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VARIATIONS IN CLAY MINERALOGY ACROSS FACIES BOUNDARIES IN THE MIDDLE DEVONIAN (LUDLOWVILLE) NEW YORK

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ABSTRACT. A series of essentially time-equivalent shales and sandstones from the Middle Devonian Hamilton Group in New York State was traced and collected from those representing the offshore marine environment through the nearshore and brackish water deposits into the nonmarine red bed facies to the east. The samples were studied by means of X-ray diffraction, X-ray fluorescence, and electron microscopy. The results of these analyses were treated statistically for reproducibility and significance of trend. The data indicate that the clay mineralogy of the shales and sandstones consists of dominant illite and subordinate chlorite. The chlorite is more susceptible to diagenetic change than is the illite. In the transition from the nonmarine to the marine environment, the evidence indicates that detrital chlorite is being supplemented by a diagenetic chlorite that seems to form more readily in the shales than in their associated sandstones. Subtle lateral variations in the clay mineralogy are discussed. Both illite and chlorite show a decrease in c-axis and an increase in a-b axis dimensions with distance from the source. Total iron content decreases with distance.

INTRODUCTION

In this study the principal objective has been to investigate the effects of environment on the clay mineralogy of ancient sediments. In many earlier investigations the interpretation of the data was complicated by the influence of a large number of unknown or poorly defined variables. Frequently, for example, several different source areas of differing physical characteristics have confused the paleoenvironmental picture to the extent that it has been difficult to isolate their effects on the resultant mineralogy.

In an effort to reduce to a minimum the effects of variables, a portion of the Middle Devonian sequence in New York State was selected for study. Here the structural geology is simple and the stratigraphy is well defined. The physical characteristics of the source area such as geographic location, composition, topography, and climate have been carefully worked out. Both marine and nonmarine depositional environments are present, and the paleoecological characteristics of their included faunas and floras have been investigated.

PREVIOUS WORK

From a stratigraphic and paleontologic point of view the Hamilton Group in New York is one of the best known sequences in the Devonian of the United States. The early work was accomplished through the efforts of many investigators, the most important of whom were Hall, Vanuxem, Grabau, Cleland, and Prosser (see Cooper, 1930). However, not until the re-examination of the area by Cooper in the 1930's was the stratigraphy clearly defined and the many misconceptions regarding the facies relationships cleared up. More recently, Cooper (1957) has also discussed the paleoecology of these rocks.

With Cooper's redefinitions as a guide, later workers have confined themselves, for the most part, to investigations of the paleontology. Aside from gross generalities, and the work of Mencher (1939) on the Catskill red beds, the petrography of the sediments is not well known.

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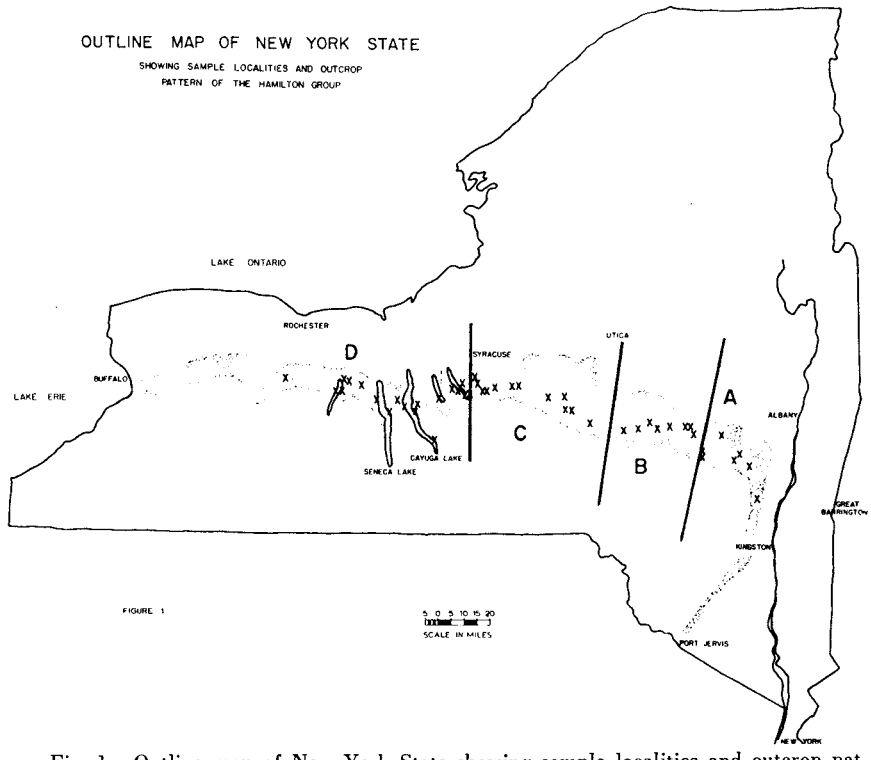

Fig. 1. Outline map of New York State showing sample localities and outcrop pattern of the Hamilton Group.

GENERAL GEOLOGIC RELATIONS

Structure

The outcrop pattern and the structural relationships of the Middle Devonian Hamilton Group as a whole are remarkably simple. The rocks form an outcrop pattern, figure 1, that extends east and west across the state of New York between Buffalo and Albany. According to Cooper (1930), the regional dip is to the southwest increasing from about 50 feet per mile in the Onondaga Valley to about 100 feet per mile in the Unandilla Valley and to about 4 degrees in Schoharie Valley. Small faults are occasionally observed.

Stratigraphy

The Devonian Stratigraphy of New York State shows remarkable examples of facies relationships. Here is a classic example of regressive relations and the gradual encroachment of nonmarine sedimentation into a geosyncline. Coupled with the regression is the gradual decrease in clastic content and the thinning of the formations from east to west roughly perpendicular to the strandline. Several sedimentary environments may be delineated and can be traced in the field. Cooper (1957) subdivides the rocks and their included faunas environmentally into (1) fluvial-lagoonal-littoral, (2) epineritic, (3) infraneritic, and

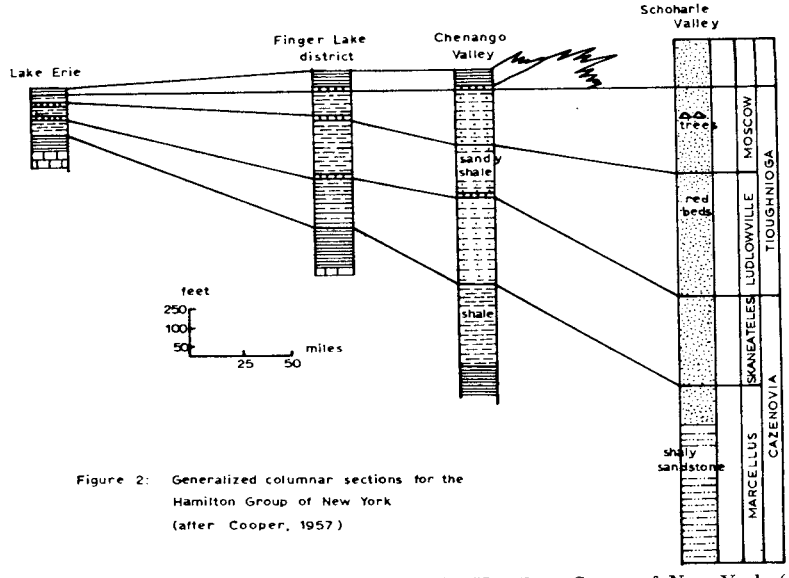

Fig. 2. Generalized columnar sections for the Hamilton Group of New York (after Cooper, 1957).

(4) epineritic biostromal. In the present study all of these environments are present except for the epineritic biostromal.

Figure 2 illustrates the generalized columnar relationships for the Middle Devonian. The present study is concerned only with the Ludlowville and its lateral equivalents to the east.

In the west-central part of New York the Ludlowville has been subdivided into several members—the King Ferry calcareous shale and limestone, the Ledyard calcareous shale, and the Centerfield limestone. In the Skaneateles Lake region a still finer subdivision has been accomplished with the Owasco, Spafford, Ivy Point, and Otisco shale members being recognized. Two coral horizons, the Joshua and Staghorn Point submembers, also have been defined. In central New York, the Ludlowville Formation has not been subdivided although it appears to be slightly coarser and more fossiliferous upwards. The dominant lithologies are dark siltstone and shale. Eastward, the Upper Panther Mountain sandstone is encountered, and finally the Middle Kiskatom red and green beds occur. Figure 3 shows these general relationships.

Capping most of the Ludlowville, and belonging to the Moscow Formation, is the Portland Point limestone. This thin shell breccia and crinoidal limestone is an exceptionally useful horizon marker and is unusual in that it cuts across facies, finally pinching out into the red bed sequence.

Source of Sediments

The source for all of the sediments in this study was a landmass of considerable relief located to the east and southeast of the geosynclinal margin. The seas themselves were shallow, probably seldom attaining any great depths (Cooper, 1957). The west and north edges of the geosyncline were apparently

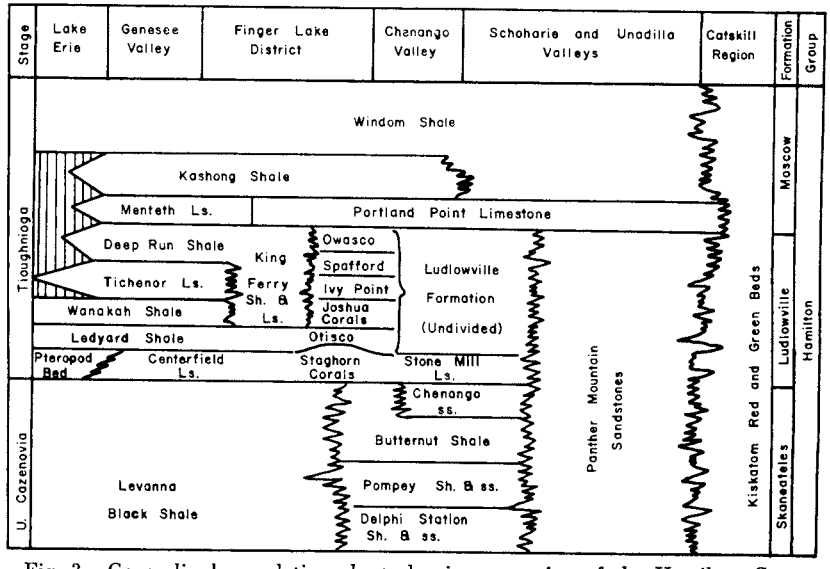

Fig. 3. Generalized correlation chart showing a portion of the Hamilton Group of New York (after Cooper and others, 1942).

low-lying landmasses contributing little or no important clastic materials. Apart from the fact that the percentage of arenaceous constituents decreases to the west, other evidence for the position of the source area can be obtained from directional sedimentary structures. Oliver (1951, p. 725) noted that occurrences of ripple marks in the sandstones under the Staghorn Point coral beds indicate that a current from the southeast prevailed. McIver (1960, p. 1926) concluded from a study of Upper Devonian paleocurrents that a linear source existed for several hundred miles along the present Atlantic coast and that "a very regular and persistent east-to-west current trend existed throughout this area during most of Late Devonian time".

The probable conditions within the source area itself, deduced from both petrographic and paleoecologic evidence, are of special interest inasmuch as the detrital minerals in the sediments are the result of the interactions of source area composition, weathering, and other variables. Mencher (1939) concluded that the source area lay nearby and was composed of metamorphic and sedimentary Paleozoic rocks of the Taconic range. Cooper (1957) believed that the plant cover was extensive and probably grew under warm and humid conditions.

SAMPLING PROCEDURES

The investigation was restricted to the Ludlowville formation of the Hamilton Group and its lateral equivalents. The lithologies were traced from the Honeoye Quadrangle south of Rochester, New York, eastward through the Finger Lakes District to the vicinity of Catskill, New York—a distance of 150 miles. This area was selected for study because it represents a transition from continental to marine deposits.

In the field, the widespread Portland Point limestone was used as a marker horizon below which samples were collected. Wherever possible the localities described by Cooper (1930, 1933, 1934) were visited and samples taken. Other localities were found by means of structural projection on topographic sheets and from outcrop patterns as shown on those quadrangles that have been mapped geologically.

As fresh a "grab" sample as possible was taken at each locality, and where shale and sandstone occurred together a sample of each was collected. The 45 localities are represented by 60 samples. Figure 1 shows the geographic distribution of these localities.

ANALYTICAL PROCEDURES

X-ray Diffraction

In the preparation of the samples for X-ray diffraction analysis, the shales and sandstones were crushed to pass a 62 micron (μ) sieve. Approximately 5 grams (10 in the case of sandstones) of the $<62\mu$ fraction was placed in 375 milliliters of distilled water and the pH adjusted to between 9.5 and 10 by the addition of ammonium hydroxide. A more complete disaggregation and dispersion was then obtained by ultrasonic treatment.

The sample was allowed to settle for the time sufficient to permit withdrawal of the $<2\mu$ fraction. Three separate withdrawals were made, combined, and concentrated by evaporation. The concentrate was sedimented on each of 5 glass microscope slides to form air-dried oriented aggregates.

In the case of 14 selected samples the $<1\mu$ and $<0.5\mu$ fractions were similarly prepared.

Nickel-filtered copper Kα radiation at 45 kv and 18 ma was used in the X-ray study.

The $<62\mu$ fraction of each sample was X-rayed as a random powder through 65° two theta (2θ) to determine the general clay mineral composition, the non-clay mineral composition, and to pick up certain nonbasal reflections of the clay minerals. The (060) reflection is of particular interest in differentiating dioctahedral and trioctahedral clay mineral species.

In the case of the oriented aggregates the $<2\mu$, $<1\mu$, and $<0.5\mu$ fractions were X-rayed through at least 30° two theta (2θ). As a check for reproducibility, a second slide of the $<2\mu$ fraction for each sample was X-rayed. In the latter instance all of the samples, selected at random, were rerun in a 48-hour period to minimize any effects that may have accrued from instrument variation.

Oriented aggregate slides of selected samples were heated to 450° C for one hour and another set of slides to 550° C for one hour. These slides were then immediately X-rayed.

At least one oriented aggregate slide for each sample was treated with ethylene glycol by allowing it to remain in a saturated atmosphere for 48 hours.

For reasons which will be discussed in a later section, selected reflections of many of the samples were rerun at various goniometer speeds and at different scalar-rate meter settings.

Electron Microscopy

Eleven selected shale samples were chosen for particle size analysis by means of electron microscopy. For each of these shales as fresh a chip as could be obtained was first washed and then placed in a test tube containing distilled water, to insure that all dust and loose particles would be removed. After 30 days the supernatant liquid was poured off and the chip again washed and placed in a clean test tube of distilled water. The 11 test tubes were then placed in an ultrasonic generator and simultaneously disaggregated. It was felt that grinding or other methods of disaggregation would tend to introduce a greater experimental bias into the particle size analysis. The ultrasonic generator, on the other hand, would provide as standard a method of disaggregation as could be obtained.

Phosphor bronze 200 mesh electron microscope grids were prepared after the method of Ribi, Brown, and Goode (1960) and coated with a substrate of 2 percent parlodion and distilled n-butyl acetate. The commonly employed "floating film" technique was used.

The dispersions obtained from ultrasonic disaggregation were diluted with distilled water until their optical densities compared with each other and with a standard dispersion of Dow polystyrene latex frequently used in electron microscopy. By means of a micropipette a drop of the clay dispersion was applied to each of two grids and allowed to dry.

The sample numbers were coded in an effort to remove operator bias and then examined in an RCA model EMU-3 electron microscope with 50 kv accelerating potential. Five random fields were photographed for each sample at an original magnification of 2300 X.

X-ray Fluorescence

Fourteen samples of both sandstones and shales from the several environments were selected for total iron analysis by means of X-ray fluorescence spectroscopy. Six grams of the $<62\mu$ powder for each sample were placed in a cylindrical mold, and 1.5 inch diameter disks were formed in an hydraulic press at 20,000 pounds per square inch.

Each disk was placed in the sample chamber of a Norelco X-ray fluorescence spectrometer fitted with an EDT crystal and flow proportional counter. Tugsten radiation at 50 kv and 45 ma was employed in an air atmosphere. The strongest peak for Fe^{++} and Fe^{+++} ($K\alpha$ at 25.20° 2θ) was counted for the time necessary to accumulate 128,000 counts. Each disk was run a total of five times. Iron was the only element investigated. A calibration curve was provided through the courtesy of R. L. Niemann of the Clay Mineralogy Laboratory of the University of Illinois.

Statistics

The data obtained experimentally were studied statistically to evaluate reproducibility and the significance of possible trends. The basic techniques used were (1) analysis of variance, and (2) linear regression and correlation. The procedures used are given in all standard statistics texts (for example, Steel and Torrie, 1960).

Analysis of variance, often referred to as the "F-test", permits an evaluation of scatter of data around means and comparison of two or more sets of data in an effort to determine whether or not they are representative of the same population. The null hypothesis that the samples analyzed represent the same population is accepted or rejected on the basis of the "F-test". The 95 percent confidence level is commonly used for the decision, inasmuch as the chance of false rejection is about equal to that of false acceptance. A 99 percent confidence level permits less chance of false rejection but greater chance of false acceptance (Volk, 1956). In this paper the 95 percent confidence level will be employed unless otherwise stated. The underlying assumptions in the analysis of variance are that the data are random samples from normal populations with statistically equal variances. The most serious source of error is the possibility of unequal variances. In all cases except for the electron microscope data (to be discussed later), the variances are homogeneous.

The geologic unit under investigation was divided into four groups A, B, C, and D. The A-group includes all the nonmarine and transitional rocks. B, C, and D are arbitrary geographical groupings (see fig. 1), which include all of the marine sediments. The analysis of variance was used to test for differences between:

(1) The two duplicate X-ray runs for illite-chlorite ratio, illite (001) sharpness, chlorite (002) sharpness, and total intensity values for 00L reflections of both illite and chlorite.

(2) The illite-chlorite ratio, and the (001) illite and (002) chlorite sharpness of sandstones and associated shales, and the same parameters for the $<2\mu$, $<1\mu$, $<0.5\mu$ samples.

(3) The duplicate runs for each sample of electron microscope particle size measurements.

(4) Groups A, B, C, and D for all the various X-ray parameters (see 1 above.

(5) The illite-chlorite ratios, and the (001) illite and (002) chlorite sharpness of marine sandstones and shales and nonmarine sandstones and shales.

In linear regression the investigator is able to fit statistically the "best" straight line through any given sets of paired data. In addition, the degree of association, or correlation, between the dependent (y) and independent (x) variables can be evaluated and tested for significance, although no cause and effect relationship is implied. The correlation coefficient is given by the symbol "r".

For this study the distance in miles from a more or less arbitrary source at Great Barrington, Massachusetts, was chosen as the independent variable against which all other parameters were tested. This location was selected to fall roughly in line with the east-southeast trend of the outcrop pattern in order to facilitate distance measurements. This does not imply that Great Barrington was the actual site of the source rocks. The slopes and correlation coefficients were calculated for the entire unit as a whole and for each of the A, B, C, D subdivisions. The significance of "r" values was tested using confidence belts presented by Steel and Torrie (1960).

All of the X-ray data were put on IBM punch cards and processed electronically with an IBM 407 tabulator and an IBM 604 computor. The programs for the analysis of variance and the regression and correlation were provided by the Statistical Services Laboratory of the University of Illinois. All other data were processed with a desk calculator.

ANALYSIS AND INTERPRETATION OF THE DATA

X-ray Fluorescence

The results of determinations of the iron content of the $<62\mu$ fraction show that there is a gradual decrease in total iron content with increasing distance from the source area. The percentage of total iron decreases from 9.6 percent in the case of a continental red shale to 4.5 percent in one of the dark marine shales. Also, there is a change in trend with the iron content increasing near the 140-mile region. Figure 4 shows these relationships plotted exponentially.

The gradual decrease in iron content with distance is considered due to a sorting process whereby individual particles of hematite, chemically reduced in the marine environment, became less and less common away from the source area. The increase in iron in the 140-mile region is due to the presence of pyrite or marcasite aggregates that occur associated with organic fragments. This region is the locality of the Joshua and Staghorn Point coral horizons.

Electron Microscopy

In an effort to evaluate particle size in the a-b axis direction, electron microscopy proved useful. From this technique it is possible in any given

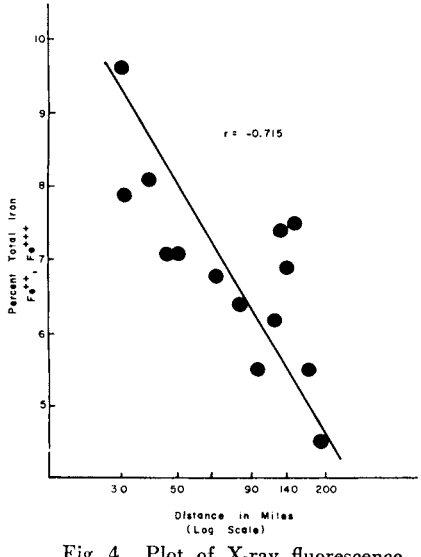

Fig. 4. Plot of X-ray fluorescence data showing percent total iron versus distance from source. r is correlation coefficient.

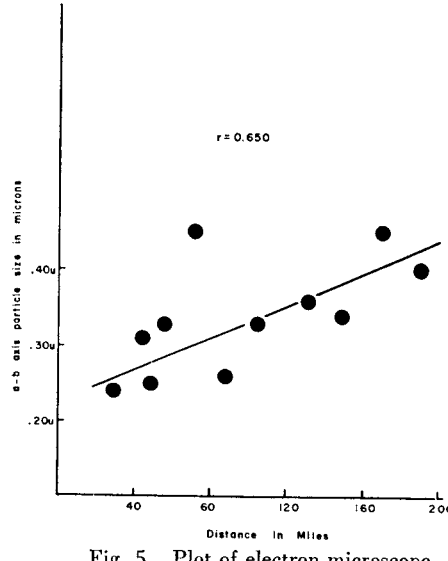

Fig. 5. Plot of electron microscope data showing a-b axis particle size versus distance from source. r is correlation coefficient.

sample to obtain a value for the mean absolute particle diameter and also some idea of particle size distribution. Unfortunately, however, the electron microscope does not distinguish between minerals, so that the values obtained are the result of chlorite plus illite.

A photographic plate containing five random fields taken at 2300 X for each sample was placed in an enlarger and magnified 8 times, so that the total magnification was 18,400 X. With the plate in the enlarger, each particle in the field of view was measured off as a line onto a piece of cross-section paper. Every particle was measured in the same direction, the assumption being that long-axis orientation was random. The validity of this procedure has been discussed by Orr and Dallavalle (1959). Each line, representing one particle, was then measured to the nearest millimeter and recorded.

The statistical handling of these data presented several problems. Because the particle size distribution was of the Poisson type (highly skewed) it was necessary, before employing the analysis of variance, to try to transform the data into a more normal distribution. A square root transformation of the general type $X = X+1$ was used. In spite of this transformation, however, the variances were still not quite homogeneous. This would slightly affect the confidence level. Nevertheless, the five treatments of each sample were analyzed for differences in mean values as a check for reproducibility. Steel and Torrie (1960, p. 129) have discussed the assumptions that underlie the analysis of variance and state:

> In the case of non-normality, the true level of significance is usually, but not always, greater than the apparent level. This results in rejection of the null hypothesis when it is true, more often than the probability level calls for; that is, too many nonexistent significant differences are claimed.

The results of the statistical treatment indicate that of the 11 samples studied only 4 of them showed a difference in means between duplicates. On the basis of the foregoing discussion it is probable that these differences within samples are somewhat more apparent than real.

The measurement of a-b particle diameter from electron micrographs leads to the seemingly anomalous conclusion that the average size of the clay flakes is increasing away from the source (fig. 5). Regression and correlation analysis indicates that the trend is significant. Powers (1954) observed a similar trend in the case of clay-sized particles of the Chesapeake Bay region, and Whitehouse, Jeffery, and Debbrecht (1959, p. 72) feel that " . . . any observations of increasing solid size with increasing distance from shore is a direct substantiation of active differential settling rather than a negation of such settling activity".

Another possible explanation concerns crystal overgrowths. It is conceivable in areas of slow accumulation that, with a clay flake as a "nucleus", growth in the a-b direction in the marine environment could take place through outward extensions of the tetrahedral and octahedral layers. Mechanisms of c-axis growth, on the other hand, are complicated, not well understood, and probably unlikely in normal diagenetic processes.

Qualitative Aspects of the Mineralogy

Random powder X-ray.—On the basis of the 00L reflections only two groups of clay minerals were identified, the illite (10Å) group and the chlorite (14Å) group. Because of the coincidence of the chlorite (002) and kaolinite (001) reflections at 7Å, the possible presence of the latter was also entertained until further tests could be made. In every sample the dioctahedral (060) peak at 1.50Å for illite was found, and in certain samples a trioctahedral (060) peak at 1.53Å for biotite and/or chlorite was observed. According to the method of Smith and Yoder (1956), the presence of both the 1M and 2M muscovite polymorphs was shown.

Oriented aggregate X-ray.—For a more detailed analysis of the flake-shaped clay minerals the sized oriented aggregate (OA) technique is useful. Here the basal reflections are greatly enhanced due to the preferred c-axis orientation's making more subtle variations in mineralogy easier to investigate.

The dry OA X-ray patterns indicated that the clay minerals are well crystallized and contain no random mixed-layer material. None of the OA slides treated with ethylene glycol showed any signs of expandable clay minerals.

Heating the slides to the region of 450°C for one hour produced little or no change in the illite reflections. Chlorite, on the other hand, experienced a decrease in intensity of all the basal reflections except 14Å (001), which was slightly increased. The samples heated to 550°C for one hour showed, in the case of illite, a decrease in 10Å (001) intensity and a marked increase in 3.33Å (003) intensity. No change occurred in the d-spacings. The chlorite 14Å (001) shifted to 13.8Å and increased in intensity. All other chlorite reflections were absent.

Figure 6 illustrates the X-ray diffractometer traces for a representative sample variously treated.

The detection of kaolinite by means of X-ray diffraction in a mixture of chlorite and kaolinite is a problem that has been given lengthy discussion in the literature. Bradley (1954), Grim and Johns (1954), and Warshaw, Rosenberg, and Roy (1960).

In the present instance the absence of kaolinite is indicated by the following:

(1) No peak was observed for kaolinite 2.37Å (003) at 37.5° 2θ.
(2) No peak for kaolinite 3.57Å (002) was resolvable from chlorite 3.54Å (004) even at a goniometer rate of $\frac{1}{8}$° per minute.
(3) The intensity of the 7Å peak relative to the other 00L chlorite reflections is of the right order of magnitude, i.e., it is not abnormally high, as might be expected were kaolinite present in significant amounts.
(4) Heating to 450°C indicated that if kaolinite is present, as shown by the small 7Å reflection that remains, it occurs in very small amounts.

Quantitative Aspects of the Mineralogy

General mineralogy.—Casual inspection of the X-ray patterns for all of the samples gives one the impression that there is little or no difference in the

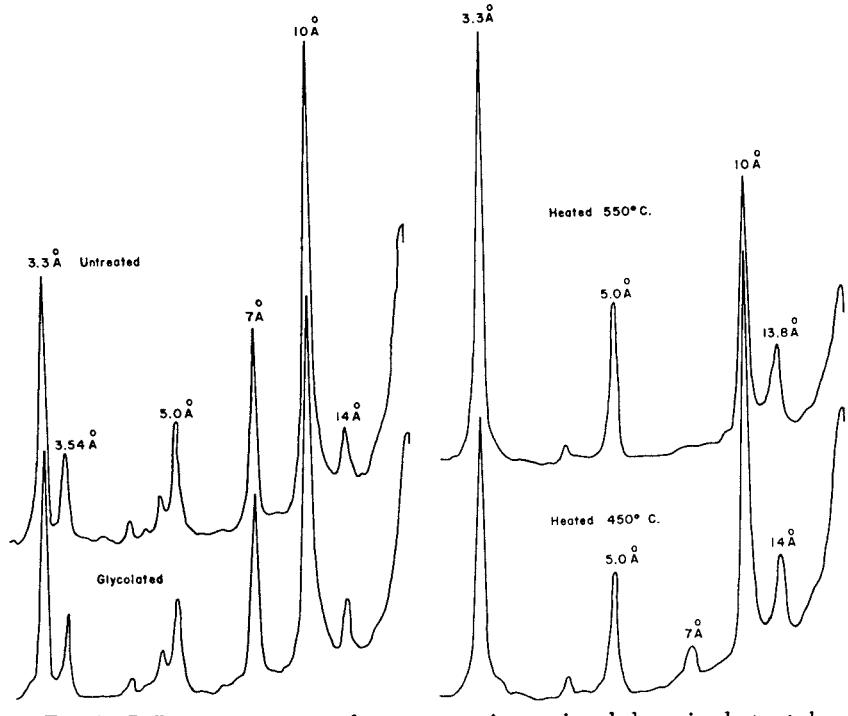

Fig. 6. Diffractometer traces of a representative marine shale variously treated.

clay mineralogy. An apparent uniformity is striking. It is only after a more detailed examination that trends and differences appear.

In the case of the nonclay mineral constituents, peaks for hematite were observed in those patterns of the red shales and sandstones. Quartz is ubiquitous, occurring in every sample, and calcite is prevalent in the shales from the more distant, offshore regions.

There is no significant difference in the clay constituents within the various size fractions ($<2\mu$, $<1\mu$, $<0.5\mu$) of any given sample. No change takes place in the illite-chlorite ratio or in the peak sharpness of these minerals. With the exception of quartz, the nonclay minerals are absent or undetectable in the $<1\mu$ and $<0.5\mu$ fractions.

Illite-chlorite ratio.—As has been pointed out by many authors, the quantitative estimation of the various clay minerals from X-ray diffraction patterns is, at best, an educated guess. This is particularly true for multicomponent mixtures in which poorly crystallized and mixed-layered materials are present. Fortunately, in the present study only two clay mineral groups are present, and both are well crystallized. For this reason the method involving peak height ratios was employed, but no attempt was made to place the quantities on a percentage or parts in ten basis.

The choice of which 00L reflections to use for determination of the ratios required considerable experimentation. Such experimentation was considered

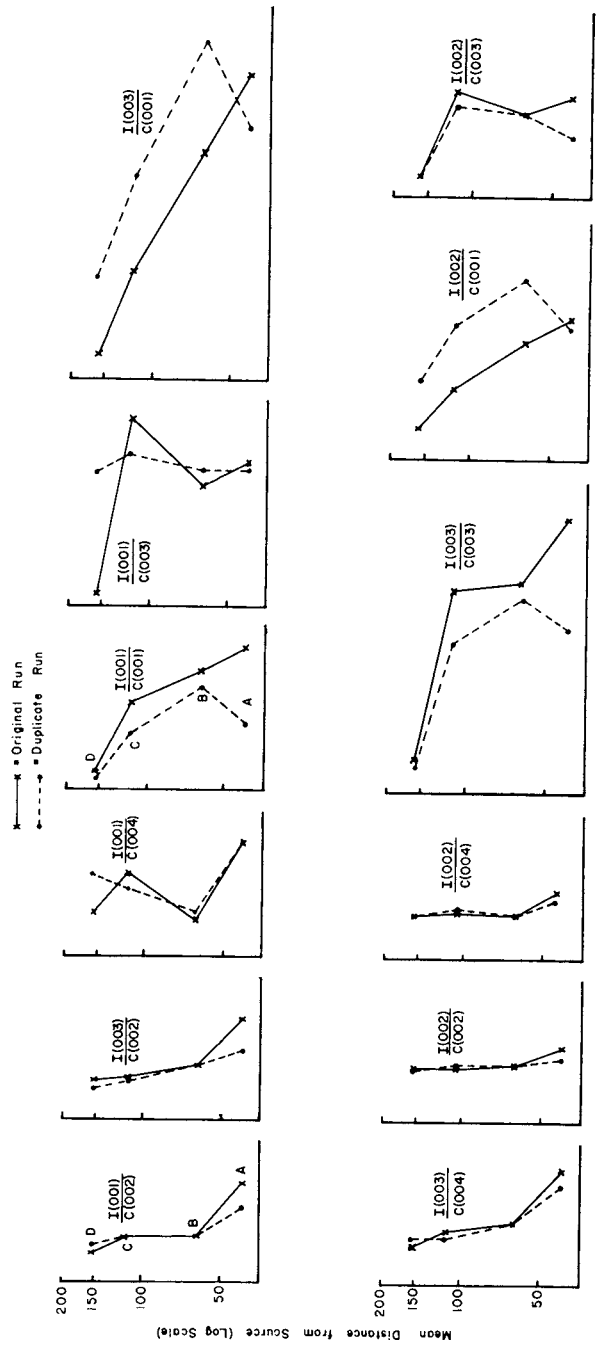

Fig. 7. Plots of illite-chlorite OOL ratio combinations versus distance from the source for comparison of original and duplicate runs.

feasible because the duplicate X-ray patterns that were run for each sample provided a basis for comparison. All combinations of illite (001), (002), and (003) with chlorite (001), (002), (003), and (004) were tried for each sample. In every case the total peak height was measured from background.

The average peak height ratio for each of the geographical subdivisions A, B, C, D was plotted against its mean straight line distance from the arbitrary source at Great Barrington, Massachusetts. The results of these data are shown in figure 7. It can be seen that the combination of any illite peak with that of chlorite (002) or (004) results in a definite trend and in mean values that are reproducible. The relative abundance of chlorite is increasing seaward. The ratio of illite (001) and chlorite (004) is an exception. On the other hand, the combination of any illite peak with chlorite (001) or (003) results in a set of mean values that vary widely.

Questions come to mind regarding the above ratios: (1) Why do the odd order chlorite reflections produce a ratio trend that is at variance with that shown by the even orders? (2) Why are the ratio values utilizing even order chlorite reflections reproducible, whereas those using the odd orders are not?

The answer to the first question is that in the case of the minerals of the chlorite group substitutions of magnesium for iron in the structure can produce marked changes in the relative intensities of the basal reflections. In particular, the intensities of (001) and (003) are strengthened by magnesium substitution to a greater degree than (002) and (004). Therefore, in comparing illite-chlorite ratios using odd order chlorite reflections, a decrease in the values may mean that a more magnesium-rich chlorite has been introduced rather than that the amount of chlorite itself has been increased.

With regard to the second question, in the present study the (001) and (003) chlorite peaks are without exception the weakest reflections present. All illite peaks are at least twice as strong. For this reason any small change in chlorite odd order intensity, whether due to cation population differences, to instrument error, to operator error in peak height measurement, or in background determination, will result in a large change in the illite-chlorite ratio. Equivalent small changes in the illite intensities, on the other hand, produce only small differences in the ratios. Table 1 serves to illustrate this point.

TABLE 1

Illite Intensity	Chlorite Intensity	Illite-Chlorite Ratio
50	5	10.0:1
50	6	8.3:1
50	7	7.1:1
51	5	10.2:1
52	5	10.4:1

According to the analysis of variance, the (001) chlorite peak intensities are the only ones that are not reproducible. All other intensity values for both illite and chlorite show no significant difference in their means for the duplicate X-ray runs at the 99 percent confidence level.

With these features in mind, the most intense reflections for illite and chlorite were used in this study to estimate the relative amounts of clay mineral groups present in each sample. The numerical value was obtained by dividing the peak height for illite (001) by that of chlorite (002).

From a statistical point of view, and according to the analysis of variance, there is no significant difference between the mean values of the illite-chlorite ratios for the two X-ray runs in any of the geographic subdivisions or for the entire group of samples. In other words, the I(001)-C(002) ratio is statistically reproducible everywhere.

The mean illite-chlorite ratio decreases significantly in the transition from the nonmarine (A) to the marine environment (B, C, D). More chlorite is present in the marine environment. Figure 8a shows a plot of I/C ratio versus distance for all of the samples. Linear regression and correlation studies show that no important changes take place with distance for the marine samples in subdivisions B and D or within the nonmarine division A. In the case of area C, however, a reproducible negative correlation exists, i.e., the I/C ratio decreases with an increase in distance.

A decrease in illite-chlorite ratio implies that the amount of chlorite has increased or the amount of illite has decreased. In the present instance it is believed that the detrital chlorite has been "regraded" in the more saline marine environment, whereas illite experienced little change. A diagenetic chlorite may also have been formed from biotite and/or vermiculite. Evidence for these statements will be given later.

The increase in the amount of chlorite with distance in subdivision C, as compared to B and D, may be due to a diagenetic response to the more calcareous environment that starts to become prominent there. Another possibility is that the iron content, increasing in the same region, may be acting as a catalyst to the brucite layer magnesium adsorption reaction as suggested by Powers (1957, p. 369). He states that: "The possibility must be considered that iron may be essential, in some yet unknown way, to the formation of diagenetic chlorite".

Peak sharpness.—The observed variations in sharpness of X-ray diffractometer peaks have long been used to estimate particle (crystallite) size and/or crystallinity in all types of materials. As a generality, a decrease in particle size is usually associated with a concomitant decrease in crystallinity. However, crystallinity, in layer silicates, is more accurately defined in terms of asymmetrical changes. Symmetrical broadening may be attributed to changes in crystallite size. The distinction between their overlapping effects is difficult to make.

Measurement of the sharpness of 00L reflections provides information concerning structural defects and mean particle size of crystallites in the c-axis direction only. Changes in the a-b directions must be evaluated from examination of hk0 sharpening.

In the case of the clay minerals under consideration here, a purely qualitative evaluation of good crystallinity is manisfested by sharp, symmetrical 00L reflections for both illite and chlorite (fig. 6). A quantitative estimation of particle size (c-axis) was attempted utilizing a modification of a scheme

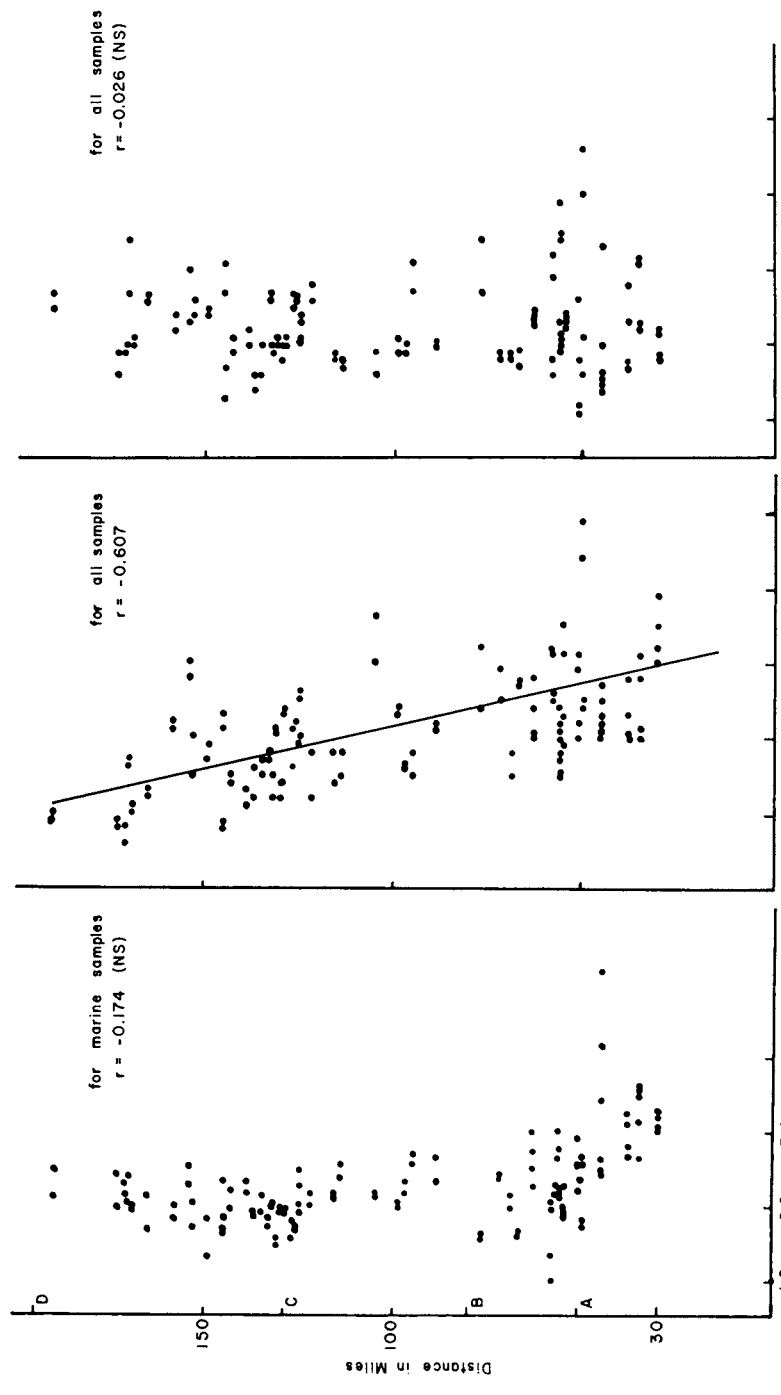

Fig. 8. (a) Plot of all illite-chlorite ratio values versus distance from the source. (b) Plot of all illite 001 peak sharpness values distance from the source. (c) Plot of all chlorite 002 peak sharpness values versus distance from the source. r is correlation coefficient.

described by Weaver (1960). The procedure employed consisted of first measuring the maximum peak height from background. Next the peak height was measured from a point 0.5° 2θ on the low-angle side, and a ratio made between the two values. A higher ratio is indicative of a larger particle size. No measurement of absolute particle size was made.

Sharpness values were thus obtained for all the oriented aggregate slides of the $<2\mu$, $<1\mu$, $<0.5\mu$ size fraction. The (001) and (002) peaks were used for illite and chlorite respectively.

At a goniometer rate of 2° per minute and a scalar-rate meter setting of 16-1-4, the (001) peak for illite is sufficiently broad and intense for accurate, reproducible measurements. However, it was necessary in the case of chlorite to rerun all of the samples at a goniometer rate of 1° per minute and at a more sensitive scalar-rate meter setting of 8-1-4 in order to obtain accurate values. For this reason the chlorite values were not directly comparable with those for illite.

The mean sharpness ratios for both illite and chlorite are completely reproducible at the 95 percent confidence level as shown by the analysis of variance.

An attempt at evaluating changes of particle size in the a-b crystallographic direction by means of hk0 broadening was unsuccessful. No hk0 peak of sufficient intensity could be found in random powder patterns that (1) was not overlapped by reflections from other minerals or (2) was not an unresolvable doublet.

Illite (001) sharpness.—As shown in figure 8b, there is a steady decrease in mean illite peak sharpness value with increasing distance from the source for all samples. That is, the 001 peak gradually broadens with increasing distance from the source. No abrupt break is evident in the change from nonmarine to marine conditions, and environment appears to exert little control on the sharpness of the illite peaks. Statistically, the negative correlation of illite peak sharpness with distance is significant and completely reproducible.

The decrease in peak sharpness is considered due to a decrease in c-axis particle size as discussed earlier. If this be true, then it is reasonable to assume that the average illite flake is becoming thinner with increasing distance from the source. Furthermore, since no break in the curve takes place at the strandline, the cleaving of the mica "books" is probably independent of the transporting medium as long as agitation takes place. In combination with the electron microscope particle size data, the conclusion may be drawn that the average clay flake becomes thinner but broader with increasing distance from shore.

Chlorite (002) sharpness.—In the case of chlorite a remarkable uniformity in peak sharpness exists. As shown in figure 8c, there are no apparent changes either with environment or with distance. The most reasonable explanation involves diagenetic processes. If it is postulated that the detrital chlorite flakes become thinner with transport as in the case of illite, then the lack of a change in sharpness must be due to the increasing influence of diagenetic chlorite. Although the parent material cannot be definitely established, this diagenetic chlorite is probably derived from biotite and vermiculite and becomes increasingly common seaward. The process of decreasing thickness of

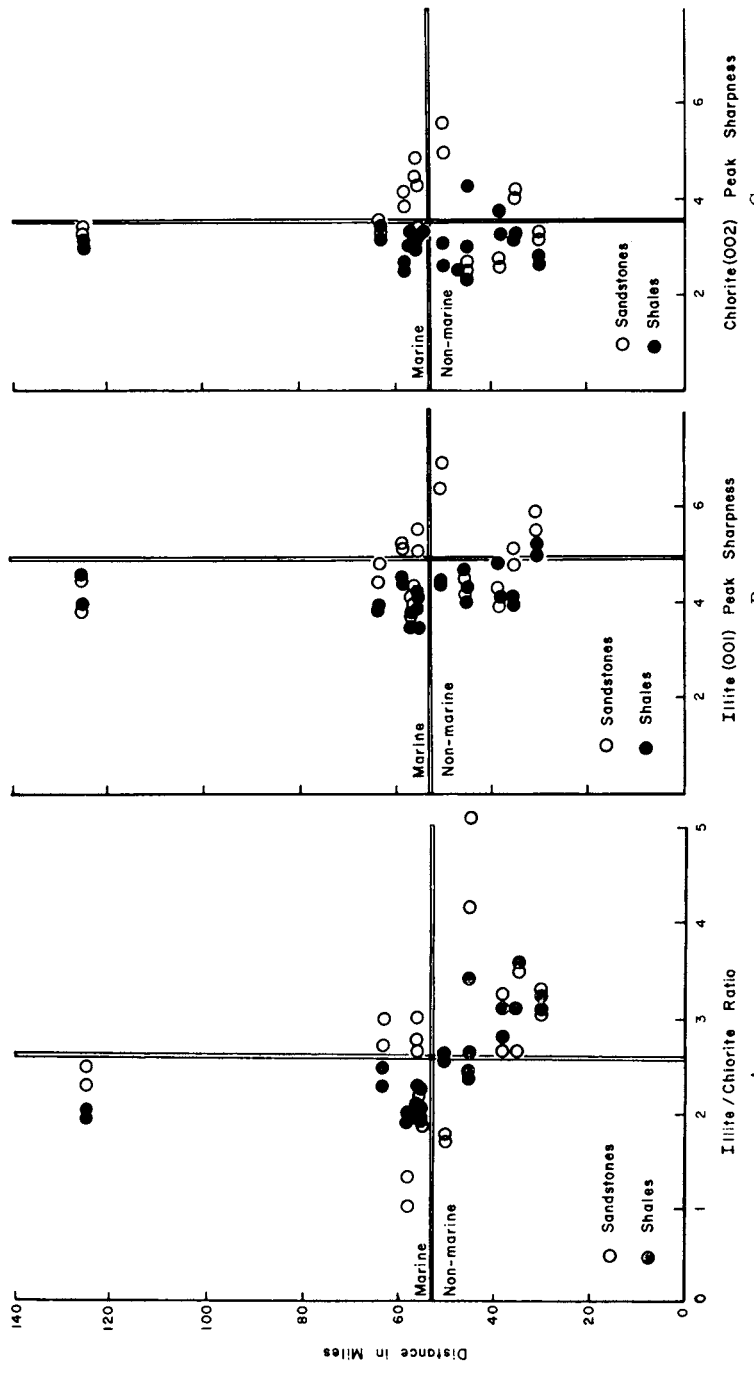

Fig. 9. (a) Plot of illite-chlorite ratio versus distance from source for sandstones and associated shales (see text for explanation of lines). (b) Plot of illite 001 peak sharpness versus distance for sandstones and associated shales. (c) Plot of chlorite 002 peak sharpness versus distance for sandstones and associated shales.

detrital chlorite flakes coupled with an increase of diagenetic chlorite (altered from thicker biotite and vermiculite) would tend to cancel each other and produce the overall effect that is observed. The altered explanation of c-axis crystal growth, mentioned earlier, is not considered feasible under normal diagenetic conditions.

Sandstone and shale environment relationships.—The clay mineralogical differences between sandstones and their associated shales have been studied, treated statistically, and related to environment of deposition. Figure 9 shows the relationships that exist. The horizontal line in each case is the marine/nonmarine boundary. The vertical line is arbitrary and is merely to aid in visualizing the statistical interpretations.

As shown by the illite-chlorite ratio (fig. 9a), there is a significant decrease in the illite content in passing from the marine to the nonmarine environment in the shales only. The large amount of scatter in the data for the sandstones does not suggest this change.

Neither illite (001) nor chlorite (002) mean values for peak sharpness show a change due to environment (fig. 9b, 9c), but both show a difference between sandstones and shales. As would be expected in a coarser deposit, the values for the sandstones are larger (sharper) than those for the shales, i.e., the average particle is thicker in the sandstones. It should be pointed out that in both intances the differences are significant at the 95 percent but not at the 99 percent confidence level. This means that the true level of confidence lies somewhere between 95 percent and 99 percent and is sufficient to show that real differences exist.

The fact that there is a difference in peak sharpness between sandstones and shales but none between environments suggests that this parameter is primarily a function of c-axis crystallite thickness rather than crystallinity. The illite-chlorite ratio on the other hand, is subject to environmental changes in the shales *only*, indicating that perhaps the diagenetic effects take place more completely in finer grained sediments.

Absolute intensity values.—Total intensity values of the major illite and chlorite 00L reflections were measured and treated statistically for the two duplicate oriented aggregate X-ray runs. Under normal conditions the use of absolute intensities is hazardous. Variables such as preferred orientation and amount of sample in position to diffract (Clark, 1955) are likely to be different from sample to sample, so that statements about the mineralogy would be tenuous. However, inasmuch as statistical tests for reproducibility were applied to the two duplicate runs of each sample, the use of absolute intensities is considered valid.

The mean values for illite (001), (002), and (003) increase seaward to a maximum in subdivision C. Then in subdivision D a decrease occurs. Figure 10 illustrates this trend.

These data combined with the peak sharpness data indicate that the average (001) illite peak becomes broader and more intense seaward to subdivision C and then continues to broaden but becomes less intense in subdivision D. At least two possibilities exist. First, there may be more of the thinner illite flakes in the seaward shales. In sample preparation this would produce a

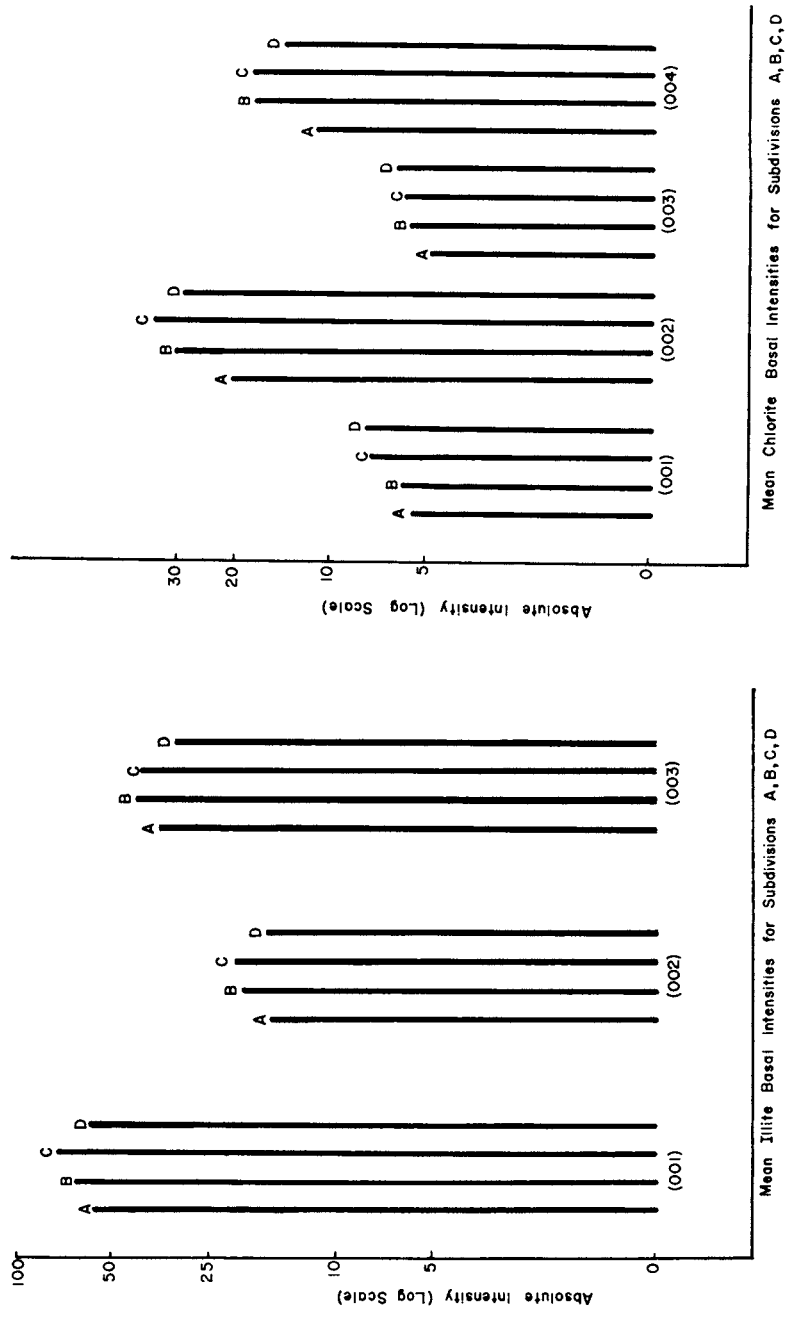

Fig. 10. Diagram to illustrate differences in mean values of illite and chlorite maximum peak intensities in geographic subdivisions A, B, C, D.

more highly oriented aggregate and when X-rayed would result in more intense but broader peaks. A second possibility is that subtle increases in perfection of crystallinity may be responsible for the increase in intensity from A to C. For example, adsorption of potassium by a partially "degraded" illite might result in small crystallinity changes that would be essentially independent of particle thickness. As stated earlier, however, the distinction between crystallinity and particle size from X-ray data is not easily made.

The decrease in intensity in subdivision D is puzzling regardless of which explanation is favored. In the case of the first possibility this would mean that for some reason there were fewer thin flakes present in these shales. The (001) sharpness, being less in subdivision D, seemingly contradicts this idea.

In the second case, a decrease in intensity would mean a subtle loss in crystal perfection perhaps related to some unknown effects in the more calcareous environment.

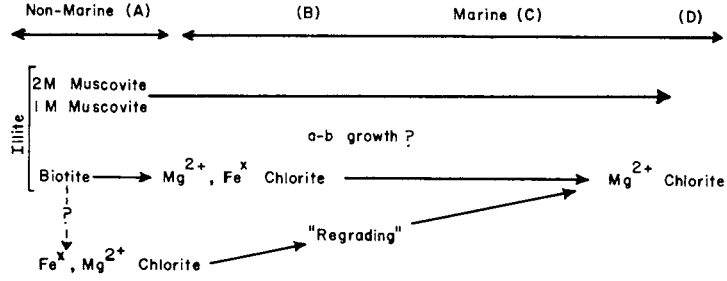

Fig. 11. Generalized diagenetic scheme proposed for Ludlowville shales and sandstones.

Examination of the chlorite intensities may help in resolving the variation in the D subdivision. The mean intensity values of the even order chlorite reflections (002, 004) behave in the same fashion as do the illite peaks. The odd order reflections (001, 003), on the other hand, show a steady increase seaward with no drop in intensity taking place in subdivision D (fig. 10).

Linear regression and correlation analyses point up some interesting facts that would have otherwise escaped detection. In particular, the chlorite 00L reflections except for (004) show reproducible, significant, positive correlations with distance for all 60 samples. What is more striking is that in subdivision C, and in C only, there is also a significant, reproducible, positive correlation with distance for *all* of the chlorite 00L reflections. It should be remembered that the illite-chlorite ratio in subdivision C showed a negative correlation. Thus, in subdivision C the chlorite intensities increase in connection with the increase in the amount of chlorite present.

What interpretations can be placed on these data? The behavior of the even order reflections, when combined with (002) sharpness data, show that in a seaward direction the peaks become more intense, yet do not broaden. In subdivision D the sharpness still maintains itself, but the intensity decreases.

As in the case of illite, at least two possibilities deserve discussion. The first of these, which postulates that more of the thinner flakes occur seaward, is held untenable because it has been demonstrated from peak sharpness that

this may not be the case. Furthermore, if better orientation due to more thinner flakes were the cause for increased intensity, then we should expect all of the 00L reflections to exhibit this increase, which they do not.

The second concept, postulating increases in perfection of crystallinity, seems more likely. In the case of chlorite the "regrading" of partially "degraded" detrital chlorite through magnesium adsorption appears to be coupled with the formation of a more highly magnesium chlorite from "brucite precipitation" into biotite and/or vermiculite structures. This latter diagenetic process is also indicated by the constant increase in intensity of the first and third order reflections. The drop in even order intensities in subdivision D is not easily explained but may be due to changes in the cation population of the structure.

The remarkable correlations with distance in subdivision C, which show an increase in chlorite 00L intensities as well as an increase in the relative amount of chlorite, indicate that some important chemical changes produced a marked increase in chlorite diagenesis but had little effect on the illite. It is significant that in subdivision C, as shown earlier, there is a relatively higher iron content which might enhance the development of chlorite.

DISCUSSION AND CONCLUSIONS

A discussion of the lateral variations in the clay mineralogy of the Ludlowville and related formations resolves itself into an evaluation of the causes, effects, and relative importance of diagenetic and detrital processes.

For the sediments in question here, the clay mineral characteristics are attributed to both detrital and diagenetic effects. The illite (001) peak sharpness as a measure of particle thickness, although decreasing away from the source, shows no marked change at the marine-continental boundary. Chlorite (002) sharpness also shows no change with environment in spite of the previously discussed overlapping effects produced by diagenesis.

Better evidence for detrital action is gained from a review of the sandstone and shale environmental relationships. The fact that there is a significant difference in both illite and chlorite peak sharpness between sandstones and shales but none between the sandstones (or shales) in one environment and those in another strongly reinforces the view that c-axis crystallite thickness is unaffected by diagenetic processes. Thickness changes seem to occur only in response to mechanical sorting and/or cleavage due to agitation during transport.

Evidence pointing toward diagenesis relies on a combination of the data derived from several parameters, the most important of which is the illite-chlorite ratio. The marked decrease in the mean value of this ratio in the marine sediments, pointing to an increase in the relative amount of chlorite, suggests the operation of diagenetic factors. In addition to the detrital chlorite, a diagenetic chlorite is being formed and deposited in the marine environment. The mechanism involved is broadly envisaged as the alteration of an original trioctahedral structure accompanied by the formation of interlayer brucite. That this change takes place more completely in the finer grain sizes is indicated by the fact that it does so only in the shales. Their associated sandstones exhibit no statistically significant change.

The change in illite-chlorite ratio, together with the remarkable reproducible positive correlations with distance shown by the chlorite basal intensities, provides added support to the diagenetic concepts.

The general diagenetic scheme is pictured diagrammatically in figure 11.

After having studied the clay mineralogy of these Middle Devonian rocks, one of the first questions that comes to mind is: How well does the present mineralogy reflect the character of the clay minerals as they were deposited? Other related questions that deserve discussion are: (1) How is the absence of kaolinite explained? (2) Why are there no expandable clay minerals (montmorillonite, vermiculite, and mixed-layer types) present? In either case there are two possibilities: (1) The minerals did not exist in the source area to begin with, or (2) they have since been diagenetically transformed to some other mineral. This latter view seems reasonable for the expandable minerals, but the writers are not inclined to invoke it in the case of kaolinite. In the marine environment the alteration of any of the expandable minerals to either illite or chlorite demands less drastic changes than would be required for kaolinite.

To say that kaolinite was not present in the source area merely begs the question, for we must then explain why it did not occur there, either. A reasonable answer seems to be that the rapid erosion of the dominantly metamorphic source area inhibited pronounced chemical weathering to the extent that kaolinite formation was negligible. There is also the possibility that the plant community, being fairly primitive, may not have contributed certain organic acids that may be necessary for active kaolinite formation. Admittedly, this is highly speculative, but nevertheless should not be ignored.

A quote from Burst (1959, p. 340) is pertinent:

> The minerals present in a sediment after diagenesis may not necessarily resemble the materials originally distributed in a basin; but the relative distribution of the diagenetic minerals may well follow the variations in environmental chemistry during original sedimentation owing to the absorption/adsorption of characteristic, submineralic building blocks at that time.

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