CHEMICAL DETERMINATION OF TETRAHEDRAL IONS IN NONTRONITE AND MONTMORILLONITE

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ABSTRACT

Samples of nontronite and montmorillonite were digested with dilute hydrochloric acid for various periods of time. Chemical determinations of the acid-soluble ions were made for each period of digestion. Curves are presented showing the rates of solution of these minerals as decreasing exponential functions of time. A change in the slopes of the curves, as plotted on semilogarithmic paper against time on the linear scale, suggests different rates of solution for the ions in the tetrahedral and octahedral layers. The initial slope of the curves represents the simultaneous rates of solution of the octahedral and tetrahedral layers with the octahedral layer predominating. The second slope of the curves represents the rate of solution of the tetrahedral layer predominantly. Extrapolation of this slope to zero time is thought to give the percent of the tetrahedrally substituted ions within very close limits. Solubility curves of nontronite suggest the presence of both iron and aluminum in the tetrahedral layer. The solubility curves for Polkville montmorillonite indicate there is no substitution for silicon in the tetrahedral layer. Experimental values of tetrahedral substitution in nontronite check very closely with values postulated from the theoretical calculations obtained from the chemical analysis of the mineral.

INTRODUCTION

Since Ross and Hendricks (1945) wrote their paper entitled "Minerals of the montmorillonite group", investigation of the structure of clay minerals has been continuous. Various workers have called attention to impurities in the samples. Chemical analysis, cation exchange capacity, x-ray diffraction, and differential thermal analysis have all contributed to an understanding of the structure of the clay minerals.

The glaring weakness in previous investigations of the distribution of ions in the crystal structure has been the inability of the analytical chemist to determine what specific ions, if any, substitute for silicon in tetrahedral coordination. In the montmorillonite group the usual assumption has been that aluminum ions make up the tetrahedral deficiency, as commonly assumed for the micas. Recently MacEwan (1951, p. 98) pointed out (in reference to nontronite) that "Fe is not considered to replace tetrahedrally coordinated aluminium." Direct proof of this assumption is conspicuous by its absence from the clay mineral literature.

With nontronite, the high iron-bearing member of the montmorillonite isomorphous series, the samples commonly contain both aluminum and

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iron in amounts either of which is sufficient to account for the deficiency of silicon. On the other hand, in many of the low-iron members of the montmorillonite series, the total iron content is not sufficient to provide the required amount of tetrahedral substitution for silicon.

Until Brindley and Youell (1951, p. 495) published their results on the determination of tetrahedral and octahedral aluminum in a chlorite, no direct analytical method had been proposed for determining what specific ions occur in tetrahedral and octahedral coordination in the clay minerals. Their results with chlorite suggested to the author that the experimental method which they used might be applicable to montmorillonite and nontronite and, hence, afford a direct analytical means of determining the ions which substitute for silicon in tetrahedral coordination.

EXPERIMENTAL

The two clay minerals selected for study were an artificially sodium-saturated Garfield, Wash., nontronite less than 50mμ (millimicrons) in average diameter (Hauser and Reed, 1936, p. 1169), and an artificially sodium-saturated Polkville, Miss., montmorillonite with a particle size ranging from 200mμ to 70 mμ.

These two clays have an extreme range of composition from a high iron content in the case of the nontronite to a high aluminum and low iron content in the Mississippi montmorillonite as shown in Table 1. The two minerals were selected because of their apparent range in composition. Theoretical calculation, on the basis of total analysis, indicates a fairly high tetrahedral substitution in the nontronite sample and an extremely small tetrahedral substitution in the montmorillonite sample.

TABLE 1. — CHEMICAL COMPOSITION OF GARFIELD, WASHINGTON, NONTRONITE AND POLKVILLE, MISSISSIPPI, MONTMORILLONITE

	Garfield Nontronite	Polkville Montmorillonite
SiO_2	42.60	53.42
Al_2O_3	5.86	16.40
Fe_2O_3	30.15	1.58
TiO_2	0.24	0.27
MnO	0.03	0.00
P_2O_5	0.07	0.03
CaO	0.19	0.09
MgO	0.24	4.33
Na_2O[1]	3.51	2.92
K_2O	0.09	0.07
H_2O	16.75	20.80
Total	99.73	99.91

[1] 2.85 percent Na_2O is exchangeable. Remaining Na_2O is extraneous, presumably owing to incomplete washing after sodium saturation.

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TABLE 2. — CALCULATED UNIT CELL CATIONS FROM THE ORIGINAL CHEMICAL ANALYSIS OF NONTRONITE

	Cations per Unit Cell	Distribution of Cations		
SiO_2	7.049	Tetra-hedral	Si	7.049
Al_2O_3	*1.1423*		Def.	*0.951?*
Fe_2O_3	3.7528			8.000
CaO	0.03364	Inter-layer	Na	0.914
MgO	0.05171		K	0.019
Na_2O	0.91370		Ca	0.034
K_2O	0.01908		Mg	0.007
MgO[1]	0.00736			

[1] Exchangeable

Nontronite

Table 2 shows the theoretical tetrahedral and interlayer cations of Garfield, Wash., nontronite calculated from the analysis. The tetrahedral deficiency thus found is 0.951 cations per unit cell. The data show that this sample contains sufficient iron or aluminum for either to satisfy the silicon deficiency.

The solution to this problem was approached by the same method as that used by Brindley and Youell. Although the rate of acid-solubility of nontronite and montmorillonite was obtained in similar manner, interpretation of the data and certain assumptions have been made that are different from their postulations and will be discussed later.

To obtain the acid-solubility rate of the two minerals, 0.5-gram samples were digested with 100 ml of ten percent hydrochloric acid at approximately constant temperature (steam bath) for various periods of time. At the conclusion of each period the contents of the platinum dishes in which the samples were digested were filtered and the filtrates retained

TABLE 3. — PERCENT OF ACID-INSOLUBLE IRON AND ALUMINUM IN NONTRONITE AFTER ACID DIGESTION

	Percent in Residue	
Digestion Period	Fe_2O_3	Al_2O_3
0.0 minutes	30.15	5.86
5.0 minutes	28.60	4.35
15.0 minutes	22.50	2.21
30.0 minutes	13.15	0.86
1.0 hour	7.25	0.58
2.0 hours	3.15	0.37
3.0 hours	1.82	0.11
4.0 hours	1.65	0.16
5.0 hours	1.15	—

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for the determination of acid-soluble iron, aluminum, and magnesium. Knowing the total content of these elements in the samples, the percentages of iron, aluminum, and magnesium remaining undissolved after each digestion period were calculated. The data are shown in Table 3.

A semilogarithmic plot of these data shows two distinct slopes in the aluminum and iron curves (Figures 1 and 2, respectively). These are interpreted as two rates of solution for iron and aluminum. If each of these elements has two rates of solution, then it is reasonable that each occupies two different positions in the crystal lattice. Since the bond strength of aluminum ions in tetrahedral coordination is believed to be greater than the bond strength in octahedral coordination, the rate of

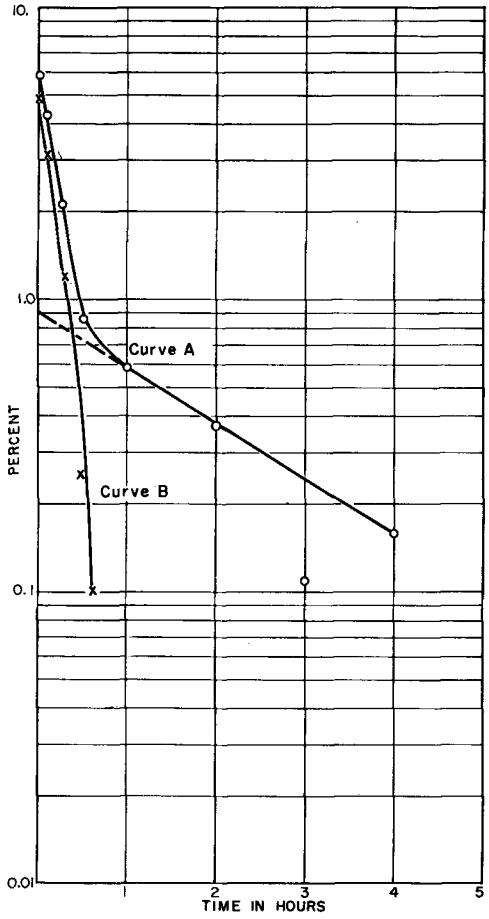

FIGURE 1. — Al_2O_3 remaining undissolved in nontronite, Garfield, Washington; expressed as percent of the original sample.

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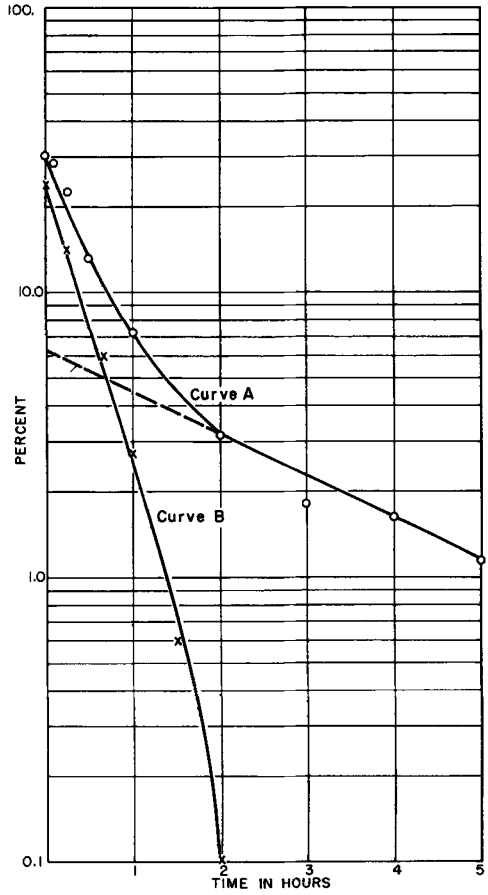

FIGURE 2. — Fe_2O_3 remaining undissolved in nontronite, Garfield, Washington; expressed as percent of the original sample.

solution of octahedral ions will be faster. This is in agreement with the observations of Brindley and Youell on chlorite. Thus, the initial rates of solution of iron and aluminum will be a summation of the octahedral and tetrahedral rates. However, if the acid digestion is carried for a long enough period, almost all the octahedral layer will be dissolved; therefore, the ions removed upon further extraction will represent predominantly the rate of solution of the tetrahedral layer. In Figures 1 and 2 it is apparent that the solution curves for tetrahedral aluminum and iron follow straight lines when plotted semilogarithmically. Thus, the rates of solution of tetrahedral iron and aluminum under isothermal conditions are primarily dependent on concentration of the metal ion. By definition this is a first-order

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reaction. Thus, the rate of solution of tetrahedral aluminum can be expressed mathematically as follows:

$$-\frac{da}{dt} = k_1 a \quad \text{.....(1)}$$

where a is the concentration of tetrahedral aluminum, K_1 is the first-order rate constant, t is the time, and $-\frac{da}{dt}$ is the rate at which the concentration decreases. Integration gives:

$$ln\ a = -k_1 t + constant \quad \text{.....(2)}$$

At $t = 0$, a equals a_o the original concentration of tetrahedral aluminum and the constant $= ln\ a_o$. Therefore,

$$ln\ a = ln\ a_o - k_1 t \text{ or } log\ a = log\ a_o - \frac{k_1 t}{2.303} \quad \text{.....(3)}$$

This equation may be written in the exponential form

$$a = a_o\ e^{-k_1 t} \quad \text{.....(4)}$$

From equation (3) it is evident that a straight line results when the logarithm of the percent residue is plotted against time. The rate constant can be obtained by determining the rectilinear slope of the line.

The rate of solution of aluminum ions from the octahedral layer will be different. If the solution of aluminum ions from the octahedral layer is also a first-order reaction, the rate of solution may be expressed as follows:

$$b = b_o\ e^{-k_2 t} \quad \text{.....(5)}$$

where b is the concentration of octahedral ions at time t, b_o is the original concentration of octahedral ions, and k_2 is the rate constant for the solution of octahedral aluminum ions. Since nontronite contains both tetrahedral and octahedral aluminum ions, the overall rate expression for solution of both ion types will be

$$a + b = a_o e^{-k_1 t} + b_o e^{-k_2 t} \quad \text{.....(6)}$$

Thus, if $k_1 \neq k_2$ a semilogarithmic plate of the percent residue against time will give a curve. From inspection of the solution curves, Figures 1 and 2, it is obvious that the rates of solution for the octahedral ions are significantly faster than for the tetrahedral ions. However, if the rate constant for the octahedral ions (k_2) is sufficiently larger than the rate constant for tetrahedral ions (k_1), the contribution of the octahedral term, $b_o e^{-k_2 t}$, in equation (6) will be diminished with time much more rapidly than the tetrahedral term. Thus, after sufficient time its contributions will be negligible and the solution curve will be a straight line representing almost wholly the tetrahedral ion. In addition, if b_o is many times larger than a_o, the solution curve will initially approximate a straight line which is a crude representation of the octahedral solution curves. The validity of this interpretation has been confirmed by graphical solutions of the curves for the reaction components.

In Figures 1 and 2 curves A represent the summations of the rates of solution of octahedral and tetrahedral aluminum and iron, respectively. If the lower portion of each curve representing predominantly tetrahedral

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ions is extrapolated to zero time, as shown by the dotted lines, the initial concentration of tetrahedral aluminum and iron is determined by the intercept on the axis at zero time. Once the tetrahedral rate has been established, the octahedral rate of solution is calculated by subtracting values on the tetrahedral slope from values on the summation curves for corresponding periods of time. Curves *B* in Figures 1 and 2 represent the rates of solution of octahedral aluminum and iron. If the summation curves *A* represent solution of only tetrahedral and octahedral ions and the extrapolated tetrahedral slopes have been accurately established, the octahedral residues should plot as straight lines. The small amount of curvature has been assumed to be due to experimental error involved in accurately measuring small quantities of the oxides.

The intercept values for aluminum and iron in Figures 1 and 2 correspond to 0.9 and 6.2 percent aluminum oxide and iron oxide, respectively. Calculated as ions per unit cell, 6.2 percent iron oxide is equivalent to 0.773 iron ions and 0.9 percent aluminum oxide is equivalent to 0.176 aluminum ions. The sum of these is 0.949 ions which is within the limits of analytical error of tetrahedral deficiency shown by theoretical calculation.

The experimental values for tetrahedral iron and aluminum in nontronite have been inserted into the calculations of lattice layer cations and are shown in Table 4.

TABLE 4.—DISTRIBUTION OF CATIONS IN LATTICE LAYERS, GARFIELD, WASHINGTON, NONTRONITE

Layer	Cations per Unit Cell	
Tetrahedral	Si	7.049
	Fe	0.773
	Al	0.176
		7.998
Octahedral	Fe	2.980
	Al	0.966
	Mg	0.052
		3.998
Interlayer	Na	0.914
	K	0.019
	Ca	0.034
	Mg	0.007

On this basis it is concluded that this particular nontronite contains relatively much more tetrahedral iron than aluminum in spite of the fact that the total aluminum content exceeds the silicon deficiency. This conclusion is in conflict with the usual view that only aluminum ions substitute for silicon ions in tetrahedral coordination.

X-ray powder diffraction analyses on several residues from the various periods of acid digestion of this sample of nontronite were made by Dr. I. H. Milne of our laboratories. These analyses suggest that two distinct reactions are involved in the progressive destruction of the crystallinity

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of the clay. The most noticeable effect during the early stages of digestion was the gradual reduction in the intensity of diffraction from the (001) plane. This diffraction almost entirely disappeared after one hour digestion, and in terms of the interpretation of the removal of aluminum oxide and iron oxide from the sample, this disappearance coincides with the solution of most of the octahedral cations. At one hour, however, there appears to have been little reduction in the intensity of diffraction from (*hk*0) planes as illustrated by the (110)(020) diffraction at 4.58A. Beyond one hour this diffraction gradually decreased in intensity until it completely disappeared after five hours digestion. This latter observation can be correlated with gradual destruction of silica sheets coincident with the solution of tetrahedral aluminum and iron. The mechanism by which silica sheets are able to remain intact after more or less complete removal of the octahedral layer is not fully understood but a similar observation has been reported by Brindley and Youell (1951).

Polkville Montmorillonite

As stated earlier, theoretical calculations from the original chemical analysis of Polkville montmorillonite indicated a very small tetrahedral deficiency of silicon. This is illustrated by the calculations shown in Table 5.

TABLE 5. — DISTRIBUTION OF CATIONS IN LATTICE LAYERS, POLKVILLE, MISSISSIPPI, MONTMORILLONITE

Layer	Cations per Unit Cell	
Tetrahedral	Si	7.993
	Al	0.007
		8.000
Octahedral	Al	2.885
	Fe	0.178
	Mg	0.965
		4.028
Interlayer	Na	0.847
	K	0.013
	Ca	0.014

The tetrahedral aluminum of Table 5 is equivalent to 0.038 percent aluminum oxide calculated on the basis of the original sample. If the previous interpretation is valid, the acid-solubility curve of aluminum should show an inflection only when less than a tenth of a percent of aluminum remains in the structure.

The acid-solubility data for Polkville montmorillonite are shown in Table 6 and the graph in Figure 3.

The slope of the line representing the undissolved aluminum is constant to 43 hours; this would indicate that tetrahedral aluminum is absent or, if present, in a very low concentration. After 43 hours digestion there still

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TABLE 6. — PERCENT OF ACID-INSOLUBLE IRON, ALUMINUM, AND MAGNESIUM, POLKVILLE, MISSISSIPPI, MONTMORILLONITE

Digestion Period Hours	Percent in Residue		
	Fe_2O_3	Al_2O_3	MgO
0.0	1.58	16.4	4.33
0.75	0.97		
1.5	0.90	14.7	3.67
3.5	0.74	11.9	3.15
7.0	0.52	9.26	2.30
30	0.02	1.00	0.02
43	—	0.30	—

remained approximately 0.3 percent aluminum in the sample, although iron and magnesium were almost entirely removed. As stated above, the theoretical calculations indicate only a few hundredths of a percent of aluminum present in tetrahedral coordination.

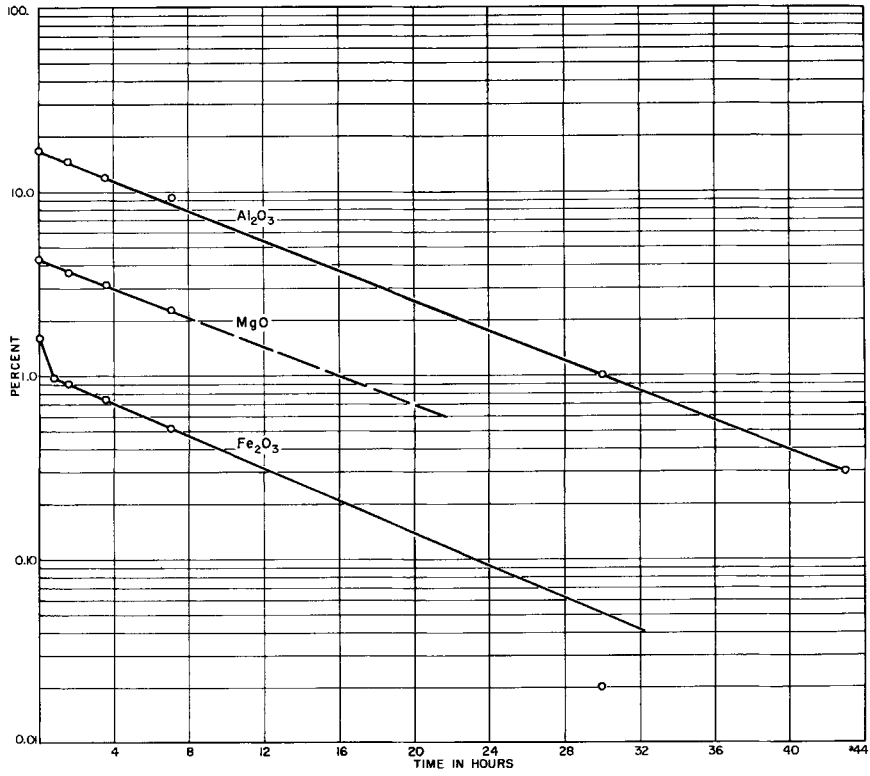

FIGURE 3. — Metallic oxide remaining undissolved in montmorillonite, Polkville, Mississippi; expressed as percent of the original sample.

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The solubility data for iron indicate that this element was dissolved as a decreasing exponential function of time. Although this paper is primarily concerned with the determination of tetrahedral ions, recent data obtained from the Polkville montmorillonite are very suggestive, especially as regards the iron.

Examination of crude specimens of Polkville montmorillonite reveals rust-colored spots disseminated throughout the clay. It is difficult, if not impossible, to hand-pick a sample so as to eliminate completely these rust spots. A typical specimen of the crude clay is seen in Plate 1. This clay is white in color except for the rust-colored areas, but when the clay is ground and separated by means of a Sharples supercentrifuge, it takes on a pink coloration indicating that the rust spots have contaminated the sample. It has long been suspected that these rust-colored areas contain some form of iron hydrate.

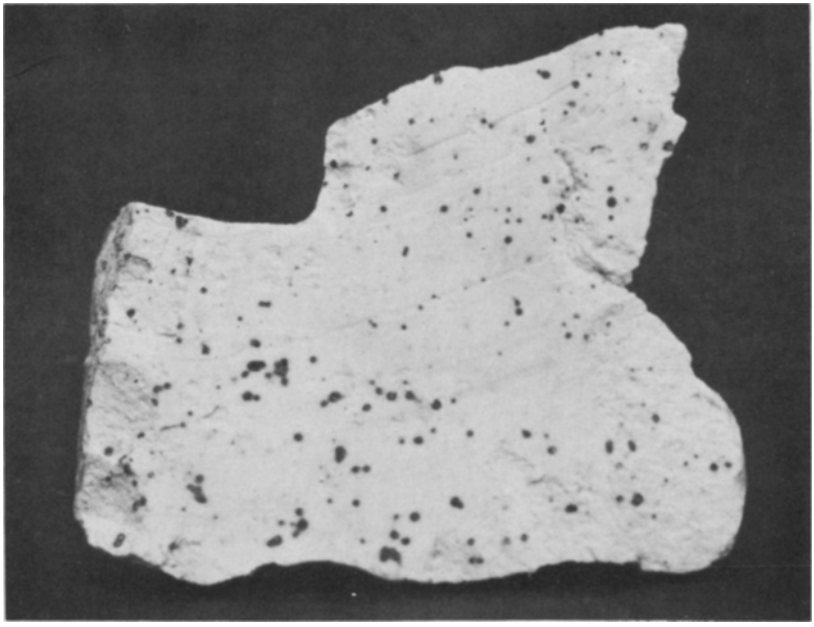

PLATE 1. — Crude Polkville, Mississippi, montmorillonite revealing rust-colored spots disseminated throughout the clay. Magnification X 3.5.

The removal of extraneous iron compounds from clay minerals has been a baffling problem for many investigators. A number of methods have been suggested. Of the methods described in the literature, several depend on the supposed reduction of the extraneous iron to the ferrous state, thereby increasing its solubility but without attacking the clay lattice iron. At best, this seems to be an uncertain method of solving the problem.

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As stated previously, iron was extracted from the Polkville sample (Figure 3) at a fairly constant rate. However, the total iron found in the sample (1.58 percent) is not obtained by extrapolating the curve to zero time. Rather, an amount is indicated corresponding to approximately 1.05 percent iron oxide. To increase the accuracy and to show more clearly the break in the iron curve, the iron-solubility data have been plotted on two-cycle semilogarithmic paper as shown in Figure 4. Since the data for aluminum and magnesium give curves approximately parallel to the iron curve, there is a strong indication that the intercept at zero time represents clay-lattice iron and that the difference between the total and this amount, that is 0.53 percent iron oxide, corresponds to extraneous iron in the sample. Obtaining the clay-lattice iron by this method depends on at least partial destruction of the mineral and not upon selective solubility of iron hydrate in preference to clay-lattice iron.

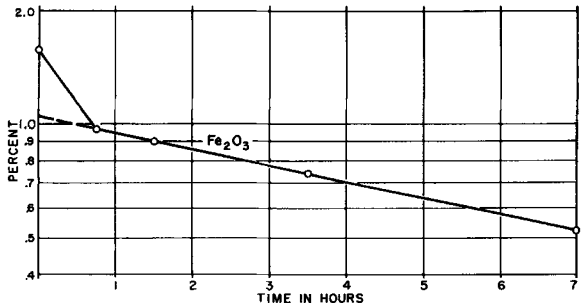

FIGURE 4. — Fe_2O_3 curve of montmorillonite, Polkville, Mississippi; reproduced from Figure 3 on two-cycle semilogarithmic paper.

Assuming that this sample contains only 1.05 percent iron oxide as lattice iron, calculation indicates a slight excess of silicon, namely, 0.0258 silicon ions per unit cell. For this value to be exactly 8.000 requires a silicon dioxide content of 52.79 percent in the sample, whereas, the amount found by chemical analysis was 53.42 percent or a difference of 0.63 percent which is in excess of the limit of error for a single determination of silicon.

The iron curve seems to indicate that clay-lattice iron can be differentiated from extraneous iron by virtue of differences in rates of solution. Insertion of the corrected iron value in the theoretical calculations yields results which indicate that there is practically no tetrahedral aluminum in this sample. The same is also suggested by the fact that the aluminum curve shows no change in slope. In other words, most if not all of the aluminum is present in this sample in octahedral coordination.

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GENERAL DISCUSSION

In considering the experimental evidence presented in relation to the results of Brindley and Youell (1951) for chlorite, it should be kept in mind that they plotted their data on the basis of the amounts dissolved, whereas the data reported herein were plotted on the basis of undissolved material expressed as percent of the original sample. Moreover, the author used a semilogarithmic plot as compared to Brindley and Youell's arithmetic plot. They postulated two separate reactions in the acid solution of chlorite and assumed that the octahedral layer was completely dissolved before the tetrahedral layer was attacked. Furthermore, they used the solution of magnesium and iron as a sort of internal indicator and reasoned that the complete solution of octahedral iron and magnesium would also determine the period of complete removal of the octahedral aluminum, and therefore, the aluminum of the two layers could be differentiated.

In contrast to their assumption for chlorite, the author proposes that for nontronite and montmorillonite, at least, the octahedral and tetrahedral layers dissolve simultaneously in ten percent hydrochloric acid but at different rates; the rate for the octahedral layer being considerably more rapid. When the acid is allowed to react for a sufficiently long period, practically all the octahedral ions pass into solution; further acid digestion, then, will represent the rate of solution of predominantly tetrahedral ions.

With samples which contain not only iron in octahedral coordination but also extraneous iron, extrapolation of the curve to zero time gives a measure of the lattice iron, the extraneous iron being then determined by difference.

The presence or absence of extraneous iron in samples which contain both tetrahedral and octahedral iron may possibly be indicated by extrapolation of the curve for octahedral iron to zero time. Should this intercept correspond to less iron than is found by total analysis, the inference would seem to be that the difference represents extraneous iron. The same may possibly hold for aluminum. However, the curve for the most soluble iron in the sample of nontronite reported herein gave an intercept corresponding to the total iron in the sample, indicating that it contains practically no extraneous iron or else that octahedral iron and the forms of extraneous iron in this sample dissolve at approximately equal rates. Further work on this problem is in progress.

An attempt was made to plot the solubility data of chlorite as reported by Brindley and Youell (1951), the iron and magnesium being plotted as decreasing exponential functions of time. However, the aluminum curve failed to give the correct tetrahedral value when extrapolated to zero time. Perhaps the acid digestion was not carried for sufficient time to establish the rate of solution of the tetrahedral layer, as only seventy-five percent of the total aluminum present was removed. It is upon this principle that the method described for nontronite and montmorillonite depends.

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CONCLUSIONS

Experimental evidence has been presented on a chemical method that may possibly quantitatively determine aluminum and iron in tetrahedral coordination as well as extraneous iron. The method depends on establishing the acid-solubility rates of iron and aluminum by plotting on semilogarithmic paper the percent of these elements remaining undissolved for any given period of digestion. The resulting curves show that the solution of these elements decreases exponentially with time. If either of the elements is present in both octahedral and tetrahedral coordination, this will be revealed by the presence of two slopes in the curve. The first slope will represent the simultaneous solution of octahedral and tetrahedral ions; the second, the rate of solution of tetrahedral ions predominantly. Extrapolation of this latter slope to zero time gives the percentage of tetrahedral iron or aluminum. Conversely, if the decreasing exponential curves of iron or aluminum show no inflection, it is concluded that silicon almost or completely fills the tetrahedral layer.

Under certain conditions, semilogarithmic plotting of the solubility data will reveal the amount of impurity present in the sample. This is well illustrated in the sample of Polkville montmorillonite.

The limited data obtained on the two minerals suggest that the rate of acid-solubility method might be applicable to other silicate sheet structures and might, therefore, permit differentiation between tetrahedral and octahedral cations in these minerals.

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DISCUSSION

G. W. Brindley. — Mr. Osthaus has extended in a most useful and thorough manner the less detailed analysis made by Brindley and Youell of the acid dissolution of a chlorite. I am indebted to Mr. Osthaus for kindly permitting me to see his typescript prior to its publication. As Mr. Osthaus states in his "general discussion," Youell and I pictured two separate reactions involving respectively the tetrahedrally- and the octahedrally-bonded layers and supposed that extraction of the octahedral cations would proceed at the same rate for all the ions in this layer. We confirmed this experimentally for Mg and Fe and assumed that octahedral Al behaved similarly. Figure 3 of Mr. Osthaus' paper largely confirms this conception, the logarithmic curves for Al, Mg, and Fe having the same negative slope, with the added merit that the experimental data now include Al.

We did not imagine that "the octahedral layer was completely dissolved before the tetrahedral layer was attacked", though it is a reasonable deduction to draw from the manner in which we handled the Al-extraction curve. Actually we drew the octahedral Al curve just below the total curve because we realized that some tetrahedral Al would be extracted from the commencement, but the scatter of our experimental points, particularly in the earlier stages of the acid attack, did not seem to warrant any more precise mathematical analysis.

Rustum Roy. — A very reasonable approach has been used by the author, and most promising results obtained. It was mentioned that there had been some doubt in other workers' minds regarding the assignation of Fe^{3+} to the tetrahedral layer. In our synthetic work we can prepare end member micas and montmorillonites with no cations other than Fe^{3+} and Si^{4+} (excepting in the interlayer positions); hence the total substitution in the tetrahedral layer is Fe^{3+} for Si^{4+}. The use of such synthetic samples may be of importance in calibrating the techniques.

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