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AN INVESTIGATION OF TOTAL AND EXCHANGEABLE MANGANESE AS A MEANS OF CORRELATING ARGILLACEOUS SEDIMENTS

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AN INVESTIGATION OF TOTAL AND EXCHANGEABLE MANGANESE AS A MEANS OF CORRELATING ARGILLACEOUS SEDIMENTS

by

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DEDICATION

To my wife, Mary, and my parents, Mr. and Mrs. L. B. Brigham, without whose financial and moral help this work could not have been completed.

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ABSTRACT

This work attempts to prove the hypothesis that total minus exchangeable cation content in argillaceous sediments gives a fixed value, representative of the amount of the cations present in the clay structure, which can be used for correlation.

Total and exchangeable manganese have been determined colorometrically in some varved glacial clays to see if the fixed value is constant within an individual varve and variable between varves.

Total manganese content proved to be similar for the three varves analyzed while exchangeable manganese varied within as well as between varves.

The differences in exchangeable manganese are shown not to be correlative with percentage of clay in the sample or with the clay mineralogy.

These differences are thought to be due to the contribution of manganese ions from manganese bearing minerals in the silt fraction.

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INTRODUCTION

Correlation of sedimentary deposits is an important tool which the geologist uses often. It is seldom that he can trace a deposit visually for this is possible only where it crops out. When he is searching for oil accumulations, the beds with which he is dealing are almost always completely concealed by overburden making it necessary to utilize the physical characteristics of a deposit in order to recognize it from well cuttings. In addition to visual comparison, some of these characteristics are mineralogy, mechanical analysis, chemical analysis, micropaleontology, and geophysical measurements. Arenaceous sediments lend themselves well to mechanical analysis because the particles are easily disaggregated and are large enough to be classified as to size and mineral composition. Carbonate rocks are often correlated chemically because of the ease of putting them into solution. Argillaceous sediments, because of their small particle size are more difficult to work with. For mechanical analysis they require the use of the laborious pipette method. For chemical analysis it is necessary to use the highly reactive hydrofluoric acid to put them into solution and their small particle size necessitates the use of X-ray techniques to determine the mineralogy. Differential thermal analysis is of questionable value for correlation.

The purpose of this research is to investigate a new method for the correlation of argillaceous sediments which might be more convenient than others that have been developed.

Metallic ions are adsorbed onto and may be removed from the surfaces of clay particles by the mechanism of ion exchange. If such exchangeable ions are characteristic of a particular clay or shale horizon, then, by the simple procedure of removing them and analyzing colorimetrically, correlations may be made. If, as seems more likely, however, the exchangeable ions are affected by circulating ground water, then the exchangeable ion content will be dependent on location and will not be characteristic of a single horizon. Moreover, total ion content, made up of exchangeable ions and fixed ions incorporated in the crystal structure, should also not be characteristic of a single horizon.

By subtracting the exchangeable ion content of a particular element from the total amount of that element present a residual value or fixed ion content would be determined which was free from the effects of ion exchange. This value should more nearly represent the amount of the element which was present in the material at its formation. Since clay is commonly the weathering product of a number of different minerals, one would expect the elemental content of a clay to vary depending upon its origin.

However, material from identical source areas, weathered and deposited under identical conditions, should have similar residual values. Therefore it seems probable that the fixed ion content of the residual could be used as a means of correlation. This research is an investigation of the fixed ion content of some glacial clays of known age to see whether correlation by this method is possible.

METHOD

For developing the procedures, it was decided that samples from a varved glacial lake deposit would be used. Varves are the fine grained bottom sediments of glacial lakes which occur in pairs of coarse and fine layers. (Flint; 1947, p.389) The coarse layers are generally silt and the fine layers clay. The advantage of using varves is two fold. Being layered they can be traced visually to provide an absolute check on correlation and since a varve is generally thought to represent deposition over a single season it may be assumed that conditions of sedimentation and source material were relatively constant for a single varve.

For this work, manganese was chosen as the ion to be analyzed. A cation was desired for which the analytical procedure was fairly simple and accurate. The addition of potassium periodate (KIO_4) to an acid solution containing trace amounts of manganese, upon heating, gives the pink permanganate color. The intensity of the color is proportional to the concentration. The color is very stable and will persist for months. A spectrographic analysis[1] was made of a sample of the varves which showed manganese to be present in determinable amounts.

[1]Courtesy of Dr. E. J. Benne and S. Bass of Agriculture Chemistry

THEORY

Clay as a term is difficult to define. It is used as a rock term to describe an "earthy, fine grained material which develops plasticity when mixed with a limited amount of water". (Grim; 1953, p.1) It is also a particle size term describing the smallest size fraction. Its maximum size is a matter of debate. Most geologists follow the Wentworth grade scale and call any material whose particle size is less than 4 microns clay. Grim (1953, p.2) believes the upper limit of clay particles should be 2 microns because above this size natural material fails to show clay mineral characteristics. Here clay is used as a mineral term. There are a number of minerals having a characteristic structure which usually occur in particles of less than 2 microns size.

There are two basic structural units which are common to most clay minerals, a silica tetrahedral layer and an octahedral layer consisting of combinations of aluminum iron or magnesium with oxygen. Most clay minerals are made up of combinations of these two layer types interspersed with sheets of water molecules. The layer combinations are relatively free to slip on these water sheets thus providing clay with its characteristic plasticity.

Ion exchange is a property of clays which is not present to any observable extent in the larger size

fractions. It is the adsorbing of ions onto the surface of the clay where they are held in exchangeable state. They will remain there until exchanged for other ions. Exchange capacity is measured in milliequivalents per hundred grams, a milliequivalent being one thousandth of a gram atomic weight. Cation exchange is much more common in clays than anion exchange and is better understood; only cation exchange will be considered here.

There are three causes for cation exchange in clay minerals. Briefly they are:

1. Broken bonds. Broken bonds at the edge of the unit cell give rise to unsatisfied charges. These charges can be satisfied by the adsorption of an ion. This type of exchange predominates in minerals such as kaolinite and halloysite. The finer the particle size, the greater will be the number of broken bonds per unit mass presented as exchange sites.

2. Substitutions within the lattice structure. When trivalent aluminum substitutes for quadrivalent silica in the tetrahedral lattice layer, or ions of lower valence for aluminum in the octahedral layer, a net negative charge is formed. This can occur either on the basal cleavage or the edges of the plate, but it is most predominent on the flat cleavage surfaces. Grim (1953, p.133) believes that the aluminum substitution for silicon produces such a tight bond with a cation that

little further exchange takes place. He states that replacement of the aluminum in the octahedral layer is probably the major substitution causing cation exchange capacity. Replacement is the major cause of cation exchange capacity in montmorillonite and vermiculite.

3. The hydrogen of exposed hydroxyls. The hydrogen of exposed hydroxyls may be available for replacement by suitable cations. This could be an important factor in the two layer types because of the exposed hydroxyls on the basal cleavage.

The ranges of exchange capacity for some of the clay minerals are shown in Table I. It can be seen that the

Table I

Cation Exchange Capacity of Clay Minerals, In Milliequivalents per 100 Grams

Kaolinite	3-15
Halloysite $2H_2O$	5-10
Halloysite $4H_2O$	40-50
Montmorillonite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiolite-attapulgite-polygorskite	20-30

clay minerals with the highest exchange capacities are montmorillonite and vermiculite. These clays have an expanding lattice. Their structure is such that between

each set of three layers water can penetrate. The distance between the layer depends on the number of layers of water molecules which penetrate and is governed by the nature of the exchange ion present. This very greatly increases the area available to exchange. However, an ion between the layers is less easily exchanged than one on the surface.

The order in which ions will replace one another varies among clay minerals. Ross (quoted in Rankama and Sahama, 1950) gives the following series for relative ease of replacement in montmorillonites:

$$Li^+ < Na^+ < H^+ < K^+ < Mg^{2+} < Ca^{2+}$$

As a general rule, the larger the ionic charge and the larger the ionic radius, the more readily will a cation be sorbed. A cation, however, will replace one higher up the series if it has a significantly greater concentration.

Chemistry of Replacement

In addition to the major elements of a mineral, other elements may fit themselves into the crystal by replacement or be present as inclusion without occupying a structural position. The latter case is the less common. In any clay sample there can be a great variety of elements present. They occur in very small quantities and are known as trace elements. Hildebrand (quoted in Sandell, 1944, p.3) states that a trace element is one occurring below the limit of quantitative analytical methods or in Sandell's

words less than 0.02 per cent. Rankama and Sahama (1950, p.34) define a trace element as any element which is not one of the eight major elements. These eight are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium, in order of their abundance. It is with these trace elements that the author seeks to correlate argilaceous sediments.

The replacement of one atom by another in a given structure is called diadochy. There are several factors which control this replacement. The radius of the replacing atom should not differ by more than 15 per cent from the radius of the atom being replaced. (Goldschmidt, 1954) It should be remembered that the size of an atom or ion will vary with the charge which it carries. If an atom loses an electron, the protons will exibit a greater force of attraction for the remaining electrons and the resulting ion will be smaller. Gaining an electron will produce the opposite effect. This size requirement is not always valid but is an approximation of the size difference allowed.

Ionization potential is an important factor in diadochy. Rankama and Sahama (1950, p.123) note that between ion pairs with small differences in ionization potential such as Si^{4+} - Ge^{4+}, K^{+} - Rb^{+}, Fe^{2+} - Co^{2+} and Mg^{2+} - Fe^{2+} diadochy occurs extensively. For pairs with large differences of ionization potential such as Na^{+} - Cu^{+} diadochy has not been observed.

As noted before, the charge of the replacing ion need not be similar. However, in cases of dissimilar charge replacement the electrostatic neutrality of the structure will be maintained by the introduction of additional ions outside the structure framework, by leaving a structure position vacant or by simultaneous substitution of another ion.

Goldschmidt (1954) gives three types of diadochy; camouflage, capture, and admission. Camouflage occurs when replacement takes place between ions of similar charge. The replacement of Fe^{2+} by Mg^{2+} is a common example of this. Capture is replacement by an element of higher charge. The process is called capture because the replacing ion is held more tightly due to its higher charge. An example is the capture of lead in potassium minerals. Admission is the opposite of capture in that an element of lower charge replaces another producing a weaker bond. An example is the substitution of lithium for magnesium in silicates.

Occurrence of Manganese as a Replacing Element

According to Rankama and Sahama, manganese is the second most abundant trace element next to titanium. In Goldschmidt's classification it is a strongly lithophile element which means that it is enriched in the silicate crust of the earth and shows a strong affinity for oxygen.

In nature it is closely related to iron and in igneous rocks its ratio with iron is constant. Independent manganese minerals are rare in igneous rocks but nearly all mineral groups contain manganese in their structure. It almost always occurs in the divalent state in igneous rocks. This is because at temperatures prevailing during the crystalization of a melt the divalent state is the most stable. Its atomic radius in this state is 0.91 kX units. This is similar in size to Fe^{2+}(0.83kX), Mg^{2+}(0.78kX), Zn^{2+}(0.83kX) and Ca^{2+}(1.06kX). These four elements can be replaced by manganese; however Fe^{2+} is most commonly replaced. In clays manganese occurs as a replacing element in the octahedral layer (Grim, 1953, p.72).

Effect of Weathering on Manganese

Two processes control the weathering of manganese. One is the leaching of the divalent manganese in solution, mainly as the bicarbonate. The other is the precipitation of the insoluble oxide and hydroxides of trivalent and quadrivalent manganese; MnO_2 being a good example of the latter. The mobility of the lowest stage and the precipitation of the higher stage of oxidation is in constrast to the situation found in vanadium and chromium. The low ionic potential of divalent manganese promotes its solution by even very weakly acid solutions. The higher oxidation potentials of Mn_2O_3 and MnO_2 leads to precipitation.

The precipitation or transportation of manganese, therefore, depends on the availability of oxygen. Humic compounds tend to promote the transportation of Mn. Another important factor is the pH of the aqueous solution. A low pH will cause solution and a high pH will bring about fixation. The presence of solid calcium carbonate will tend to bring non-reversible precipitation of manganese as the dioxide.

The effect of the oxidation reduction on exchangeable manganese in soil is shown in the following diagram:

$$\underset{\text{Manganic Oxides}}{Mn_2O_3\ MnO_2} \underset{Ox.}{\overset{Red.}{\rightleftharpoons}} \underset{\text{Manganous Oxide}}{MnO} \underset{Ox.}{\overset{Red.}{\rightleftharpoons}} \text{Exchangeable} \underset{Ox.}{\overset{Red.}{\rightleftharpoons}} \text{Water Soluble}$$

It can be seen that as theoxidation state is reduced, the solubility of themanganese is increased. Under reducing conditions the insoluble manganic oxide convert to the mobile manganous state. Further reduction makes the Mn soluble enough to be able to take up exchange positions on the clay as ionic manganese. A small percentage of the manganese is in water soluble condition. This system is in dynamic equilibrium and as oxidation reduction conditions change the amount of exchangeable manganese will be shifted. Fujimoto and Sherman (1948) investigating manganese toxicity in soil found that adding sulfur to increase the acidity increased to a great extent the amount of exchangeable manganese as did adding organic matter. They found that the amount of exchangeable

manganese could be reduced below toxic levels by adding crushed limestone.

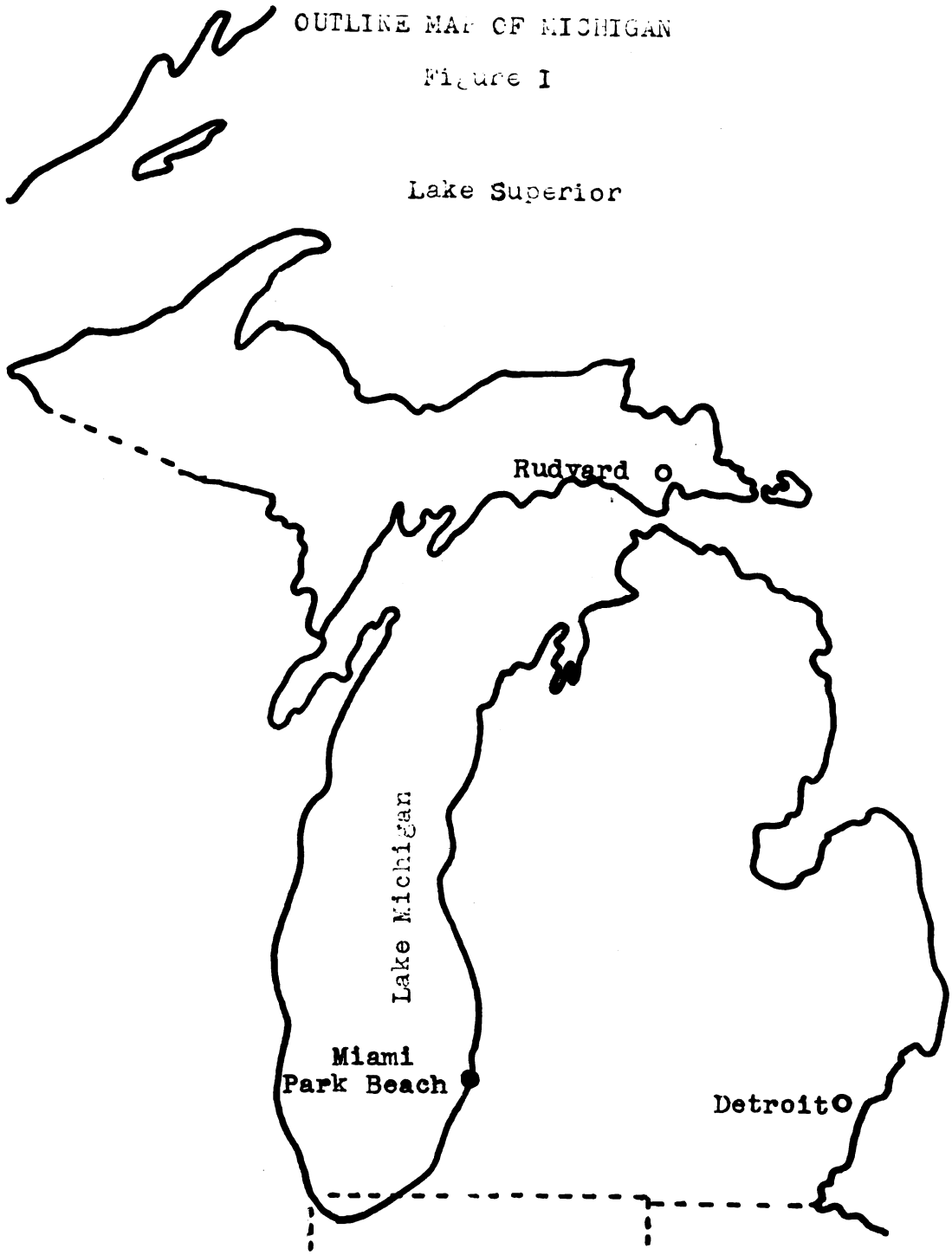
In summary, it is seen that the disposition of manganese after weathering from the parent igneous material is dependent on conditions of oxidation reduction which govern its solubility.

LOCATION AND SAMPLING

The varves selected for sampling are those described by Bergquist in his paper in the 1950 proceedings of the Michigan Academy of Science Arts and Letters. They are exposed in the bluffs along Lake Michigan at Miami Park Beach, four miles north of South Haven, Michigan (map). The bluff stands 90 feet above lake level at this point. The upper 35 feet is a bluish-grey pebbly clay till. Below this is a 36 foot section of varved sediments which are described by Bergquist (1950) as glaciolacustrine. These in turn rest upon another till distinguishable only by position from the one above. The varves themselves differ from the typical varves in that they are extremely variable in thickness, from a few inches to two feet for both the clay and sand layers. Bergquist (1950) states that the lack of uniformity may possibly be due to near-shore deposition of the sediments in an iceborder lake of relatively short duration. The sand layers grade upward into the clay layers in what the writer chooses to call the transitional zone. However, the separation between the sand layers and the underlying clay layers is at times sharp and other times transitional. The sand is rather fine, light yellow in color, and completely unconsolidated. The clay layer contains two zones, a blue zone sharply separated from an upper brown zone. The transitional zone is composed of finely interstratified silt and clay.

OUTLINE MAP OF MICHIGAN

Figure I

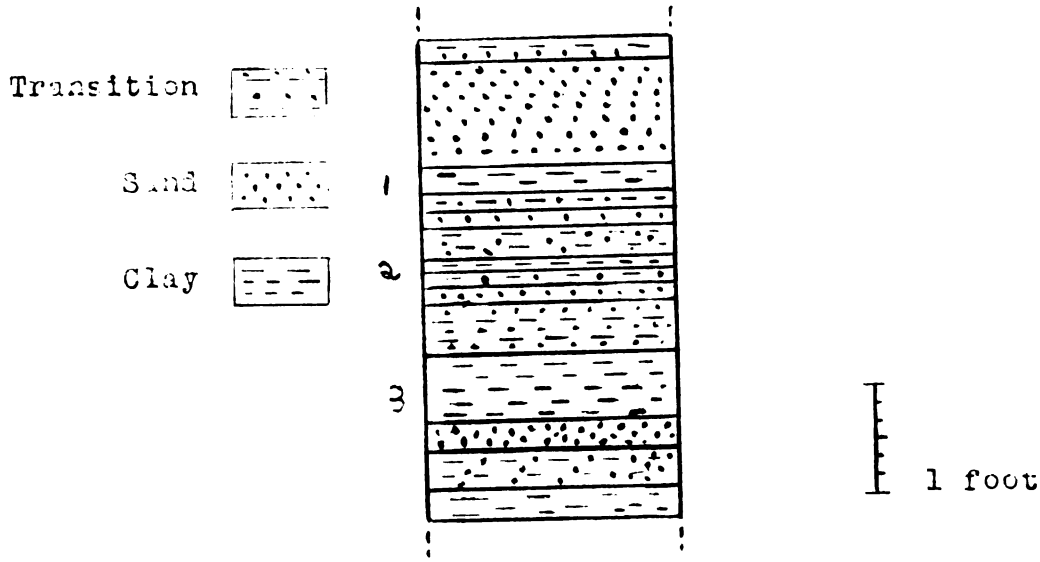


Sample site o

The sample site is in a deep gully which is situated at the end of the northernmost road leading into Miami Park Beach. About twenty feet below the contact between the upper drift and the varved sediments a sixteen feet long four feet deep trench was dug to expose a section of the varves free from slope wash. The section with thicknesses and sample numbers is shown below.

Figure II

SECTION OF VARVES



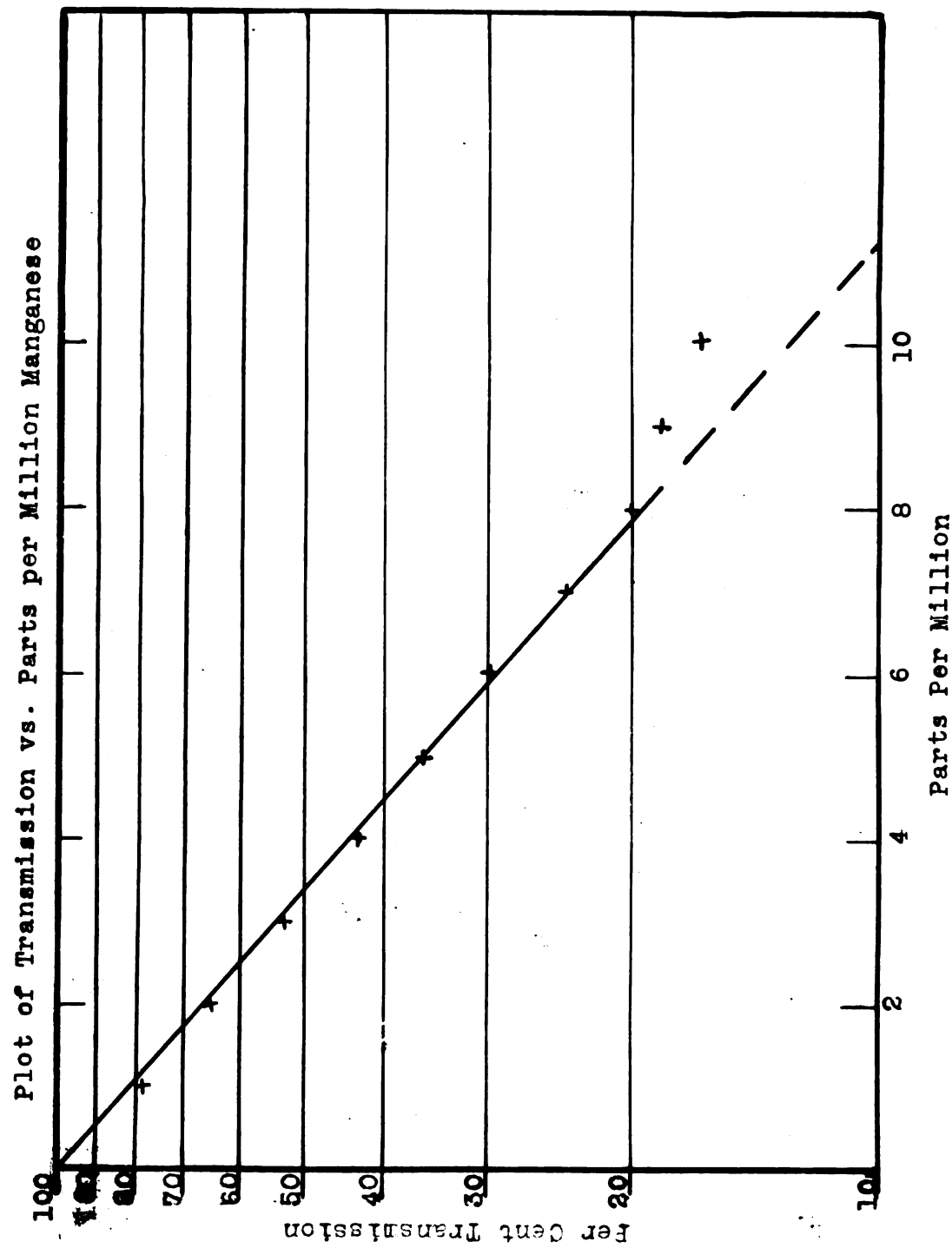
Clay layers 1, 2, and 3 were sampled at the eastern end of the trench, at the center of the trench, and at the western end. Enough of the clay layer was taken to fill a four hundred milliliter beaker. Care was taken to sample equally the blue and brown zones. The samples were then air dried and ground in an agate morter.

PROCEDURES AND RESULTS

Colorimetric Methods

A colorimetric method fundamentally consists of treating a solution of a substance with a reagent in such a way as to produce a color which is proportional in intensity to the amount of the substance in the solution. (Snell & Snell, vol. 1, 1948, p.1) According to the Lambert Beer Law, the amount of light which will be absorbed by a solution is directly proportional to the concentration of the absorbing molecules. This is expressed mathematically by the equation $\log \frac{I}{I_o} = a_s bc$ where I is the intensity of light transmitted by the sample and I_o is the intensity of light striking the sample. "a_s" is the absorbancy coefficient of the particular solute and depends upon the wavelength of light, the solvent, and the temperature. The thickness of sample through which the light passes is denoted by b and c is the concentration of the solute. The writer chose a wavelength which gave a maximum absorbancy coefficient for manganese, 525μ, and plotted the per cent transmission $\frac{I}{I_o}$ for a range of concentration from 1 to 10 ppm manganese. A blank containing all the reagents but no manganese was used to calibrate the colorimeter at 100 per cent transmission $\frac{I_o}{I_o}$. The resultant plot (fig. II) is a straight line on semi-log paper and therefore agrees very well with the Lambert Beer Law. In determining the amount of

Figure III


Plot of Transmission vs. Parts per Million Manganese
Per Cent Transmission
100
70
60
50
40
30
20
10
2
4
6
8
10
Parts Per Million

exchangeable and total manganese present in the samples sufficient solvent was used to bring the parts per million within the range of the standards. The method used to develop the color is that given in Snell and Snell (1948, vol. II, p.394). It was modified because the concentration of sulphuric acid used caused precipitation of calcium sulfates which clouded the solution. Calcium sulfate is soluble in dilute sulphuric acid but insoluble in concentrated. When the amount of sulphuric acid was cut from 2 ml to 1 ml the precipitate disappeared.

In all cases duplicated samples were run and if they varied by more than 1 per cent transmission were redone. Best results were obtained when an additional half gram of potassium periodate was added after color development began.

Total Manganese

The procedure for the analysis of total manganese is essentially that given in Snell and Snell (vol. II, 1948, p.383) for soils. Periodate was used for color development rather than the per sulfate method as recommended. Two hundred milliliters of solvent were used in developing the color.

Samples M_1, M_2, M_3, W_3, and E_3 were analyzed to determine the variability between varves and that within varves. The results are shown on the following page.

Sample No.	To Trans.	ppm in Solution	Sample Size 1 Gram ppm in Sample
M1	64	2.1	420
M2	65	2.2	440
M3	64	2.1	420
W3	64	2.1	420
E3	65	2.2	440

Within the limits of accuracy of the method there are no discernable differences in total manganese between or within the varves.

Exchangeable Manganese, Resin Method

For determination of the exchangeable cation content it was decided that a new method utilizing exchange resins would be investigated. A letter of inquiry was sent to the Rohm and Haas Company, Resinous Products Division, regarding the use of their research grade cation exchange resin, amberlite IR 120. They expressed an interest in the project and sent a complimentary pound of the resin.

IR 120 cation exchange resin is an artificial organic compound with high exchange capacity. It is composed of sulfionic acid groups which have at their surfaces large numbers of exchange sites. These exchange positions can be filled by any cation. However, preference is shown for ions of larger ionic size and or higher valence. If cations of lower valence and or smaller ionic size are present in sufficient concentration they will replace the

other cations. This same type of reaction occurs in anion exchange resins except that the exchange sites have positive instead of negative charges. These characteristics make exchange resins extremely useful both in industry and in research.

Resins are generally charged with small, low valence ions. When solutions containing ions of higher charge or larger size are passed through them they pick up these ions in exchange for the low valence ions with which they are saturated. The ions adsorbed in this manner can be recovered by flushing the resin with a high concentration of the charging ions. This is known as stripping or eluting. The greater the affinity of the resin for the adsorbed ion the higher will need be the concentration of stripping ions to displace it. Normally hard to separate substances, the rare earths for example, can be separated by placing them on the resin and very carefully adjusting the concentration of the elutant.

For the determination of exchangeable manganese, it was necessary to know what concentration of elutant, in this case HCl, would be required to completely remove the manganese from the resin. Known amounts of manganese were placed on the resin and then were stripped off by various strength elutants. It was found that about 10 milliequivalents of HCl per milliliter of resin at a concentration of 30 per cent were necessary to completely remove the manganese.

Tests were run to determine the length of time required to place a given amount of manganese on the resin. Four parts per million manganese in 50 ml water were shaken with four 50 ml portions of resin for 10, 20, 30, and 40 minutes. In all four there was complete absorption of the manganese.

For most exchange work the resin is placed in a glass column and the ion bearing solutions are passed through it. The solutions can then be followed by the elutant. To approximate these conditions, three grams of clay were shaken with a liter of water. This suspension was allowed to pass through a column of resin, however, the resin very effectively screened out the clay. It was feared that to effectively disperse the clay would upset the manganese equilibrium thereby giving erroneous results so this method was abandoned.

The next attempt was to mix the clay and the resin directly in a small volume of water. A gram of sample E₂ was added to 25 ml of resin in 100 ml of water. The mixture was shaken for an hour. After the first few shakes the cork was blown from the flask. The identity of the gas being evolved was established as CO_2. A possible explaination would be that exchange released a sufficient quantity of hydronium ions to cause breakdown of the carbonates. After shaking, the clay was rinsed from the resin by repeated decantations with distilled

water. Fifty milliliters of 30 per cent HCl was added and shaken with the resin for half an hour. This was poured off and another 50 ml was added and shaken as before. The process was repeated a third time. The first, second, and third decantations were analyzed separately and the following amounts of manganese were determined:

		1 gm resin 100 ml solvent
first stripping	61% trans.	2.4 ppm
second stripping	89% trans.	0.6 ppm
third stripping	97% trans.	0.1 ppm
	Total	3.1 ppm

From these results it was decided that this would be the procedure followed.

Another test was made to observe the effect of pH on exchangeable manganese. Four two gram samples of W1 were treated with .1 normal HCl to give PH's of 7, 5, 3, and 1. A fifth sample was left at the pH of the soil, 8.7. The samples were treated as before with the exception that the three strippings were boiled to dryness together.

pH	Per Cent Trans.	ppm
8.7	44	4.0
7.0	43	4.1
5.0	43	4.1
3.0	42	4.2
1.0	41	4.3

It was felt that a determination made at the soil pH would be most characteristic since pH varies between soils.

The amounts of exchangeable manganese in the varved samples as determined by the resin method are shown below:

Table II

Sample No.	Per Cent Trans.	1 gm clay ppm in sol.	100 ml solvent ppm in clay
E1	61	2.4	240
E2	56	2.8	280
E3	52	3.2	320
M1	57	2.7	270
M2	57	2.7	270
M3	50	3.4	340
W1	60	2.5	250
W2	56	2.8	280
W3	53	3.1	310

It can be seen from the results that variation in the amount of exchangeable manganese within a single varve is nearly of the same magnitude as the variation between varves. This could be due either to inadequacies in the method or to variables such as percentage of clay and type of clay which affect the exchange capacity.

Exchangeable Manganese, Ammonium Acetate Method

An attempt was made to check the effectiveness of the resin method by comparing the results with those obtained by a commonly used method. Saturating the clay with a high concentration of cations such as ammonium or barium will exchange off the cations absorbed on the clay. The amounts of these can then be determined in the leachate. A procedure involving the use of ammonium acetate is given by Schollenberger and Simon (1945). The samples were shaken in 250 ml of neutral 1 normal ammonium acetate for two hours. The leachate was then filtered off in a Buchner funnel and three additional 25 ml portions of ammonium acetate were passed through the clay cake. The acetate was boiled off and the residue analyzed as before.

Table III

Samples No.	Per Cent Trans.	ppm Soln.	ppm in Clay
E1	57	2.8	22.4
E2	45	3.9	31.2
E3	46	3.8	30.4
M1	45	3.9	31.2
M2	43	4.1	32.8
M3	43	4.1	32.8
W1	57	2.8	22.4
W2	46	3.8	30.4
W3	39	4.6	36.8

The amount of manganese exchanged by this method is less than with the resin by a factor of ten. However, the relative amounts are similar. It would appear that the resin method gives results at least as valid as these.

Exchange Capacity

The possibility that the variability was due to exchange capacity was also investigated. The ammonium saturated clay from the preceeding experiment was rinsed free of excess ammonia with ethyl alcohol. The absorbed ammonium ions were then forced from the exchange sites by leaching with 10 per cent NaCl. The exchange capacity was determined by Kjeldahl distillation of the ammonia and titration with .1 normal HCl. The method is given by Schollenberger and Simon in the reference sited above with the exception that Kjeldahl distillation was used in place of Nesslerization.

Exchange Capacity Expressed as Mec/100g.

E1 8.08	M1 7.03	W1 6.85
E2 5.36	M2 5.93	W2 5.03
E3 9.06	M3 8.18	W3 8.35

There are definite differences in the exchange capacity as given by this method but they do not seem to correlate with the exchangeable manganese. To pursue this line further it was decided that a mechanical and mineralogical analysis of the clay was indicated.

Mechanical Analysis

The procedure for mechanical analysis is essentially that given by Krumbein and Pettijohn (1938, p.152). Tenth normal sodium hydroxide was used as a dispersing agent and the settling cylinders were thermostated in a bath at 25°C. An interesting refinement was a jig which allowed the pipette to be held in place laterally over the cylinder and then lowered smoothly into the suspension an exact measured distance.

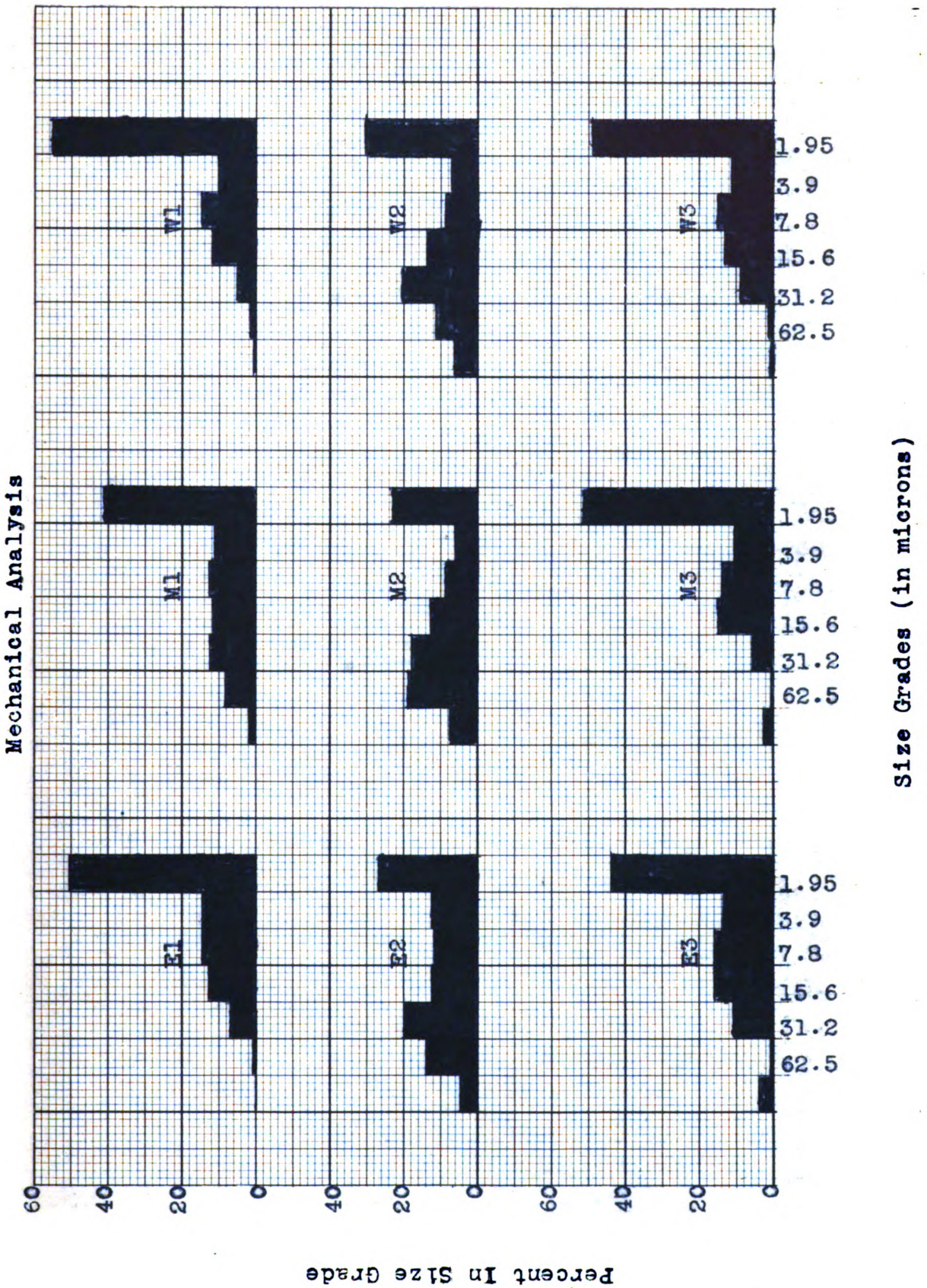
The results of the mechanical analysis are shown numerically in table IV and graphically in figure IV. The amount of clay present in each layer is seen to be fairly consistent within the layer but does not correlate with the amount of exchangeable manganese as determined by either method.

Table IV

PARTICLE SIZE DISTRIBUTION OF SAMPLES
(SIZE IN MICRONS)

Sample Number	62.5	62.5 -31.2	31.2 -15.6	15.6 -7.8	7.8 -3.9	3.9 -1.95	1.95
E1	0.3%	0.8%	3.7%	12.4%	14.8%	14.6%	50.5%
E2	4.7%	14.2%	20.0%	12.4%	11.7%	12.4%	26.8%
E3	3.4%	0.2%	10.0%	15.4%	15.0%	12.8%	43.8%
M1	1.8%	8.6%	12.8%	12.0%	12.4%	10.8%	41.6%
M2	8.0%	19.5%	18.9%	13.3%	8.9%	7.5%	23.9%
M3	2.1%	0.5%	5.3%	14.6%	13.1%	12.0%	51.8%
W1	0.2%	1.6%	4.9%	12.0%	15.1%	10.2%	56.1%
W2	6.5%	10.7%	21.6%	13.8%	9.3%	7.5%	30.6%
W3	0.2%	1.2%	9.2%	12.8%	15.0%	11.6%	50.0%

Figure IV


Mechanical Analysis
W1
W2
W3
M1
M2
M3
E1
E2
E3
1.95
3.9
7.8
15.6
31.2
62.5
Size Grades (in microns)
60
40
20
0
Percent In Size Grade

X-RAY ANALYSIS

The use of X-rays has gained much popularity as a means of determining clay mineralogy. It is quite a reliable method and procedures are easy. A short explanation will suffice for an understanding of the results.

Procedure

The clay fraction was separated from the silt by repeated decantation. A measured portion of the suspension was evaporated to dryness and the residue weighed to determine the concentration of clay. Next a plaster block about an inch square and an eighth of an inch thick was placed over a suction flask. Enough suspension was sucked through the block to plate out about 30 milligrams of clay. Twelve milliliters of three per cent glycerol solution were then passed through the block in three portions. After air drying the block was X-rayed. A similar amount of 0.1 normal KCl solution was passed through the block. The block was heated in an oven at 110°C for two hours and X-rayed again. The block was then heated to 500°C for two hours and X-rayed a third time. The three X-ray tracings were studied to determine the mineralogy.

Theory

Reflection of X-rays by clay minerals is governed by the inter-layer distances (d), the angle of reflection (2θ), and the wavelength of the rays (λ), according to

Bragg's equation $n\lambda = 2d \sin \theta$. By observing the angle 2θ at which maximum reflection occurs, and referring to a table (Parrish and Irwin, 1933) using the proper wavelength, interlayer spacing can be read directly.

Interpretation of Results

As noted before montmorillonite and vermiculite are three layer minerals with expanding lattices. Treatment with glycerol will insert two layers of this material between each set of three layers of montmorillonite. This will expand the montmorillonite so that the distance from the top layer of the set to the top layer of the next including the glycerol layers set will be 17.7 angstroms. If a peak occurs at this distance it is an indication of montmorillonite. Vermiculite will allow only one layer of glycerol and will show a peak at 14.3 angstroms interlayer distance. Mica (usually illite) and kaolinite will not be affected by this treatment. Their peaks occur at 10A° and 7A° respectively.

Treating with potassium and heating to 110°C drives out the interlayer glycerol from montmorillonite and vermiculite and collapses the distance to 10 angstroms. If this collapse is noted it is further indication of the presence of these minerals. If a peak remains at 14.3 angstrom it shows the presence of chlorite which has the same interlayer distance as vermiculite but is not collapsable.

Heating to 500°C breaks down the exposed hydroxyl layer of kaolin and the disappearance of this peak is an indication of the mineral. Below 7A° the peaks are higher orders of the ones outlined above with the exception of a peak due to quartz at 3.3A°.

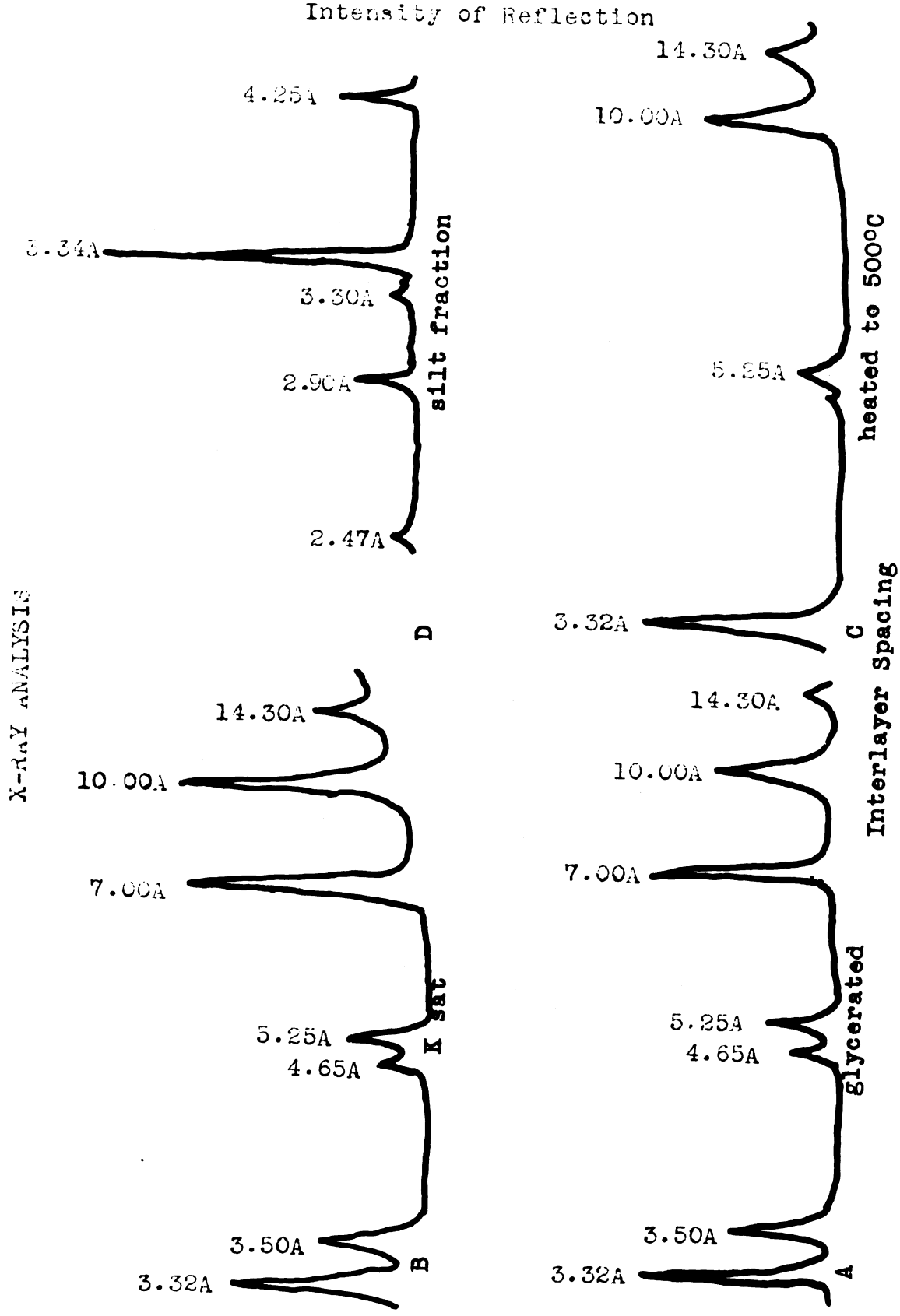
Results

Analyses were run on the clay and silt fractions of samples M_1, M_2, M_3, W_3, and E_3 to determine if there were correlative differences. There were no differences in the results so only those of one sample (M_1) will be shown here. The clay peaks which occur in figure V are listed below with their possible significance.

14A°	Chlorite Vermiculite
7A°	Kaolin 2nd order of 14A°
5A°	2nd order of 10A°
4.65	3rd order of 14A°
3.5	2nd order of 7A°
3.3	3rd order of 10A° quartz

There is not enough of a peak at 17.7A° to show the presence of montmorillonite. The peak at 14A° does not disappear upon heating and therefore is due to chlorite not vermiculite. The peak at 10A disappears upon heating

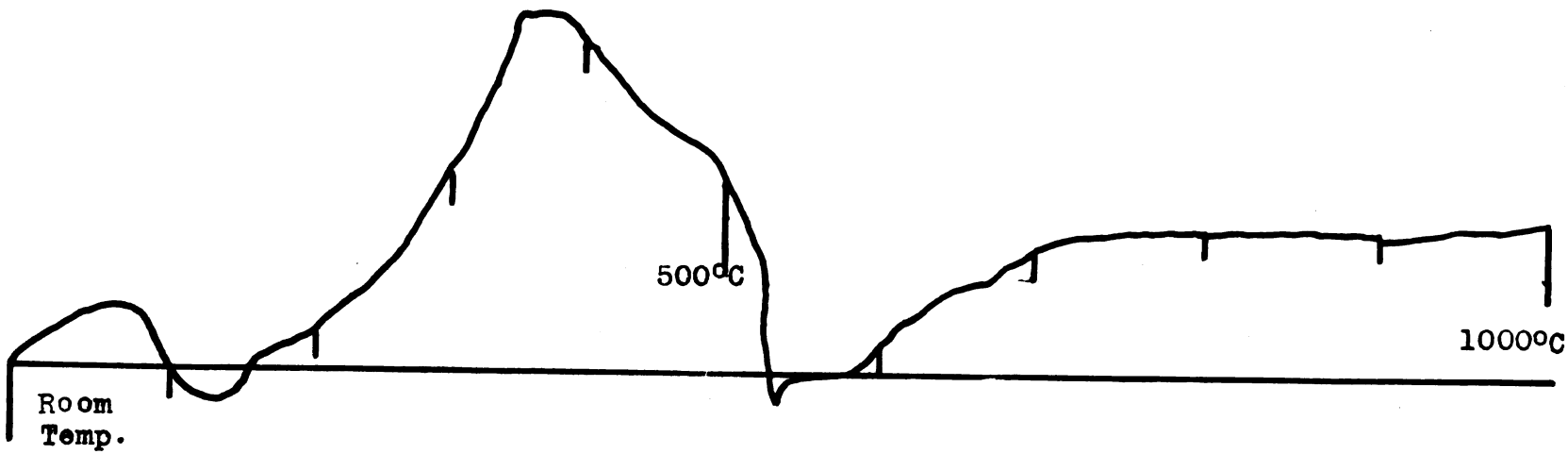
Figure V


Intensity of Reflection
X-RAY ANALYSIS
Interlayer Spacing
A
glycerated
3.50A
3.32A
5.25A
4.65A
B
K sat
14.30A
10.00A
7.00A
3.50A
3.32A
C
heated to 500°C
14.30A
10.00A
5.25A
3.32A
D
silt fraction
4.25A
3.34A
3.30A
2.90A
2.47A

to 500° proving mica (probably illite). The peak at 7°A indicates kaolin but this will have to be confirmed by a differential thermal analysis. Therefore, on the basis of the X-ray tracings the clay can be supposed to be a mixture of chlorite, illite, and kaolinite.

Figure shows an X-ray tracing of the silt fraction of sample M1. The minerals responsible for the peaks are tentatively identified as (4.25A) quartz and feldspars, (3.34A) quartz (3.25A and 3.20A) feldspars, (2.90A) dolomite, (2.47A) quartz. (ASTM, 1952) Calcite occurs in the silt fraction but in this sample has been destroyed by acid treatment.

A differential thermal analysis wave for sample M_1 is shown in figure VI. At 150° the volatilization of the adsorbed water caused an endothermic reaction. The combustion of organic matter is responsible for the exothermic peak at 350°C. The small peak at 550°C is due to the conversion of the standard. At 570°C the water of the kaolin octahedral layer is driven off giving rise to an endothermic peak. This supports the X-ray data and proves the presence of kaolinite.



DIFFERENTIAL THERMAL ANALYSIS

ADDITIONAL ANALYSIS

Because of the lack of differences in total manganese between varves, it was decided to run total and exchangeable manganese on samples from more widely separated locations to see if measureable differences actually did occur. Samples from undifferentiated glacial lake clays from Detroit, Michigan, Rudyard, Michigan, and from the Fort Union clay of western North Dakota were analyzed. The following results were obtained:

	Total ppm	Exchangeable ppm	Residual ppm
Detroit	640	330	310
Rudyard	560	280	280
Fort Union	2500	1700	640

It can be seen that entirely different source areas may yield different values.

DISCUSSION OF RESULTS AND CONCLUSIONS

The idea initiating this work on trace element correlation in clays was that non-exchangeable ionic content in a clay sediment would serve as a correlatable value. The results fail to bear this out. Manganese was chosen as the element to be analyzed and which total manganese remained essentially constant for the three varves in the glacial lake clay which was studied, exchangeable manganese increased generally downward and was not completely correlative within the same varve. This trend is anomalous with clay content and exchange capacity. The fact that the governing exchange capacity seem to exert little effect on the amount of manganese picked up by the resin absorption method of analysis leads the writer to believe that manganese oxides in the silt fraction of the clay contribute a larger amount of manganese than does the clay fraction. This idea is borne out by the fact that varying the pH from 6.7 to 1 produced only slight increases in exchangeable manganese. The increase in "exchangeable" manganese downward may possibly be explained by increasingly reducing conditions with depth.

Non-exchangeable cation content, while not shown here to be effective may yet, by further research, prove to be of value. The results from different areas proves that total and exchangeable manganese does vary in clays.

For further work, the writer suggests that clay samples be dispersed by shaking in dilute ammonium hydroxide. The ammonia would fill the exchange sites thereby allowing the separation of the clay fraction free from exchange effects. Total analysis of a clay thus prepared should give the residual content of the ion analyzed without the masking effect of contributions from the silt fraction.

BIBLIOGRAPHY

1. American Society for Testing Materials (1954) Cumulative Alphabetical and Grouped Numerical Index of X-Ray Diffraction Data.

2. Bergquist, S. G., (1950) "An Unusual Occurrence of Varved Deposits in Southwestern Michigan", Papers of the Michigan Academy of Science, Arts, and Letters Proceedings, University of Michigan Press, Ann Arbor.

3. Flint, R. F., (1947), Glacial Geology and the Pleistocene Epoch. John Wiley and Sons, Inc., New York.

4. Fujimoto, C. K., and Sherman, L. G., (1948) "Behavior of Manganese in the Soil", Soil Science, Williams and Wilkins Company, Baltimore.

5. Goldschmidt, V. M., (1954) Geochemistry, Oxford University Press, London.

6. Grim, R. E., (1953) Clay Mineralogy, McGraw-Hill Book Co., Inc., New York.

7. Krumbein, W. C., and Pettijohn, F. J., (1938) Manual of Sedimentary Petrography, Appleton-Century-Crofts, Inc., New York.

8. Parrish, W., and Irwin, E. W.,(1953) Data for X-ray Analysis, Vol., 1, Charts for Solution of Bragge's Equation (λ versus θ and 2θ), Phillip's Laboratories, Inc., New York.

9. Rankama, K., and Sahama, Th. G., (1950) Geochemistry, University of Chicago Press, Chicago

10. Sandell, E. B., (1944) Colorimetric Determination of Trace Metals, Interscience Publishers, Inc., New York

11. Schollenberger, C. J., and Simon, R. H., (1945) "Exchange Capacity and Exchangeable Bases, Ammonium Acetate Method", Soil Science, Williams and Wilkins Company, Baltimore.

12. Snell, F. D., and Snell, C. T., (1943) Colorimetric Methods of Analysis, Vol. I, D. Van Norstrand Co., Inc., New York

_____,(1954) Colorimetric Methods of Analysis, Vol. II, D. Van Norstrand Co.,Inc. New York

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