THE IMPORTANCE OF EXCHANGEABLE MAGNESIUM AND CATION-EXCHANGE CAPACITY IN THE STUDY OF MONTMORILLONITIC CLAYS*

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ABSTRACT

In calculating the formulas of members of the montmorillonite group all the magnesium is generally assigned to the Al layer. However, determination of exchangeable cations in 14 montmorillonitic clays, 10 of them the identical specimens for which analyses were quoted by Ross and Hendricks (*U. S. Geological Survey, Prof. Paper* **205-B**), showed that in all of them some of the magnesium was exchangeable, the amount ranging from 0.11 to 1.62 per cent. In two samples exchangeable magnesium amounted to about $\frac{1}{3}$ of the total magnesium. These results indicate that the presence of exchangeable magnesium in the montmorillonitic clays is more common than is generally recognized.

Ross and Hendricks, assigning all magnesium to the Al layer in calculating the formulas of montmorillonites, found that the number of ions in octahedral coordination ranged from 2.02 to 2.24. However, a recalculation of the formulas of some of these samples on which exchangeable cations were determined showed that, when total magnesium is corrected for exchangeable magnesium and only non-exchangeable magnesium is assigned to the Al layer, and when the determined rather than an average cation-exchange capacity is used, the number of cations in octahedral coordination does not exceed 2.02, even in those samples in which the number of cations is as much as 2.13 when all the magnesium is assigned to the Al layer. Apparently, in montmorillonite then, substitution of Mg for Al in the Al layer is ion for ion, with no extra ions added in an effort toward internal compensation of charge.

By the Marshall method of calculation, the number of atoms in the octahedral layer in excess of 4.00, when all the magnesium is assigned to the octahedral layer, permits an estimation of the amount of exchangeable magnesium present and, from this, an estimation of the cation-exchange capacity of the sample. On the other hand, when only non-exchangeable magnesium is assigned to the octahedral layer, the number of atoms in this layer is very close to the theoretical 4.00, and the charge on the cell checks the charge of the external cations and the determined cation-exchange capacity, which it does not do when all the magnesium is assigned to the octahedral layer.

INTRODUCTION

In the structural interpretation of analyses of clays of the montmorillonite group magnesium is generally assumed to be part of the crystal lattice and is assigned to the octahedral group, proxying aluminum. Calcium, sodium, and potassium are, on the other hand, thought to be too large to occupy positions in the crystal lattice without undue distortion of the lattice, and are, consequently, considered to be exchange cations, although potassium may be only partly replaceable. The possibility that magnesium may occupy exchange positions, as well as octahedral positions, thus playing a dual role, has been recognized, but generally neglected in interpreting the structure of these clays.

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Of the cations commonly found in natural waters—calcium, magnesium, sodium, and potassium—magnesium ranks second only to calcium in replacing power.[1] Its superior replacing power as compared with that of sodium is indicated by the results obtained by Kelley and Liebig[2] on treating a bentonitic clay with sea water. Although sea water contains approximately 4.3 equivalents of sodium to 1 equivalent of magnesium, its action on a bentonitic clay, which had been converted to calcium clay before treatment with sea water, resulted in the replacement of somewhat more magnesium than sodium.

With few exceptions, natural waters contain some of all the common bases—calcium, magnesium, sodium, and potassium. When such a solution comes in contact with a cation-exchange mineral like montmorillonite, cations in the mineral are replaced by cations from the solution, the relative extent of replacement depending on the cations in the mineral at the time of contact, on the relative concentration of the cations in the solution, and on their respective replacing powers. As calcium is the predominant cation in most natural waters, and as calcium has the highest replacing power of the cations normally found in natural waters, it is not surprising that in naturally occurring montmorillonites calcium is generally the dominant exchangeable cation. But as most natural waters also contain some magnesium, and as magnesium ranks next to calcium in replacing power, it is to be expected that most montmorillonites would also contain some magnesium as an exchangeable cation.

In their comparison of the cation-exchange capacity of 22 samples of clays with the sum of the milliequivalents per gram of Ca^{+2}, Na^{+1}, and K^{+1}, Ross and Hendricks[3] found that in nine of the samples the sum of these cations was considerably less than the determined cation-exchange capacity. In four of these samples alkalies had not been determined and there was the possibility that Na and K might account for the low summation, but in the other five samples the presence of exchangeable magnesium seemed a possible cause of the low summation. Even in those samples in which the sum of the milliequivalents of Ca, Na, and K equaled or exceeded the determined cation-exchange capacity the possibility of exchangeable magnesium was not to be ignored.

As several of the samples upon which Ross and Hendricks compared

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[1] Schachtschabel, P., Adsorption by clay minerals, etc.: *Koll. Beih.*, **51**, 199–276 (1940).

[2] Kelley, W. P., and Liebig, G. F., Jr., Base-exchange in relation to composition of a clay with special reference to effect of sea water: *Am. Assoc. Petroleum Geologists, Bull.* **18,** no. 3, 358–367 (1934).

[3] Ross, C. S., and Hendricks, S. B., Minerals of the montmorillonite group: *U. S. Geol. Survey, Prof. Paper* **205-B,** p. 39 (1945).

cation-exchange capacity with the sum of the milliequivalents per gram of Ca, Na, and K had been analyzed in the laboratory of the U. S. Geol. Survey, it was possible for the author to obtain some of the identical materials for a study of exchangeable magnesium. Several other samples were supplied by Ross. Although these latter samples were from the same localities as some listed by Ross and Hendricks, reanalysis showed they were not identical. In all, 14 samples were obtained for the study. The source locality of these samples is shown in Table 1; those that are identical with the samples listed by Ross and Hendricks are identified by the use in the table of the same number as used by Ross and Hendricks. The study of these samples included, in addition to determination of exchangeable magnesium, determination of exchangeable Ca, Na, K, and H, total cation-exchange capacity, and water-soluble salts.

SOLUBLE SALTS AND CATION-EXCHANGE

Two-gram portions of the samples, ground to pass 80-mesh, were shaken with 200 ml of distilled water in a stoppered Erlenmeyer flask, allowed to settle overnight, the water decanted off through a filter paper, split into three portions, and Ca, Mg, Na, K, SO_4, and Cl determined. Material that had been transferred to the filter paper during the decantation was transferred back to the proper flask with a jet of distilled water.

After the samples were dried over a low steam bath, they were shaken with two successive 20-ml portions of normal NH_4Cl (neutralized), allowed to settle about 10 minutes, and the supernatant liquid decanted through a filter paper after each treatment. The samples were then washed with successive 20-ml portions of 95 per cent ethyl alcohol, decanting each portion through the filter paper, until the filtrate did not give a test for Cl with $AgNO_3$. The filtrates, consisting in each case of the NH_4Cl solution used in the treatments and the alcohol washings, were tested for acidity with a few drops of methyl red. The acidity of those filtrates which gave an acid reaction was determined by titration with 0.1 normal Na_2CO_3. The filtrates were then evaporated to dryness on a steam bath, the residue taken up with water slightly acidified with HCl, made up to volume and divided into two equal portions. On one portion R_2O_3, Ca, and Mg were determined; on the other SO_4, Na, and K. The final Na and K determination was made by means of a flame photometer. Material that had been transferred to the filter papers during the NH_4Cl treatments and the alcohol washings was washed back into the proper flask and the NH_4 content of the treated clays was determined by distilling with 2 grams of $Ba(OH)_2$, catching the distillate in a flask containing 50 ml of 2 per cent boric acid and a few drops of a (5-1) bromcresol green methyl red indicator.[4] After distillation of NH_4 was complete, the amount of NH_4 present in the distillate representing the total cation-exchange capacity of the sample was determined by titration with 0.1 normal HCl.

On several samples in which the dominant exchange cation was Na, it was not feasible to determine water-soluble salts by digesting the sample overnight with distilled water and filtering, because such samples settled so very slowly. On these samples Cl was determined by digesting a separate portion with water slightly acidified with nitric acid, filtering, neutralizing the filtrate with $CaCO_3$, and titrating it with standard $AgNO_3$ solution. Sulfate was determined on all the samples on the filtrate from the cation-exchange treatment. Qualitative tests for CO_3 on all the samples showed that only one sample, No. 12, contained CO_3.

Discussion of Results

The sum of the milliequivalents per gram of the cations found in the cation-exchange filtrate minus the sum of the milliequivalents per gram of soluble anions and the resulting total, representing the cation-exchange capacities of the samples, are shown in Table 1, together with the determined cation-exchange capacities of the samples. For all the samples there is very good agreement between the determined cation-exchange capacitity and the total cation-exchange capacity obtained by subtracting the sum of the milliequivalents per gram of the soluble anions from the sum of the milliequivalents per gram of the cations found in the cation-exchange filtrate. In most of the samples no soluble anions were found; the cations found in the filtrate from the cation-exchange treatment of these samples are apparently therefore all exchangeable cations, and the sum of their milliequivalents per gram represents the cation-exchange capacity of the sample. The only samples found to contain soluble anions were those in which Na is the dominant exchange cation. In these samples part of the cations found in the cation-exchange filtrate belong to the soluble anions found and the equivalent of these anions was subtracted from the sum of the cations to obtain the total of the exchangeable cations. The total thus obtained is in good agreement with the determined cation-exchange capacity for every sample in which soluble anions were found. In all these samples, however, the amount of soluble anions found was relatively small, indicating that by far the greater proportion of the cations found in the cation-exchange filtrate were exchangeable cations. As already pointed out, because of the colloidal na-

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[4] Ma, T. S., and Zuazaga, G., Micro-Kjeldahl determination of nitrogen, A new indicator and an improved rapid method: *Ind. Eng. Chem.*, Anal. Ed., **14,** 280–282 (1942).

TABLE 1. EXCHANGEABLE CATIONS, SOLUBLE ANIONS AND CATION-EXCHANGE CAPACITIES OF SOME MONTMORILLONITE CLAYS

No.	Location	Cations						Soluble Anions			Total Cation-Exchange Milliequivalents per gram	Determined Cation-Exchange Milliequivalents per gram
		CaO	MgO	Na_2O	K_2O	H		CO_2	SO_3	Cl		
		Milliequivalents per gram						Milliequivalents per gram				
3	Amargosa Valley, Calif.	[0.13+	0.16+	0.82+	0.03+	0.00]	minus	[0.00+	0.01+	0.03]=	1.10	1.11
6	Tatatila, Mexico	[.83+	.13+	.00+	.00+	.00]	"	[.00+	.00+	.00]=	.96	.98
10	Nieder-Bayern, Germany	[.59+	.26+	.00+	.00+	.00]	"	[.00+	.00+	.00]=	.85	.86
12	Ardmore, S. Dak.	[.35+	.08+	.65+	.02+	.00]	"	[.11+	.02+	.00]=	.97	.97
13	Irish Creek, Va.	[.77+	.16+	.00+	.00+	.00]	"	[.00+	.00+	.00]=	.93	.94
14	Hector, Calif.	[.11+	.06+	1.06+	.02+	.00]	"	[.00+	.04+	.06]=	1.15	1.15
20	Lemon, Miss.	[.44+	.39+	.00+	.00+	.06]	"	[.00+	.00+	.00]=	.89	.89
22	Atzcapozalco, Mexico	[.24+	.48+	.12+	.04+	.00]	"	[.00+	.00+	.00]=	.88	.88
24	Santa Rosa, Mexico	[.14+	.80+	.02+	.01+	.00]	"	[.00+	.00+	.00]=	.97	.98
28	Greenwood, Maine	[.94+	.08+	.00+	.00+	.00]	"	[.00+	.00+	.00]=	1.02	1.03
	Fort Steel, Wyo.	[.30+	.26+	.00+	.00+	.25]	"	[.00+	.00+	.00]=	.81	.80
	Pala, Calif.	[.36+	.59+	.02+	.00+	.00]	"	[.00+	.00+	.00]=	.97	.98
	Belle Fourche, S. Dak.	[.07+	.26+	.61+	.01+	.00]	"	[.00+	.11+	.00]=	.84	.85
	Upton, Wyo.	[.09+	.05+	.76+	.01+	.00]	"	[.00+	.07+	.00]=	.84	.86

ture of the materials it was not feasible to determine the soluble salts in these samples on a water extract; consequently the exact cations belonging to the soluble anions are not known.

Of the 10 samples that were identical with those listed by Ross and Hendricks, the value obtained for cation-exchange capacity in the present study agreed with that given by them for only three, Nos. 3, 13, and 20. For the other seven samples higher values, ranging from 0.17 to 0.31 milliequivalents per gram, were obtained. The values given by them for observed cation exchange ranged between 0.66 and 1.00 milliequivalents per gram, the mean value being 0.84. In the present study the values, for all the samples examined, ranged between 0.80 and 1.15, with a mean value of 0.95. This discrepancy may be due to the different procedures used in the two studies for the determination of cation-exchange capacity.

Of particular interest is the fact that magnesium was found in the cation-exchange filtrate of all the samples. In several of the samples, Nos. 12, 14, and that from Upton, Wyo., the soluble anions were more than equivalent to the magnesium found; and there is the possibility that in these samples the magnesium found in the cation-exchange filtrate was present in the sample as carbonate, sulfate, and/or chloride. In all the other samples, however, there seems to be little doubt that magnesium is present as an exchangeable cation. In three samples, Nos. 22, 24, and that from Pala, Calif., it is the dominant exchange cation and amounts to 24.5, 32.0, and 28.8 per cent, respectively, of the total magnesium in the samples. Two of these samples, Nos. 22 and 24, were ones whose sum of the milliequivalents per gram of Ca, Na, and K, in Ross and Hendricks' table, was much lower than the observed cation-exchange capacity. In the Fort Steel, Wyo., sample the exchangeable magnesium is almost equivalent to exchangeable calcium, the dominant cation, and amounts to 14.6 per cent of the total magnesium in the sample. These results indicate that the presence of exchangeable magnesium in the montmorillonite clays is more common than is generally recognized and that it may constitute an important proportion of the total magnesium in the clay.

The close agreement between the sum of the milliequivalents of exchanged cations—treating calcium and magnesium entirely as divalent cations—with the determined cation-exchange capacity suggests that these cations are actually present as divalent cations and that no significant portion of them is present as univalent basic cations as postulated by Bower and Truog.[5] These investigators found that the cation-exchange

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[5] Bower, C. A., and Truog, F., Base-exchange capacity as influenced by the nature of the cation employed and basic salts: *Soil. Sci. Soc. Am. Proc.*, 5, 86–89 (1940).

capacity of a bentonite is significantly higher when determined with divalent cations than when determined with univalent cations; they attributed the higher values obtained with divalent cations to the formation of a basic salt with the weak clay acid to a varying degree, depending on the strength of the base which the cation in question forms. According to their results, cation-exchange is 7 and 12 per cent higher, respectively, when determined with calcium and magnesium acetate than when determined with sodium, potassium, or ammonium acetate. If basic cations of calcium and magnesium form such significant proportions of the exchange cations of a natural calcium or magnesium montmorillonite, failure to consider this in the summation of the milliequivalents of the exchange cations would result in a considerable discrepancy between such a summation and the cation-exchange capacity as determined with a univalent cation, particularly for such samples as those from Santa Rosa, Mexico (No. 24), and from Pala, Calif., in which magnesium is the dominant exchangeable cation.

Effect of Exchangeable Magnesium and Observed Cation-Exchange Capacity on the Calculated Formula

Formulas for the samples used in the cation-exchange studies, calculated according to the method of Ross and Hendricks, are given in Table 2. On the left side of the table appears the formula obtained when all the magnesium is assigned to the octahedral group and when 0.33, the average value for cation-exchange capacity obtained by Ross and Hendricks, was used. On the right side of the table appears the formula obtained when the value used for magnesium in octahedral coordination was obtained by subtracting the amount of magnesium found in the cation-exchange filtrate from the total magnesium content of the sample and when the determined value for cation-exchange, not an average value, was used in the calculation.

In suggesting $[Al_{1.67}\overset{\overset{Na_{.33}}{\uparrow}}{Mg_{.33}}]Si_4O_{10}[OH]_2$ as the most suitable generalized formula for montmorillonite, Ross and Hendricks stated that "the only serious flaw in it is that the total number of ions in octahedral coordination is 2.00, whereas in all actual specimens this number is exceeded. In the formulas obtained by them, the number of ions in octahedral coordination ranged from 2.02 to 2.27, with the number of ions in octahedral coordination being apparently somewhat higher toward the beidellite end. This increase in the number of ions in octahedral coordination was interpreted as evidence of a tendency toward internal compensation of charge as the amount of aluminum in tetrahedral coordination is increased.

TABLE 2. FORMULAS FOR MONTMORILLONITE CLAYS

No.	Locality	Mg all in lattice—mean cation-exchange	Non-exchangeable Mg in lattice—observed cation-exchange
3	Amargosa, Valley, Calif.	$\underbrace{[Al^{+3}_{1.40}Fe^{+3}_{.14}Fe^{+2}_{.01}Mg^{+2}_{.53}]}_{2.08}[Si^{+4}_{3.98}Al^{+3}_{.02}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.37}Fe^{+3}_{.14}Fe^{+2}_{.01}Mg^{+2}_{.50}]}_{2.02}[Si^{+4}_{3.97}Al^{+3}_{.03}]O_{10}[OH]_{2_{x.48}}$
6	Tatatila, Mexico	$\underbrace{[Al^{+3}_{1.63}Mg^{+2}_{.42}]}_{2.05}[Si^{+4}_{3.94}Al^{+3}_{.06}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.61}Mg^{+2}_{.40}]}_{2.01}[Si^{+4}_{3.92}Al^{+3}_{.08}]O_{10}[OH]_{2_{x.45}}$
10	Nieder-Bayern, Germany	$\underbrace{[Al^{+3}_{1.44}Fe^{+3}_{.21}Mg^{+2}_{.40}]}_{2.05}[Si^{+4}_{3.92}Al^{+3}_{.08}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.46}Fe^{+3}_{.21}Mg^{+2}_{.35}]}_{2.02}[Si^{+4}_{3.93}Al^{+3}_{.07}]O_{10}[OH]_{2_{x.36}}$
12	Ardmore, S. Dak.	$\underbrace{[Al^{+3}_{1.48}Fe^{+3}_{.15}Fe^{+2}_{.02}Mg^{+2}_{.40}]}_{2.05}[Si^{+4}_{3.92}Al^{+3}_{.08}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.47}Fe^{+3}_{.15}Fe^{+2}_{.02}Mg^{+2}_{.38}]}_{2.02}[Si^{+4}_{3.91}Al^{+3}_{.09}]O_{10}[OH]_{2_{x.43}}$
13	Irish Creek, Va.	$\underbrace{[Al^{+3}_{1.50}Fe^{+3}_{.14}Mg^{+2}_{.42}]}_{2.06}[Si^{+4}_{3.91}Al^{+3}_{.09}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.48}Fe^{+3}_{.14}Mg^{+2}_{.39}]}_{2.01}[Si^{+4}_{3.91}Al^{+3}_{.09}]O_{10}[OH]_{2_{x.45}}$
14	Hector, Calif.	$\underbrace{[Al^{+3}_{1.49}Fe^{+3}_{.13}Fe^{+2}_{.01}Mg^{+2}_{.44}]}_{2.07}[Si^{+4}_{3.90}Al^{+3}_{.10}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.46}Fe^{+3}_{.13}Fe^{+2}_{.01}Mg^{+2}_{.42}]}_{2.02}[S^{+4}_{3.87}Al^{+3}_{.13}]O_{10}[OH]_{2_{x.50}}$
20	Lemon, Miss.	$\underbrace{[Al^{+3}_{1.43}Fe^{+3}_{.16}Fe^{+2}_{.01}Mg^{+2}_{.52}]}_{2.12}[Si^{+4}_{3.87}Al^{+3}_{.13}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.45}Fe^{+3}_{.16}Fe^{+2}_{.01}Mg^{+2}_{.44}]}_{2.06}[Si^{+4}_{3.89}Al^{+3}_{.11}]O_{10}[OH]_{2_{x.39}}$
22	Atzcapozalco, Mexico	$\underbrace{[Al^{+3}_{1.34}Fe^{+3}_{.30}Mg^{+2}_{.44}]}_{2.08}[Si^{+4}_{3.87}Al^{+3}_{.13}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.37}Fe^{+3}_{.31}Mg^{+2}_{.34}]}_{2.02}[Si^{+4}_{3.89}Al^{+3}_{.11}]O_{10}[OH]_{2_{x.41}}$
24	Santa Rosa, Mexico	$\underbrace{[Al^{+3}_{1.56}Mg^{+2}_{.57}]}_{2.13}[Si^{+4}_{3.85}Al^{+3}_{.15}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.62}Mg^{+2}_{.39}]}_{2.01}[Si^{+4}_{3.89}Al^{+3}_{.11}]O_{10}[OH]_{2_{x.44}}$
28	Greenwood, Maine	$\underbrace{[Al^{+3}_{1.74}Fe^{+3}_{.01}Mg^{+2}_{.30}]}_{2.05}[Si^{+4}_{3.83}Al^{+3}_{.17}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.71}Fe^{+3}_{.01}Mg^{+2}_{.29}]}_{2.01}[Si^{+4}_{3.81}Al^{+3}_{.19}]O_{10}[OH]_{2_{x.45}}$
	Fort Steel, Wyo.	$\underbrace{[Al^{+3}_{1.51}Fe^{+3}_{.13}Mg^{+2}_{.39}]}_{2.03}[Si^{+4}_{3.97}Al^{+3}_{.03}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.53}Fe^{+3}_{.13}Mg^{+2}_{.34}]}_{2.00}[Si^{+4}_{3.98}Al^{+3}_{.02}]O_{10}[OH]_{2_{x.36}}$
	Pala, Calif.	$\underbrace{[Al^{+3}_{1.66}Fe^{+3}_{.01}Mg^{+2}_{.45}]}_{2.12}[Si^{+4}_{3.78}Al^{+3}_{.22}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{3+}_{1.69}Fe^{+3}_{.01}Mg^{+2}_{.32}]}_{2.02}[Si^{+4}_{3.81}Al^{+3}_{.19}]O_{10}[OH]_{2_{x.42}}$
	Belle Fourche, S. Dak.	$\underbrace{[Al^{+3}_{1.55}Fe^{+3}_{.18}Fe^{+2}_{.02}Mg^{+2}_{.28}]}_{2.03}[Si^{+4}_{3.89}Al^{+3}_{.11}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.57}Fe^{+3}_{.18}Fe^{+2}_{.02}Mg^{+2}_{.23}]}_{2.00}[Si^{+4}_{3.91}Al^{+3}_{.09}]O_{10}[OH]_{2_{x.35}}$
	Upton, Wyo.	$\underbrace{[Al^{+3}_{1.56}Fe^{+3}_{.17}Fe^{+2}_{.03}Mg^{+2}_{.25}]}_{2.01}[Si^{+4}_{3.94}Al^{+3}_{.06}]O_{10}[OH]_{2_{x.33}}$	$\underbrace{[Al^{+3}_{1.55}Fe^{+3}_{.17}Fe^{+2}_{.03}Mg^{+2}_{.24}]}_{1.99}[Si^{+4}_{3.93}Al^{+3}_{.07}]O_{10}[OH]_{2_{x.35}}$

The value of 0.33 for the exchange cations in the generalized formula for montmorillonite was used because 26 of their 54 samples had a total equivalence of Na+Ca/2+K approximately equal to 0.33, which was in agreement with the mean value of 0.84 milliequivalents for cation-exchange capacity found by Ross and Hendricks.

In the formulas shown in Table 2 of the samples used in this study, the number of ions in octahedral coordination ranges from 2.01 to 2.13 when all the magnesium is assigned to the octahedral group and when an average cation-exchange value of 0.33 is used. When, however, only non-exchangeable magnesium is assigned to the octahedral group and when the determined cation-exchange value is used, the number of ions in octahedral coordination for the same samples is very close to the theoretical 2.00, ranging from 1.99 to 2.03 except for one sample, No. 20, for which the number of ions was 2.06 as compared with 2.12 by the first method of calculation.

Correction of total magnesium for exchangeable magnesium and use of the determined cation-exchange value in calculating the formula has little effect on the number of ions in octahedral coordination if the exchangeable magnesium is small and if the cation-exchange capacity is near the average value of 0.33 used by Ross and Hendricks. For example, the sample from Upton, Wyo., had only 0.10 per cent exchangeable magnesium and a cation-exchange capacity of 0.86 milliequivalents per gram as compared with the mean value of 0.84 found by Ross and Hendricks. The number of ions in octahedral coordination is 2.03 when all the magnesium is calculated as in octahedral coordination and 0.33 is used as the cation-exchange value and 2.00 when total magnesium is corrected for exchangeable magnesium and the determined cation-exchange value is used. However, if a sample has high exchangeable magnesium and/or high cation-exchange capacity, correction of total magnesium for exchangeable magnesium and use of the determined cation-exchange value in calculating the formula has considerable effect on the number of ions found to be in octahedral coordination. The highest exchangeable magnesium was found in sample No. 24, in which it amounted to 1.62 per cent, approximately one-third of the total magnesium content of the sample. The cation-exchange capacity is also fairly high, being 0.98 milliequivalents per gram. When all the magnesium of this sample is calculated as in the octahedral group and an exchange value of 0.33 is used, the number of ions in octahedral coordination is 2.13 as compared with 2.01 ions in octahedral coordination when only non-exchangeable magnesium is calculated as in the octahedral group and the determined cation-exchange value is used. The number of positions occupied in the octahedral group by Mg fell from 0.57 to 0.39 and Al in tetrahedral coordination fell from 0.15 to 0.11. Sample No. 14 has very little exchangeable magnesium, only 0.11 per cent, but very high cation-exchange capacity, 1.15 milliequivalents per gram. Correcting for exchangeable magnesium in this sample has no effect on the number of ions in octahedral coordination, but use of the determined cation-exchange value instead of 0.33 lowers the number of ions in octahedral coordination from 2.07 to 2.02, and raises the Al in tetrahedral coordination from 0.10 to 0.13. It is apparent, therefore, that correction of total magnesium for exchangeable magnesium and the use of the determined cation-exchange value is of considerable importance in calculating the formulas of the montmorillonites; of as much importance as any of the other analytical values. When these modifications are made in calculating the formula, the number of ions found to be in octahedral coordination is very close to the theoretical value of 2.00. This suggests that substitution of Mg for Al in the octahedral group is ion for ion, and that there is little or no tendency toward internal compensation of charge by the filling of extra positions.

INFORMATION FURNISHED BY MARSHALL'S METHOD OF CALCULATION

A comparison of the number of atoms in the octahedral layer of the unit cell by Marshall's method[6] of calculation when (1) all the magnesium is assigned to the octahedral layer, and (2) when only non-exchangeable magnesium is assigned to this layer is shown in Table 3.

In recalculating the analysis for sample No. 24, the number of atoms in the octahedral layer is 4.400 when all the magnesium is assigned to this layer, and 4.032 when only non-exchangeable magnesium is assigned to the same layer. The 0.400 in excess of 4.00 found in the first calculation is equivalent to 1.78 per cent of MgO, as compared with 1.62 per cent of exchangeable magnesium as MgO found on determination. When all the magnesium is assigned to the octahedral layer that layer appears to carry a plus charge of 0.060, the total charge on the cell amounts to only -0.156, and the charge due to the cations—CaO, Na_2O, and K_2O—is only -0.154. But when only non-exchangeable magnesium is assigned to the octahedral layer, that layer has a negative charge of 0.668, the total charge on the cell is 0.884, and the charge due to the exchangeable cations is 0.881. Determined cation-exchange capacity was 0.886. For the sample from Fort Steel, Wyo., there are 4.113 atoms in the octahedral layer when all the magnesium is assigned to that layer as compared to 3.990 atoms when correction is made for exchangeable magnesium and

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[6] Marshall, C. E., The colloid chemistry of the silicate minerals: *Am. Soc. Agron* Monograph Ser., **1**, p. 58, Academic Press, Inc., New York, N. Y. (1949).

the charge on this layer rises from 0.458 to 0.704. The total charge on the unit cell is only −0.482 when all the magnesium is assigned to the octahedral layer and is −0.728 when only non-exchangeable magnesium is assigned to that layer. The charge due to the exchangeable cations is 0.729 as compared with a determined cation-exchange capacity of 0.718. The excess atoms found in the octahedral layer when all the magnesium is assigned to that layer are equivalent to 0.49 per cent MgO. Exchangeable MgO in the cation-exchange filtrate was 0.52 per cent. Thus when the formula is calculated from the analysis by Marshall's method and all magnesium assigned to the octahedral layer, it is possible to estimate, from the excess atoms over 4.00 in the octahedral layer, the amount of exchangeable magnesium present in the sample to within a few tenths of a per cent. It is also possible to estimate the cation-exchange capacity of the sample by subtracting the excess atoms over 4.00 from the number of atoms of MgO before calculating the charge on the octahedral layer. For example, if 0.400 is subtracted from 1.140 (the number of atoms of magnesium in the octahedral layer when all the magnesium is assigned to that layer) and the remainder (0.740) used in calculating the charge on that layer, a total charge for the unit cell, or the cation-exchange capacity, for sample No. 24 of 0.956 is obtained, whereas the determined cation-exchange capacity of this sample was 0.890. If the same calculation is made for the sample from Fort Steel, Wyo., an estimated cation-exchange capacity of 0.708 is obtained, compared to a determined cation-exchange capacity of 0.718. When exchangeable magnesium is low, assignment of all magnesium to the octahedral layer involves no considerable error, although even in such a sample the number of atoms obtained in the octahedral layer is somewhat high and the charge on the unit cell is proportionately low. Sample No. 14 had only 0.11 per cent exchangeable magnesium on determination. If this is assigned with non-exchangeable magnesium to the octahedral layer, the number of atoms obtained in this layer on calculation is 4.066 and the charge on the unit cell is 0.953 as compared with 4.040 atoms in the octahedral layer and a charge of 1.009 on the unit cell when total magnesium is corrected for exchangeable magnesium. The determined cation-exchange of this sample was 1.000. If the excess atoms above 4.000 obtained in the octahedral layer when all the magnesium is assigned to that layer are converted to their equivalent in terms of MgO, they indicate an exchangeable MgO of 0.31 per cent—0.20 per cent higher than the exchangeable MgO found on determination but indicative of the degree of magnitude of the exchangeable magnesium and within the limits of the analytical error involved when all the analytical values used in the calculation are taken into consideration.

TABLE 3. COMPARISON OF NUMBER OF ATOMS IN THE OCTAHEDRAL LAYER OF THE UNIT CELL WHEN (1) ALL Mg IS ASSIGNED TO OCTAHEDRAL LAYER AND (2) ONLY NON-EXCHANGEABLE Mg IS ASSIGNED TO OCTAHEDRAL LAYER

All Mg assigned to octahedral layer							Only non-exchangeable Mg assigned to octahedral layer						
	Percentage composition	G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell		Charge		Percentage composition	G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell		Charge
Sample No. 24—Santa Rosa, Mexico													
SiO_2	51.50	3.430	31.143	7.786	7.786		SiO_2	51.50	3.430	31.143	7.786	7.786	
					.214	−.214						.214	− .214
					8.000							8.000	
Al_2O_3	19.44	1.144	10.387	3.462 →	3.248		Al_2O_3	19.44	1.144	10.387	3.462 →	3.248	
Fe_2O_3	.10	.004	.036	.012	.012	+.060	Fe_2O_3	.10	.004	.036	.012	.012	− .668
MgO	5.07	.251	2.279	1.140	1.140		MgO	3.45	.171	1.553	.776	.776	
					4.400	−.154						4.036	− .884
CaO	.40	.014	.127	.127	.127		CaO	.40	.014	.127	.127	.127	
Na_2O	.06	.002	.018	.018	.018		MgO	1.62	.080	.727	.727	.727	
K_2O	.04	.001	.009	.009	.009		Na_2O	.06	.002	.018	.018	.018	
		4.846			E = .154		K_2O	.04	.001	.009	.009	.009	
									4.846			E = .881	.881
Excess atoms in octahedral layer equiv. to 1.78 per cent MgO							Detd. cation-exchange		.098			.890	
Fort Steel, Wyo.													
SiO_2	53.37	3.554	31.903	7.976	7.976		SiO_2	53.37	3.554	31.903	7.976	7.976	
					.024	−.024						.024	− .024
					8.000							8.000	
Al_2O_3	17.53	1.032	9.261	3.087 →	3.063		Al_2O_3	17.53	1.032	9.261	3.087 →	3.063	
Fe_2O_3	2.25	.084	.758	.253	.253	−.472	Fe_2O_3	2.25	.085	.758	.253	.253	− .704
MgO	3.58	.176	1.580	.790	.790		MgO	3.03	.150	.674	.674	.674	
					4.106	−.496						3.990	− .728

TABLE 3 (*continued*)

All Mg assigned to octahedral layer

Percentage Composition		G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell		Charge
CaO	.84	.030	.269	.269	.269	
Na_2O	.00	.000	.000	.000	.000	
K_2O	.02	.000	.004	.004	.004	
H		.025	.224	.224	.224	
		4.901			E = .497	
Excess atoms in octahedral layer equivalent to 0.48 per cent MgO						
Sample No. 14—Hector, Calif.						
SiO_2	53.02	3.532	30.945	7.736	7.736	
					.264	− .264
					8.000	
Al_2O_3	18.50	1.089	9.543	3.181 →	2.917	
Fe_2O_3	2.33	.088	.771	.257	.257	
FeO	.13	.004	.035	.017	.017	− .692
MgO	4.04	.200	1.753	.876	.876	
					4.067	− .956
CaO	.32	.011	.096	.096	.096	
Na_2O	3.28	.106	.929	.929	.929	
K_2O	.08	.002	.017	.017	.017	
		5.032			1.042	
Soluble anions		.010			.088	
		5.022			E = .954	
Excess atoms in octahedral layer equivalent to 0.31 per cent MgO						

Only non-exchangeable Mg assigned to octahedral layer

Percentage composition		G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell		Charge
CaO	.84	.030	.269	.269	.269	
MgO	.52	.026	.232	.232	.232	
Na_2O	.00	.000	.000	.000	.000	
K_2O	.02	.000	.004	.004	.004	
H		.025	.224	.224	.224	
		4.901			E = .729	
Detd. cation-exchange		.080			.718	
SiO_2	53.02	3.532	30.945	7.736	7.736	
					.264	− .264
					8.000	
Al_2O_3	18.50	1.089	9.543	3.181 →	2.917	
Fe_2O_3	2.33	.088	.771	.257	.257	
FeO	.13	.004	.035	.017	.017	− .744
MgO	3.93	.194	1.700	.850	.850	
					4.041	−1.008
CaO	.32	.011	.096	.096	.096	
MgO	.11	.006	.052	.052	.052	
Na_2O	3.28	.106	.929	.929	.929	
K_2O	.08	.002	.017	.017	.017	
		5.031			1.094	
Soluble anions		.010			.088	
		5.021			E = 1.006	
Detd. cation-exchange		1.150			1.008	

Thus, by the Marshall method, the number of atoms obtained in the octahedral layer in excess of 4.00, when all magnesium is assigned to the octahedral layer, permits an estimation of the amount of exchangeable magnesium present and of the cation-exchange capacity of the sample. On the other hand, when exchangeable magnesium is determined and only non-exchangeable magnesium is assigned to the octahedral layer, the number of atoms in this layer is very close to the theoretical 4.00, even when exchangeable magnesium is high (as in sample No. 24) and the charge on the unit cell checks the charge of the external cations and the determined cation-exchange capacity, provided, of course, that correction has been made for soluble salts that may be present.

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