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FINE - GRAINED SEDIMENTS WITH THE AID OF THE
SPECTROGRAPH AS APPLIED TO THE
MISSISSIPPIAN - DEVONIAN SEQUENCE IN
OGEMAW COUNTY, MICHIGAN

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
John Hardin Hefner
1957



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OF FINE-GRAINED SEDIMENTS WITH THE
AID OF THE SPECTROGRAPH
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OGEMAW COUNTY, MICHIGAN

BY
JOHN HARDIN HEFNER

A THESIS

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ABSTRACT

A review of methods for correlating stratigraphic units indicates that there is a paucity of ways to establish time-line horizons in the geologic column. In attempting to determine another method of locating time-line horizons, the hypothesis was set forth that at certain times in geologic history, rare elements, or common elements in abnormal amounts, were deposited from the sea over a wide sedimentation area simultaneously and thus would be time-line horizons.

The hypothesis was tested by analyzing the solubles of sediments from the Mississippian-Devonian sequence in the Michigan Basin. A spectrograph was used to make the analyses, and since qualitative results were negative, a rapid method of making semi-quantitative determinations with this instrument was devised. The elements in the samples tested which seemed to show variations in their relative quantities were calcium, magnesium, barium and strontium. Final tests were made concerning the relative quantities of barium and magnesium in samples from rotary wells in the Michigan Basin.

The results obtained by plotting the relative ratios of barium to magnesium against depth were capable of being correlated, but these correlations are not believed to be time-line correlations. It appears that the samples were contaminated in such a manner as to make the results that were obtained a type of rock unit correlation. Therefore, the tests of the hypothesis that time-lines could be established by semi-quantitative analysis of the elements involved were inconclusive.

The fact that results which could be correlated were obtained indicates that the spectrographic procedure which was developed here may be worthy of use in other similar work. Also, the hypothesis that time-lines can be established by determining variations in the amount of elements precipitated from the sea has not been proven or disproven here. Perhaps this idea would merit further investigation.

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INTRODUCTION

In recent years, stratigraphers have made many advances in solving the problems encountered in correlating stratigraphic units. One of the most important realizations has been that the environment in which a sediment is deposited has a great influence on the resulting strata. With this realization, stratigraphers have recognized that former correlation methods are not all equivalent to one another, and therefore it has become necessary to review and classify methods of correlation. A good review of correlation problems and methods of correlation is given by Krumbein and Sloss (1951, Chapter 10). In general, It may be said that stratigraphic correlation is the demonstration of equivalency of stratigraphic units, and that this equivalency may be expressed in rock, biostratigraphic or time-rock units.

In studies involving geologic history, paleogeography and facies mapping, great use is made of time-rock units, that is, strata that were deposited within a specific interval of geologic time. However, time-line horizons, which are the boundaries for time-rock units are, as yet, established in only a few portions of the geologic column. Rock units and biostratigraphic units are very common and correlations of these units are not too

difficult, but they may not be parallel to time-lines so they are not necessarily time-rock units.

Formations, members and other rock units are determined by the physical characteristics of the strata, and since these physical characteristics are easily observable, rock unit correlation is the most common method in use. Also, since nearly all geophysical methods of prospecting are based upon physical characteristics of the strata such as ability to reflect or refract sound waves, spontaneous potential, resistivity, radioactivity and so forth, all correlations made by using these geophysical methods would be rock unit correlations. Rock units do not necessarily have any direct relationship to time-lines because the type of sediment deposited is dependent upon the environment of deposition. Gradual tectonic movements may cause an environmental condition to change position as time passes. This causes strata to transgress time and is evidenced in many geologic sections by overlap, offlap and other time transgressive stratigraphic relationships. Also, lithologic facies changes can occur where two or more different environments exist adjacent to each other making the determination of time-lines in such a situation extremely difficult. Rock units have been used as time-parallel horizons in many studies because of a lack of any other horizon which will serve as a better time marker. However, stratigraphers realize that in doing this, they may be introducing considerable error into their studies, and thus they cannot place too much confidence in their results.

Biostratigraphic units are strata characterized by their fossil assemblage and are usually called biozones. Since the

organisms comprising the fossil assemblage are dependent upon the environment in which they could live, biostratigraphic units are subject to the same limitations as rock units in regard to using them as time-rock units. Often, biozones will transgress time, and biofacies will result from two or more adjacent environmental conditions. However, many organisms living in the past were adaptable enough to be able to exist in many different environments. Thus, biozones based upon these organisms can be considered to be time-parallel, and are the best working tool that the stratigrapher has available for establishing time-line horizons in the geologic column. Using these time-parallel fossils, various stratigraphers and stratigraphic commissions have established fairly reliable time-rock divisions of systems and series in North America. However, for lesser time-rock divisions, fossils can be used only locally and their time-parallelism is more in doubt. Another difficulty in using fossils for establishing time-rock units is that great thicknesses of strata are often encountered in which no fossils can be found, or if fossils are scarce, the lowest and highest fossil in the section may not be discovered causing incorrect location of the boundaries. This is especially true in subsurface work where macrofossils are seldom seen and almost all paleontological studies are limited to the use of microfossils.

Other methods have been tried for establishing time-line horizons. The radioactive "time-clock" of uranium has been used to date certain time-rock units, but inaccuracy of determinations and nonoccurrence of uranium in some sediments makes this of little value to the stratigrapher. Certain natural phenomena

have occurred in the past to place some time-line horizons in the geologic section. Volcanic ash was, at times, blown over wide areas of ancient seas, and then settled to form bentonite layers which are time-parallel. Cyclical sedimentation and, on a smaller scale, varves afford time-line horizons which the stratigrapher may use. However, it can be seen that there are few usable time-line markers available to the stratigrapher and that any type of time-line horizon which could be added to this list would substantially aid future geologic studies.

Statement of problem- Since there is an apparent lack of satisfactory methods by which time-rock correlations can be made at the present time, it seems evident that any research along this line would be useful. One of the newer approaches to the establishment of time-lines in ancient sediments has been the use of geochemistry.

It has been hypothesized that during the deposition of sediments certain comparatively rare elements may become simultaneously entrapped in all sediments being deposited in a basin. If such a horizon of an element could be found by some geochemical method, this would provide an excellent time-line marker just as a bentonite layer does. Since it is known that clastic sediments vary with environment of deposition, as is shown by lithofacies changes, it does not seem likely that examination of clastic components of sediments would yield any widespread time-line markers. On the other hand, if the water in a basin were of consistent composition throughout the basin, and if a rare element were introduced into the water, the mobility of the

element in solution would cause the element to be spread over the entire area of the basin. Subsequent deposition of the element by chemical precipitation would provide a time-line marker. Thus, since the element would be chemically precipitated into the sediment, it should be possible to extract it by treatment with chemicals so that it could be analyzed apart from the variable clastic portion of the sediments.

Section analyzed- The section chosen for this study is a thick sequence of Mississippian-Devonian strata in the Michigan Basin. This sequence is made up almost entirely of shales, slightly calcareous, with small sandstone lenses appearing in the Berea and Bedford formations. The stratigraphic sequence studied consists of the Antrim, Bedford, Berea, Sunbury and Coldwater formations with a total thickness of approximately 1500 feet. This section was chosen primarily for development of a technique and not because any special correlation problems are involved. The sandier Berea-Bedford sediments can be differentiated from the shales above and below and the Sunbury shale is much blacker than the Antrim and Coldwater shales. The top of the Sunbury formation is probably the most distinctive horizon in the sequence. Although this study was made mostly on shales, it should be emphasized that the methods used can be applied to any rock type and not to shales alone.

Area studied- Since the main objective of this study was to locate a horizon which could be used for correlation, samples from fairly closely spaced wells were used. Four wells were chosen in Foster, West Branch and Mills Townships, Ogemaw County,

Michigan and sample cuttings from these wells were obtained from the Michigan Geological Survey. However, a similar study was being carried on at the same time in Grant and Sheridan Townships in Clare County, Michigan and data from this study were made available to the writer for use in longer range correlation. A map indicating the locations of the wells used in these studies appears on page 36.

General method of attack- Since only the non-clastic fraction of the sediments contain the elements which were synchronously deposited by chemical precipitation from the sea, only the solubles of the sediments were analyzed. When analyzing the solubles from clastic sediments, only small amounts will be available, so it was decided that the analyses could best be made spectrographically because with this instrument large samples are not needed. Also, with the spectrograph the presence of an element which may occur in a very small amount in the sample can be determined quickly and a record on film may be permanently retained.

At first, it was hoped that time-line horizons could be located in the sequence of shales by means of trace element or minor element analyses. Spectrograms of samples from one well were analyzed qualitatively to determine whether or not there were any trace or minor element horizons in the stratigraphic column. In this examination, the elements calcium, barium, strontium, magnesium and iron were the only elements identified, and they were present in all of the samples. Thus, there were no trace or minor element horizons found, nor were there any horizons

characterized by the absence of any of the above named elements. These results were much the same as the qualitative results obtained by Sloss and Cooke (1946) in a similar study of the Madison Limestone. In other words, qualitatively, all of the samples were remarkably similar in character.

While making the qualitative studies, it was noticed that the various samples contained different amounts of the five elements found. This was evidenced by the varying density of the spectrographic lines of each of the elements in different samples. For example, one sample would have dark barium lines and light magnesium lines while another sample would have light barium lines and dark magnesium lines. This indicated that perhaps a quantitative study might provide time-line correlations which qualitative studies were unable to do. That is, a stratum, such as one of low barium-high magnesium content, might be found which could be traced throughout the basin as a time-line marker. It seemed evident that the best method of attacking this problem was to determine a ratio of the concentrations of the two elements for each sample, and then this ratio, which may have significantly high or low values, could be used for correlation purposes. Thus, the problem at this point was essentially a two-fold one. The first part was to develop a quantitative spectrographic procedure which was rapid and also retained enough accuracy so that results capable of interpretation could be obtained. The second part of the problem was to interpret the data obtained and determine whether or not any relationship for time-rock correlation existed in the sediments as hypothesized earlier.

SPECTROSCOPY

Many theories of light are involved in spectrographic work and their discussion would be much too complex to be included in this study. Further information along these lines may be obtained from any of the many books which have been written on the subject of spectroscopy. Three excellent books which the writer used for reference are those compiled by Ahrens (1950), Brode (1943) and Harrison, Lord and Loofbourow (1948). However, a resumé of these theories is appropriate here because the entire study is based upon spectrographic determinations.

Terminology- A spectroscope is an instrument which uses a refracting prism or a reflecting grating to disperse light into a spectrum of its component wave lengths. When light entering the spectroscope is passed through a slit and diffracted by a grating, the different wave lengths are completely separated and the spectrum consists of many lines which are made by each component wave length of light. A spectrograph is an instrument which records the spectrum on photographic emulsion, and the resulting picture of the spectrum is a spectrogram.

Origin of spectra- When atoms are subjected to an excitation force such as an arc or spark, they are known to emit light of definite wave length values. The excitation force pushes electrons into the outer levels of the atom where they are unstable. The electrons fall back to their normal level, losing the energy that was imparted to them by the excitation force by emission of light. The frequency of the emitted light is directly

proportional to the amount of energy lost by the falling electron, which in turn is the same as the amount of energy the atom absorbed from the excitation force. Theoretical and experimental work has demonstrated that this absorption and emission of energy takes place in accordance with fixed and well-defined rules, and electrons which are forced away from the nucleus can "jump" only to certain predetermined positions. Also, the electrons can return to their original positions only through a certain number of finite moves, either returning from their unstable positions to their normal positions in one move, or stopping at an intermediate level before returning to their original position. Each different electron movement in one atom involves a different amount of energy, and thus each emits light of its own unique wave length. All of the different wave lengths of light emitted by the electron movements within atoms of one element make up the spectrum of that element. Since atomic structures of the elements are all different, each element will produce its own characteristic spectrum.

Qualitative spectrographic technique- Since each element gives its own identifying spectrum when arced, the problem of qualitative determination of elements in an unknown resolves into spotting each elemental spectrum on a spectrogram. This problem may be approached in several ways. If certain elements are suspected of being present in the unknown, a pure sample of each of these elements can be arced so that the spectrograms of the known and unknown samples are in juxtaposition. If each major line of a known sample coincides with a line of the unknown sample, the

suspected element is actually present.

Other lines on an unknown spectrogram, which cannot be accounted for in the above manner, can be identified by measuring their wave length values and referring these to appropriate tables. The wave lengths are best measured by arcing an iron spectrogram adjacent to the unknown spectrogram. Then by referring to published charts of the iron spectrum, in which the wave lengths of the iron lines are given, the wave lengths of the unknown lines can be interpolated from the adjacent iron lines of known values. It will be found that a line whose wave length has been determined could possibly have been caused by several elements. However, upon measuring more lines it will turn out that all of the lines belong to the spectra of one or two elements. The presence of these elements can then be checked by identification of the principle line of the elements or by juxtaposition of spectrograms of pure samples of these elements with spectrograms of the unknown as described above. This process is carried out until all lines in the unknown spectrogram are identified as belonging to the spectra of one of the identified elements.

Quantitative spectrographic technique- A line of a particular element on a spectrogram may vary in density depending upon how bright the light of that wave length is in the spectrum. One of the factors controlling the intensity of the light, and thus the density of the line on the spectrogram, is the amount of the element which is present in the sample. Thus, if other factors affecting the density of a line on a spectrogram can be eliminated or be held constant, a quantitative determination of

the element can be made by measuring the density of the line. The density of the line can be determined by using a densitometer to measure the amount of light which the line can transmit.

The factors which effect the density of a line besides the amount of element in the sample include such variables as the exposure time, character of the arc, time lapse between arcing and exposure, development time of the spectrogram and the character of the photographic emulsion. Quantitative spectrochemical procedures have been developed for elimination of these variables so that the exact percentage of an element in an unknown sample can be determined. These procedures include the use of internal standards, the use of known samples, and the calibration of the photographic emulsion.

The photographic emulsion must be calibrated to determine how it reacts to different intensities of light. This is accomplished by exposing the plate to light of known relative intensities by use of a step density tablet or other means. Then optical densities of the different relative intensities are measured and plotted one against the other. These points are connected to produce the characteristic curve of the emulsion from which optical density readings of lines in the known and unknown samples can be converted to their relative intensities.

Samples with known concentrations of the elements being tested can be prepared and arced onto the same spectrogram as the unknown sample. Then by comparing the relative intensities of the known and unknown samples, the quantity of the element in the unknown could be determined. However, since other factors besides quantity affect the intensities, these variables must be

eliminated too. Therefore, an internal standard must be used in the known and unknown samples. An internal standard is another element which is present in the samples in large or constant quantities and is spectrochemically related to the elements being analyzed. The internal standard may be introduced into the samples or it may be already present in the material being analyzed. The optical densities of a line of the internal standard are also measured and their relative intensities determined. Then a ratio of the relative intensity of the element being measured to the relative intensity of the internal standard is calculated, and this ratio is used in further work. The use of the internal standard will compensate for sample variations in exposure time, character of the arc, and development time. That is, if a sample were exposed for a longer time, the relative intensities of both the element being measured and the internal standard would be increased, but the ratio between the two would remain the same. Care must be exercised in the selection of an element for an internal standard or this will not always be the case. The previously mentioned references discuss the important spectrochemical factors which must be considered in selecting an internal standard.

The above described relative intensity ratio is computed for all samples on the spectrogram. Then by plotting this ratio of the known samples against their concentrations, a "working curve" is established. The relative intensity ratio of the unknown sample can then be inserted into this "working curve" and the concentration of the element in the sample can be determined.

In summary, quantitative spectrographic procedure involves the following steps: (1) Arcing the unknown and several known samples onto the spectrogram. (2) Development of the spectrogram. (3) Calibration of the photographic emulsion and construction of the characteristic curve. (4) Measurement of optical density of lines of the test materials and internal standard in all samples and determination of the background reading for each line measured. (5) Conversion of optical density values to relative intensity values by use of the characteristic curve. (6) Calculation of ratios of relative intensities for all samples. (7) Construction of the "working curve" from known sample concentrations and their relative intensity ratios. (8) Quantitative determination of the test material by insertion of relative intensity ratio of the unknown into the "working curve".

Semi-quantitative spectrographic technique- As can be seen above, the determination of the absolute percentage value of a constituent in a sample by spectrochemical methods can be quite an arduous task. This is especially true if there are many samples to be treated or if there are several elements in each sample which need to be analyzed quantitatively. Since this study involves many samples with several elements to be determined in each, it was deemed necessary to develop a method of analysis which would speed up the process and would still obtain reliable results. The nature of the desired results in this study as well as the similar spectrographic behavior of the elements involved allow several short-cut methods to be applied.

As mentioned earlier, a ratio of the concentrations of two

of the elements in each sample would be the best values to use for correlation purposes. In using this ratio of the concentrations of two elements, it is not necessary to determine the absolute percentages of the elements in order to calculate the ratio. That is, the ratio can be calculated just as effectively from the ratio values of the relative intensities of the two elements. This refinement of normal spectrographic technique eliminates the necessity of using known solutions for construction of a "working curve", and thus reduces the amount of work involved for each sample a great deal since arcing and reading of line densities of known samples is eliminated.

Also, since ratios of element concentrations are to be used in the correlations, the use of an internal standard is not necessary with the elements analyzed. The reason for this is that the spectrochemical behavior of the elements analyzed are so similar that the same internal standard could be used for both elements, and thus, the intensity readings of the internal standard cancel out in calculating the ratio used in correlation. That is, using the elements barium and magnesium for example, the ratio would be calculated in the following manner:

$$C.R. = \frac{[Ba]}{[Mg]} = \left(\frac{\frac{R.I. \text{ of Ba}}{R.I. \text{ of Internal Standard}}}{\frac{R.I. \text{ of Mg}}{R.I. \text{ of Internal Standard}}} \right) K = \left(\frac{R.I. \text{ of Ba}}{R.I. \text{ of Mg}} \right) K$$

C.R. = Ratio used in Correlation; R.I. = Relative Intensity;
K = Constant.

The constant, K, in the above equation arises from the fact that even if the magnesium and barium lines which are measured have the same density, they do not necessarily have the same concentration in the sample. The determination of this constant is not deemed

to be important in this study so that the correlation ratio used is just a ratio of the relative intensities of the chosen lines of the elements.

One final short-cut was employed. By standardizing the procedures in developing the spectrogram, it was found that the characteristic curves of different spectrograms varied very little. Therefore, an empirical characteristic curve was established (figure 1) and used for all spectrograms. Tests indicated that any error introduced by this step would be less than other errors which are inherent in the sampling procedure. A table was made of the values from the characteristic curve so that easier conversion of optical densities to relative intensities could be accomplished. This table appears on page 39.

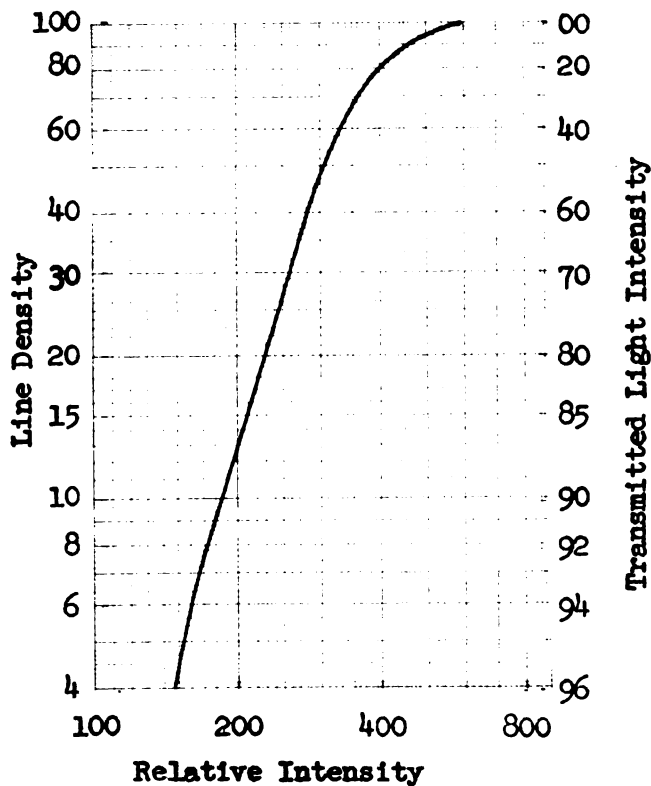


Figure 1. Empirical characteristic curve of photographic emulsions.

Thus, with the above mentioned refinements, the semi-quantitative procedure involves only the following steps: (1) Arcing several unknown samples onto each spectrogram since known samples are not needed. (2) Development of the spectrogram. (3) Measurement of optical densities of selected lines in the samples and determination of their background readings. (4) Conversion of the readings to relative intensities by use of the table.

Selection of lines for measurement of optical density- A line of the spectrum of each element to be determined must be chosen for measurement of its optical density. The line which is selected for a particular element will then represent the concentration of that element in the sample. The lines chosen for each element should be of approximately the same intensity in most of the samples. This being the case, exposure time can be regulated so that most readings of optical density will be converted to their relative intensities using the straight portion of the characteristic curve, and result in more reliable correlation ratios being obtained. Another factor that must be considered in choosing a line for measurement is that there must not be any interfering lines from spectra of other elements in the sample. Also, when samples are arced on carbon electrodes, carbon unites with nitrogen in the air to form cyanogen which produces a band spectrum. This cyanogen "background" often covers a sizable portion of the spectrogram, depending upon how long the sample is arced. Obviously, the lines measured must not fall within the area covered by the cyanogen "background". When these requirements in choosing a line are satisfied, any

further choice of available lines may be made for convenience or "film saving" reasons.

EQUIPMENT

The instrument used in this study was a Cenco grating spectrograph equipped with a replica grating. The excitation source was a D. C. arc and the spectrograms were produced on Ansco Isopan cut sheet film. Quarter inch standard spectrographic carbons manufactured by National Carbon Company were cut into two inch lengths and used for electrodes. Strips of soft wood were cut and drilled for use as electrode and sample bottle holders. Standard sample bottles, such as those used by the Michigan Geological Survey for storage of well samples were used for preparation of the well cuttings. Chemically pure concentrated hydrochloric acid was diluted to 6 N with distilled water and used for sample treatment. A separatory funnel was used to introduce the acid to the samples. A hot plate in a fume hood was needed to simmer the samples in the acid, and a drying oven was used in preparing the electrodes. Standard darkroom equipment was needed for development of the spectrograms.

The densitometer used for the density determinations was constructed especially for this type of study. Paige (1952), who constructed the densitometer, gives the details for the construction of the instrument, in which an extra-sensitive light meter was used to obtain the optical density readings. Construction of the densitometer was necessary because no densitometer equipped to handle celluloid film was available.

DEVELOPMENT OF LABORATORY TECHNIQUE

The development of a concise laboratory technique was an important part of this study. Therefore, a resumé of the more significant technique developments which were made will be included here, while a complete step by step procedure will be outlined later.

Obtaining the samples- The samples used in this study were rotary well cuttings obtained from the Michigan Geological Survey. Approximately one gram of cuttings from each interval, which was usually ten feet, were placed in sample bottles and used for analysis. Since ratios of element concentrations were to be used in the final calculations, the quantity of cuttings treated was not a critical factor in the research. Care was taken not to include any cuttings which appeared to be extraneous to the whole sample.

Preparing the samples- The sample bottles containing the cuttings were placed in the bottle holders, put on a hot plate



Figure 2. Treating the samples with acid.

in a fume hood, and nearly filled with 6 N hydrochloric acid (figure 2). The hot plate was turned on and the cuttings simmered to hasten the action of the acid. This also disaggregated the sample so that complete solution could take place. The bottles were then removed from the hot plate and set aside to allow all insoluble particles to settle out of the solution.

Making the electrodes- Preliminary tests indicated that standard spectrographic carbons were sufficiently free of the elements being tested to make it unnecessary to assume the added expense of using spectrochemically pure carbons for the electrodes. Tests were also made to determine what kind of electrode surface was most suitable for these experiments. It was decided that flat-topped electrodes worked the best, and that arc wandering was reduced if the positive electrode was partially sharpened. Therefore, the carbons were cut into two inch lengths, and both ends leveled and polished on emery cloth and the positive electrodes were partially beveled with a small pencil sharpener. The electrodes became contaminated upon firing a sample, but by using both ends, each electrode could be used for two samples.

Loading the electrodes- The negative electrodes were placed in the electrode holders and heated in the drying oven to remove any moisture and make them more porous. Then an eyedropper was used to introduce a drop of liquid from each sample onto the surfaces of the electrodes (figure 3). The eyedropper was rinsed in two different beakers of distilled water after each use. Care was taken to record what sample was put on each electrode so that the data would not get mixed. The electrodes with the droplets

on them were left in the drying oven to evaporate the liquid and leave the salts of the samples baked onto the electrodes. The electrodes were kept in the drying oven until just before they were to be arced because the salts would absorb moisture from the air readily and this increased the difficulty of maintaining a steady arc.



Figure 3. Loading the electrodes.

Arcing the samples and developing the spectrogram- These two processes were so interwoven that the techniques involved are best described together. Since there are so many steps to be performed in this portion of the work, it was found that two people performing the operation together greatly facilitated the procedure. One person could be kept busy changing the electrodes, adjusting their height and arcing the sample while the other

operated the shutter, moved the plate holder for each sample, and recorded the sample numbers and their positions on the film. Also, while one person was developing the spectrograms, the other could be cutting film and loading the plate holder for the next samples.

Sheet film, cut to size to include only the desired portion of the spectrogram, was used (figure 4). Two plate holders were employed and the unused portions of the plate holders were blocked off by taping old film into them so the films for the spectrograms could be fitted only into their proper positions. One plate holder was marked with tape, and the film placed in it was notched so that the spectrograms could be identified in the dark and not be transposed in the developing process.

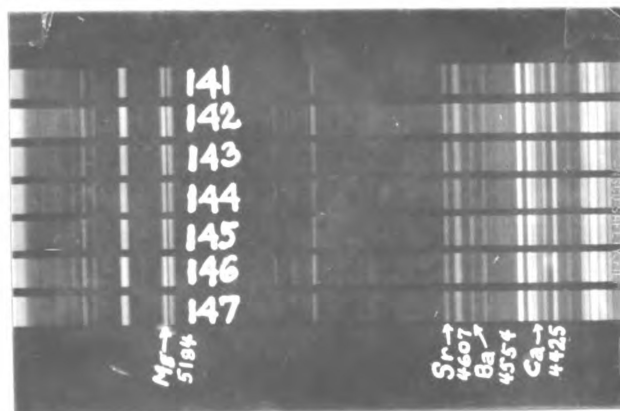


Figure 4. Positive print of a typical group of sample spectra showing the lines used for analysis.

In this portion of the work, it was necessary to develop a method of operation which would save time and would keep from transposing the sample spectrograms. The individual sample spectra could not be marked until the spectrogram was developed and dried, but by organizing the procedure, spectrograms were

kept separated in the following way: The spectrogram developing process provided three "resting places" for the spectrograms. These were in the fix, in the final wash and on the dryer. Thus, it was possible to have two spectrograms (one notched) on the dryer, two in the wash and two in the fix while two more were being prepared by arcing samples on the spectrograph. A rotation between these resting places was maintained, marking the sample spectra with their code number as they came off the dryer, and thus, the time per sample analysis was greatly reduced.

Preliminary testing also provided some technique improvements in the arcing of the samples. Ordinarily the time lapse between arcing the sample and exposure of the film is quite an important spectrochemical factor to be considered in performing an analysis of this type. However, tests showed that one sample could be exposed after any of several different time lapses and still obtain the same results. Also, a sample electrode could be arced twice with the same results being obtained. This was because the elements measured in the sample were quite similar in their spectrographic behavior, and all elements were present in sufficient quantities so that they were not burned up readily. Thus, knowing this, if a good steady arc was not obtained immediately, it was all right to wait until the arc stabilized before exposing the film. Also, an occasional spectrum would be unaccountably poor on the spectrogram. This would be noticed as soon as the spectrogram had been placed in the fix, so this sample could be re-run immediately from the same electrode which

was used for that sample before. These methods were important time-saving procedures.

Reading optical densities- The densitometer was so constructed as to allow film strips the width of the spectrum to pass by the slit as in a movie projector (figure 5). Therefore,



Figure 5. Densitometer constructed for use with celluloid film strips.

the spectrograms were cut into the individual spectra and spliced together to form the film strip. To do this, a razor blade and straight edge were used to cut the spectrogram on the side opposite the emulsion, after which bending along the cut would break off the strip. The emulsion was scraped off of one end of a strip, the opposite side of the other end was scraped, and then the strips were spliced with regular splicing cement. The seven

strips in a spectrogram were spliced together and the ends of the long strip were notched so they could be hooked together in a loop through the densitometer.

The densitometer was equipped with a dial so that by setting it with the "starting line" in the proper place, the line to be measured could be quickly passed over the slit. A light intensity adjustment made it possible to take constant background readings for all lines, so the density readings for the lines could be converted to relative intensities directly by use of the chart shown on page 39. It will be noticed that the density readings shown in the chart have an inverse relationship to those shown on the empirical characteristic curve. The reason for this is that the photocell used in the densitometer was a sensitive light meter, and consequently it was calibrated to register light intensity instead of line density. Therefore, low readings were obtained from lines of high optical density and vice-versa. The chart was made up to correct for this change automatically.

Calculating relative ratios- Of the five elements, calcium, magnesium, barium, strontium and iron, which were present in the samples, density readings were first recorded on the lines of all elements except iron. The lines which had been selected to represent these four elements were those of the following wave lengths (figure 4): Calcium- 4425 Å; magnesium- 5184 Å; barium- 4554 Å; strontium- 4607 Å. Iron was discarded because small pieces of iron from the drilling bit were noticed in the original sample cuttings. Although those pieces of iron which were seen were removed, it was believed that other pieces may have

remained to contaminate the sample as far as the quantity of iron was concerned. On some spectrograms, the cyanogen background was great enough to interfere with the selected calcium line. Tests on the samples which had calcium lines that could be measured seemed to indicate that the use of the calcium lines in the ratios would not provide any data which would be usable for correlation. Therefore, rather than try to reduce the cyanogen background on the poor samples, the calcium line was not used and emphasis was concentrated upon what information could be obtained from the barium, magnesium and strontium lines.

Since it was not known what ratios might be most usable in correlation, various ratios were calculated for samples from wells in a selected portion of the strata in order to determine what would be the best ratio to use. Ratios of magnesium to strontium, barium to strontium, and barium to magnesium were calculated. All of these ratios appeared to be somewhat usable, but the ratio of barium to magnesium seemed to exhibit a greater magnitude of change and appeared to be the best ratio. It was then noticed that strontium seemed to act somewhat as an internal standard in the samples, and for samples in which the barium-strontium ratio was low, the magnesium-strontium ratio was high, thus explaining why the barium-magnesium ratio had a greater amplitude of change. Also, it was noticed that the magnitude of the barium-strontium ratio was about twice as great as the magnitude of the magnesium-strontium ratio. Tests showed that by doubling the intensity of magnesium in the magnesium-strontium ratio, the magnitude difference between the barium-strontium ratio and the magnesium-strontium ratio was minimized. Therefore,

it appeared that the best ratio to use was one involving the relative intensity of barium and twice the relative intensity of magnesium. This doubling of the magnesium intensity is strictly empirical and it is not believed to have adversely affected the final results.

One more refinement of the ratio was used to help stabilize the results. This was the placement of barium in both the numerator and denominator of the ratio to cause the results to behave more like percentages. Therefore, the ratio of relative intensities which was used throughout the study was that of barium to twice the magnesium plus barium. That is, with R. I. referring to relative intensity, the ratio used was:

$$\frac{\text{R. I. of Barium}}{2(\text{R. I. of Magnesium}) + \text{R. I. of Barium}}$$

Plotting the ratios- When the samples were obtained, the depth at which they were collected was recorded. Knowing the elevation of the wells, the positions of the samples in relation to sea level was determined. Then the ratio which was calculated for each sample was plotted on a horizontal scale against its sea level elevation on the vertical scale. Since each sample represented an interval of strata, the points were plotted at the middle values of the intervals. When all the points for a well were plotted, they were connected by straight lines to make a "dog-tooth" curve to be used in correlation. Occasionally, there would be a gap in the sampling, so points on each side of such a gap were connected by a dashed line, indicating the lack of data. These curves which resulted from plotting the ratios of barium to magnesium are shown in plate I.

For reasons which will be explained later, it was deemed necessary to plot a "trend curve" for each well. The values for this curve were obtained by averaging the ratio values for every three adjacent points and plotting this value at the elevation of the middle point. These curves are shown in plate II.

PROCEDURE

Applying the various techniques outlined previously, the following procedure was followed in analyzing the samples:

1. Put about one gram of sample cuttings from each interval into their respective sample bottles and label.
2. Place sample bottles in the bottle holders and onto the hot plate. Nearly fill all bottles with 6 N hydrochloric acid.
3. Turn on hot plate to simmer the samples until they are well disaggregated.
4. Remove samples from hot plate and allow insoluble particles to settle.
5. Prepare negative electrodes by cutting carbons into two inch lengths and polishing ends with emery cloth. Put them in the electrode holders and place them in the drying oven.
6. Load the electrodes by placing a drop of sample liquid on each with an eyedropper. Rinse eyedropper in two beakers of distilled water between each loading.
7. When all electrodes are loaded, close oven carefully and allow the liquid to evaporate leaving the sample salts on on the electrodes. Do not remove electrodes from the oven until just before they are ready to be arced.
8. Prepare the positive electrodes by polishing the ends and

sharpening them slightly.

9. In darkroom, cut film and place it in plate holder. Put plate holder on spectrograph and adjust it to proper height. Remove baffle.
10. Install electrodes into clamps on spectrograph. Adjust negative electrode to proper height so that center of gap will be level with the center of the slit.
11. Close power switch. Arc the sample by lowering the positive electrode to contact the negative electrode and then raising it immediately to obtain the optimum electrode gap of about one half inch.
12. When arc is burning steadily, open shutter and expose for about four seconds. This time may be lengthened if the arc wanders. Close shutter.
13. Open power switch. Remove electrodes from clamps and replace them in electrode holder.
14. Move plate holder into position for next spectrum.
15. Record the sample number and its position on the spectrogram.
16. Repeat steps 10 to 15 for all samples (seven) on one spectrogram.
17. Close baffle and remove the plate holder from spectrograph.
18. In darkroom, remove film from plate holder and develop as follows: Two and one half minutes in Kodak D-19 developer, one half minute in running wash water, and approximately ten minutes in acid fix. Wash for convenient time and dry.
19. After spectrogram is dry, put the identifying sample number on each spectrogram.
20. Cut film into individual spectra and splice them together

as described previously.

21. Insert spliced film strip in densitometer and hook ends together. Line up "starting line" with edge of film track and set calibrated dial to starting point.
22. Turn on light. Rotate film to position for obtaining background reading. Adjust light so that background reading is 100 on light meter.
23. Pass the lines to be read slowly over the slit and observe and record the lowest readings.
24. Obtain the relative intensity for each line by use of the chart.
25. Calculate the correct ratio for each sample.
26. Determine the correct sample elevation and plot the ratio curves.

INTERPRETATION OF RESULTS

The dogtooth curves of the barium-magnesium ratios for each of the wells are plotted in plate I. Since the Sunbury formation is the most distinctive horizon in the portion of the stratigraphic column analyzed, the top of the Sunbury was plotted and used as a reference line in correlation. This horizon which was determined on well logs, is shown as a black line on plate I.

The Sunbury formation also appears to be distinctive as far as the barium-magnesium ratio is concerned because the ratio is low within the Sunbury in all wells. The red line correlating the lowest ratio values within the Sunbury does not exactly parallel the line at the top of the Sunbury, but this is not to be expected since variations may be caused by the Coldwater-Sunbury

contact being either gradational or abrupt. However, a general relationship is apparent. Other correlations of the high and low points of the dogtooth ratio curves have been made as indicated by the red lines in plate I. Since the ratio correlations show a general relationship to the distinctive Sunbury formation, it is believed that the correlations in the Coldwater and lower formations may be as good, and thus a means of subdividing these formations is established.

Besides having high and low values which could be correlated, it was also noticed that each of the ratio curves had distinctive trends. It was difficult to determine exactly what the trends were on the dogtooth curves, so a trend curve for each well was constructed as shown in plate II. Each trend curve was made by averaging the ratios of three adjacent points and plotting this average at the elevation of the middle point. Then the trend curve of the average ratios was "painted" by making the line of the curve wide enough to cover every plotted point. For reference purposes, "base lines" were arbitrarily drawn for each curve, and these are the black lines in plate II.

The trend curves show two significant relationships. First, all wells show a definite change in the trend of the average ratios at about the location of the Sunbury formation in the stratigraphic column. In the Coldwater formation, the trend curves all lie to the right of the base line except for minor variations in each well, while in the Sunbury and lower formations the trend has shifted so that the greater part of all curves lie to the left of the base line. The other relationship which appears to be present is that the position of the base line

varies from well to well. That is, the ratio value of the base line which separates the upper and lower trends is different in each well.

The relationships which have been pointed out in the dogtooth and trend curves all are dependent upon the relative occurrence of barium to magnesium in the samples. If it is assumed that the quantity of barium and magnesium present in the sample is derived by precipitation of the elements into the sediments, it may be supposed that the amount of these elements in the sediments is in turn dependent upon the concentration of each element in the sea water in which the sediments were deposited. Rankama and Sahama (1949, p. 295) list the amounts of elements supplied to sea water and the amount of each present in sea water. By making barium-magnesium ratios from these data, it is seen that the ratio is much higher in the source than in the sea water. Thus, a higher ratio of barium to magnesium would be expected to be deposited near the shore, a fact that is supported by Rankama and Sahama who say that barium is associated with near shore sediments.

In this study, sediments most indicative of near shore deposition are the sands and sandy shales of the Berea formation. This formation, as picked on the electric logs, is thinner than the sample interval in six of the seven wells analyzed and therefore any distinguishing characteristics may well be masked by the adjacent strata. However, well no. 4 in Ogemaw County penetrates 114' of the Berea sandstone between the elevations of -322' and -436'. This sandstone was probably deposited closer to shore than the shales above and below were, but both the dogtooth and

trend curves show a very low barium-magnesium ratio for this interval instead of a high one as would be expected. Therefore, the assumption that the concentration of barium and magnesium in the samples is the result of precipitation of the elements from sea water is probably incorrect. Perhaps the cause of the anomalous occurrence of a low barium-magnesium ratio in the Berea sandstone lies in the fact that the samples which were analyzed in this study were rotary drill cuttings. Drilling mud used in rotary drilling usually contains barite to increase its specific gravity. Thus, although the cuttings were washed and separated from the drilling mud, there is still a great possibility that the samples may have been contaminated by the barite. Therefore, it is possible that the barium content which was determined in these samples did not originate by precipitation from the sea, but was introduced to the cuttings from the drilling mud.

The fact that the samples probably were contaminated by the barite does not make it necessary to discard the results obtained, because it appears that contamination of the samples may have taken place as a selective process. If it is supposed that all of the samples were subject to contamination by barite in the drilling mud, and if when the samples were washed, it was much easier to remove the contaminating mud from the sands than from the shales, the cuttings analyzed would be expected to have a higher barium-magnesium ratio in the shaly sections than in the sandy sections. This may explain why the Berea sandstone in well no. 4 has such a low ratio while the shales on both sides have a high ratio.

Since the barium-magnesium ratios may be strongly influenced

by the drilling mud, the correlations which were made on the dogtooth curves cannot be considered to be time-line correlations. Instead, the correlations might be a type of rock unit correlation if the barium content in the samples varies according to the sediment type. Supposing this to be the case, interpretations as to the environment of deposition can be made from the results which were obtained. The low ratio trend values in the Sunbury and underlying formations possibly indicate that these sediments were deposited nearer to the shore than were the overlying Coldwater shales, and the high and low points on the dogtooth curves may indicate that the shore line fluctuated many times during the deposition of these sediments. Also, it could generally be assumed that a well near the center of the basin might have a base line of higher ratio than would a well near the shore line. Since well no. 3 in Clare County and well no. 4 in Ogemaw County have base line values of 270 and 275 respectively and the other wells have values of 300 or more, it may be concluded that the positions occupied by these two wells were nearer the shore than the other wells during the interval in which these sediments were deposited. By comparing the relative localities of the wells on the location map on page 36, it is seen that this possible conclusion is in accordance with the results of other studies which indicate that the nearest shore line during this time was to the southeast in the Findlay arch area. This agreement adds support to the assumption that the correlations which have been made may be some type of rock unit correlations.

One other factor which may have influenced the results obtained in this study is the fact that cave-ins often occur in

the drill hole, especially when a shale section is being drilled. Thus, the cuttings analyzed may have contained some slump material from higher in the well rather than just the cuttings for the calculated depth. However, by not using any cuttings which seemed to be extraneous to the sample as a whole, it is believed that much of this possible error was eliminated. In portions of the section where closely spaced sample control was present, the plotted points almost always fell on some sort of curve, with no great deviations by any one point. Thus, it appears that the results were not greatly affected by slumping in the well, but this is not definitely known.

CONCLUSIONS

The results obtained in this study could not prove or disprove the hypothesis that time-line correlations could be made by quantitative examination of elements in the solubles of sediments because the samples were apparently contaminated. However, it is suggested that further research along this line would have merit, especially if work were first carried out on closely spaced outcrop samples of known relationships, so that the method could be tested against known results. In working with outcrop samples an important factor that should be considered would be the effects of differential weathering on the samples. Should the hypothesis prove to be true, the method could then be extended to include greater outcrop areas, cores, and possibly well cuttings if non-contaminated elements were analyzed.

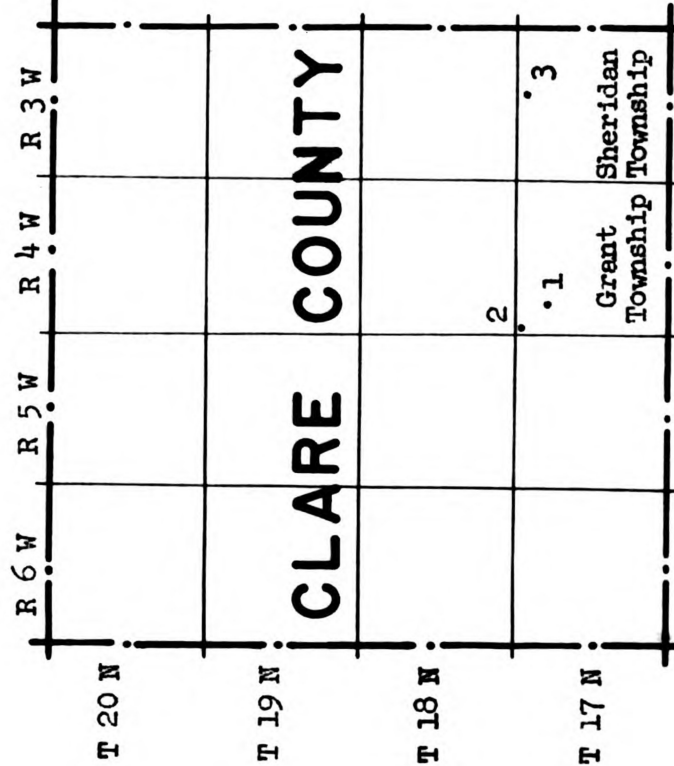
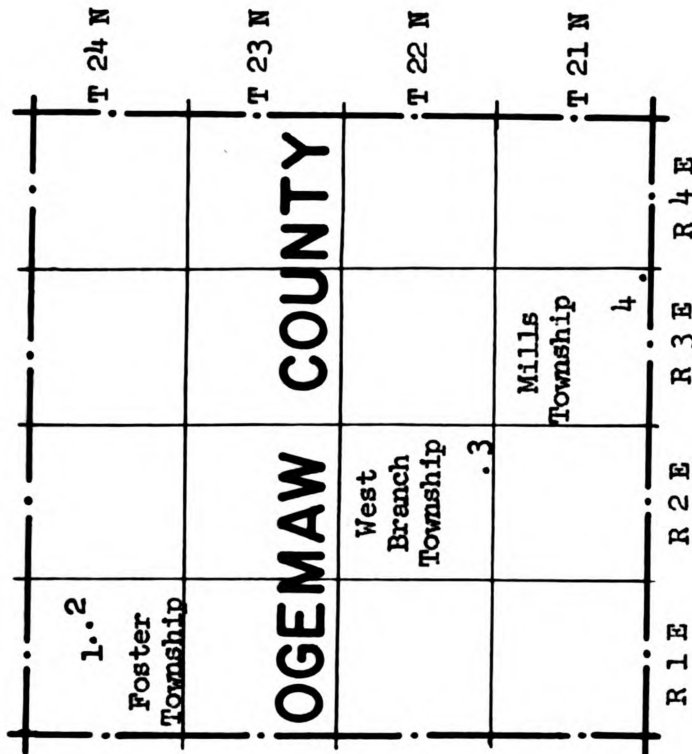
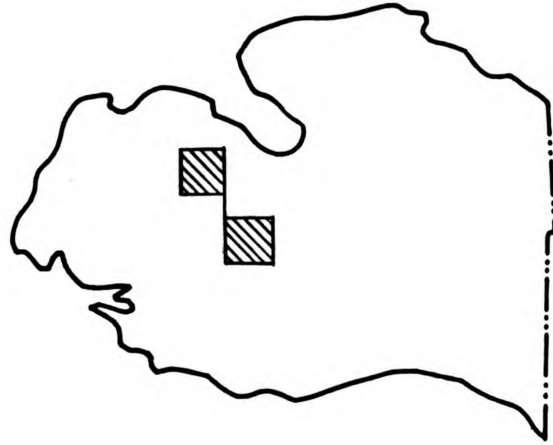
The correlations which were made in this study appear to be valid rock unit correlations, but there are much better methods

available for making rock unit correlations, so this is of little significance. However, the fact that results which were capable of being correlated were obtained indicates that the spectrochemical ideas introduced here may have merit and could be worthy of use in further research.

The spectrographic technique which was developed was thoroughly tested and gave reproducible determinations even though many time-saving practices were employed. It is believed that if the spectrograph is to be used by the stratigrapher to make quantitative type determinations for correlation, a procedure such as used for this study must be employed or the time and costs of running many samples will be prohibitive. Further work along this line might be facilitated by use of a spark source for exciting the samples. The ease of firing and timing a spark source would probably reduce possible errors due to selective volatilization of the constituent materials. Selective volatilization was not of great importance in this study because of the spectrographic nature of the elements analyzed, but in a study involving other elements, this could be an important factor to be considered.

Finally, the possibility of extending the methods developed in this paper to other types of sedimentary rocks should be emphasized. Facies studies of intervals bounded by time-lines are becoming increasingly important to the stratigrapher, so that if a spectrographic method such as developed here could be used for locating time-lines in any type sediment, it would certainly be a significant contribution to the field of stratigraphy and sedimentation.

LOCATION MAP
of Ogemaw and
Clare Counties,
Michigan



WELL LOCATION INDEX

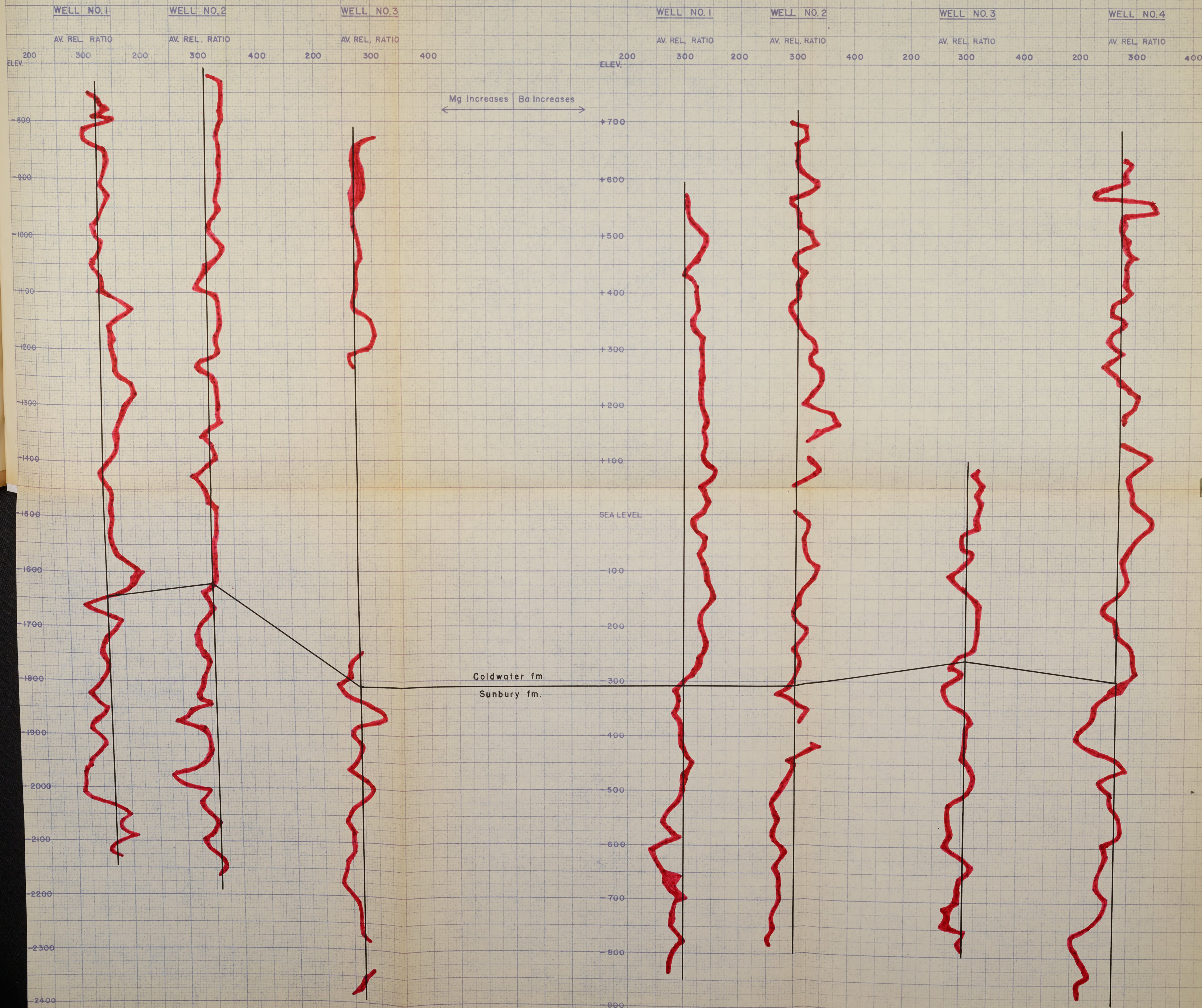
#	Permit #	Location of well
Ogemaw County		
1.	16755	CN $\frac{1}{2}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$ Section 15, T 24 N, R 1 E.
2.	16529	CN $\frac{1}{2}$ SW $\frac{1}{4}$ NW $\frac{1}{4}$ Section 14, T 24 N, R 1 E.
3.	4831	NE $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ Section 35, T 22 N, R 2 E.
4.	4623	SE $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ Section 36, T 21 N, R 3 E.
Clare County		
1.	9904	C NW $\frac{1}{4}$ NW $\frac{1}{4}$ Section 8, T 17 N, R 4 W.
2.	866	NE $\frac{1}{4}$ NW $\frac{1}{4}$ NW $\frac{1}{4}$ Section 6, T 17 N, R 4 W.
3.	8352	CE $\frac{1}{2}$ SE $\frac{1}{4}$ NW $\frac{1}{4}$ Section 3, T 17 N, R 3 W.

Figure 6. Well Location Index Map

CURVES SHOWING TRENDS OF AVERAGE RELATIVE RATIOS OF BARIUM TO MAGNESIUM

CLARE COUNTY

OGEMAW COUNTY



OPTICAL DENSITY* - RELATIVE INTENSITY CHART

1. 585	21. 397	41. 326	61. 279	81. 225
2. 570	22. 392	42. 323	62. 277	82. 220
3. 555	23. 388	43. 321	63. 275	83. 217
4. 540	24. 384	44. 319	64. 272	84. 213
5. 525	25. 382	45. 316	65. 270	85. 208
6. 510	26. 379	46. 313	66. 268	86. 204
7. 500	27. 375	47. 311	67. 266	87. 199
8. 490	28. 370	48. 309	68. 264	88. 194
9. 482	29. 365	49. 306	69. 262	89. 185
10. 475	30. 360	50. 304	70. 260	90. 180
11. 470	31. 357	51. 300	71. 256	91. 175
12. 460	32. 353	52. 297	72. 254	92. 170
13. 451	33. 351	53. 295	73. 249	93. 165
14. 442	34. 349	54. 292	74. 247	94. 160
15. 439	35. 343	55. 290	75. 245	95. 155
16. 433	36. 340	56. 289	76. 241	96. 150
17. 425	37. 337	57. 287	77. 238	
18. 416	38. 334	58. 285	78. 235	
19. 409	39. 332	59. 283	79. 232	
20. 401	40. 330	60. 280	80. 227	

* The values in the left hand columns are actually light intensities rather than optical densities as explained on page 24.

DATA

The data listed on the following pages was obtained by the procedures described previously and used to construct the curves of plates I and II. The data for the four wells in Ogemaw County are the only figures included here, but data for the three wells in Clare County are given by Paige (1952). Only the values needed to plot the curves in plates I and II are listed with this paper. Since the line densities were converted to relative intensities by use of the chart on page 39, only the relative intensity values will be included here.

The first column of the following data sheets gives the sample code number and the second column lists the mean elevation of the sample interval. The third and fourth columns give the relative intensity values of magnesium and barium respectively, while the fifth column lists the value of twice the relative intensity of magnesium plus the relative intensity of barium. The sixth column gives the ratio of the values in column four to the values in column five, and is the value that is plotted against the sample elevation in the dogtooth curves of plate I. The seventh column is the average of the ratio values of three adjacent samples and this average is listed opposite the middle sample of the three. Column seven values were plotted against the sample elevation to locate the points by which the trend curves in plate II were plotted.

WELL NO. 1, OGEMAW COUNTY (PERMIT # 16755). ELEVATION: 1243'

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
1	580	490	388	1368	280	
2	570	277	260	814	319	301
3	560	332	290	954	304	307
4	550	460	388	1308	297	306
5	540	287	266	840	317	306
6	530	525	460	1510	305	308
7	520	332	287	951	302	315
8	510	260	266	786	338	323
9	500	482	475	1439	330	339
10	490	277	297	851	349	338
11	480	323	323	969	333	334
12	470	351	330	1032	320	324
13	460	289	268	846	317	327
14	450	238	249	725	344	310
15	440	270	199	739	270	304
16	430	482	409	1373	298	296
17	420	321	300	942	319	316
18	410	297	295	889	332	321
19	400	525	475	1525	311	319
20	390	490	451	1431	315	320
21	380	277	275	829	333	321
22	370	540	500	1580	316	328
23	360	-	-	-	-	-
24	350	360	365	1085	336	311
25	340	330	256	916	280	311
26	330	525	490	1540	318	317
27	320	319	349	987	354	335
28	310	330	330	990	333	333
29	300	321	290	932	311	329
30	290	245	256	746	344	331
31	280	319	326	964	338	333
32	270	540	500	1580	316	331
33	260	309	316	934	338	326
34	250	300	287	887	324	335
35	240	470	490	1430	342	326
36	230	525	475	1525	312	332
37	220	275	285	835	341	326
38	210	297	285	879	324	328
39	200	279	262	820	320	328
40	190	510	525	1545	340	332
41	180	482	490	1454	337	340
42	170	283	295	861	343	340
43	160	280	287	847	339	333
44	150	416	388	1220	318	332
45	140	249	256	754	340	338
46	130	260	287	807	356	339
47	120	280	264	824	320	337
48	110	295	297	887	335	330

WELL NO. 1, OGEMAW COUNTY (PERMIT # 16755), Continued.

Sample Number	Sea Level Elevation	<u>Relative Intensities</u>			<u>Ba-Mg Ratio</u>	Average Ratio
		<u>Mg</u>	<u>Ba</u>	<u>(2Mg + Ba)</u>	<u>Ba ÷ (2Mg + Ba)</u>	
49	100	287	290	864	336	335
50	90	311	311	933	333	339
51	80	245	262	752	349	354
52	70	285	349	919	380	354
53	60	297	297	891	333	348
54	50	283	279	845	330	326
55	40	460	425	1345	316	338
56	30	277	323	877	368	338
57	20	510	500	1520	329	347
58	10	208	217	633	343	335
59	00	277	277	831	333	335
60	-10	500	490	1490	328	315
61	-20	227	180	634	284	319
62	-30	292	306	890	344	320
63	-40	256	254	766	332	341
64	-50	313	332	958	347	334
65	-60	323	309	955	324	338
66	-70	332	345	1009	342	323
67	-80	345	300	990	303	330
68	-90	337	357	1031	346	331
69	-100	353	370	1076	344	341
70	-110	311	311	933	333	339
71	-120	304	311	919	339	338
72	-130	297	309	903	342	347
73	-140	297	334	928	360	351
74	-150	249	268	766	350	354
75	-160	245	266	756	352	346
76	-170	266	270	802	336	338
77	-180	289	280	858	326	327
78	-195	266	249	781	318	327
79	-210	309	313	931	336	330
80	-220	264	266	794	335	338
81	-230	292	306	890	344	344
82	-240	279	306	864	354	335
83	-250	321	285	927	307	336
84	-260	260	275	795	346	324
85	-270	304	285	893	319	331
86	-280	321	313	955	328	317
87	-290	300	264	864	305	320
88	-300	482	470	1434	327	299
89	-310	311	225	847	265	293
90	-320	334	268	936	286	281
91	-330	287	238	812	293	292
92	-340	319	270	908	297	293
93	-350	442	360	1244	289	286
94	-360	401	300	1102	272	281
95	-370	285	225	795	283	286
96	-380	334	292	960	304	295

WELL NO. 1, OCEMAW COUNTY (PERMIT # 16755), Continued.

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
97	-390	313	264	890	297	300
98	-400	300	256	856	299	293
99	-410	290	227	807	282	297
100	-420	330	295	955	309	295
101	-430	323	268	914	294	305
102	-440	316	287	919	312	305
103	-450	482	500	1464	341	319
104	-460	306	268	880	305	314
105	-470	272	227	771	295	299
106	-480	313	264	890	297	309
107	-490	289	290	868	334	299
108	-500	525	379	1429	266	302
109	-510	292	256	840	305	286
110	-520	337	272	946	288	292
111	-530	309	245	863	284	284
112	-540	319	249	887	281	272
113	-550	482	323	1287	251	268
114	-560	510	379	1399	271	262
115	-570	510	365	1385	264	273
116	-580	304	241	849	284	279
117	-590	295	241	831	290	295
118	-600	309	277	895	310	265
119	-610	470	227	1167	195	241
120	-620	334	185	853	217	210
121	-630	332	185	849	218	225
122	-640	316	199	831	240	254
123	-650	345	300	990	303	268
124	-660	349	245	943	260	299
125	-670	316	316	948	333	265
126	-680	326	165	817	202	289
127	-690	323	319	965	331	279
128	-700	334	292	960	304	308
129	-710	351	283	985	288	283
130	-720	311	213	835	256	282
131	-730	297	256	850	302	279
132	-740	345	268	958	279	284
133	-750	311	232	854	272	276
134	-760	500	384	1384	277	286
135	-770	277	247	801	309	293
136	-780	323	268	914	293	303
137	-790	280	247	807	306	286
138	-800	297	208	802	259	283
139	-810	313	247	873	283	277
140	-820	297	241	835	288	273
141	-830	275	180	730	247	275
142	-840	326	264	910	290	274
143	-850	304	241	849	284	

WELL NO. 2, OGEMAW COUNTY (PERMIT # 16529). ELEVATION: 1238'

<u>Sample Number</u>	<u>Sea Level Elevation</u>	<u>Relative Intensities</u>			<u>Ba-Mg Ratio</u>	<u>Average Ratio</u>
		<u>Mg</u>	<u>Ba</u>	<u>(2Mg + Ba)</u>	<u>Ba ÷ (2Mg + Ba)</u>	
1	710	365	290	1020	284	
2	700	416	311	1143	299	284
3	690	451	334	1236	270	314
4	680	241	287	769	373	312
5	670	416	345	1177	293	313
6	660	442	332	1216	273	293
7	650	416	379	1211	313	297
8	640	351	309	1011	305	302
9	630	401	323	1125	287	293
10	620	420	337	1177	286	298
11	610	304	287	895	321	305
12	602	319	285	923	309	327
13	595	297	319	913	350	336
14	585	409	442	1260	350	337
15	575	330	297	957	311	311
16	565	375	280	1030	272	287
17	555	351	283	985	287	286
18	545	332	295	959	308	300
19	535	337	295	969	305	305
20	525	370	319	1059	304	301
21	515	321	280	922	304	328
22	505	416	353	1185	298	328
23	495	357	439	1153	381	328
24	485	392	345	1129	306	333
25	475	321	292	934	313	307
26	465	319	275	913	301	292
27	455	279	199	757	263	290
28	445	349	309	1007	307	300
29	435	304	300	908	330	314
30	425	370	323	1063	304	304
31	415	351	270	972	278	299
32	405	351	323	1025	315	301
33	395	292	262	846	310	302
34	385	375	292	1042	280	293
35	375	323	262	908	289	285
36	365	397	316	1110	285	289
37	355	357	297	1011	294	294
38	345	375	326	1076	303	299
39	335	357	304	1018	299	309
40	325	401	384	1186	324	314
41	315	300	280	880	318	331
42	305	353	382	1088	351	332
43	295	375	365	1115	327	336
44	285	392	384	1168	329	321
45	275	345	306	996	307	323
46	265	388	388	1164	333	341
47	255	365	451	1181	382	346
48	245	360	345	1065	324	346

WELL NO. 2, OGEMAW COUNTY (PERMIT # 16529), Continued.

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
49	235	316	313	945	331	337
50	225	330	365	1025	356	326
51	215	460	379	1299	292	320
52	205	442	401	1285	312	309
53	195	401	334	1136	323	327
54	185	392	416	1200	346	366
55	175	290	439	1019	430	366
56	165	370	353	1093	323	375
57	155	397	433	1227	352	337
58	145	409	416	1234	337	335
59	135	470	433	1373	315	318
60	105	439	379	1257	302	322
61	95	332	357	1021	349	329
62	85	357	360	1074	335	343
63	75	277	290	844	344	330
64	65	365	330	1060	311	314
65	55	353	283	989	286	298
66	5	292	247	831	297	298
67	-5	376	340	1092	311	314
68	-15	345	345	1035	333	325
69	-25	345	340	1030	330	324
70	-35	397	353	1147	308	319
71	-45	334	311	979	318	311
72	-55	382	337	1101	306	318
73	-65	330	326	986	330	315
74	-75	351	313	1015	308	322
75	-85	360	349	1069	327	325
76	-95	297	306	900	340	342
77	-105	326	365	1017	359	339
78	-115	397	370	1164	317	336
79	-125	353	349	1055	331	321
80	-135	370	340	1080	315	312
81	-145	360	292	1012	289	306
82	-155	382	351	1115	314	302
83	-165	323	280	926	302	307
84	-175	375	330	1080	306	295
85	-185	340	260	940	277	295
86	-195	409	353	1171	301	301
87	-205	392	379	1163	326	323
88	-215	433	451	1317	342	321
89	-235	416	349	1181	295	308
90	-245	409	330	1148	288	293
91	-255	382	321	1085	296	305
92	-265	304	300	908	330	308
93	-275	425	360	1210	298	309
94	-285	-	-	-	-	-
95	-305	388	330	1106	298	295
96	-315	397	323	1117	289	287

WELL NO. 2, OGEMAW COUNTY (PERMIT # 16529), Continued.

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
97	-325	375	283	1033	274	261
98	-335	490	277	1257	220	294
99	-345	285	360	930	287	302
100	-355	353	300	1006	298	323
101	-375	384	306	1074	284	308
102	-417	283	309	875	353	330
103	-422	357	392	1106	354	347
104	-427	283	283	849	333	330
105	-437	300	260	860	304	307
106	-442	353	280	986	284	292
107	-447	360	290	1010	287	285
108	-452	-	-	-	-	-
109	-457	360	285	1005	284	297
110	-465	360	340	1060	320	292
111	-482	349	262	960	273	284
112	-487	306	213	825	258	277
113	-492	375	323	1073	300	277
114	-497	-	-	-	-	-
115	-502	382	285	1049	272	272
116	-515	433	280	1146	244	262
117	-525	375	277	1027	270	255
118	-535	416	277	1109	250	263
119	-545	382	283	1047	270	263
120	-555	442	326	1210	270	270
121	-565	475	349	1299	269	267
122	-575	375	268	1018	263	258
123	-585	433	277	1143	242	259
124	-595	439	330	1208	273	261
125	-605	409	300	1118	268	278
126	-615	384	319	1087	284	285
127	-625	442	365	1249	292	274
128	-635	382	238	1002	237	264
129	-645	388	279	1055	264	257
130	-655	439	326	1204	270	273
131	-665	384	306	1074	285	270
132	-675	353	256	962	256	272
133	-685	392	297	1081	274	267
134	-695	416	311	1143	272	273
135	-705	384	287	1055	272	273
136	-715	353	268	974	275	266
137	-725	370	249	989	252	259
138	-735	357	238	952	250	257
139	-745	409	300	1118	269	258
140	-755	416	285	1117	256	266
141	-765	-	-	-	-	-
142	-775	392	292	1076	272	249
143	-785	349	194	892	218	251
144	-795	392	280	1064	263	

WELL NO. 3, OGEMAW COUNTY (PERMIT # 4831). ELEVATION: 856'

Sample Number	Sea Level Elevation	<u>Relative Intensities</u>			<u>Ba-Mg Ratio</u>	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
1	100	247	247	741	333	
2	88	227	175	629	279	323
3	73	217	241	675	358	316
4	55	241	217	699	311	335
5	37	247	249	743	335	321
6	25	256	238	750	318	334
7	15	225	241	691	349	328
8	5	213	199	625	318	324
9	-5	232	204	668	306	319
10	-15	249	249	747	333	320
11	-25	220	208	648	321	324
12	-35	241	225	707	318	296
13	-47	247	165	659	250	295
14	-60	238	220	696	316	296
15	-70	238	225	701	321	317
16	-80	227	208	662	314	314
17	-90	235	208	678	307	305
18	-100	235	194	664	293	293
19	-110	321	264	906	280	276
20	-119	283	194	760	255	282
21	-134	232	208	672	310	302
22	-152	232	241	705	342	327
23	-165	235	232	702	330	333
24	-175	235	227	697	326	325
25	-185	232	217	681	318	324
26	-195	238	232	708	328	324
27	-205	321	311	853	326	324
28	-215	235	220	290	319	329
29	-225	227	235	689	341	325
30	-235	-	-	-	-	-
31	-245	245	225	715	315	326
32	-255	249	238	736	323	295
33	-266	241	250	632	248	287
34	-276	245	199	689	289	279
35	-288	238	204	680	300	301
36	-297	241	220	702	313	297
37	-302	235	180	650	277	278
38	-312	309	199	817	244	266
39	-335	227	175	629	278	275
40	-352	247	213	707	302	301
41	-362	238	225	701	322	313
42	-375	323	295	941	314	323
43	-385	227	225	679	332	307
44	-395	232	175	639	274	312
45	-405	232	227	691	329	307
46	-417	330	306	966	317	310
47	-430	256	204	716	285	304
48	-440	238	213	689	310	299

WELL NO. 3, OGEMAW COUNTY (PERMIT # 4831), Continued

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba + (2Mg + Ba)	
49	-450	254	220	966	317	310
50	-460	235	225	695	323	315
51	-470	232	217	681	319	323
52	-480	235	227	697	326	321
53	-490	235	220	690	319	321
54	-500	316	295	927	319	317
55	-512	235	213	683	312	297
56	-524	311	217	839	259	278
57	-537	232	165	629	263	279
58	-560	247	225	719	314	277
59	-580	249	170	668	255	287
60	-590	235	194	664	293	272
61	-600	227	165	619	267	271
62	-610	319	217	855	254	286
63	-622	227	232	686	338	306
64	-637	232	225	689	327	324
65	-650	235	208	678	307	313
66	-660	247	217	711	306	299
67	-672	235	185	655	283	299
68	-689	235	208	678	307	297
69	-701	238	204	680	300	299
70	-712	334	272	940	290	270
71	-727	312	175	799	220	281
72	-742	227	227	681	333	268
73	-755	269	180	718	250	311
74	-765	-	-	-	-	-
75	-777	235	254	724	350	296
76	-790	330	266	926	288	303
77	-800	326	241	893	270	

WELL NO. 4, OGEMAW COUNTY (PERMIT # 4623). ELEVATION: 800'

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
1	643	311	213	835	255	
2	633	442	313	1197	262	280
3	626	375	357	1107	322	293
4	618	287	241	815	296	289
5	612	365	241	971	248	280
6	605	379	311	1069	296	276
7	595	442	249	1233	283	286
8	595	313	241	867	278	256

WELL NO. 4, OGEMAW COUNTY (PERMIT # 4623), Continued.

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
9	575	490	256	1236	207	224
10	567	425	194	1044	188	223
11	562	510	384	1404	273	244
12	555	460	345	1265	272	329
13	547	340	540	1220	442	334
14	541	360	289	1009	287	335
15	535	360	275	995	277	276
16	530	272	194	738	263	276
17	525	306	247	859	288	280
18	519	326	266	918	290	284
19	512	345	262	952	275	269
20	506	500	319	1319	242	272
21	498	365	309	1039	298	274
22	492	379	297	1055	281	291
23	485	365	289	1019	293	275
24	477	397	268	1062	252	284
25	469	379	334	1092	306	284
26	461	353	292	998	293	301
27	455	439	382	1260	303	286
28	448	490	349	1329	263	281
29	440	433	330	1196	276	282
30	432	290	256	836	306	285
31	425	379	285	1043	273	288
32	416	365	289	1019	284	278
33	407	433	330	1196	276	283
34	400	304	247	855	289	294
35	396	330	304	964	316	286
36	387	460	311	1231	252	283
37	378	451	351	1253	280	260
38	367	284	254	1022	248	261
39	359	470	323	1263	256	260
40	352	401	304	1106	275	279
41	343	306	270	882	306	282
42	336	442	321	1205	266	279
43	328	401	290	1092	265	259
44	322	384	238	1006	246	257
45	314	357	249	963	259	252
46	306	460	309	1229	252	261
47	298	392	282	1076	272	266
48	290	360	272	992	274	281
49	283	351	297	999	297	268
50	276	442	266	1150	232	251
51	268	510	295	1315	224	242
52	261	388	289	1065	271	256
53	254	451	340	1242	373	264
54	246	439	292	1170	249	271
55	238	351	289	991	292	274
56	229	439	345	1223	282	291

WELL NO. 4, OGEMAW COUNTY (PERMIT # 4623), Continued.

Sample Number	Sea Level Elevation	Relative Intensities			Ba-Mg Ratio	Average Ratio
		Mg	Ba	(2Mg + Ba)	Ba ÷ (2Mg + Ba)	
57	222	387	240	1134	299	291
58	217	375	309	1059	292	310
59	207	345	353	1043	338	303
60	194	357	375	989	278	301
61	182	460	370	1290	287	283
62	170	330	262	922	284	281
63	130	357	266	980	272	279
64	121	332	260	924	282	296
65	113	357	360	1074	334	327
66	105	409	470	1288	365	331
67	87	332	277	941	294	310
68	62	409	306	1124	272	288
69	47	409	349	1167	299	295
70	40	392	360	1144	314	301
71	20	409	334	1152	290	300
72	10	337	283	957	296	316
73	-5	384	439	1207	363	336
74	-22	316	340	972	350	339
75	-35	384	337	1105	305	320
76	-45	392	345	1129	306	303
77	-61	375	319	1069	298	299
78	-69	353	292	998	293	293
79	-77	365	295	1025	288	281
80	-85	388	277	1053	263	282
81	-97	365	304	1034	294	284
82	-117	351	295	997	296	291
83	-140	375	295	1045	282	281
84	-160	397	285	1079	264	256
85	-170	470	270	1210	223	251
86	-180	357	260	974	267	250
87	Duplicate	-	-	-	-	-
88	-190	482	337	1301	259	272
89	-200	357	292	1006	290	277
90	-208	382	300	1064	282	274
91	-216	416	275	1107	249	273
92	-223	401	326	1128	289	277
93	-231	388	319	1095	292	294
94	-239	326	279	931	300	300
95	-247	401	375	1177	308	306
96	-262	345	311	1001	311	303
97	-287	360	295	1015	290	311
98	-302	451	451	1353	333	286
99	-307	375	232	982	236	293
100	-312	382	345	1109	311	267
101	-318	475	323	1273	254	284
102	-326	439	353	1231	286	258
103	-335	439	270	1148	235	252
104	-345	475	290	1240	234	235

WELL NO. 4, OGEMAW COUNTY (PERMIT # 4623), Continued.

<u>Sample Number</u>	<u>Sea Level Elevation</u>	<u>Relative Intensities</u>			<u>Ba-Mg Ratio</u>	<u>Average Ratio</u>
		<u>Mg</u>	<u>Ba</u>	<u>(2Mg + Ba)</u>	<u>Ba ÷ (2Mg + Ba)</u>	
105	-355	482	297	1261	236	240
106	-365	416	279	1111	251	237
107	-375	500	285	1285	223	234
108	-385	490	289	1269	228	215
109	-395	510	245	1265	193	211
110	-406	500	270	1270	212	205
111	-419	510	270	1290	209	224
112	-431	475	319	1269	251	248
113	-439	392	311	1095	284	280
114	-453	352	311	1015	306	289
115	-460	321	247	889	278	297
116	-465	392	349	1133	308	275
117	-472	482	300	1264	238	259
118	-480	525	313	1363	230	244
119	-491	433	309	1175	263	250
120	-503	540	375	1455	258	268
121	-514	439	349	1227	284	267
122	-528	510	357	1377	259	268
123	-548	439	311	1189	261	286
124	-575	451	460	1362	338	287
125	-585	416	297	1129	263	282
126	-596	388	241	1017	245	254
127	-607	470	321	1261	254	257
128	-615	442	330	1214	272	266
129	-630	525	392	1442	272	260
130	-655	433	266	1132	235	247
131	-675	370	227	967	235	245
132	-685	470	337	1277	264	257
133	-695	470	353	1293	272	268
134	-704	375	287	1037	267	265
135	-712	379	260	1018	255	262
136	-723	482	345	1309	264	256
137	-737	370	245	985	249	242
138	-752	500	268	1268	212	218
139	-767	475	225	1175	192	200
140	-779	510	247	1267	195	202
141	-792	475	264	1214	218	213
142	-807	540	313	1393	225	217
143	-818	451	235	1137	207	228
144	-827	433	290	1156	251	227
145	-835	540	311	1391	224	236
146	-845	475	290	1240	234	214
147	-855	490	220	1200	183	211
148	-865	482	268	1232	217	214
149	-875	570	365	1505	242	215
150	-885	540	245	1325	185	

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