$ .

In order that the results of the swelling tests should represent the swelling of the actual montmorillonites in the bentonites and pegmatite clays used, the clays, after conversion to the Na form, were separated by suspension from associated minerals—feldspar, quartz, etc. The supernatant liquid containing the clay fraction was then siphoned off, evaporated to dryness, and the clay crushed. One gram of material passing 20 mesh but retained on 40 mesh was set aside for the swelling test; the remainder of the material was crushed to pass 80 mesh and used for the analysis of the clay fraction of the samples and for redetermination of free  $\text{SiO}_2$  and free  $\text{Al}_2\text{O}_3$  in the clay fraction of those specimens that had

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TABLE 3. FORMULAS FROM CLAY FRACTIONS FOR MONTMORILLONITES  
(Sample numbers the same as in table 1)

No.	Locality	Formulas	Swelling volume, ml.
1.	Amargosa Valley, Calif.	$[Al_{1.37}^{+3}Fe_{.15}^{+3}Mg_{.50}^{+2}][Si_{3.96}^{+4}Al_{.04}^{+3}]O_{10}[OH]_2 \times_{.47}$	21
2.	Greenwood, Maine	$Al_{1.66}^{+3}Fe_{.01}^{+3}Mg_{.34}^{+2}][Si_{3.83}^{+4}Al_{.17}^{+3}]O_{10}[OH]_2 \times_{.47}$	50
3.	Fort Steel, Wyo.	$[Al_{1.49}^{+3}Fe_{.10}^{+3}Mg_{.43}^{+2}][Si_{3.95}^{+4}Al_{.05}^{+3}]O_{10}[OH]_2 \times_{.39}$	35
4.	Belle Fourche, S.D.	$[Al_{1.60}^{+3}Fe_{.19}^{+3}Mg_{.22}^{+2}][Si_{3.84}^{+4}Al_{.16}^{+3}]O_{10}[OH]_2 \times_{.38}$	43.5
5.	Upton, Wyo.	$[Al_{1.55}^{+3}Fe_{.20}^{+3}Mg_{.25}^{+2}][Si_{3.90}^{+4}Al_{.10}^{+3}]O_{10}[OH]_2 \times_{.36}$	35
6.	Tatatila, Mexico	$[Al_{1.53}^{+3}Fe_{.06}^{+3}Mg_{.40}^{+2}][Si_{3.94}^{+4}Al_{.06}^{+3}]O_{10}[OH]_2 \times_{.45}$	43
7.	Nieder-Bayern, Germany	$[Al_{1.45}^{+3}Fe_{.21}^{+3}Mg_{.34}^{+2}][Si_{3.95}^{+4}Al_{.05}^{+3}]O_{10}[OH]_2 \times_{.39}$	23
8.	Rideout, Utah	$[Al_{1.55}^{+3}Fe_{.06}^{+3}Mg_{.39}^{+2}][Si_{3.97}^{+4}Al_{.03}^{+3}]O_{10}[OH]_2 \times_{.44}$	32.5
9.	San Antonio, Tex.	$[Al_{1.57}^{+3}Fe_{.12}^{+3}Mg_{.30}^{+2}][Si_{3.99}^{+4}Al_{.01}^{+3}]O_{10}[OH]_2 \times_{.38}$	43
10.	Santa Rosa, Mexico	$[Al_{1.63}^{+3}Fe_{.01}^{+3}Mg_{.36}^{+2}][Si_{3.90}^{+4}Al_{.10}^{+3}]O_{10}[OH]_2 \times_{.48}$	66
11.	Burns, Miss.	$[Al_{1.41}^{+3}Fe_{.16}^{+3}Mg_{.43}^{+2}][Si_{3.99}^{+4}Al_{.01}^{+3}]O_{10}[OH]_2 \times_{.43}$	26
12.	Aberdeen, Miss.	$[Al_{1.44}^{+3}Fe_{.34}^{+3}Mg_{.24}^{+2}][Si_{3.86}^{+4}Al_{.14}^{+3}]O_{10}[OH]_2 \times_{.32}$	23

been found to contain several per cent of these impurities before the separation of associated minerals. As shown in Table 2, the clay fraction of some of the specimens contained several per cent of free or soluble  $SiO_2$ . X-ray examination of these clay fractions showed this free  $SiO_2$  to be present predominantly as cristobalite, with a trace of quartz.

Formulas derived from the analyses of the clay fractions are given in Table 3. These formulas were calculated according to the method of Ross and Hendricks, after correcting for free  $SiO_2$ , if present, and exchangeable Mg, and using the determined cation-exchange value. The determined cation-exchange capacity ranged between 0.77 and 1.15 milliequivalents per gram (the mean value being 0.97), indicating a 50 per cent difference among the specimens in the extent to which the structure was unbalanced. Substitution of  $Fe^{+3}$  for  $Al^{+3}$  ranged from none up to 0.34, substitution of  $Mg^{+2}$  for  $Al^{+3}$  ranged between 0.22 and 0.50, and total substitution of  $Al^{+3}$  in the octahedral layer by Fe and Mg ranged between 0.35 and 0.65. There were several specimens in which all, or very nearly all, of the unbalance in the structure was in the octahedral layer, as several

specimens had little or no substitution of  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$  in the tetrahedral layer. In others, however, almost half of the unbalance of the structure was in the tetrahedral layer. In only one sample, however, was the substitution due entirely to one element, Mg. This was the Tatatila specimen, with no substitution of  $\text{Fe}^{+3}$  for  $\text{Al}^{+3}$  in the octahedral layer and only  $0.01\text{Al}^{+3}$  substituted for  $\text{Si}^{+4}$  in the tetrahedral layer. Thus the specimens used in the study varied widely in type and amount of replacement, in total cation-exchange capacity, and in the distribution of charge between the Al and Si layers.

#### DETERMINATION OF SWELLING

The procedure used for the determination of swelling was as follows:

One gram of air-dried material, crushed to pass 20 mesh but to be retained on 40 mesh, was added, in divided portions, to 100 ml. of distilled water contained in a 100-ml. graduate. Montmorillonite aggregates of this grain size are just heavy enough to sink of their own weight in water. Each portion added amounted to 0.10 to 0.15 gram of material, which was gently tapped from the end of a small spatula blade into the water. Addition of similar portions was repeated at 5-minute intervals until the whole sample had been added. Twenty-four hours after the last portion had been added the volume of the gel was measured on the graduate.

This method for measuring free swelling is capable of giving results that are comparable if the samples are prepared under uniform conditions of room temperature and humidity and if they are added to the water at the same rate.

The results of the swelling tests are given in Table 3.

#### DISCUSSION OF RESULTS

The variation in swelling volume between 21 and 66, a more than three-fold difference, strongly supports the assumption that the swelling of montmorillonites is greatly influenced by factors other than the effect of the exchangeable cation, which was the same, i.e. Na, in all the specimens. As the amount of Na present varied with the total cation-exchange capacity, it seemed possible that the differences in swelling volume might be due to differences in the amount of Na present, i.e. to differences in total exchange capacity. However, comparison of cation-exchange capacity with swelling volume (Fig. 1) indicated that, although the Santa Rosa sample, which had the highest cation-exchange capacity, had also the highest swelling volume and the Aberdeen sample, which had the lowest exchange capacity, had the lowest swelling volume, a more detailed examination showed certain discrepancies. For example, the Aberdeen, Nieder-Bayern and Amargosa Valley samples, which had quite dif-

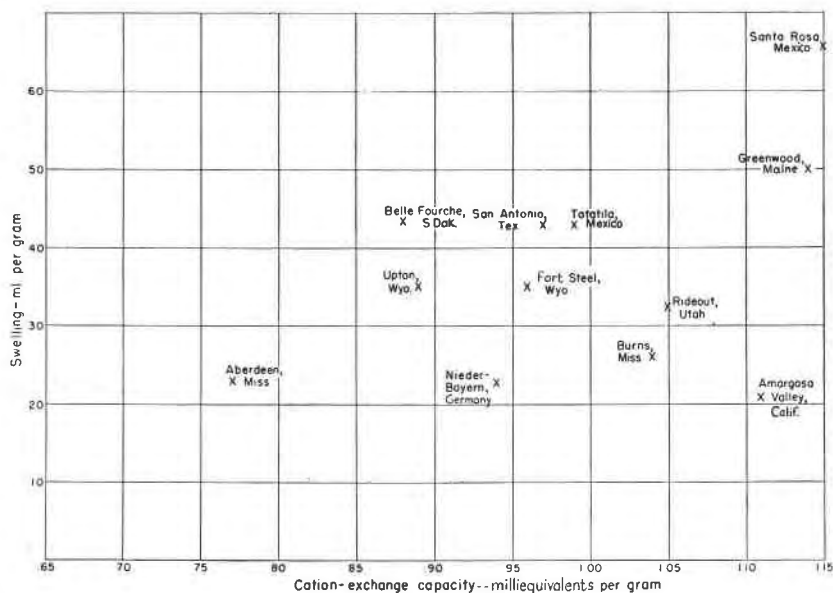


FIG. 1. Relation between swelling and cation-exchange capacity.

ferent exchange capacities, 0.77, 0.94, and 1.11 respectively, had approximately the same swelling volumes, 23, 23, and 21 mls., respectively. On the other hand, the Amargosa Valley and Greenwood samples had almost the same exchange capacities, 1.11 and 1.14, but their swelling volumes were quite different, 21 and 50 mls., respectively.

As an excess negative charge originating in the outer tetrahedral layers is presumed to be stronger and more adequate to hold the units together and prevent expansion in water than an excess charge originating in the octahedral layers, it would be expected that of two samples having the same total charge, one in which the charge originated almost wholly in the octahedral layer would swell more than one in which a considerable part of the charge originated in the tetrahedral layers. The samples from Fort Steel (No. 3, Table 3) and Belle Fourche (No. 4, Table 3) have almost the same total charge, 0.39 and 0.38 respectively. In the Fort Steel sample this charge originates almost wholly in the octahedral layer; in the Belle Fourche sample almost half the charge originates in the tetrahedral layers. Yet the Belle Fourche sample had a swelling volume of 43.5 ml., while the Fort Steel sample swelled to only 35 ml. Similarly the Amargosa Valley and Greenwood samples had the same total charge, 0.47, but the Greenwood sample, with 0.17 tetrahedral charge, swelled more than the Amargosa Valley sample with only 0.04 tetrahedral charge.

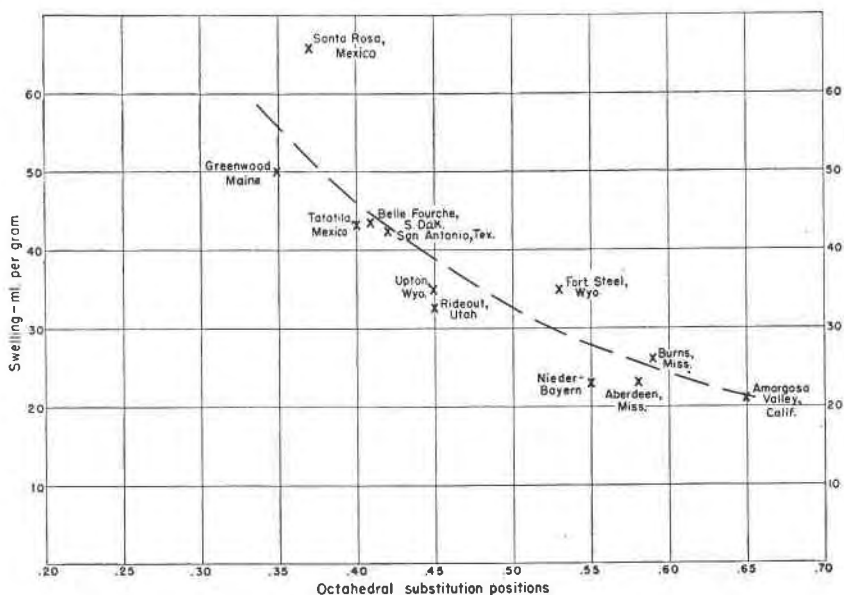


FIG. 2. Relation between swelling and octahedral substitution.

Other samples with the same total charge and the same tetrahedral charge, as, for example the Nieder-Bayern and San Antonio samples, had quite different swelling volumes. These examples indicate that neither total charge nor tetrahedral charge has, apparently, much influence on the swelling volume.

Inspection of the formulas of the last-mentioned pair of samples—Nieder-Bayern and San Antonio—shows that although the total charge and the tetrahedral charge, or substitution of  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$ , is the same in both samples, the amount of substitution in the octahedral layer is quite different, being 0.55 and 0.43 respectively, and that the sample with the greater octahedral substitution has the lower swelling volume. Examination of the other pairs of samples cited above shows the same relationship. In each pair the sample with the higher octahedral substitution has the lower swelling volume.

When the swelling volume of each specimen is plotted against octahedral substitution (Figure 2) there is apparent a much closer relationship than when swelling is plotted against cation-exchange capacity (Figure 1). The Burns and Aberdeen samples, with quite different cation-exchange capacities (1.04 and 0.77, respectively) have almost the same amount of octahedral substitution and almost the same swelling volumes. Similarly Tatatila and Belle Fourche have very different cation-exchange



capacities but the same amount of octahedral substitution and the same swelling volumes.

The fact that  $\text{Fe}^{+3}$  substitution has a significant effect on swelling is apparent when the formulas and swelling volumes of the Tatatila, Fort Steel, and Burns samples are compared.

		Swelling volume ml.
Tatatila	$[\text{Al}_{1.58}^{+3}\text{Fe}_{.00}^{+3}\text{Mg}_{.40}^{+2}][\text{Si}_{3.99}^{+4}\text{Al}_{.01}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.45}$	43
Fort Steel	$[\text{Al}_{1.49}^{+3}\text{Fe}_{.10}^{+3}\text{Mg}_{.42}^{+2}][\text{Si}_{3.99}^{+4}\text{Al}_{.01}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.39}$	35
Burns	$[\text{Al}_{1.41}^{+3}\text{Fe}_{.16}^{+3}\text{Mg}_{.43}^{+2}][\text{Si}_{3.99}^{+4}\text{Al}_{.01}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.43}$	26

In these samples the amount of  $\text{Fe}^{+3}$  substitution increases from 0.00 in the Tatatila sample to 0.16 in the Burns sample and the swelling volume decreases from 43 ml. for the Tatatila sample to 26 ml. for the Burns sample. As the make-up of the tetrahedral layers is the same and the amount of  $\text{Mg}^{+2}$  substitution in the octahedral layers is essentially the same in all three samples, it seems reasonable to conclude that the differences in  $\text{Fe}^{+3}$  substitution are responsible for the differences in swelling volume. For these three samples an increase of 0.16 in  $\text{Fe}^{+3}$  substitution was accompanied by a decrease of 17 ml. in swelling volume. The Belle Fourche and Aberdeen samples similarly show a decrease in swelling volume with increase in  $\text{Fe}^{+3}$  substitution, other substitutions remaining essentially constant.

		Swelling volume, ml.
Belle Fourche	$[\text{Al}_{1.60}^{+3}\text{Fe}_{.19}^{+3}\text{Mg}_{.22}^{+2}][\text{Si}_{3.84}^{+4}\text{Al}_{.16}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.33}$	43.5
Aberdeen	$[\text{Al}_{1.44}^{+3}\text{Fe}_{.34}^{+3}\text{Mg}_{.21}^{+2}][\text{Si}_{3.96}^{+4}\text{Al}_{.04}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.32}$	23

In this pair of samples an increase of 0.15 in  $\text{Fe}^{+3}$  substitution is accompanied by a decrease of 20.5 ml. in swelling.

The effect of  $\text{Fe}^{+3}$  substitution on swelling volume is similar to that of  $\text{Mg}^{+2}$  substitution. Between the San Antonio and Amargosa samples there is a difference of 22 ml. in swelling volume corresponding to a difference of 0.19 in  $\text{Mg}^{+2}$  substitution, all other substitutions remaining the same.

		Swelling volume, ml.
San Antonio	$[\text{Al}_{1.56}^{+3}\text{Fe}_{.12}^{+3}\text{Mg}_{.31}^{+2}][\text{Si}_{3.96}^{+4}\text{Al}_{.04}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.40}$	43
Amargosa	$[\text{Al}_{1.37}^{+3}\text{Fe}_{.15}^{+3}\text{Mg}_{.50}^{+2}][\text{Si}_{3.96}^{+4}\text{Al}_{.04}^{+3}]\text{O}_{10}[\text{OH}]_2 \times_{.47}$	21

Thus  $\text{Fe}^{+3}$ , although it does not contribute to the charge on the structure or to cation-exchange capacity, appears to have much the same effect on the swelling property as  $\text{Mg}^{+2}$ , which does contribute to the charge and cation-exchange capacity.

On the other hand, differences in the amount of  $\text{Al}^{+3}$  substituted for  $\text{Si}^{+4}$  in the tetrahedral layer apparently have little effect on the swelling volume. For example, in the Belle Fourche and Tatatila samples, the tetrahedral substitution of  $\text{Al}^{+3}$  for  $\text{Si}^{+4}$  differs considerably, being 0.16 and 0.01 respectively, but they had the same swelling volume; they also have essentially the same amount of octahedral substitution. The Aberdeen and Burns samples also differ considerably in tetrahedral substitution, but they, too, have essentially the same octahedral substitution and nearly the same swelling volume. Thus,  $\text{Al}^{+3}$  substituted for  $\text{Si}^{+4}$  appears to have little effect on the swelling volume although it does contribute to cation-exchange capacity, and gives rise to an excess negative charge on the outer layers of the structure, where it would be expected to have more effect in preventing expansion than substitution in the middle layer.

#### RELATIVE EFFECT OF $\text{Fe}^{+2}$ AND $\text{Fe}^{+3}$ ON SWELLING

The examples cited indicate that  $\text{Fe}^{+3}$  in octahedral positions affects the swelling to about the same extent and in the same way as  $\text{Mg}^{+2}$  even though it does not affect the charge on the layer. The effect of  $\text{Fe}^{+2}$  relative to  $\text{Fe}^{+3}$  is shown by comparing the swelling volumes of two specimens of bentonite identical in chemical composition except for the proportionate amounts of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  present.

In natural exposures and near the surface the bentonite commonly known as the "Wyoming" bentonite is pale olive green or cream in color. However, under a few feet of cover many of the blocks, into which the bentonite has cracked due to drying and shrinkage, have a small central core of blue-gray material. With greater depths under cover the proportion of blue-gray to olive-green material increases and under 40 feet or more of cover the blocks are, as a rule, wholly made up of blue-gray material. Analyses (Table 4) of the blue-gray and olive-green phases of the same block, and the derived formulas, show that the two-color phases are essentially identical in chemical composition except for the state of oxidation of the iron. The total iron content of the two phases is the same but in the blue-gray phase two-thirds of the iron is present as  $\text{Fe}^{+2}$ , and in the olive-green phase two-thirds is present as  $\text{Fe}^{+3}$ . Swelling tests showed that the blue-gray phase had a swelling volume only two-thirds as great as that of the olive-green phase (Table 4).

Nine months after the first examination, a redetermination of the FeO content of the blue-gray material from block No. 1 showed a decrease of

TABLE 4. ANALYSES OF BLUE-GRAY AND OLIVE-GREEN "WYOMING" BENTONITE, BELLE FOURCHE, SOUTH DAKOTA

	Bicolored block No. 1		Bicolored block No. 2	
	Blue-gray phase	Olive-green phase	Blue-gray phase	Olive-green phase
SiO <sub>2</sub>	54.34	54.62	54.34	54.07
Al <sub>2</sub> O <sub>3</sub>	19.92	20.08	20.12	20.24
Fe <sub>2</sub> O <sub>3</sub>	1.11	2.36	1.13	2.45
FeO	2.17	1.03	2.06	.74
TiO <sub>2</sub>	.11	.11	.14	.14
CaO	.33	.40	.53	.55
MgO	2.21	2.15	2.02	1.92
Na <sub>2</sub> O	2.65	2.26	2.44	2.35
K <sub>2</sub> O	.45	.35	.49	.40
MnO	.01	.01	.01	.01
SO <sub>3</sub>	.18	.16	.15	.17
H <sub>2</sub> O— (300° C.)	11.73	11.78	12.18	11.90
H <sub>2</sub> O+	4.50	4.58	4.62	4.89
Total	99.71	99.89	100.23	99.83

	Formulas	Swelling volume, ml.
Blue-gray (No. 1)	$[Al_{1.60}^{+3}Fe_{.06}^{+3}Fe_{.13}^{+2}Mg_{.22}^{+2}][Si_{3.91}^{+4}Al_{.09}^{+3}O_{10}[OH]_2 \times .41]$	39.5
Olive-green (No. 1)	$[Al_{1.61}^{+3}Fe_{.13}^{+3}Fe_{.06}^{+2}Mg_{.20}^{+2}][Si_{3.92}^{+4}Al_{.08}^{+3}O_{10}[OH]_2 \times .36]$	60
Blue-gray (No. 2)	$[Al_{1.62}^{+3}Fe_{.06}^{+3}Fe_{.13}^{+2}Mg_{.20}^{+2}][Si_{3.92}^{+4}Al_{.08}^{+3}O_{10}[OH]_2 \times .38]$	40
Olive-green (No. 2)	$[Al_{1.62}^{+3}Fe_{.13}^{+3}Fe_{.05}^{+2}Mg_{.19}^{+2}][Si_{3.90}^{+4}Al_{.10}^{+3}O_{10}[OH]_2 \times .37]$	60

one percent—2.17 to 1.17—and the swelling volume had increased from 39.5 to 48 ml. Eleven months after the first determination of FeO in this specimen, the FeO content had decreased to 1.05 per cent—as compared with 1.03 per cent FeO in the olive-green phase at the start of the tests—and the swelling volume was 66 ml. as compared with 60 ml. for the olive-green material at the start. During this 11-month period the color of the blue-gray material when wet had changed from blue-gray to olive-green. The blue-gray material from block No. 2 showed a similar increase in swelling volume with decrease in FeO content.

These data suggest that there is a close relationship between the state of oxidation of iron and the swelling volume and that Fe<sup>+2</sup> in octahedral positions has a greater depressing effect than Fe<sup>+3</sup> on the swelling volume.

## INTERPRETATION OF RESULTS

It is apparent from this comparison of the swelling volumes of 12 samples of Na-saturated montmorillonite that there is a significant relation between the composition and the swelling volume of montmorillonite. A montmorillonite that has a relatively high degree of octahedral substitution has, for example, a lower swelling volume than one that has a relatively low degree of octahedral substitution. The effect on the swelling volume is not limited to those substitutions that induce a charge on the structure, such as the substitution of  $Mg^{+2}$  or  $Fe^{+2}$  for  $Al^{+3}$ . Substitution of  $Fe^{+3}$  for  $Al^{+3}$  seems to have about the same effect on the swelling volume as substitution of  $Mg^{+2}$  for  $Al^{+3}$ . Apparently, therefore, the effect of substitutions of other atoms for Al is not necessarily related to the charge induced by the substitution, but rather to some other change in the structural relations brought about by the substituted atoms.

Hartley (1935) differentiated charged colloids into two classes: (1) those of which the bulk of the particle is made up of insoluble material in regard to which there is no equilibrium and whose charge is due chiefly to preferential adsorption of foreign ions and (2) those of which the particle is made up of a definite ionizing compound with regard to which there is true equilibrium and whose charge is due to ionization of this compound. The term "colloidal electrolytes" may be applied to this second class. From structural considerations Marshall (1936) concludes that the clays of the montmorillonite group may be placed in the second class and may be looked upon as colloidal electrolytes. The substitutions found in the montmorillonite structure result in a net negative charge on the ultimate clay particle, which is balanced by cations held by electrostatic attraction. When such a particle is dispersed in water, these cations dissociate to a greater or less degree. Thus a suspension of montmorillonite in water may be likened to a dissociated electrolyte, one of whose ions falls within the colloidal range of dimensions.

Dissociation of the exchangeable cations leaves some of the structural units of montmorillonite negatively charged. Thus charged, the units have a tendency to repel one another, and the montmorillonite appears to swell. The more complete the dissociation and the greater the number of units carrying a charge, the greater is the swelling; the less complete the dissociation, the fewer are the units carrying a charge and the less is the swelling. The greater swelling of Na-montmorillonite as compared with Ca-montmorillonite may be reasonably explained, therefore, by the greater dissociation of Na-montmorillonite, by which a greater number of structural units are left with a negative charge.

The greater dissociation of exchange cations associated with a charge on the Al layer as compared with cations associated with a charge on the

Si layer as an explanation of the swelling relationships of montmorillonite and beidellite has already been mentioned.

If swelling is thus assumed to be related to dissociation, the decrease in swelling found to accompany increase in the amount of substitution of iron and magnesium for aluminum in gibbsite positions suggests that these substitutions affect in some way the degree of dissociation of the exchangeable cations, even though, as in the replacement of  $\text{Al}^{+3}$  by  $\text{Fe}^{+3}$ , the charge on the layer may not be affected. Because of their lesser polarizing power as compared with  $\text{Al}^{+3}$ , the substitution of these atoms for  $\text{Al}^{+3}$  may be accompanied by a change in the polarization of neighboring atoms, which is reflected throughout the structure, thus altering the energy relationships of the whole structure. The more extensive the substitution, the more the internal energy relationships of the structure will be affected. Such an alteration in the energy relationships of the structure may well affect the bonding energy and hence the degree of dissociation of the exchangeable cations on dispersion of the montmorillonite in water. The decrease in swelling found to accompany increase in octahedral substitution seems to indicate that the effect of the substitution is in the direction of decrease in the degree of dissociation of the montmorillonite. Although a colloidal electrolyte like montmorillonite cannot be strictly compared with a soluble electrolyte, the change in the strength of acetic acid brought about by the substitution of one or more of the H atoms by positive or negative atoms or groups—such as Cl, OH or  $\text{CH}_3$ —and the increase in the strength of ammonium hydroxide caused by the substitution of one or more of the H atoms by  $\text{CH}_3$  groups are examples of the way in which the degree of dissociation of a compound can be changed by substitutions.

This interpretation of the decreased swelling found to accompany increase in substitution in the octahedral group in montmorillonite is, admittedly, speculative, and further work is required to clarify the relation between substitutions in the montmorillonite structure and swelling.

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