A SPECTROCHEMICAL ANALYSIS OF THE INSOLUBLE RESIDUES OF THE DUNDEE LIMESTONE OF PRESQUE ISLE COUNTY, MICHIGAN

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by

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ABSTRACT

A spectrochemical analysis of the insoluble residues of the Dundee Limestone of Presque Isle County, Michigan was done to determine their use in correlation. Fourteen samples were taken; four laterally and ten vertically. A qualitative analysis showed no change in the elements present. A semi-quantitative analysis showed a change in the blackness of the spectral lines of calcium, cobalt, vanadium, magnesium, and beryllium at different horizons. The relative blackness of these spectral lines, hence the relative concentrations of the elements, remained the same in the residues of the same horizons.

Correlation between the four horizons was made based on the semi-quantitative data obtained from the relative blackness of the spectral lines of the five afore-mentioned elements.

Stanley Harold Elman

ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to all those who aided him in this study. Among those who merit acknowledgement are Mr. Paul Thornley and Mr. Duanne Dewey of the Michigan Limestone Quarry who assisted the author in procuring the samples used, Dr. H. B. Stonehouse of the Geology Department of Michigan State University for his encouragement and interest, and Drs. Schwendeman and Sternberg of the Chemistry Department of Michigan State University who placed at the disposal of the author the spectrographic and photographic equipment used in this study.

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INTRODUCTION: BACKGROUND AND PURPOSE

The application of insoluble residue studies to surface and subsurface correlation and identification of calcareous rocks has become widespread in the last two decades. The publication of methods of preparation and terminology by McQueen and Martin (1931) gave the initial impetus to this type of study which has evolved into a major segment of the geologic investigations performed by petroleum companies.

Up until now, all of the work done with insoluble residues has been with the macroscopic and near-macroscopic fractions.

> "Clay and fine silt are generally decanted in routine work. Little or no work has been done with the fine residues, and their value for correlation and identification is yet to be determined." (Ireland: Leroy, 1950,p. 143)

Spectrochemical analysis has been employed for many years; however its use has undergone a rapid advancement in the last fifty years. Up until now, the majority of the publications dealing with the use of spectrography in geologic research and investigation have been confined to qualitative and quantitative analysis of ore-bearing rocks and igneous and/or metamorphic complexes. It is the belief of the writer that this method of investigation can be applied to problems of correlation that arise in the interpretation of sedimentary formations.

Little or no work has been done with the fine fraction of insoluble residues. Insoluble residues reflect the sea bottom conditions, the classic conditions, the action of the currents, and the conditions existing on the adjacent land-masses during deposition. These factors may change independently or together and over long periods of time or rather abruptly. If the conditions mentioned above remained constant over a long period of time, no lithologic change would take place in the sediment; hence, no stratigraphic breaks would occur. If conditions did change, however,, but to such a small degree or in some particular way so that no visible lithologic change could be seen in the sediment, formations deposited under different conditions might be considered to be of the same "environment". A study of the residues would show this assumption to be false. In areas where the residues consisted almost entirely of fines, the investigation would not be undertaken due to lack of suitable method of analysis. It is the contention of the author that in such cases as described above, a spectrochemical investigation of the fines could yield useful results.

The samples used in this study were chosen from the Dundee Formation in the Michigan Basin, since the Dundee has been well investigated and insoluble residue studies have been made (see Bibliography). Also petroleum production in the basin from this formation is relatively important.

At first, well cuttings were considered as the basis of the investigation. After running some tests and looking at various sets of well samples from different sections of the state, it was decided that the contamination introduced by the drilling tools, the drilling mud, and the cavings would be so great as to prohibit a true investigation. Quarry samples were chosen because of their purity and the Michigan Limestone Quarry at Rogers City, Michigan was chosen as the sampling site (see figures 1 and 2). As was later discovered during the digestion of the limestone, the Dundee at this locality is exceptionally pure; yielding less than 1 per-cent (by volume) of residue. In most of the samples, the fines ran as high as 95 per-cent by volume of the total residue; the remainder being composed of quartz, gypsum and fossil fragments. The large proportion of fines made this location ideal for the study being performed.

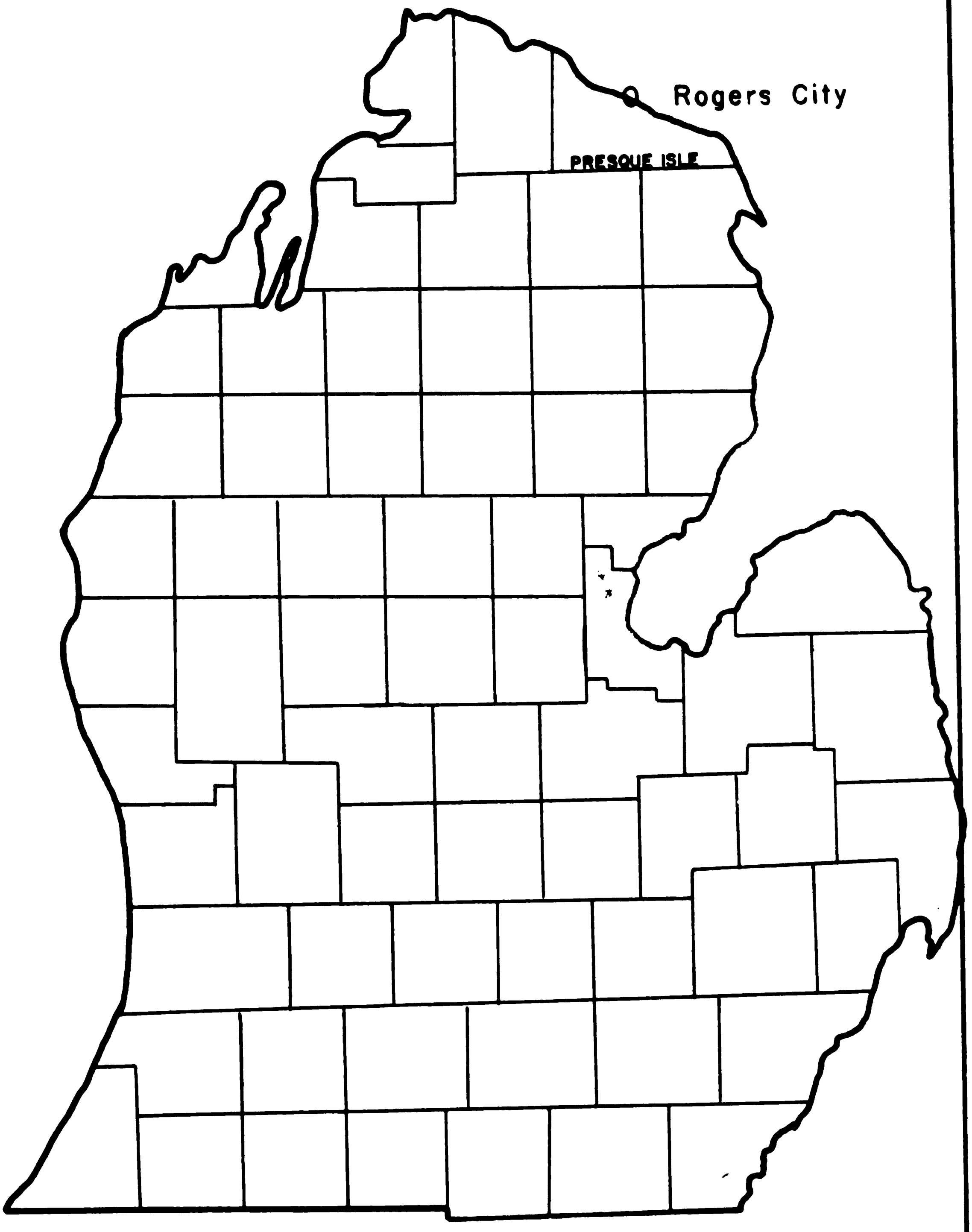

Figure I: Location Map

Southern Peninsula of Michigan

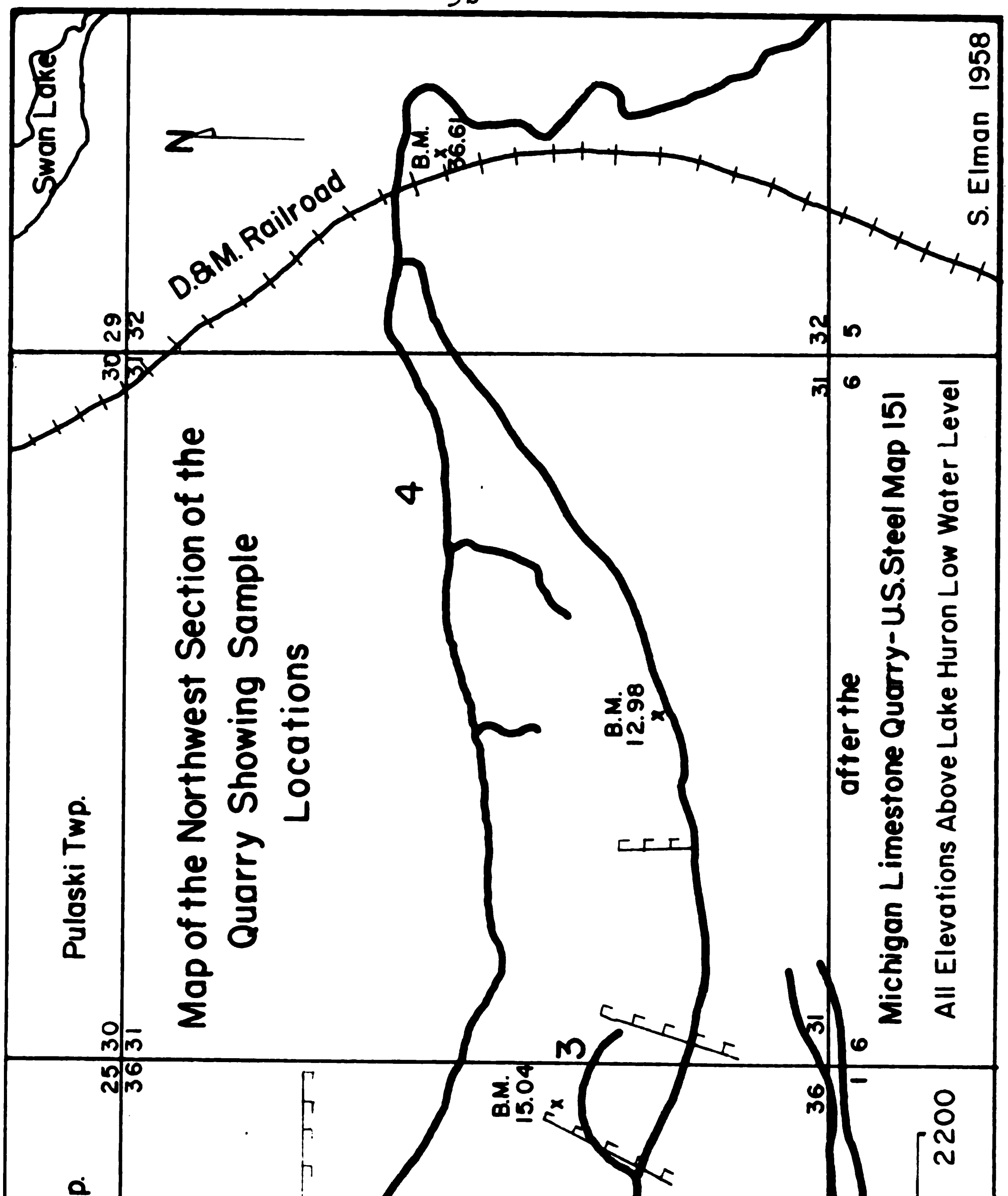
Map of the Northwest Section of the Quarry Showing Sample Locations
after the Michigan Limestone Quarry-U.S. Steel Map 151
All Elevations Above Lake Huron Low Water Level
S. Elman 1958
Swan Lake
D.&M. Railroad
N
Rogers Twp.
Pulaski Twp.
25
36
30
31
29
32
31
6
32
5
36
1
31
6
B.M. 36.61
B.M. 12.98
B.M. 15.04
1
2
3
4
0
1100
2200
feet

Figure 2

DESCRIPTION AND AREAL EXTENT OF THE DUNDEE FORMATION

The Dundee Formation is quite widespread and underlies nearly all of the Southern Peninsula of Michigan. It is Middle Devonian in age and was first defined by Lane (1893, p.25). The Dundee is overlain throughout most of the state by the Rogers City Limestone which is a brownish-buff dolomitic limestone or dolomite. In Southeastern Michigan where the Rogers City is absent, the Dundee is overlain unconformably by the Bell Shale member of the Traverse Group. Throughout the Southern Peninsula of Michigan, the Dundee Formation rests unconformably on the Detroit River Group. The lower extremity of the Dundee is usually placed at the appearance of the first anhydrite bed of the Detroit River Group.

The surface extent of the Dundee Formation is very limited with the only outcrops being found

> "in a narrow belt in the southeastern part of the Peninsula and along the shore of Lake Huron from Mackinaw City, Cheboygen County to Presque Isle, Presque Isle County." (R.A.Smith,1915,p.159)

The thickness of the Dundee ranges from 100 feet in the southeastern portion of the Southern Peninsula to over 200 feet in the northern part. Thicknesses of 400 feet or better have been encountered in wells drilled in Tuscola County, Michigan.

The Dundee is chiefly a high calcium limestone with some magnesium impurity near the base. It is generally gray to buff to brown in color, crystalline, and locally very fossiliferous.

The beds of the Dundee in the Michigan Limestone Quarry are dark gray to buff, crystalline and especially high in calcium carbonate.

> "The average of 235 analyses of the upper fifty feet of cores (from this quarry) gave 97.85 per-cent of calcium carbonate, 1.26 per-cent of magnesium carbonate and 0.34 per-cent of silica". (R.A.Smith, 1915, p.251)

BASIC THEORY OF SPECTROSCOPY

An atom, when excited, is known to emit radiant energy of definite wavelength. The excitation process causes an electron to be elevated to a higher state than is normal for the particular atom in question. The return of the electron to its normal orbital position is accompanied by a loss of energy which is radiated. The energy lost by the electron during the return can be represented by the energy difference between the two states and this may be equated to $h\nu$ where h is the Planck constant (6.62×10^{-27} erg-second) and ν is the frequency of the energy radiated (in vibrations per second). From this, it can be seen that the electron energy loss may be measured in terms of the frequency of the radiant energy.

The radiant energy, when dispersed, produces a spectrum that is thus unique for the particular atom or molecule. The means of excitation may be an arc, spark, flame, or discharge tube. A mixture of unknown elements, therefore, can be identified by the interpretation of the spectra emitted during excitation. Since the concentration of the element present is directly proportional to the radiation, and the radiation emitted is proportional to the amount of blackening or the "optical density" of the spectral line produced on the photographic plate, a measure of the element present in the unknown sample can be determined.

Various books, tables, and charts have been published listing the most persistant lines of the elements by wavelength. The tables used for identification in this study can be found in Brode (1943), Ahrens (1950), Harvey (1950), and Harrison (1939). Also used as an aid in identification was the spectral chart of the most persistant lines of R. U. Powder; this chart also containing the persistant lines of the iron spectrum which was used as an external standard.

The complete spectrum or, as Brode states "the spectral distribution of energy" (Brode,1943,p.3), runs from the ultra-sonic (large wavelength, low frequency) to cosmic rays (small wavelength, high frequency). The portion of the spectrum used in this study ranges from 2929A to 4383A or from the near ultra-violet into the visible range. This portion was used for the two following reasons: (1) within its boundries can be found the most persistant lines of most of the common elements, and (2) the instrument used would not photograph the spectrum at higher wavelengths. In some cases, however, photographic plates were exposed at lower wavelengths so as to confirm the identification of certain elements suspected.

SAMPLES

LOCATION AND FIELD PROCEDURES

The samples used in this study were obtained from the Michigan Limestone Quarry at Rogers City located on the shore of Lake Huron in Presque Isle County of the Southern Peninsula of Michigan (see figure 1). The quarry, which is owned and operated by the Michigan Limestone Division of United States Steel, is the largest limestone quarry in the world. It was selected as the sampling site because it was felt that truly representative samples of the Dundee Formation were to be obtained there and the exposure was suitable for the purpose. Figure 2 shows the locations of the samples. This section of the quarry was selected for sampling as a persistent chert bed occurs, varying in thickness from 2 inches to 8 inches and lying immediately below a dolomite zone (see figures 3 and 4) which could be used as a horizon marker; all samples were taken below the chert. Small pockets of soft, gray shale were encountered in sections of the quarry and slumping zones occured locally. These sites were avoided for it was felt that samples from these locals would not be representative of the Dundee Formation.

At locations 1, 2, 3, and 4 (see figure 2), a sample was taken three feet below the chert zone. This gives the study an East-West lateral extent of one and one-half miles and a North-South lateral extent of approximately one-fourth mile.

At locations 1 and 3, 10 additional samples (5 at each locality) were taken at varying distances below the initial sample.

Fig.3: The Northwest Section of the Michigan Limestone Quarry

Fig.4: Sample Location One showing steepness of slope and chert bed near top

Due to the character of the quarry face, which was vertical in many places, sample A (the first sample below one) is 13 feet below the chert. Samples B, C, D, and E, however were taken at two-foot intervals. For the same reasons, Sample F (the first sample below 3) is 9 feet below the chert with G, H, I, and J at two-foot intervals. This method of sampling gives 3 additional lateral horizons with samples A, B, and C being at the same distance below the chert zone as samples H, I, and J. Other samples were not taken due to the steepness of the quarry wall and/or the thickness of the talus slope. Care was taken to eliminate sample contamination at the sampling site. After getting a sample at the quarry face, it was broken by pounding on another piece of limestone, thus preventing any contamination from the hammer. The samples were broken by this method to a convenient size (approximately 3 by 3 inches). Samples were placed in paper sample bags which were marked as to location and position below the chert.

SAMPLES

PREPARATION:

Because contamination of any sort would cause errors of substantial import, a carefully controlled laboratory technique was developed. A cleaning solution composed of 70 ml. of sodium dichromate and 2000 ml. of concentrated sulfuric acid was prepared and all glassware was then soaked in this solution. The glassware was then washed twice in distilled, de-ionized water and left to dry. The acid used to digest the limestone samples was 12 normal hydrochloric acid diluted one to one with distilled, de-ionized water to 6 normal. The 6 normal acid was then distilled to two-thirds its original volume with the impurities remaining in the residue. The samples were then placed in 400 ml. beakers and the distilled hydrochloric acid was added until the reaction had ended. The samples were not broken or crushed prior to digestion. A list of the sample weights and the approximate amount of acid needed for digestion can be found in Table A. The samples were not heated during solution so that volatile constituents were retained. The residues were filtered and dried in a warm oven (150°F) overnight. They were then placed in small, screw top vials, marked, and stored. Samples of the solution were also preserved in vials.

Some of the residues obtained contained fossil fragments. These were removed by picking them off the filter paper with a toothpick. They were placed in their own vials and labeled accordingly. A microscopic inspection of the fossil fragments revealed the original shell material had been completely replaced by silica; much of which was in the form of minute quartz crystals. The shape of the hard parts, however, was preserved. From the size and shape of the fragments, they were identified as brachiopods with some crinoid stems present.

Due to the fact that the material contained in these fossil fragments was deemed secondary, they were not analyzed with the residue but on a separate photographic plate.

TABLE A

Sample No.	Weight (in gms)	Amount of Acid (ml)
1	43	200
2	40	200
3	43	200
4	93	300
A	89	300
B	163	600
C	119	450
D	107	400
E	136	500
F	116	450
G	71	275
H	70	275
I	81	300
J	101	400

SAMPLES

DESCRIPTION OF RESIDUES:

During the process of transfer of the residues from the filter paper to the vials, the non-fines were segregated from the fines by use of a toothpick and placed in their own vials. The following is a description of these non-fines.

Sample One: Siliceous, fossiliferous material, very fragmentary; massive gypsum and fragmentary quartz.

Sample Two: Siliceous, fragmental fossiliferous material, tentatively identified as brachoipods, iron stain; some fragments of quartz found, no massive gypsum.

Sample Three: Consisted wholly of fines.

Sample Four: Siliceous brachoipod fragments, some with complete shells and hinge line, quartz crystals formed on inside parts of shells causing a geode-like affect; massive gypsum and fragments of quartz present, some iron stain.

Sample A: Silicified brachoipod fragments, some badly crushed, coated with fines and iron stain.

Sample B: Silicified brachiopod fragments coated with fines and iron stain; fragments of quartz with some well defined crystals.

Sample C: Silicified brachiopod fragments coated with fines and iron stain; gray to white massive microcrystalline gypsum.

Sample D: Silicified brachiopod fragments coated with iron stain; gray to white massive, microcrystalline gypsum; milky to white quartz fragments.

Sample F: Silicified brachiopod fragments, some large with complete shells and hinge line visible, iron stain coating; milky to white quartz fragments; gypsum of two types: (1) gray to white massive microcrystalline, and (2) colorless, vitreous crystals.

Sample G: Silicified brachiopod fragments with iron stain, some crinoid stem fragments; gray to white massive microcrystalline gypsum; milky to white quartz fragments.

Sample H: Silicified brachiopod fragments with iron stain; gray white massive microcrystalline gpysum; milky to white quartz fragments.

Sample I: Silicified brachiopod fragments with iron stain; gray to white massive microcrystalline gypsum; milky to white quartz fragments; fossils badly crushed.

Sample J: Silicified brachiopod fragments with iron stain;

gypsum of both types abundant; milky to white quartz fragments; crinoid stem fragments.

Sample E: Silicified brachiopod fragments coated with fines and iron stain; gray to white massive microcrystalline gypsum; milky to white quartz fragments.

SAMPLES

SPECTROGRAPHIC TECHNIQUES:

The instrument used for these analyses was a Bausch and Lomb Large Littrow Spectrograph which utilizes a quartz Littrow prism for dispersing. The computed dispersion of this instrument for the section of the spectrum used in this study was about 5.8 A/mm. The excitation source used was a Direct Current Arc energized at 70 volts and 4 amperes; anode excitation was used throughout. Kodak Spectrum Analysis Number One plates of size 10.2 by 25.4 cms. were used as the recording device. Development of the plates was by use of Kodak Developer D-19 for 4 minutes at 70°F. This was followed by a 30 second stop bath, a 15 minute acid fix and a 30 minute washing period. All plates were exposed with a slit width of 10 microns and a slit height of 5 millimeters with an overlap of approximately one millimeter. National spectroscopic carbon electrodes, one-fourth inch by 12 inches, manufactured by the National Carbon Company, were used.

The samples were burned according to the following format: Five milligrams of the sample was placed in a shallow cup drilled in the end of the lower electrode. A toothpick was used to transfer the sample from the bottle to the electrode so as to eliminate the contamination that would have been introduced by a metal strip. The upper electrode was partially beveled producing a smooth burn. The gap length between the electrodes was held at approximately one-fourth inch during all of the arcings in order to produce the best results. The amperage and voltage were controlled through a rheostat on the power supply unit. Arcing of the electrodes was done by means of a striker electrode which was run from the upper to the lower electrode causing the arc to jump the gap. The shutter was then opened and the sample burned until the cup had been completely consumed. Complete consumption was considered necessary because

> "some elements form highly refactory carbides with the electrode and persist in the arc long past their expected or noticeable burning time". (Harvey,1950,p.125)

The plate was then racked up 4 millimeters (so as to give an overlap of one millimeter) and the operation repeated for the next sample. This was continued until a convenient number of spectra (usually 4 or 6) were photographed on the same plate. The carbon electrodes were replaced by iron electrodes and the iron spectra were recorded above and below the sample series and were used for alinement and external standard identification purposes.

The fossil fragments found in some of the samples were burned in the same manner as the residues.

Many methods have been outlined for the preparation and arcing of liquid samples. The author found the following method to be highly satisfactory. The electrodes were pre-arced (the upper slightly beveled, the lower flat) for approximately 2 minutes. This caused a porosity to develop in the lower electrode. The lower electrode was then dipped approximately one-fourth inch into the liquid allowing it to soak up into the electrode. Immediate arcing followed; burning the lower electrode one-fourth inch down from the top (approximately 5 minutes). Although this caused heavy cyanogen bands, the spectral lines present were sharp and clear. The liquids were analyzed in series as were the residues with iron spectra above and below.

A few words on the method employed in identification is considered necessary for a complete understanding of the spectrochemical technique and such a discussion follows.

For the most part, the identifications were made by comparison with standard charts and tables. Such can be found in the publications already mentioned. When this method was not feasible, the wavelength of the unknown spectrum line was determined by the method outlined in Ahrens (1950,pp.62-63). A positive identification was made by the location and naming of the most persistant lines of the elements and in most cases at least 2 lines were identified before final confirmation was given to the existance of an element in the spectra of the residue or liquid.

SPECTROGRAPHIC RESULTS

QUALITATIVE:

Figures 5 through 12 are reproductions of the photographic plates utilized in this study. A list of the elements found on these plates is shown in Table B.

Figure 7 shows the spectrum of residue number 1 photographed at a lower wavelength of the spectrum than the other plates. This was done to check the existance of silicon, antimony, and bismuth. Figure 7 also contains the spectra of the liquids of samples 1 through 4. An inspection of Table B will show that only one spectrum line was used for the identification of each of the elements antimony and strontium in the liquid spectra. These lines are the most persistant of these elements and, in the case of strontium, the next most persistant line is beyond the scope of the instrument used.

An inspection of the plates photographed yielded no qualitative difference between the residues. That is, the same elements persisted throughout all of the residues arced, thus confirming the findings of Sloss and Cooke (1946). The spectra of the liquids, which were photographed and identified so as to complete the research, contained their own suite of elements but these also were monotonously persistant throughout the samples.

TABLE B

SPECTRAL LINES USED IN ELEMENT IDENTIFICATION

I: Lines used in insoluble residue identifications:

Element	Spectral Lines - Wavelength in A
Iron(Fe)	3099.9, 3100.3, 3100.7
Magnesium(Mg)	3091.9, 3329.9, 2942.1
Aluminum(Al)	3944.0, 3092.9, 3082.2
Vanadium(V)	3185.4, 3184.0, 3183.4
Beryllium(Be)	3131.1, 3130.4, 3321.3
Molybdenum(Mo)	3132.6, 3194.0
Calcium(Ca)	3158.9, 3179.3, 3933.7
Antimony(Sb)	3267.5, 2769.9, 2528.5
Titanium(Ti)	3242.0, 3322.9, 3329.5
Zinc(Zn)	3345.5, 3345.0, 2800.9
Cobalt(Co)	2424.9, 3453.5, 3502.3
Silicon(Si)	3905.5, 2528.8, 2506.9
Bismuth(Bi)	3067.7, 2497.7
Sodium(Na)	3302.9, 3302.2

II: Lines used in the liquid identifications:

Iron(Fe)	3099.9, 3100.3, 3100.7
Calcium(Ca)	3644.4, 3179.3, 3158.9
Vanadium(V)	3183.4, 3183.9, 3185.4
Titanium(Ti)	3192.0, 3371.5, 3981.8
Magnesium(Mg)	4352.1, 3093.1, 3091.1
Antimony(Sb)	3232.5
Strontium(Sr)	4077.7

III: Lines used in the fossil identifications:

Iron(fe)	3020.7, 3471.3, 3608.9
Silicon(Si)	2881.6, 3905.5
Magnesium(mg)	2928.7, 3329.9
Aluminum(Al)	3082.2, 3092.7, 3539.4
Vanadium(V)	3102.3, 3183.4, 3185.4
Calcium(Ca)	3158.9, 3179.3, 3844.4
Titanium(Ti)	3239.0, 3989.8
Copper(Cu)	3247.6, 3273.9, 3602.0
Zinc(Zn)	3035.8, 3345.0, 3345.5

PLATES

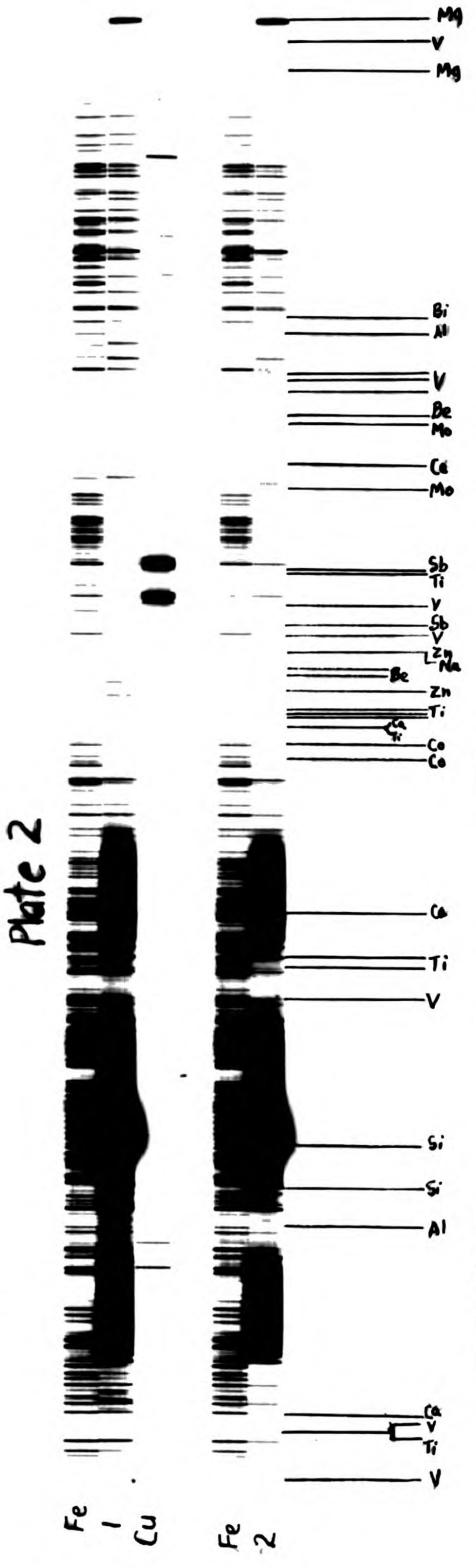

Figure 5: Spectra of Iron and Residues 1 and 2 (4383 to 2929A)

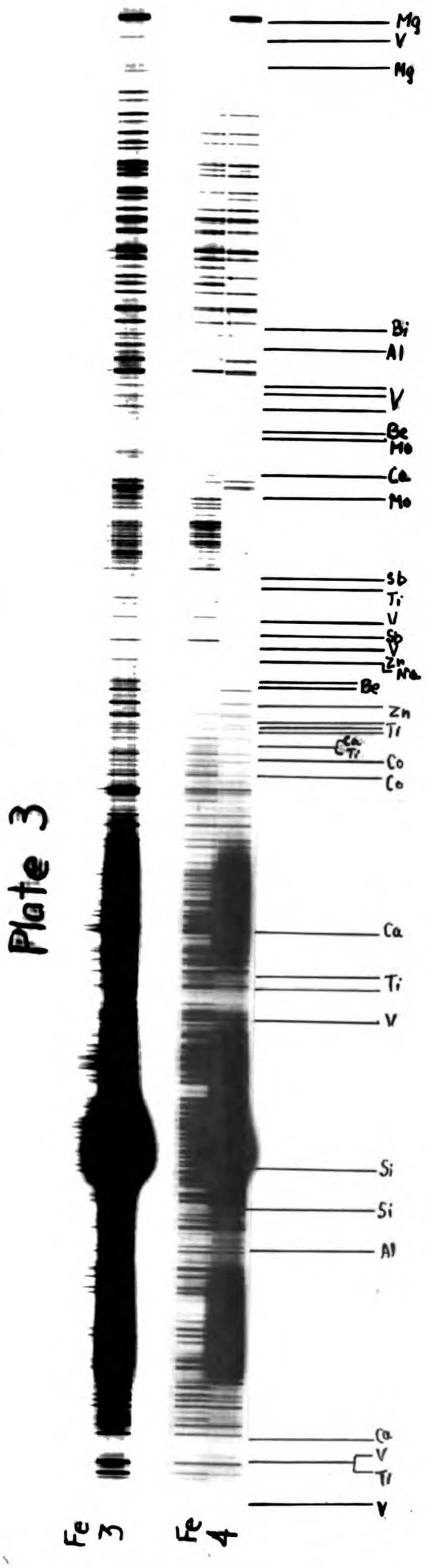

Figure 6: Spectra of Iron and Residues 3 and 4 (4383 to 2929A)

PLATES

Plate 6

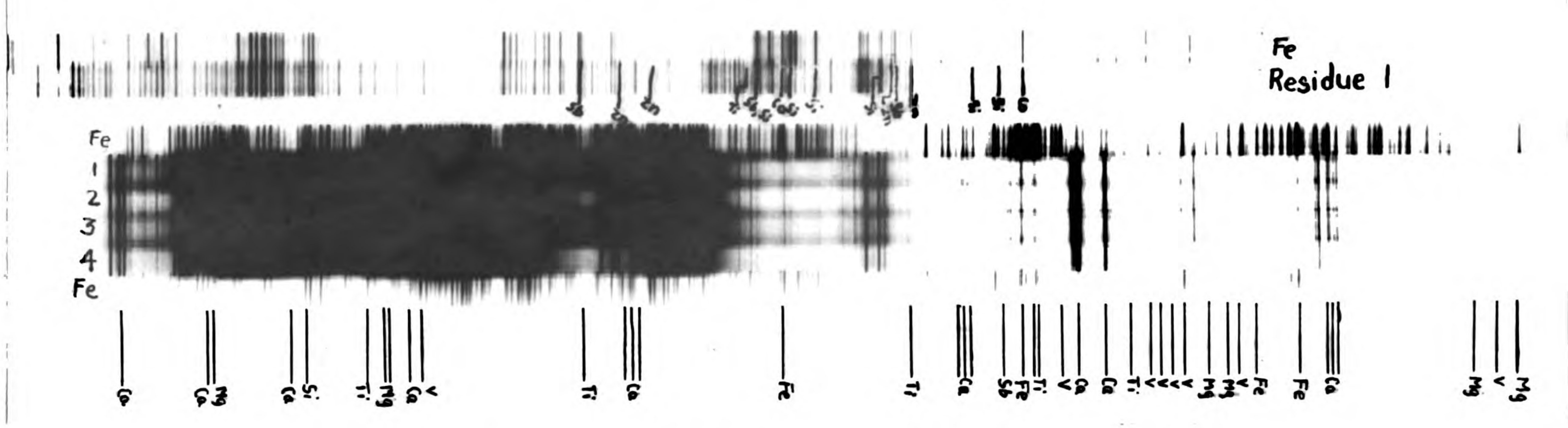

Figure 7: Spectra of Iron and Residue 1 (2973 to 2327A)
Spectra of Iron and Liquids 1 - 4 (4383 to 2929A)

Plate 7

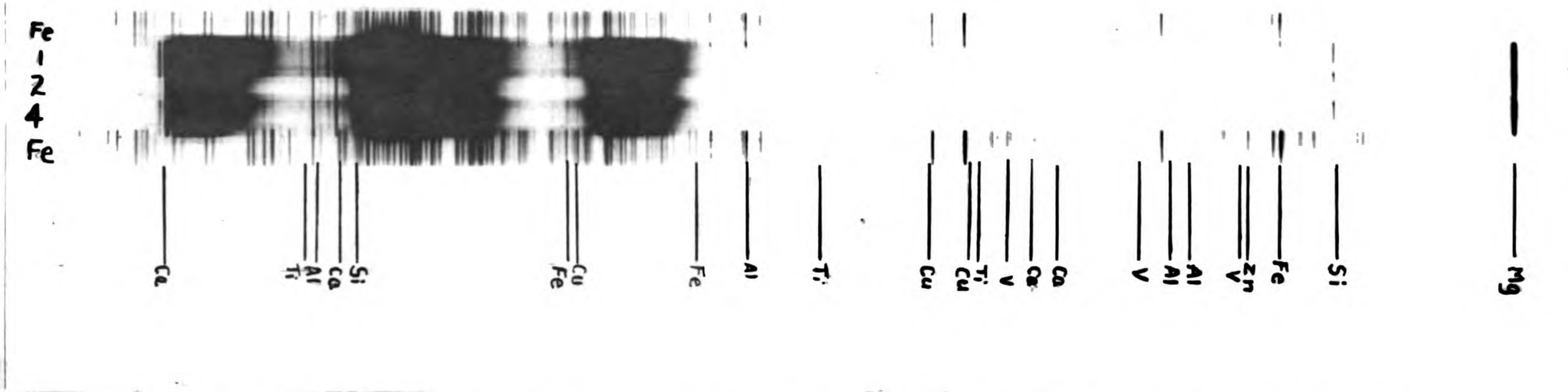

Figure 8: Spectra of Iron and Fossils from Residues 1,2, and 4 (4383 to 2929A)

PLATES

Plate 8

Figure 9: Spectra of Iron and Residues 1,A,B,C,D,E (4383 to 2929A)

Plate 9

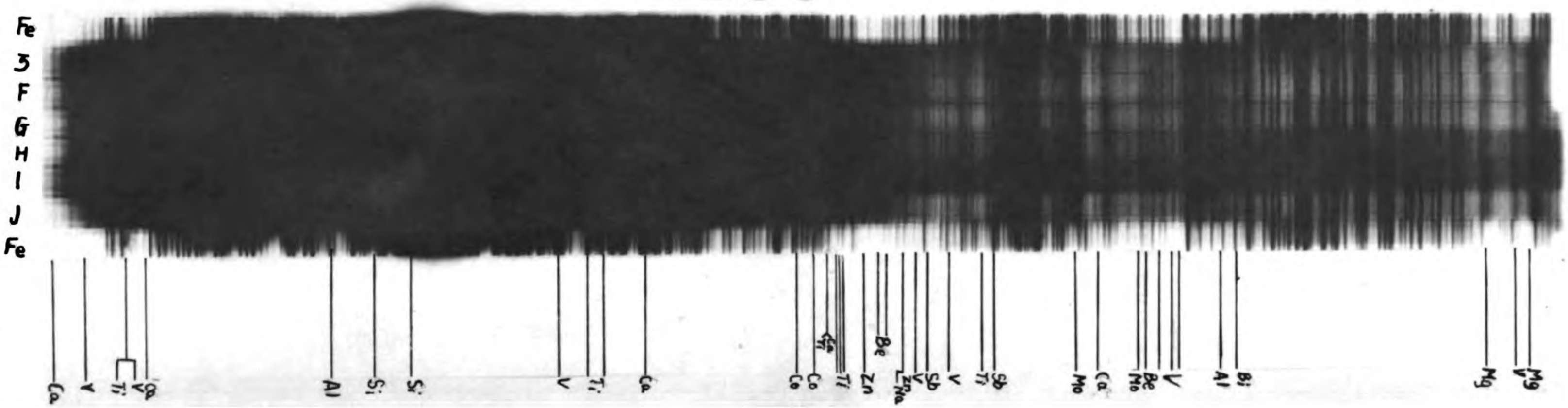

Figure 10: Spectra of Iron and Residues 3,F,G,H,I,J (4383 to 2929A)

PLATES

Plate 10

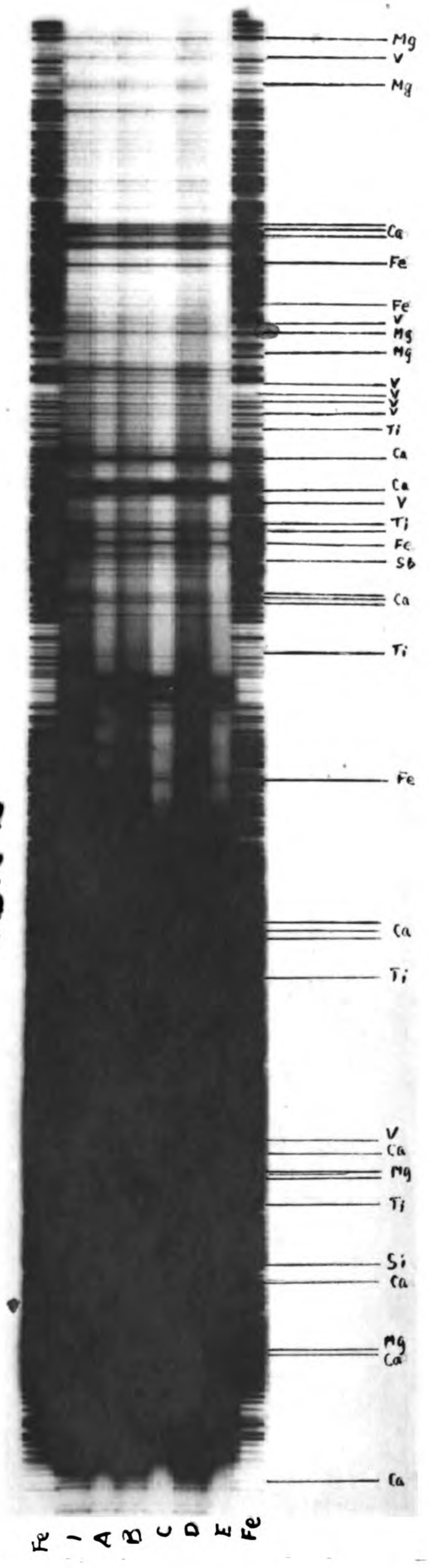

Figure 11: Spectra of Iron and Liquids 1,A,B,C,D,E (4383 to 2929A)

Plate 11

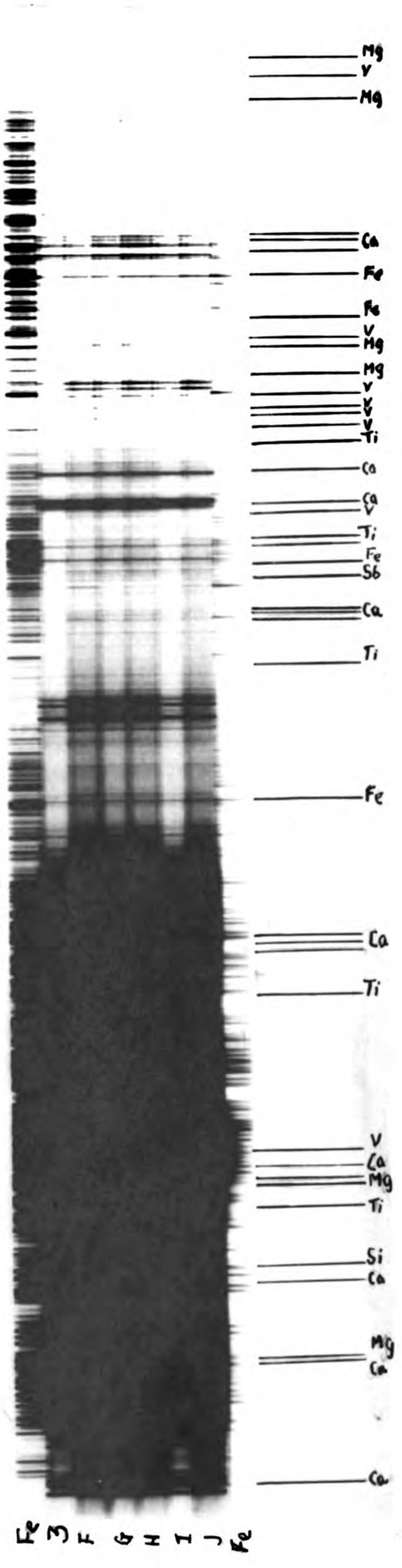

Figure 12: Spectra of Iron and Liquids 3,F,G,H,I,J (4383 to 2929A)

The following is an interpretation of the photographic plates. The elements mentioned occur in all the unknown spectra, unless otherwise specified.

The iron spectrum was persistant throughout all of the spectra analyzed. Its presence was determined by the strong iron triplet at 3100A followed by 4 evenly spaced spectral lines. A faint magnesium line was identified at 3091A and was confirmed by a strong magnesium line at 3329A. Magnesium was more abundant in the liquid than the residue spectra. Aluminum was found only in the fossil and residue spectra and was identified by lines at 3082 and 3092A. Vanadium was identified by a strong triplet at 3185, 3184, and 3183A. Beryllium was exclusive to the residue spectra and a strong line at 3321 with a weaker but persistant doublet at 3130 and 3131A confirmed its presence. Molybdenum was likewise only in the residue spectra with spectral lines at 3132 and 3194A. Calcium, which was most abundant in the liquid spectra, produced very strong lines at 3933 and 3179A. Antimony was found only in the residue and liquid spectra. The antimony line at 3267A was confirmed by exposing a plate at a lower range with the consequent identification of antimony lines at 2769 and 2528A. Titanium was identified by strong lines at 3242 and 3322A. Zinc, found only in the residue and fossil spectra, was identified by a doublet at 3345A and confirmed by a strong line at 2800A. Cobalt, found only in the residue spectra, produced strong lines at 3453 and 3502A. Silicon was present in both the residue and fossil spectra and was identified by strong lines at 3905 and 2528A. Bismuth and sodium were peculiar to the residue spectra and were identified by the spectral lines 2497, 3067, and 3302.9, 3302.3A respectively. Strontium was found only in the liquid spectra and copper only in the fossil spectra. The strontium was identified by a strong line at 4077A and the copper by the very persistant doublet at 3247 and 3273A.

TABLE C

QUALITATIVE RESULTS

Sample #	ELEMENTS															
	Fe	Mg	Al	V	Be	Mo	Ca	Sb	Ti	Zn	Co	Si	Bi	Na	Sr	Cu
1	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
2	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
3	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
4	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
A	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
B	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
C	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
D	u	u	w	u	x	x	u	v	u	w	x	w	x	x	y	z
E	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z
F	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z
G	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z
H	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z
I	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z
J	u	u	w	u	x	x	u	v	u	x	x	w	x	x	y	z

u: element found in residue, liquid, and fossil spectra
v: element found in residue and liquid spectra
w: element found in residue and fossil spectra
x: element found in residue spectra
y: element found in liquid spectra
z: element found in fossil spectra

SPECTROGRAPHIC RESULTS

SEMI-QUANTITATIVE:

Due to the fact that the same elements persisted throughout the samples used, the author inspected the findings to determine whether a semi-quantitative determination could be made. An investigation of plates 2 and 3 (Fig. 5 and 6) showed the component elements of the residues to be of approximately the same optical density; the samples thus having roughly the same concentration of the elements present. This was to be expected for the samples used in these arcings were from the same horizon in the formation (3 feet below the chert zone). Plates 8 and 9 (Figs. 9 and 10), which contain the spectra of the residues obtained from (a) residues 1, A, B, C, D, E and (b) residues 3, F, G, H, I, J, did however show a variation in the optical densities of some of the elements present. Residues A, B, and C of plate 8 are from the same horizons as residues H, I, and J of plate 9. Therefore, these spectra were used for the semi-quantitative optical density work.

A semi-quantitative blackness scale was devised. The scale ran from 1 to 10 with 1 describing the blackness of a line barely visibly and 10 one totally black.

The elements calcium, cobalt, beryllium, vanadium, magnesium were those used in the semi-quantitative investigations. They all showed a marked variation in the samples that were not from the same horizon.

The 3453A line of cobalt has a blackness of 4 in the spectrum of residue A, 5 in B and 4 in C. The same values were assigned to the cobalt 3453A line in residue spectra H, I, and J. The values of 2, 4, and 3 were assigned to the beryllium doublet 3030 - 3131A for the spectra of residues A, B, and C with the same values for the beryllium doublet in H, I, and J. The same results were obtained when a comparison of the blackness of the vanadium 3183A line and the magnesium 3329A line; that is, the blackness of the spectral lines of the same elements in the residues at the same horizons was the same. There was some discrepancy between the calcium content of the spectrum of residue C and residue J but the blackness comparisons of the other four elements were consistant with the results obtained from the other samples.

Since the blackness of a spectral line on a film or plate (relative to an arbitrary scale) is directly proportional to the optical density of the line which is proportional to the concentration of the element in the sample, it was concluded that the relative concentrations of the elements mentioned above were the same in the residues of the same horizons.

A semi-quantitative investigation of the spectral lines of the liquid samples yielded no positive results for there were no density variations between the samples of the same horizon. The relative blackness of the principal spectral lines (Ca 3644A, Mg 4352A, and V 3183A) remained the same throughout the liquid spectra. It was therefore concluded that the relative concentrations of these elements was constant throughout the acid soluble constituents of the section analyzed or variations were too small to be recognized.

The spectral lines photographed of the fossil content of samples 1, 2, and 4 were done to complete the analysis and cannot be considered indicative of any correlation for the fossil casts are definitely of secondary origin. Two fossils of the same genus and species may contain within their hard parts different elements but if found in the same bed and peculiar to that bed, would be considered indicative of that horizon regardless of their elemental make-up.

TABLE D

QUANTITATIVE RESULTS - RESIDUE SPECTRA

Sample #	ELEMENTS				
	Ca 3159A	Co 3453A	Be 3030A	V 3183A	Mg 3329A
1	1	2	2	2	3
2	1	2	2	2	3
3	1	2	2	2	3
4	1	2	2	2	3
A	3	4	2	4	5
H	3	4	2	4	5
B	5	5	4	6	7
I	5	5	4	6	7
C	4	4	3	5	6
J	2	4	3	5	6

Numbers indicate Relative Blackness. Relative Blackness scale runs from 1 to 10 with 1 describing the blackness of a line barely visible and 10 one totally black.

INTERPRETATION OF RESULTS

At the time of the deposition of the Dundee Formation the elemental composition of the sea water from which it was precipitated was constant. This was shown by the monotonous persistance of the same elements throughout all of the samples studied, both vertically and horizontally. The similarity in composition of the residues indicates very stable conditions during the deposition of the section studied. The concentration variations that were discovered indicate a quantitative fluctuation of the chemical composition of the clastic particles during deposition and possibly a variation in sedimentation or source conditions. The vertical extent of this study was not great enough to determine whether these fluctuations were periodic.

Of the 4 sets of samples taken at the same levels, correlation by the relative blackness method was shown to be effective.

CONCLUSIONS

As was stated at the beginning of this report, little or no work previous to this study has been done with the fines of insoluble residues. The Dundee Formation in the locality chosen for this study yields a very high percentage of fines in its residue and from the results obtained from a spectrochemical study of them, the following conclusions have been reached.

(1) The fines of insoluble residues, formerly decanted in insoluble study, can be utilized by means of a spectrochemical analysis.

(2) A qualitative study of the residues yielded no variations in the elements present, thus indicating a constant elemental condition in the sea of deposition.

(3) A semi-quantitative study of the residues yielded concentration differences from one horizon to another. This study also indicated concentration similarities in samples of the same horizons.

(4) These concentration similarities were correlated across the quarry in 4 different horizons.

(5) Thus, correlation by means of a semi-quantitative procedure was performed successfully in this area.

SUGGESTIONS FOR FURTHER STUDY

The use of spectrochemical analysis for geologic research is in its infant stage. The work that has been done so far is just a promise of what can be done. In this study, I have tried to show the application of this method to the study of insoluble residues; especially the fines thereof. At this time, I would like to offer some suggestions for further study along these lines.

(1) The present study can be expanded to include other sections of Dundee in the state of Michigan. In particular, an analysis of the limestone at Petosky (by use of cores) on the western side of the state could furnish information leading to correlation across the northern end of the Southern Peninsula.

(2) A system could be devised so that well-cuttings can be used in this type of investigation, thus correlating throughout the state. A series of controlled washings in different solutions could be developed that would remove most of the contaminants present. Much laboratory experimentation would be necessary before well-cuttings can be used successfully for this type of investigation.

(3) Other sedimentary carbonates can be used for the same type of study.

(4) Finally, analyses of other limestone and/or carbonate formations can be made with the results tabulated. This could lead to a solution of some of the carbonate correlation problems.

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