THE CORRELATION OF CINCINNATIAN ENVIRONMENTS BY SPECTROGRAPHIC ANALYSES OF ASSOCIATED FOSSILS

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THESIS

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THE CORRELATION OF CINCINNATIAN ENVIRONMENTS BY SPECTROGRAPHIC ANALYSES OF ASSOCIATED FOSSILS

By

DUANE C. UHRI

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ABSTRACT

Biogeochemical methods of research have become increasingly important in recent years and have aided geologists in solving numerous problems. One such problem pertains to the Cincinnati Arch area. Some geologists argue that during Cincinnatian time, two arms of a sea existed in this area and that the formations from the Greendale through the Arnheim were deposited in the southern branch and those formations immediately above the Arnheim in the northern branch. Others claim that the two arms of the sea were united and remained as one continuous sea throughout this time. If the former were correct, it would not be improbable that the composition of the water in the two branches differed slightly in dissolved constituents. If the latter were true, it seems likely that the sea water would have had a uniform distribution of dissolved material except for minor local variations.

Since many marine organisms have the capacity to fractionate elements to a certain degree during their growth stages and since the raw materials used in the formation of their skeletal frameworks are extracted mainly from the surrounding sea water, the presence of a particular organism in a given locality and the chemical composition of its skeleton should be indicative of its environment. If one were to find that for a particular species of marine organism the compositions of several members remained essentially the same or that there existed a certain ratio of component elements characteristic of that species for a given set of environmental conditions, a large difference in the compositions or elemental ratios of several specimens would suggest the existence of considerably different environments for the various members examined.

Attempts were made at solving the Cincinnati Arch problem by means of investigations into the compositions of supposedly northern and southern fossilized brachiopods which showed no evidences of diagenetic alterations. Brachiopods were chosen as the class of organisms to be analyzed for several reasons: 1) brachiopods were sessile-benthonic forms and are probably found in marine strata in the immediate vicinity of their former habitat; 2) brachiopod genera and species can be identified with much greater certainty and ease than many other types of organisms; 3) there is considerable skeletal material in relation to the size of the individual; and 4) brachiopod shell punctae and tubules produce only a limited amount of porosity thereby reducing possibilities of alteration by diagenetic processes.

Spectrographic analyses and chemical tests yielded the following results: 1) the major and trace elements in all the brachiopod specimens were similar; 2) the quantities of certain elements varied between specimens; 3) all of the brachiopods belonged to the calcareous group; 4) the fossils contained less than 1.5 % Mg^{++} by weight; and 5) the ratios of $MgCO_3/CaCO_3$ differed between the same species as well as between different genera and species.

The analyses of certain specimens seemed to support the theory that there had been two branches of the sea in the Cincinnati Arch area. Other fossil analyses gave rise to much uncertainty in such an interpretation.

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INTRODUCTION

Biogeochemical Research

In recent years, many of the investigations into paleontological problems have been concerned with biogeochemical methods of research. A number of these methods deal with the chemical and isotopic compositions of marine fossils, present-day marine organisms, and sediments. Examples which may be cited are: 1) the oxygen isotope studies of carbonate-secreting marine organisms by H. C. Urey, S. Epstein, and H. A. Lowenstam to obtain paleotemperature relationships; 2) the investigations of Keith E. Chave into the biogeochemistry of magnesium in calcareous skeletal material to arrive at a correlation between magnesium content and skeletal mineralogy, water temperature, phylogenetic level of the organism, salinity and depth of the water, and the age or size of the individual; 3) the effect of chemical scavengers of marine waters as observed by E.D. Goldberg; and 4) the determination of the origin and classification of chemical sediments in terms of the oxidation-reduction potentials and hydrogen-ion concentrations of their environments by Krumbein and Garrels.

It seems likely that biogeochemistry will be the answer to various paleontological problems and help to support or to weaken numerous controversial theories.

Cincinnati Arch Area

One such controversy pertains to the Cincinnati Arch area. During the early part of the Paleozoic era, most of the continent of North America was covered by shallow seas which, due to their shallowness, fluctuated areally to a great extent. Some geologists argue that during Cincinnatian time, a northern and a southern arm of one of these seas existed in this arch area and that the two branches were separated by an east-west trending barrier in the vicinity of southwestern Ohio. Others claim that no barrier existed but that the two arms of the sea were united and remained as one continuous sea throughout this time.

If the former were correct, it would not be improbable that the composition of the water in the two branches differed slightly in dissolved constituents. If the latter were true, it seems likely that the sea water would have had a uniform distribution of dissolved material except for minor local variations.

Fractionation of Elements by Marine Organisms

It is a well-known fact that many marine organisms have the capacity to fractionate elements to a certain degree during their growth stages. V. T. Bowen and D. Sutton have found that large amounts of nickel are extracted from sea water by sponges. Numerous articles mention that iodine is much more concentrated in various seaweeds than in the surrounding environment. According to E. D. Goldberg, strontium and yttrium are extracted from marine waters by red and green algae, vanadium by the mucus of tunicates, and silicon by sponges. H. C. Urey, S. Epstein, and H. A. Lowenstam have discovered that belemnites incorporate O^{16} and O^{18} into their skeletons in a definite ratio.

Therefore, since a particular marine organism can exist only under certain environmental conditions because the raw materials used in the formation of its skeletal framework are extracted mainly from the surrounding sea water, the presence of that organism in a particular locality and the chemical composition of its skeleton should be indicative of its environment. If one were to find that for a particular species of marine organism the compositions of several members remained essentially the same or that there existed a certain ratio of component elements characteristic of that species for a given set of environmental conditions, a large difference in the compositions or elemental ratios of several specimens would suggest the existence of considerably different environments for the various members examined. This seems possible since H. A. Lowenstam and others have found that the ecology of many marine organisms indicate a class-distinct mineralogical selection related to their modes of life.

Methods of Investigating the Cincinnati Arch Problem

A solution or an aid to the solution of the previously mentioned controversy might be obtained by means of investigations into the compositions and elemental ratios of supposedly northern and southern fossilized fauna which show no evidences of diagenetic alterations. The spectrographic determination of the existence of trace elements in the former group and of the absence of the same elements in the latter group would suggest that there had been two arms of the sea, whereas the detection of the same elements in both groups would support the idea of a continuous sea. Another method would be to spectrographically determine the ratios of magnesium carbonate to calcium carbonate for the various members since the magnesium content increases at the expense of the calcium and is affected by the temperature, salinity, and depth of the water.

These were the two methods attempted by the author and a discussion of the methodology, apparatus, and data is now in order.

APPARATUS, METHODOLOGY, AND DATA

Selection and Source of Materials

Brachiopods were chosen as the class of organisms to be used for several reasons: 1) brachiopods were sessile-benthonic forms and are probably found in marine strata in the immediate vicinity of their former habitat; 2) brachiopod genera and species can be identified with much greater certainty and ease than many other types of organisms; 3) there is considerable skeletal material in relation to the size of the individual; and 4) brachiopod shell punctae and tubules produce only a limited amount of porosity thereby reducing possibilities of alteration by diagenetic processes.

The specimens were obtained from and identified by W. H. Shideler of Miami University at Oxford, Ohio. The relationships between the geological formations and the specimens are shown in Table I.* According to Professor Shideler, the sites of their collections are as mapped in Figure 1. He also stated that many believe the formations from the Greendale through the Arnheim were deposited during the invasion

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*The reference numbers opposite the generic names will be used hereafter instead of the actual names.

TABLE I

ORDOVICIAN BRACHIOPODS AND STRATIGRAPHIC RELATIONSHIPS

Strata			Brachiopods	
Series	Group	Formation	Genus and Species	No.
Cincinnatian	Richmond	Elkhorn		
		Whitewater-Saluda	Rhynchotrema dentatum	17,18
		Liberty	Rafinesquina alternata	13,14
		Waynesville	Rafinesquina alternata Leptaena richmondensis	11,12 7,8
		Arnheim	Rhynchotrema dentatum Rafinesquina alternata Leptaena richmondensis	15,16 9,10 5,6
	Maysville	Mt. Auburn		
		Corryville		
		Bellvue		
		Fairmount	Orthorhynchula linney	3,4
		Mt. Hope		
	Eden	McMicken		
		Southgate		
		Economy		
		Fulton		
Mohawkian	Cynthiana	Rogers Gap		
		Gratz		
		Bromley		
		Greendale	Orthorhynchula linney	1,2

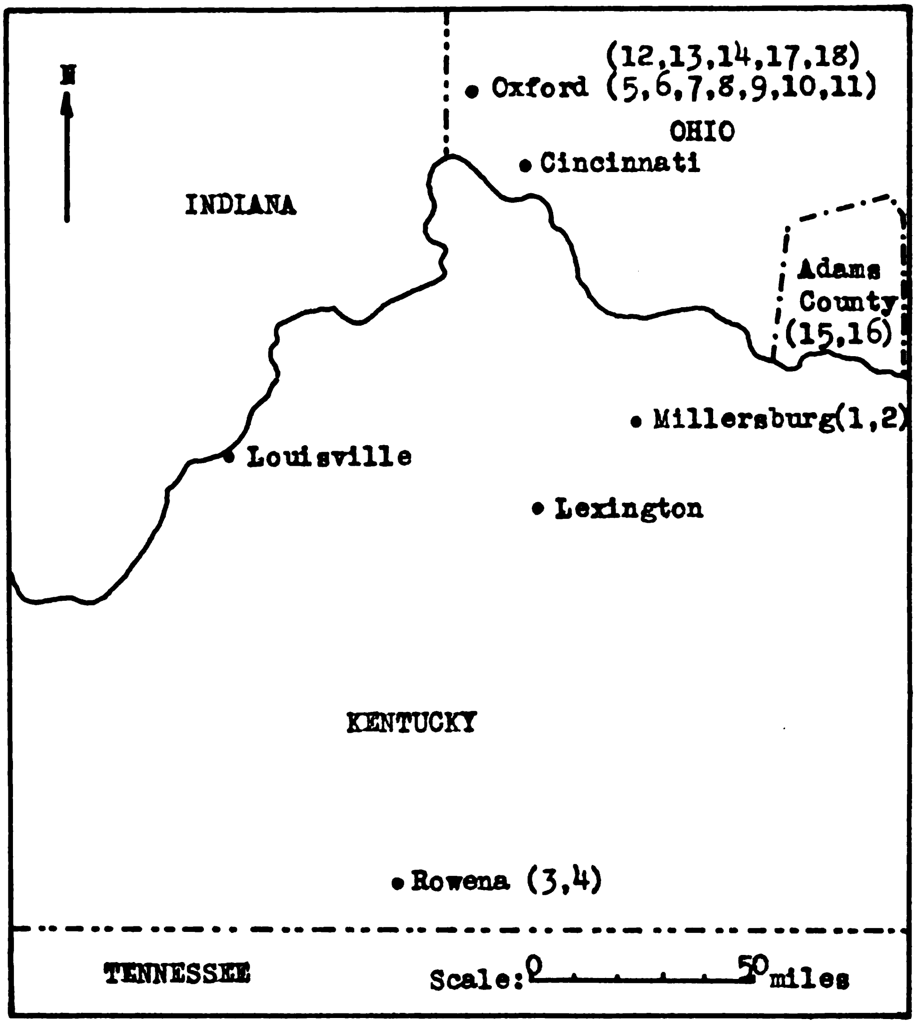

Fig. 1. Collection sites of brachiopod specimens

of the area by the southern branch of the sea and the formations immediately above the Arnheim, during a later invasion by the northern branch, the associated fossils being the remains of southern and northern fauna respectively.

Preparation of Specimens for Analysis

From each group of brachiopods of the same genus, species, stratum, and collection site, the two specimens which appeared to be the most well preserved were selected for the following investigations. Most of the adhering sediment was removed from the exteriors of the shells after which the fossils were washed in distilled water, dried, and pulverized in a steel percussion mortar. The mortar was washed, rinsed with dilute hydrochloric acid, and rewashed with distilled water before breaking up a different shell. The entire material of each specimen was sieved to less than 100 mesh to produce a homogeneous powder with particles of a fairly uniform size. During the pulverization, it was observed that the interior cavity between the valves of each specimen was filled with secondary silica, but no attempt was made to remove it.

Determination of Constituent Elements

Small amounts of the fossil powders were placed into the cavities of carbon spectrograph electrodes and, using the Littrow spectrograph, a spectrum between 2450 and 3450 A was obtained for each. Detailed studies showed the presence of large amounts of calcium and silicon, some magnesium, aluminum, sodium, phosphorus, and boron, and traces of lead, zinc, and other elements. The source of the lead and zinc, however, was probably the sieve through which the powders were shaken. The major and trace elements appeared to be the same when the various spectra were compared but a difference in the amounts of certain constituents was observable.

Relationship between $CaCO_3$ and $MgCO_3$ in Brachiopods

It was then decided to consider the relationships between the $CaCO_3$ and $MgCO_3$ contents of the fossils. Several analyses by F. W. Clarke and W. C. Wheeler (1917) show that there were two types of brachiopods: 1) those with calcareous skeletons and 2) those with a highly phosphatic composition. The calcareous forms contained small amounts of $CaSO_4$ and $Ca_3P_2O_8$, whereas the phosphatic types were composed mainly of $Ca_3P_2O_8$ with small quantities of $MgCO_3$, $CaCO_3$, and $CaSO_4$ which were similar in magnitude. This made it necessary to deviate from an entirely spectrographic analysis and to employ wet chemical methods for the determination of $CO_3^=$ ion contents since the presence of Ca^{++} ions in the $Ca_3P_2O_8$ and $CaSO_4$ would affect a spectrographically obtained $CaCO_3/MgCO_3$ ratio. A wet chemical procedure had to be followed because, of $CaCO_3$ and $MgCO_3$, only the Ca^{++} and Mg^{++} ion concentrations may be obtained from the usual spectrographic procedures.

Trial Magnesium and Calcium Determinations

So to prepare spectrographic standards within the proper range, one-gram samples of several fossil powders were dissolved in dilute hydrochloric acid and diluted to 100 ml. After several minutes of agitation, they were allowed to stand 48 hours to permit the silicates and other insolubles to settle to the bottoms of the flasks. With lithium as an internal standard and solutions of varying Ca^{++} and Mg^{++} ion concentrations, trial runs showed approximately 20-30 % Ca^{++} ion and 0.1-0.6 % Mg^{++} ion concentrations.

Quantity of Sample Required

The weights of a number of fossil powders approximated one gram each and, since it was desired to hold down to a minimum any experimental error due to variability in sample sizes, three 0.3 gram samples of each fossil powder were used for analysis. One of these was used in the preparation of a solution for the spectrograph and two were employed for $CO_3^=$ determinations.

Procedure for $CO_3^=$ Determinations

The $CO_3^=$ ion concentration of an individual sample was completely determined before another sample was started. The apparatus is shown in Figure 2 and the procedure followed was similar to that for the usual determination of $CO_3^=$ in a slightly alkaline solution.

The 0.3 gram sample of fossil material was placed into a 200 ml. Erlenmeyer flask. To this flask (#1) were added 75 ml. of distilled water. Flasks #2 and #3 each contained 100 ml. of NaOH solution.[1] The flasks were placed in their proper positions, tightly stoppered, and, after the system had been carefully checked for the leakage of air, 5 ml. of concentrated sulphuric acid were added slowly.[2] After flask #1 had received the total amount of acid, it was heated to boiling. Heat was applied slowly so as to allow the volume of gas bubbling into flasks #2 and #3 to react with the NaOH

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[1] NaOH solution = 5 grams wet-weight of NaOH crystals dissolved in 2 liters of distilled water

[2] H_2SO_4 was used because of its low volatility as compared with other acids.

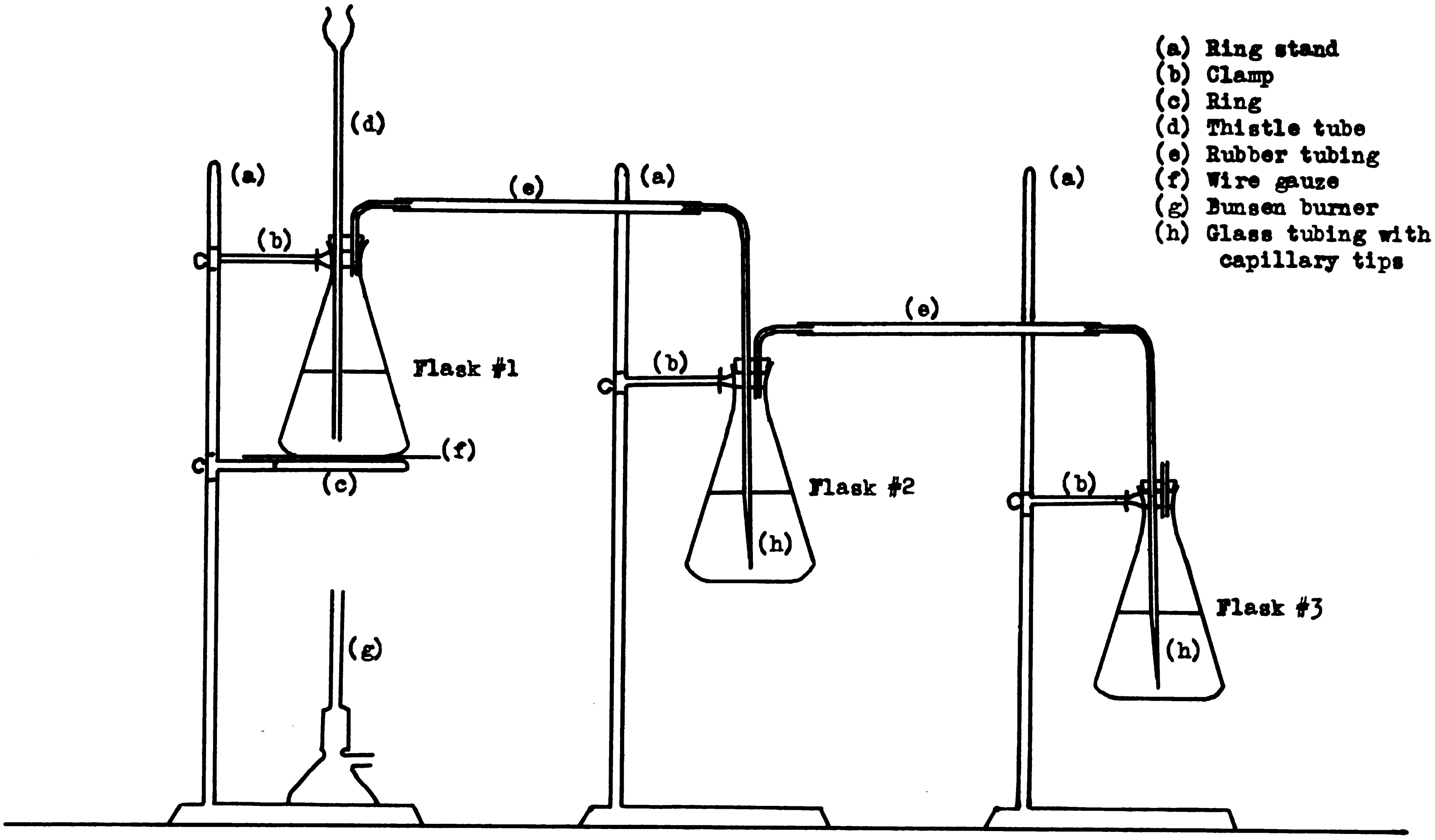

Fig. 2. Apparatus for $CO_3^{=}$ determinations

according to:

$$2\ NaOH + CO_{2(g)} \longrightarrow Na_2CO_3 + H_2O$$

When it became evident that steam was beginning to pass through the system, the time of completion of the trial was set for 3 minutes thereafter.

Flasks #2 and #3 were then removed for titration. To each flask were added 3 drops of phenolphthalein indicator.[3] Dilute hydrochloric acid was added dropwise until the solutions reached the phenolphthalein endpoint. The reaction which occurred may be expressed by:

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$HCl + Na_2CO_3 \longrightarrow NaHCO_3 + NaCl$$

and resulted in solutions with a pH of 7. A reading was made on the burette. After each solution had received 6 drops of brom-phenol-blue indicator, it was titrated with dilute hydrochloric acid of known normality to a blue-gray color with the use of potassium biphthalate (0.1 N) as a color standard for the brom-phenol-blue. Another reading was taken on the burette to determine the quantity of HCl required for the process:

$$HCl + NaHCO_3 \longrightarrow H_2CO_3 + NaCl$$

during which the pH of 7 was lowered to a pH of 4. The moles of HCl required for the titration of the $NaHCO_3$ were equal,

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[3] The solutions were titrated in the same flasks to prevent possible loss of liquid in a transferring procedure.

therefore, to the moles of $CO_3^=$ ion contained in the solution.

Several blanks were run according to the above procedure and it was found that the number of moles of $CO_3^=$ should be reduced by 0.0002140 moles due to CO_2 in the NaOH, air, and water.[4] The results of these determinations are recorded in Tables II and III.

Knowing the quantity of $CO_3^=$ and Mg^{++} present, it would not be difficult to calculate the amount of Ca^{++} since the total carbonate consisted of $CaCO_3$ and $MgCO_3$.

Procedure for Spectrographic Analyses of Mg^{++} Concentrations

The ideal situation would have been to prepare solutions for the spectrograph from the remaining liquids in flasks #1 of the $CO_3^=$ ion determinations but, due to the possibility of impurities being introduced during the process and due to the precipitation of $CaSO_4$ upon dilution, fresh samples of the fossil material were used. A 0.3 gram sample of each fossil powder was dissolved in hydrochloric acid and diluted to 100 ml.

Since it had been previously found by a trial run that the Mg^{++} ion concentrations varied approximately between 0.1 %

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[4] Originally, 3 flasks of NaOH solution were used but the amount of CO_2 in the third flask proved to be negligible and only two flasks were employed.

TABLE II

TITRATIONS WITH HYDROCHLORIC ACID

Sample	Milliliters of HCl Required*					
	Trial 1			Trial 2		
	Flask 2	Flask 3	Total	Flask 2	Flask 3	Total
1	(a) 30.29	(a) 13.28	(a) 43.57	(a) 32.05	(a) 12.40	(a) 44.45
2	(a) 31.58	(a) 13.82	(a) 45.40	(a) 30.69	(a) 13.77	(a) 44.46
3	(b) 32.29	(b) 13.23	(b) 45.52	(b) 32.13	(b) 13.06	(b) 45.19
4	(c) 22.27	(c) 4.51	(c) 26.78	(c) 21.96	(c) 5.33	(c) 27.29
5	(c) 18.01	(c) 4.12	(c) 22.13	(c) 17.62	(c) 4.62	(c) 22.24
6	(d) 21.19	(d) 5.95	(d) 27.14	-	-	-
7	(e) 26.92	(e) 6.91	(e) 33.83	(e) 25.43	(e) 8.89	(e) 34.32
8	(f) 27.29	(f) 7.13	(f) 34.42	(f) 27.13	(f) 7.86	(f) 34.99
9	(d) 24.40	(d) 7.09	(d) 31.49	(d) 24.08	(d) 8.07	(d) 32.15
10	(d) 27.00	(d) 7.42	(d) 34.42	(d) 26.05	(d) 7.94	(d) 33.99
11	(e) 28.22	(e) 5.46	(e) 33.68	(e) 28.13	(e) 6.23	(e) 34.46
12	(f) 26.29	(f) 7.60	(f) 33.89	(f) 24.59	(f) 9.02	(f) 33.61
13	(f) 28.00	(f) 7.01	(f) 35.01	(f) 26.25	(f) 8.12	(f) 34.37
14	(g) 20.39	(g) 5.36	(g) 25.75	(g) 19.08	(g) 6.39	(g) 25.47
15	(g) 23.37	(g) 5.65	(g) 29.02	(g) 22.12	(g) 7.03	(g) 29.15
16	(g) 18.92	(g) 5.55	(g) 24.47	(g) 18.75	(g) 5.70	(g) 24.45
17	(g) 21.88	(g) 7.11	(g) 28.99	(g) 22.44	(g) 7.41	(g) 29.85
18	(g) 22.71	(g) 7.11	(g) 29.82	(g) 22.29	(g) 7.13	(g) 29.42

*Normalities were: (a)=0.06044, (b)=0.06044, (c)=0.09076, (d)=0.08150, (e)=0.07645, (f)=0.07687, and (g)=0.08139.

TABLE III

PERCENTAGE WEIGHT DETERMINATIONS FOR $CO_3^=$

Sample	% Difference	Average	Moles $CO_3^=$	% by Wt.
1	1.9	(a) 44.01 ml.	0.0026599	48.9
2	2.1	(a) 44.93 ml.	0.0027156	50.0
3	0.7	(b) 45.36 ml.	0.0027415	50.6
4	1.5	(c) 27.04 ml.	0.0024542	44.8
5	0.5	(c) 22.19 ml.	0.0020239	36.2
6	-	(d) 27.14 ml.	0.0022119	40.0
7	1.4	(e) 34.08 ml.	0.0026054	47.8
8	1.6	(f) 34.71 ml.	0.0026682	50.8
9	2.1	(d) 31.82 ml.	0.0025933	47.6
10	1.2	(d) 34.21 ml.	0.0027881	51.5
11	1.9	(e) 34.02 ml.	0.0026008	47.7
12	0.8	(f) 33.75 ml.	0.0025944	47.6
13	1.8	(f) 34.69 ml.	0.0026666	49.1
14	1.1	(g) 25.61 ml.	0.0020844	37.4
15	0.5	(g) 29.09 ml.	0.0023676	43.1
16	0.1	(g) 24.46 ml.	0.0019908	35.5
17	2.9	(g) 29.42 ml.	0.0023945	43.6
18	1.3	(g) 29.62 ml.	0.0024108	43.9

and 0.6 %, it was decided that the standards for magnesium should have Mg^{++} ion concentrations of 1.5 %, 1.0 %, 0.7 %, 0.5 %, and 0.1 %. Due to the fact that 10 ml. of fossil solution contained 0.030 grams of fossil powder, 10 ml. of solutions with the above Mg^{++} ion concentrations should contain 0.450 mg., 0.300 mg., 0.210 mg., 0.150 mg., and 0.030 mg. of magnesium respectively. A solution for the magnesium standards was prepared by dissolving 0.5 gram $MgCO_3$ in 1:1 HCl and diluting to 250 ml. The amounts of magnesium solution necessary to duplicate the Mg^{++} ion concentrations in 10 ml. aliquots of the various solutions are listed in Table IV.

Strontium was chosen for the internal standard since it is desirable to use an element which has an ionization potential similar in magnitude to that of the analyzed element. What was assumed to be a sufficient amount of strontium solution was used as an internal standard with the magnesium standards and fossil solutions, but it was found that a greater quantity should have been added for these plates 1, 2, and 3. It was determined by the spectrum analysis of several Sr^{++} ion concentrations that 8 grams of $SrCl_2 \cdot 6 H_2O$ should be dissolved in 1:1 HCl and diluted to 100 ml. in order to obtain an internal standard which could be used on a 1 ml.-addition basis.

To 10 ml. aliquots of the fossil solutions were added 1 ml. of strontium solution and 5 ml. of distilled water to

TABLE IV

STANDARD MAGNESIUM SOLUTIONS

Reference number	I	II	III	IV	V
Magnesium ion concentration	1.5 %	1.0 %	0.7 %	0.5 %	0.1 %
Amount of internal standard	1 ml.	1 ml.	1 ml.	1 ml.	1 ml.
Amount of magnesium solution	0.779 ml.	0.519 ml.	0.364 ml.	0.259 ml.	0.052 ml.
Amount of water	14.221 ml.	14.481 ml.	14.636 ml.	14.741 ml.	14.948 ml.
Total volume	16.000 ml.	16.000 ml.	16.000 ml.	16.000 ml.	16.000 ml.

TABLE V

STEP SECTOR DATA FOR PLATES 4, 5, AND 6

Sector number = n		1	2	3	4	5	6	7	8
$(1.585)^n$		1.585	2.512	3.981	6.310	10.00	15.85	25.12	39.81
Percent transmission	Plate 4	83.0	65.0	40.8	23.8	12.3	7.6	3.8	2.2
	Plate 5	90.8	76.0	56.0	29.7	18.0	10.2	5.0	2.6
	Plate 6	85.7	70.0	49.3	27.5	18.3	10.5	6.0	3.7

make a total of 16 ml. In the preparation of the magnesium standards, the same amount of strontium solution was mixed with the proper amounts of magnesium solution and diluted to 16 ml.

Carbon electrodes were then cut and polished so as to reduce their porosity and to assure an even arcing. Three electrodes were made for each fossil solution by evaporating 25 lambda of the solutions on the polished surfaces.[5] Each spectrum ranged from 2450 to 3450 A and was run at 9 amperes direct current for 20 seconds, except the iron spectra, which were 2-second exposures. Each plate included the spectra of the 5 magnesium standards, iron through a step sector, and several fossil solutions. The plates were developed according to the usual darkroom procedures and the spectrum lines of Mg 2779.8 and Sr 2931.8 were located for percentage-transmission determinations on the Jarrel-Ash densitometer.

Calibration curves and working curves for quantitative analysis may follow a number of patterns and be based on various optical relationships. The calibration curves for these plates were obtained with the aid of a step sector. As in most texts on spectroscopy, Ahrens (1950) includes the equation $E = It$, where E is the exposure, I is the incident light intensity, and t is the time. If the intermittency effect is considered as negligible, it should be possible to

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[5] 1 lambda = 0.001 cubic centimeters

duplicate a number of exposures, which were made by a constant I and varying t, by holding t constant and varying I. Therefore, E = kt = kI. The result of placing a step sector before the spectrograph slit during the photographing process is a spectrum which is divided into sections of different exposures. The sector used had 7 steps for which I_0/I = 1.585, where I_0 is the intensity of line emission and I is the intensity of the line as actually measured.[6] Knowing then, that a particular step had an exposure which was 1.585 times that of the preceding step, a calibration curve was prepared for each plate by plotting the Log % transmission of the line Fe 2832.43 vs. Log $(1.585)^n$, where n is the step number. Figures 3, 4, and 5 show these curves and Table V lists their data.

The percentage-transmissions of the Sr 2931.8 and Mg 2779.8 lines were determined for the standard magnesium samples and the fossil solutions. The logarithms of the relative intensities of these lines were then obtained by locating the percentage-transmissions on the ordinate of the proper calibration curve and reading the relative intensities on the abcissa. The working curves for the quantitative determination of the magnesium contents resulted from plotting the ratios of the relative intensities of the Mg 2779.8 lines of

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[6] The step sector may be regarded as having 8 steps if complete exposure is counted as a step.

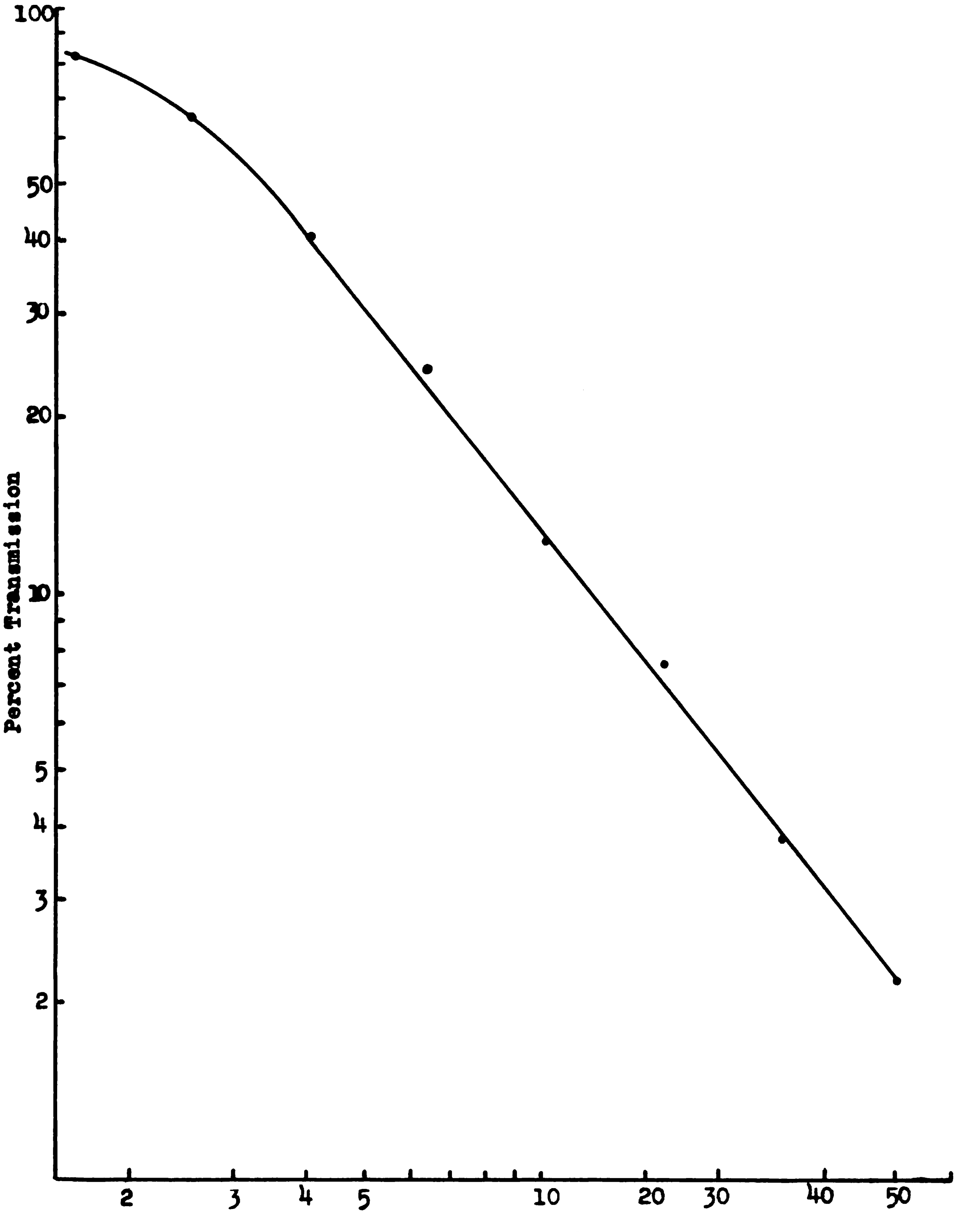

Fig. 3. Calibration curve for plate 4

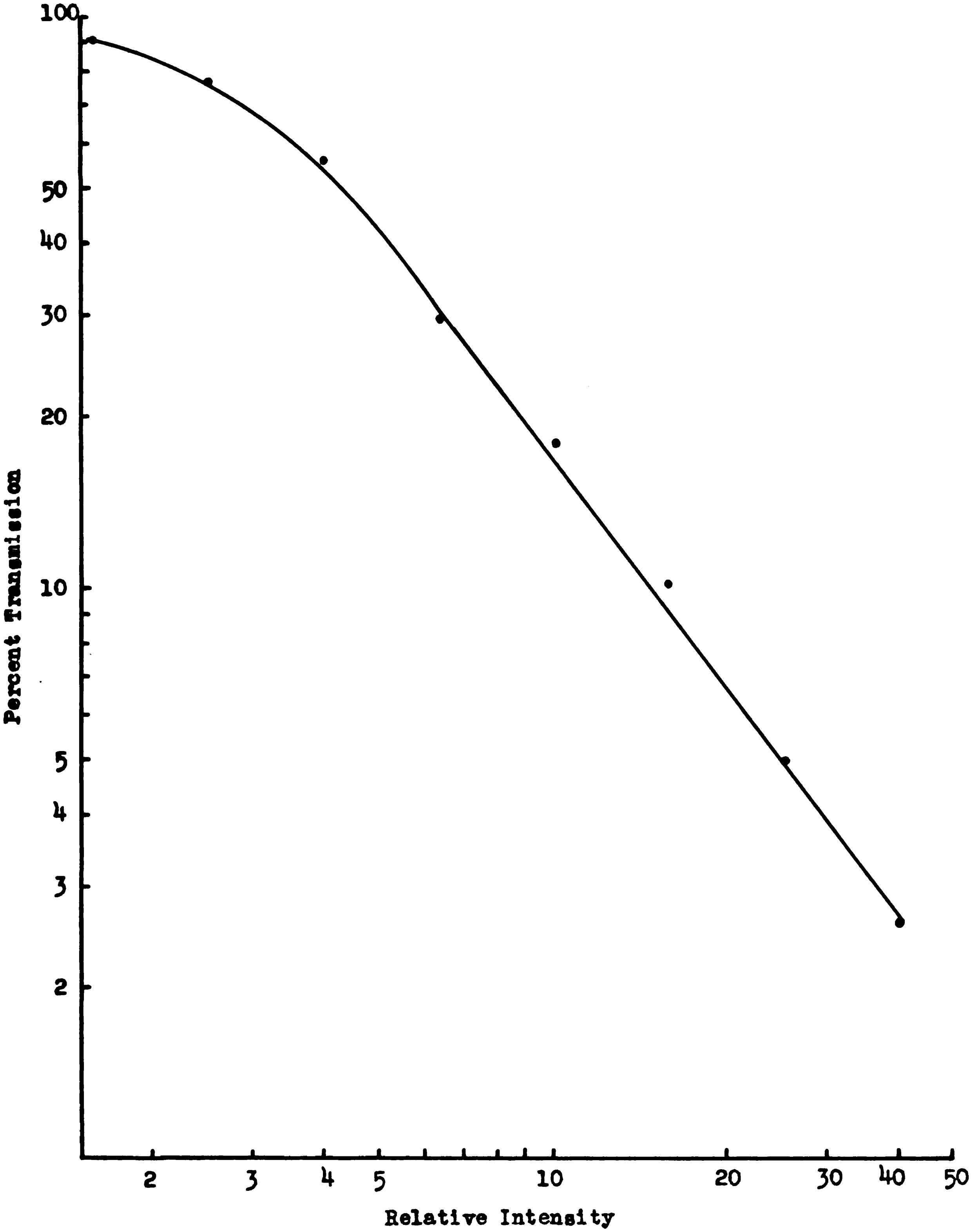

Fig. 4. Calibration curve for plate 5

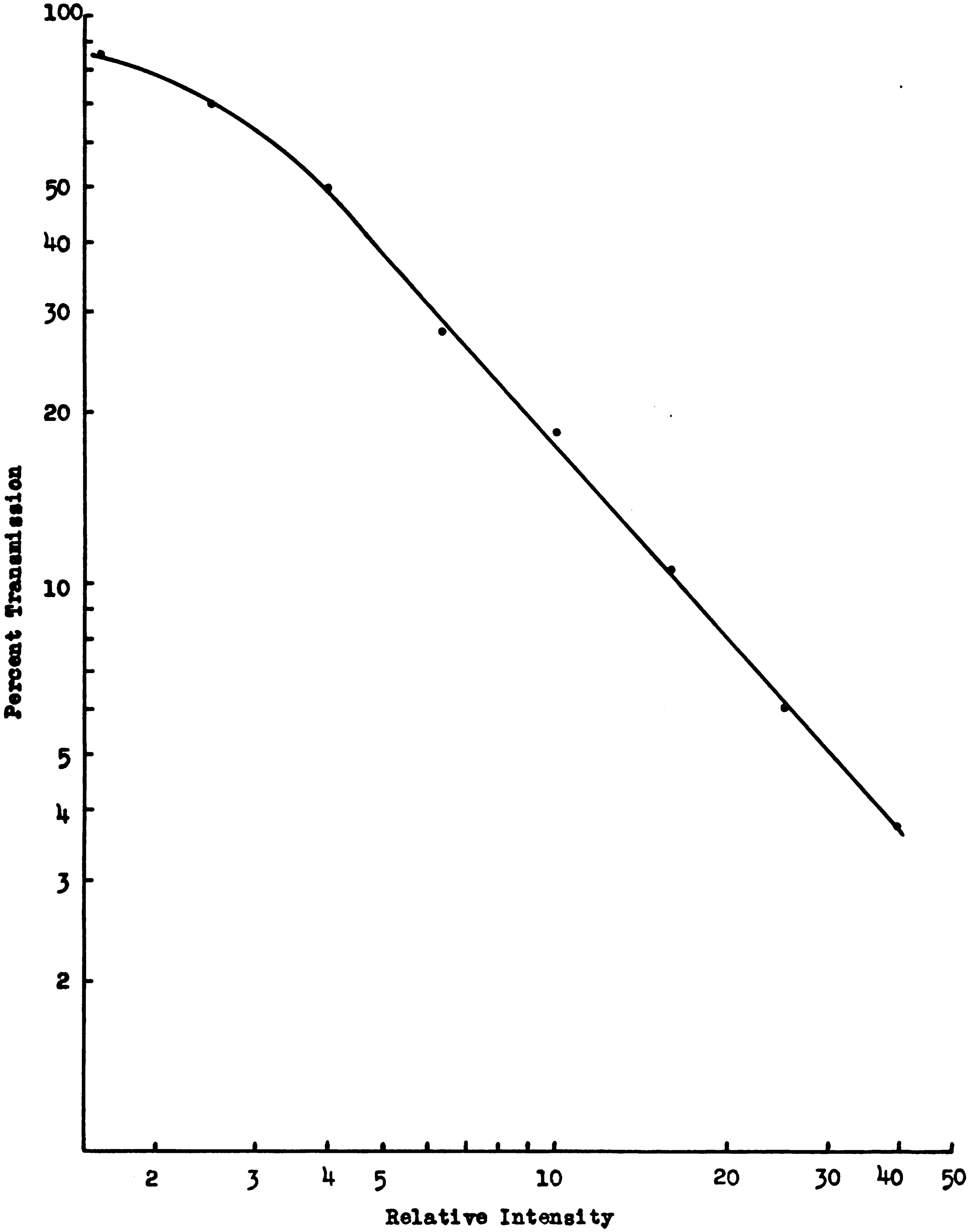

Fig. 5. Calibration curve for plate 6

the standard magnesium solutions to the relative intensities of the Sr 2931.8 lines in the same spectrum vs. the percentage Mg^{++} ion concentrations as in Figures 6, 7, and 8.[7] According to theory, by locating the RI Mg^{++}/RI Sr^{++} ratios for the fossil solutions on the curves, one may obtain the percentage magnesium ion concentrations for these solutions.[8]

Since three portions of the same fossil material were run separately, the values obtained for each magnesium ion concentration should be similar in magnitude and a measure of the accuracy of the method. However, the results show considerable deviations. Some believe that such deviations or spreads of points for a single sample are due to very low concentrations of the analyzed element. Ahrens (1950) shows how the reproducibility of the relative intensities of K 4047 varies with the concentration of K_2O. This may have been the case here. The standard deviation from the mean value of each solution was as shown in Table VII. The average standard deviation was ± 20.1 %, suggesting that Sr 2931.8 was possibly not a practical line to be used with Mg 2779.8.

A similar procedure was then attempted, omitting the internal standard and producing a working curve by plotting the logarithm of RI_{Mg} vs. the Mg^{++} ion concentration. Providing that the conditions under which each sample is arced are

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[7] See Table VI.
[8] See Table VII.

TABLE VI

WORKING CURVE DATA FOR PLATES 4, 5, AND 6

Plate	Standard	Percent Mg^{++}	Percent transmission		Relative intensity		Log $\frac{RI_{Mg}}{RI_{Sr}}$
			Sr	Mg	Sr	Mg	
4	I	1.5	52.3	28.8	3.18	5.25	0.2180
	II	1.0	53.0	44.3	3.15	3.73	0.0734
	III	0.7	46.8	39.0	3.56	4.13	0.0645
	IV	0.5	43.2	49.0	3.81	3.40	-0.0496
	V	0.1	38.5	61.7	4.18	2.69	-0.1911
5	I	1.5	46.9	26.6	4.53	7.10	0.1952
	II	1.0	54.0	38.9	3.97	5.35	0.1296
	III	0.7	38.0	36.3	5.45	5.67	0.0172
	IV	0.5	38.6	42.6	5.35	4.95	-0.0338
	V	0.1	39.3	59.0	5.29	3.59	-0.1684
6	I	1.5	57.2	36.5	3.29	5.15	0.1946
	II	1.0	48.5	41.5	4.00	4.60	0.0607
	III	0.5	48.2	52.0	4.02	3.64	-0.0431
	V	0.1	53.5	79.9	3.62	1.93	-0.2731

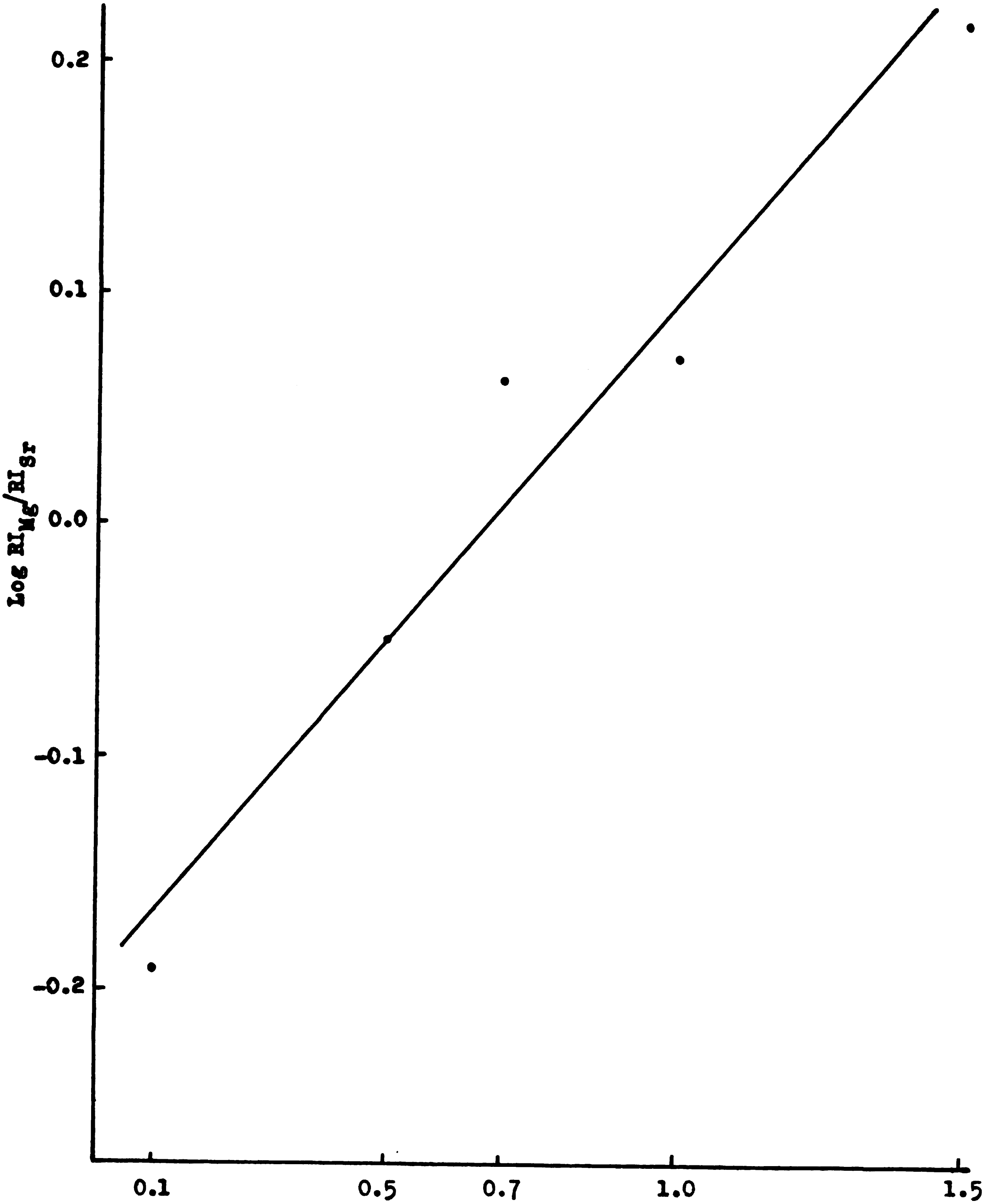

Fig. 6. Working curve for plate 4

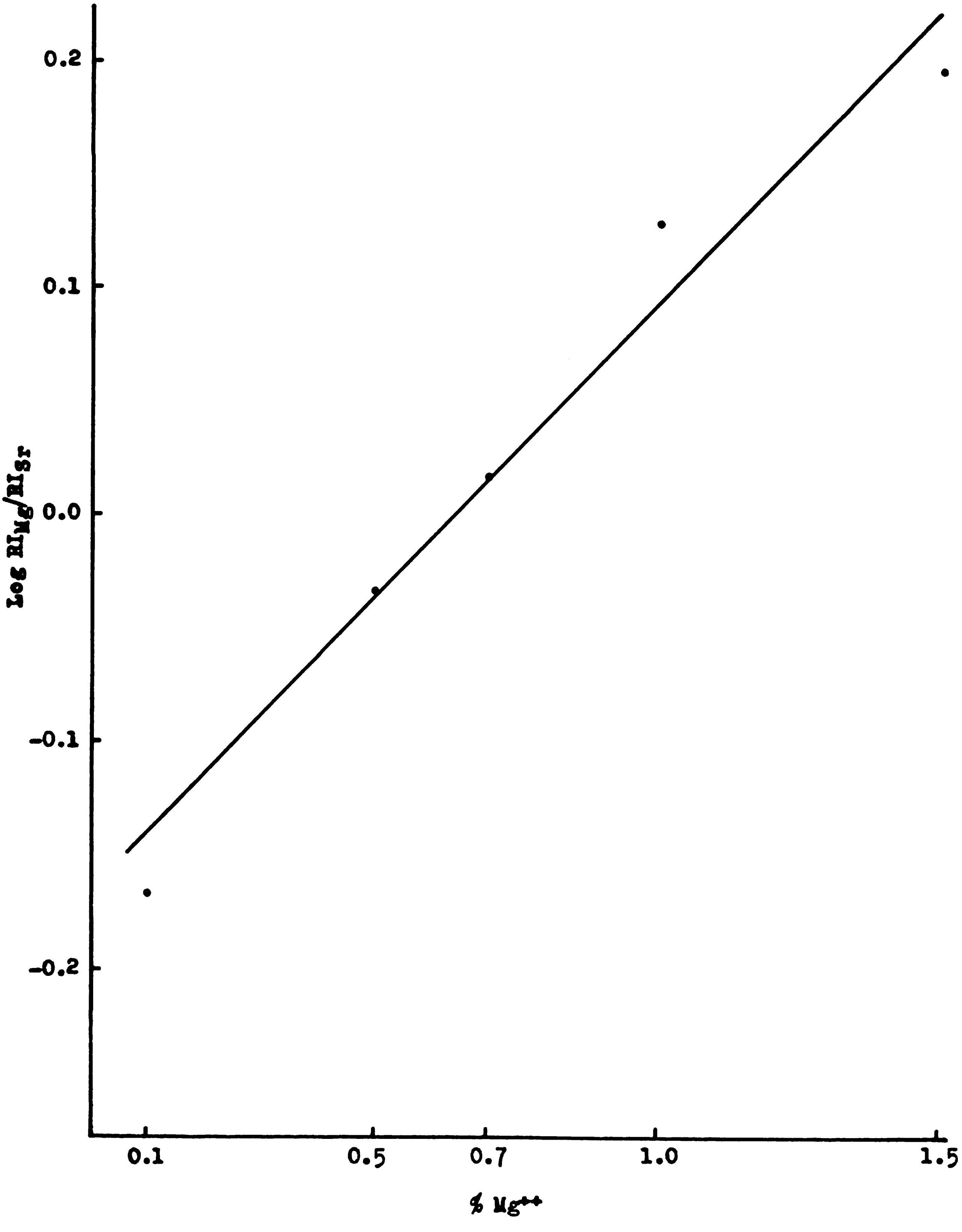

Fig. 7. Working curve for plate 5

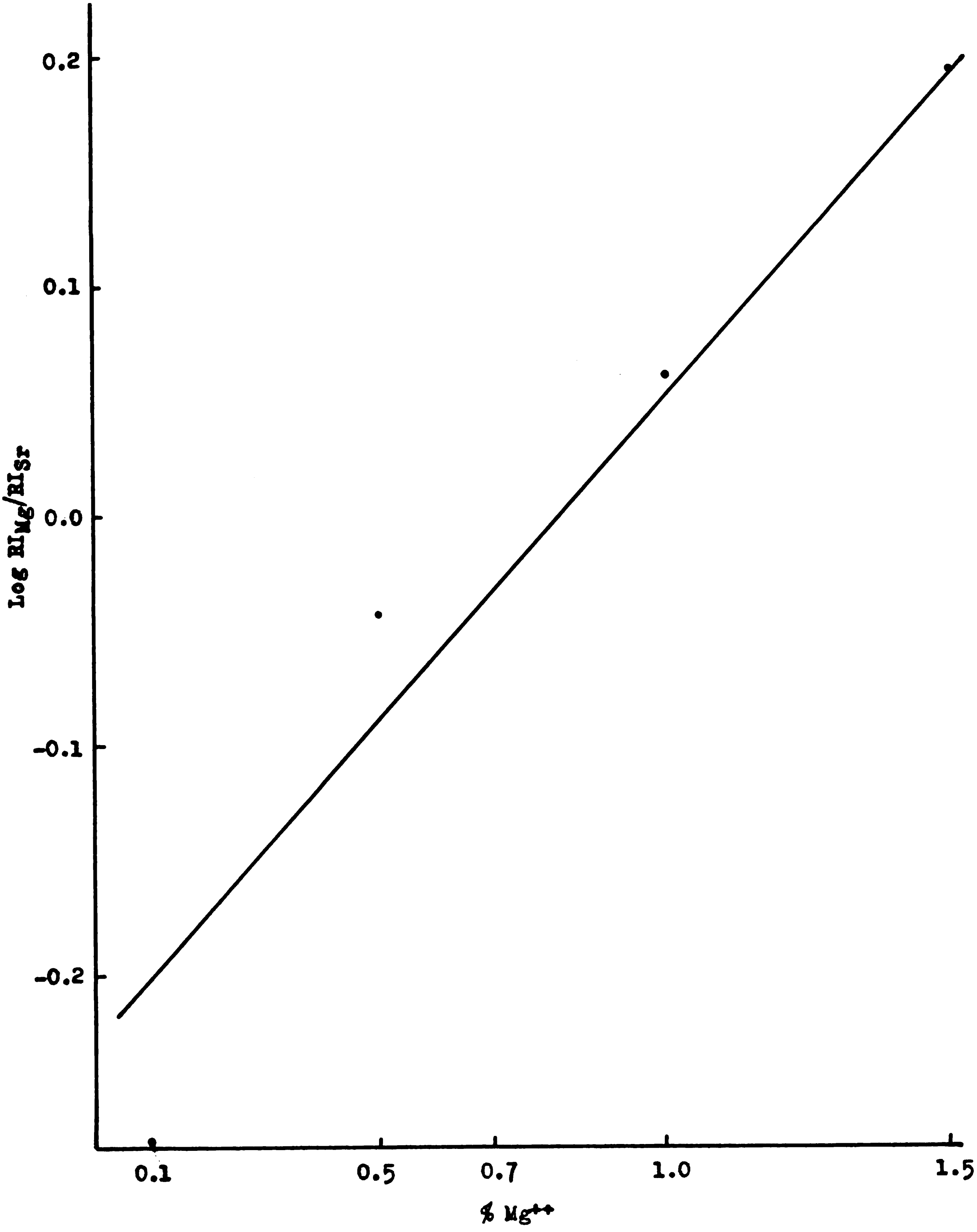

Fig. 8. Working curve for plate 6

TABLE VII

SPECTROGRAPHIC DATA FOR FOSSIL MATERIALS

Plate	Specimen	Trial	Percent transmission		Relative intensity		Log $\frac{RI_{Mg}}{RI_{Sr}}$	Percent Mg^{++}	Mean	% Dev.	(% Dev.)^2	Standard deviation*
			Sr	Mg	Sr	Mg						
4	1	(a)	39.8	49.4	4.05	3.35	-0.0825	0.39		21.9	479.6	
		(b)	45.6	57.2	3.65	2.90	-0.0999	0.33	0.32 %	3.1	9.6	± 23.6 %
		(c)	40.8	55.5	4.00	3.00	-0.1250	0.24		-25.0	625.0	
	2	(a)	37.0	54.5	4.30	3.05	-0.1492	0.16		-44.8	2007.0	
		(b)	49.0	58.1	3.40	2.85	-0.0767	0.41	0.29 %	41.4	1713.9	± 43.4 %
		(c)	38.3	50.6	4.20	3.30	-0.1047	0.31		6.9	47.6	
	3	(a)	42.3	46.9	3.85	3.55	-0.0353	0.55		1.9	3.6	
		(b)	38.0	44.0	4.20	3.75	-0.0492	0.50	0.54 %	-7.4	54.8	± 6.7 %
		(c)	44.0	47.4	3.75	3.50	-0.0299	0.57		5.6	31.4	
	4	(a)	40.0	40.3	4.05	4.03	-0.0022	0.68		-16.0	256.0	
		(b)	47.8	40.9	3.50	4.00	0.0580	0.87	0.81 %	7.4	54.8	± 13.9 %
		(c)	49.8	42.5	3.35	3.85	0.0605	0.88		8.6	74.0	

TABLE VII CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		Log $\frac{RI_{Mg}}{RI_{Sr}}$	Percent Mg^{++}	Mean	% Dev.	(% Dev.)^2	Standard deviation
			Sr	Mg	Sr	Mg						
4	5	(a)	42.9	34.8	3.85	4.50	0.0677	0.90		-3.2	10.2	
		(b)	50.2	38.9	3.30	4.15	0.0995	1.01	0.93 %	8.6	74.0	± 7.5 %
		(c)	39.2	32.8	4.10	4.70	0.0593	0.88		-5.4	29.2	
	6	(a)	53.3	51.3	3.10	3.25	0.0205	0.74		1.4	2.0	
		(b)	54.5	52.8	3.05	3.15	0.0140	0.72	0.73 %	-1.4	2.0	± 1.7 %
		(c)	59.3	57.0	2.80	2.90	0.0152	0.72		-1.4	2.0	
5	7	(a)	35.3	38.0	5.80	5.45	-0.0270	0.53		-13.1	171.6	
		(b)	40.0	40.0	5.20	5.20	0.0000	0.64	0.61 %	4.9	24.0	± 11.5 %
		(c)	39.2	39.0	5.30	5.35	0.0041	0.66		8.2	67.2	
	8	(a)	39.4	40.5	5.25	5.15	-0.0084	0.60		1.7	2.9	
		(b)	37.5	40.1	5.50	5.20	-0.0244	0.55	0.59 %	-6.8	46.2	± 6.1 %
		(c)	35.9	36.5	5.70	5.65	-0.0050	0.62		5.1	26.0	
	9	(a)	36.0	35.3	5.70	5.80	0.0075	0.67		19.6	384.2	
		(b)	34.5	37.5	5.90	5.50	-0.0305	0.52	0.56 %	-7.1	50.4	± 16.6 %
		(c)	32.8	36.8	6.10	5.60	-0.0371	0.50		-10.7	114.5	

TABLE VII CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		Log $\frac{RI_{Mg}}{RI_{Sr}}$	Percent Mg^{++}	Mean	% Dev.	(% Dev.)^2	Standard deviation
			Sr	Mg	Sr	Mg						
5	10	(a)	30.5	42.0	5.85	5.00	-0.0682	0.38		-9.5	90.3	
		(b)	32.6	34.4	6.15	5.90	-0.0180	0.57	0.42 %	35.7	1274.5	± 34.2 %
		(c)	31.9	39.5	6.30	5.25	-0.0791	0.32		-31.2	973.4	
	11	(a)	35.3	38.6	5.80	5.40	-0.0310	0.52		10.6	112.4	
		(b)	32.3	38.2	6.20	5.40	-0.0600	0.41	0.47 %	-12.8	163.8	± 11.8 %
		(c)	36.8	41.3	5.60	5.05	-0.0449	0.47		0.0	0.0	
	12	(a)	37.3	34.9	5.55	5.85	0.0229	0.73		0.0	0.0	
		(b)	40.1	40.0	5.20	5.20	0.0000	0.64	0.73 %	-12.3	151.3	± 12.3 %
		(c)	55.6	44.5	3.85	4.30	0.0480	0.82		12.3	151.3	
6	13	(a)	46.1	59.0	4.20	3.20	-0.1181	0.40		-2.4	5.8	
		(b)	45.0	58.6	4.30	3.25	-0.1216	0.38	0.41 %	-7.3	53.3	± 7.5 %
		(c)	46.1	58.3	4.20	3.30	-0.1047	0.44		7.3	53.3	
	14	(a)	46.4	35.5	4.15	5.30	0.1063	1.19		16.7	278.9	
		(b)	44.0	40.7	4.35	4.65	0.0290	0.88	1.02 %	-19.6	384.2	± 18.4 %
		(c)	50.4	45.0	3.85	4.30	0.0480	0.98		-3.9	15.2	

TABLE VII CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		Log $\frac{RI_{Mg}}{RI_{Sr}}$	Percent Mg^{++}	Mean	% Dev.	(% Dev.)^2	Standard deviation
			Sr	Mg	Sr	Mg						
6	15	(a)	54.2	43.9	3.60	4.40	0.0872	1.12		3.7	13.7	
		(b)	42.5	36.6	4.50	5.15	0.0586	1.02	1.08 %	-5.6	31.4	± 4.8 %
		(c)	42.8	34.6	4.50	5.40	0.0792	1.09		0.9	0.8	
	16	(a)	38.2	28.8	4.95	6.20	0.0978	1.16		-10.1	102.0	
		(b)	50.0	32.9	3.90	5.65	0.1629	1.39	1.29 %	7.8	60.8	± 6.3 %
		(c)	44.4	30.6	4.30	6.00	0.1447	1.33		3.1	9.6	
	17	(a)	46.0	56.1	4.20	3.45	-0.0854	0.51		6.3	39.7	
		(b)	45.3	58.7	4.25	3.25	-0.1165	0.40	0.48 %	-16.7	278.9	± 15.4 %
		(c)	49.1	57.0	4.00	3.35	-0.0771	0.54		12.5	156.3	
	18	(a)	43.0	50.7	4.45	3.85	-0.0629	0.59		1.7	2.9	
		(b)	47.5	52.6	4.10	3.70	-0.0446	0.65	0.58 %	12.1	146.4	± 14.0 %
		(c)	49.5	59.0	3.95	3.20	-0.0915	0.49		-15.5	240.3	

*Standard deviation = ± square root of $\frac{\text{sum of (\% Dev.)}^2}{\text{no. of trials - 1}}$.

identical, the omission of the internal standard line is permissible. Variations in these conditions are effected by changes in the length of exposure, the amount of sample, the nature of the electrode, the arcing current, plate characteristics, and developing procedure. All of these were taken into consideration and carefully regulated. The working curve and data for this method, which are to be found in Tables VI, VII, and VIII and Figure 9, show no great increase in the constancy of results.

Ahrens (1950) shows that for small concentrations of K^+ ion, the curve of a plot of the logarithm of RI_{K^+} vs. the concentration of K_2O changes from an essentially straight line at higher concentrations to a curve at lower concentrations. Assuming that the concentrations of Mg^{++} ion in the fossil solutions were low enough to fall within this curved portion of the graph, a working curve was prepared by actually drawing a curved line through the proper points instead of the usual straight line. But no appreciable advantage was observed. This curve is shown in Figure 10 and the Mg^{++} ion concentrations so obtained are recorded in Table IX.

It was decided then to investigate the relationships between the relative intensities of Mg 2779.8 and Ca 3006.9 and thus eliminate possible error due to Sr 2931.8 and slightly varying conditions of arcing the samples. The Ca and Mg lines of a particular spectrum were, of course, produced under identical conditions since the two elements were mixed

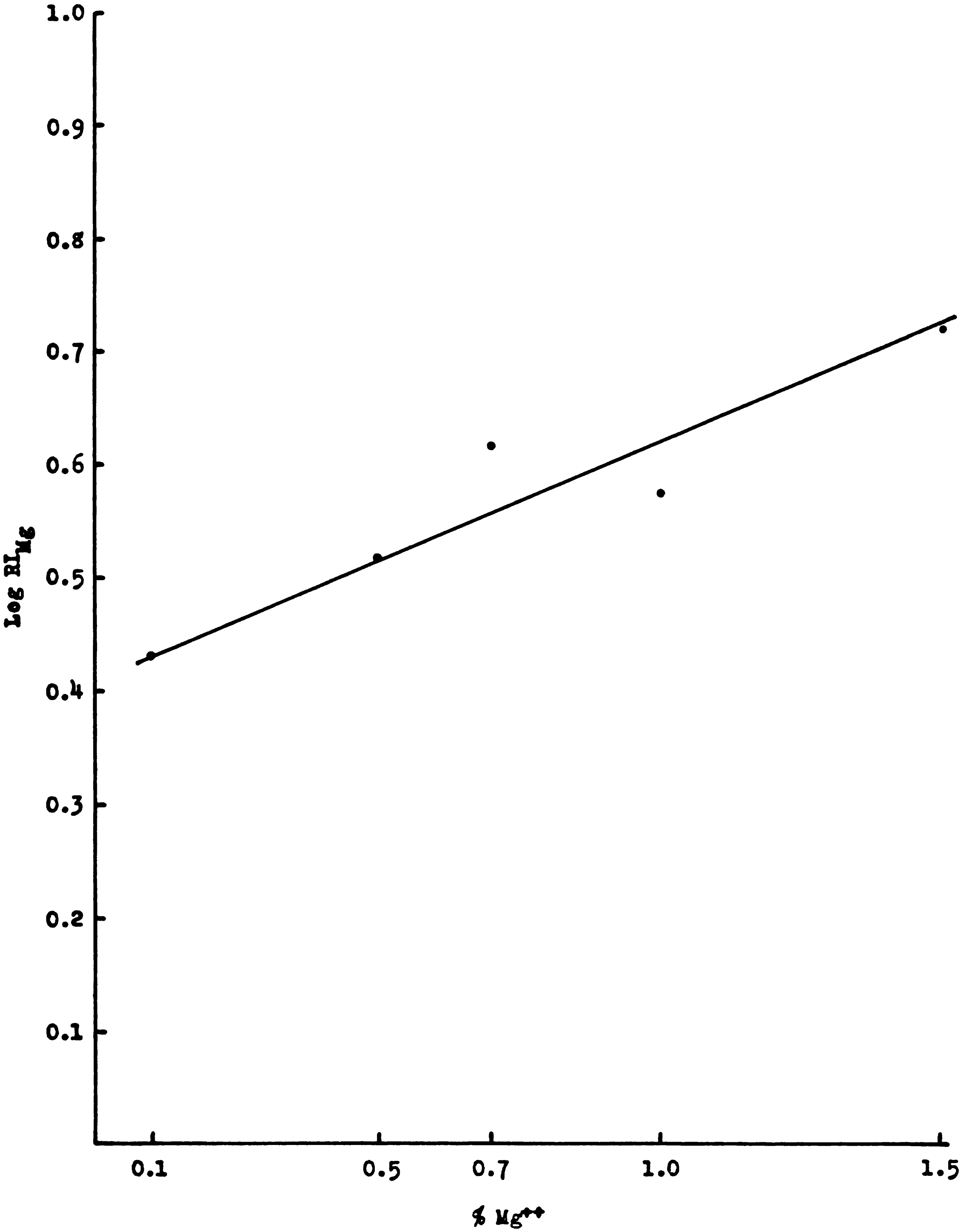

Fig. 9. Non-internal standard working curve for plate 4

TABLE VIII

NON-INTERNAL STANDARD DATA AND PERCENTAGES Mg^{++} OBTAINED

Plate	Specimen	Trial	Log RI_{Mg}	% Mg^{++}	Avg.	% Dev.	Std. Dev.
4	1	(a)	0.5250	0.55		44.7	
		(b)	0.4624	0.26	0.38 %	-31.6	± 40.3 %
		(c)	0.4771	0.32		-15.8	
	2	(a)	0.4543	0.22		-31.3	
		(b)	0.4548	0.22	0.32 %	-31.3	± 52.4 %
		(c)	0.5185	0.51		59.4	
	3	(a)	0.5502	0.67		-4.3	
		(b)	0.5740	0.78	0.70 %	11.4	± 10.5 %
		(c)	0.5441	0.64		-8.6	
	4	(a)	0.6053	0.93		3.3	
		(b)	0.6021	0.92	0.90 %	4.8	± 5.4 %
		(c)	0.5855	0.84		-6.6	
	5	(a)	0.6532	1.16		2.7	
		(b)	0.6180	0.99	1.13 %	-12.4	± 11.7 %
		(c)	0.6721	1.25		10.6	
	6	(a)	0.5119	0.49		25.6	
		(b)	0.4983	0.41	0.39 %	5.1	± 29.9 %
		(c)	0.4624	0.26		-33.3	

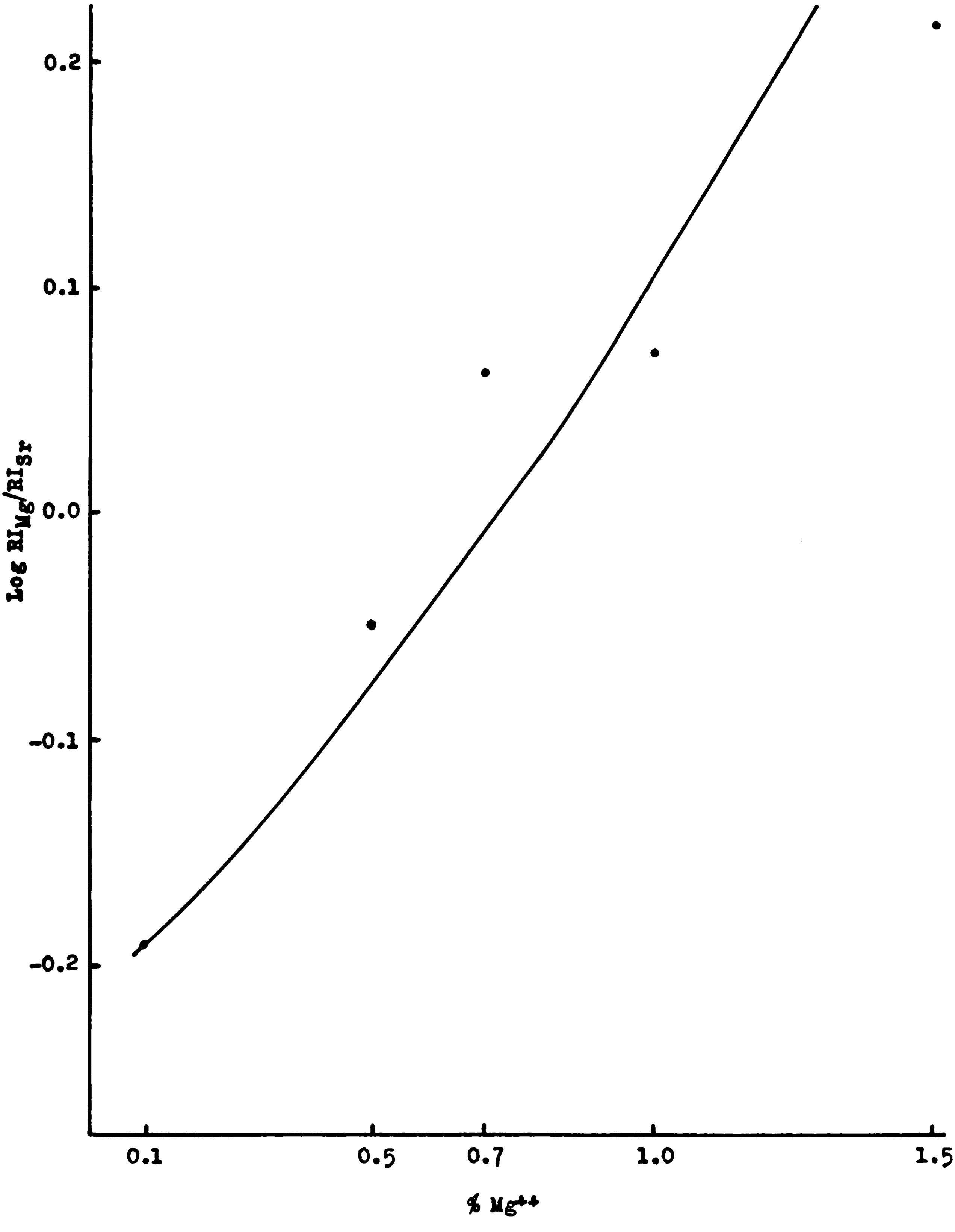

Fig. 10. "Curved" working curve for plate 4

TABLE IX

"CURVED" WORKING CURVE DATA AND PERCENTAGES Mg^{++} OBTAINED

Plate	Specimen	Trial	$\log \frac{RI_{Mg}}{RI_{Sr}}$	% Mg^{++}	Avg.	% Dev.	Std. Dev.
4	1	(a)	-0.0825	0.48		11.6	
		(b)	-0.0999	0.43	0.43 %	0.0	± 11.6 %
		(c)	-0.1250	0.38		-11.6	
	2	(a)	-0.1492	0.27		-30.8	
		(b)	-0.0767	0.49	0.39 %	25.6	± 28.5 %
		(c)	-0.1047	0.41		5.1	
	3	(a)	-0.0353	0.62		1.6	
		(b)	-0.0492	0.58	0.61 %	-4.9	± 4.3 %
		(c)	-0.0299	0.64		3.3	
	4	(a)	-0.0022	0.72		-13.3	
		(b)	0.0580	0.88	0.83 %	6.0	± 11.5 %
		(c)	0.0605	0.89		7.2	
	5	(a)	0.0677	0.91		-2.2	
		(b)	0.0995	0.99	0.93 %	6.5	± 5.7 %
		(c)	0.0593	0.89		-4.3	
	6	(a)	0.0205	0.79		1.3	
		(b)	0.0140	0.77	0.78 %	-1.3	± 1.6 %
		(c)	0.0152	0.77		-1.3	

together and arced on the same electrode. Due to the fact that the relative intensities of Mg 2779.8 and Sr 2931.8 were employed to arrive at percentage Mg^{++} ion concentrations, it should be permissible to state that the ratios of the relative intensities of Mg 2779.8 to Ca 3006.9 are proportional to and depend upon the percentage composition ratios of Mg^{++}/Ca^{++}. Therefore, the percentage-transmissions of the Ca 3006.9 lines were determined and are recorded in Table X along with their relative intensities, which were obtained from the calibration curves. The same table shows that deviations do exist in the ratios of RI_{Mg}/RI_{Ca}. Although, in many instances, two of the three values for each solution were nearly the same, it was considered not feasible to discard the third value and to average the two which were similar since these values might represent the extreme end of the range. Therefore, the three values for each fossil solution were averaged together.

TABLE X

RELATIVE INTENSITY Mg/Ca RATIOS FOR PLATES 4, 5, AND 6

Plate	Specimen	Trial	Percent transmission		Relative intensity		RI_{Mg}/RI_{Ca}	Average	% Dev.	Standard deviation
			Ca	Mg	Ca	Mg				
4	1	(a)	20.5	49.4	6.60	3.35	0.508		6.8	
		(b)	23.5	57.2	6.10	2.90	0.476	0.477	-0.6	± 6.5 %
		(c)	21.2	55.5	6.70	3.00	0.448		-6.1	
	2	(a)	18.0	54.5	7.60	3.05	0.402		-9.3	
		(b)	23.6	58.1	6.10	2.85	0.467	0.443	5.4	± 8.0 %
		(c)	19.4	50.6	7.20	3.30	0.459		3.6	
	3	(a)	20.0	46.9	7.00	3.55	0.508		-0.4	
		(b)	19.0	44.0	7.30	3.75	0.513	0.510	0.6	± 0.6 %
		(c)	20.5	47.4	6.85	3.50	0.510		0.0	
	4	(a)	23.8	40.3	6.10	4.03	0.662		0.8	
		(b)	24.4	40.9	5.95	4.00	0.671	0.657	2.1	± 2.6 %
		(c)	24.0	42.5	6.05	3.85	0.637		-3.0	

TABLE X CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		RI_{Mg}/RI_{Ca}	Average	% Dev.	Standard deviation
			Ca	Mg	Ca	Mg				
4	5	(a)	25.0	34.8	5.85	4.50	0.769		-1.3	
		(b)	28.7	38.9	5.20	4.15	0.800	0.779	2.7	± 2.3 %
		(c)	22.8	32.8	6.10	4.70	0.769		-1.3	
	6	(a)	31.4	51.3	4.90	3.25	0.662		1.4	
		(b)	33.6	52.8	4.65	3.15	0.677	0.653	3.7	± 4.5 %
		(c)	32.5	57.0	4.75	2.95	0.621		-4.9	
5	7	(a)	18.5	38.0	9.40	5.45	0.581		0.0	
		(b)	19.6	40.0	9.05	5.20	0.575	0.581	-1.0	± 1.1 %
		(c)	19.7	39.0	9.10	5.35	0.588		1.2	
	8	(a)	21.2	40.5	8.50	5.15	0.606		-0.8	
		(b)	21.3	40.1	8.50	5.20	0.613	0.611	0.3	± 0.6 %
		(c)	19.1	36.5	9.20	5.65	0.613		0.3	
	9	(a)	17.2	35.3	9.90	5.80	0.585		-1.0	
		(b)	18.5	37.5	9.40	5.50	0.585	0.591	-1.0	± 1.7 %
		(c)	18.3	36.8	9.30	5.60	0.602		1.9	

TABLE X CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		RI_{Mg}/RI_{Ca}	Average	% Dev.	Standard deviation
			Ca	Mg	Ca	Mg				
5	10	(a)	15.2	42.0	10.08	5.00	0.495		-7.6	
		(b)	15.6	34.4	10.06	5.90	0.585	0.536	9.1	± 8.4 %
		(c)	17.5	39.5	9.90	5.25	0.529		-1.3	
	11	(a)	15.1	38.6	10.09	5.40	0.535		1.5	
		(b)	14.5	38.2	10.12	5.40	0.535	0.527	1.5	± 2.7 %
		(c)	17.6	41.3	9.90	5.05	0.510		-3.2	
	12	(a)	18.8	34.9	9.20	5.85	0.637		-5.5	
		(b)	21.9	40.0	8.20	5.20	0.634	0.674	-5.9	± 3.4 %
		(c)	29.2	44.5	6.30	4.75	0.752		11.6	
6	13	(a)	22.5	59.0	7.90	3.22	0.408		-2.4	
		(b)	22.2	58.6	7.95	3.25	0.408	0.418	-2.4	± 2.2 %
		(c)	24.0	58.3	7.50	3.28	0.437		4.5	
	14	(a)	26.9	35.5	6.70	5.20	0.775		12.0	
		(b)	23.8	40.7	7.50	4.70	0.625	0.692	-9.7	± 3.5 %
		(c)	27.8	45.0	6.35	4.30	0.676		-2.3	

TABLE X CONTINUED

Plate	Specimen	Trial	Percent transmission		Relative intensity		RI_{Mg}/RI_{Ca}	Average	% Dev.	Standard deviation
			Ca	Mg	Ca	Mg				
6	15	(a)	30.7	43.9	6.00	4.40	0.735		7.1	
		(b)	20.3	36.6	8.65	5.30	0.613	0.686	-10.6	± 3.3 %
		(c)	21.5	34.6	8.20	5.80	0.709		3.4	
	16	(a)	17.8	28.8	9.50	6.40	0.676		-6.1	
		(b)	24.8	32.9	7.25	5.65	0.781	0.720	8.5	± 2.9 %
		(c)	20.8	30.6	8.50	6.00	0.704		-2.2	
	17	(a)	21.4	56.1	8.30	3.45	0.415		-1.2	
		(b)	22.7	58.7	7.85	3.25	0.413	0.420	-1.7	± 2.4 %
		(c)	22.5	57.0	7.90	3.40	0.431		2.6	
	18	(a)	18.0	50.7	9.70	3.85	0.397		-5.5	
		(b)	20.0	52.6	8.80	3.70	0.420	0.420	0.0	± 2.4 %
		(c)	24.5	59.0	7.35	3.25	0.442		5.2	

ANALYSIS OF DATA

If, in Table II, all the carbonate in specimen #1 were $CaCO_3$, then $CaCO_3$ would comprise 73.4 % by weight of the sample and the brachiopod would belong to the previously mentioned calcareous group. Similar calculations show that all the brachiopods examined have calcareous rather than phosphatic skeletons. Somewhat lower values for the $CaCO_3$ contents than those found by Clarke and Wheeler (1917) are due to the fact that not only pure shell material but also secondary silica were pulverized and weighed together. Since the $CO_3^{=}$ ion is the major anion, $MgCO_3/CaCO_3$ ratios should have considerable significance.

Of the two methods used to arrive at a relationship between Ca and Mg, the method of obtaining ratios between the relative intensities of Mg 2779.8 and Ca 3006.9 appears to be the better due to the smaller standard deviations.[9] In order that these ratios might be more easily visualized, the values for plates 4, 5, and 6 have been graphed as a histogram (Figure 11).

The first thing one may observe is that the $MgCO_3/CaCO_3$ ratios for two specimens of the same genus, species, stratum,

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[9] It was decided to obtain a $MgCO_3/CaCO_3$ ratio instead of a $CaCO_3/MgCO_3$ ratio since a small change in the $MgCO_3$ content would be more significant in the overall ratio.

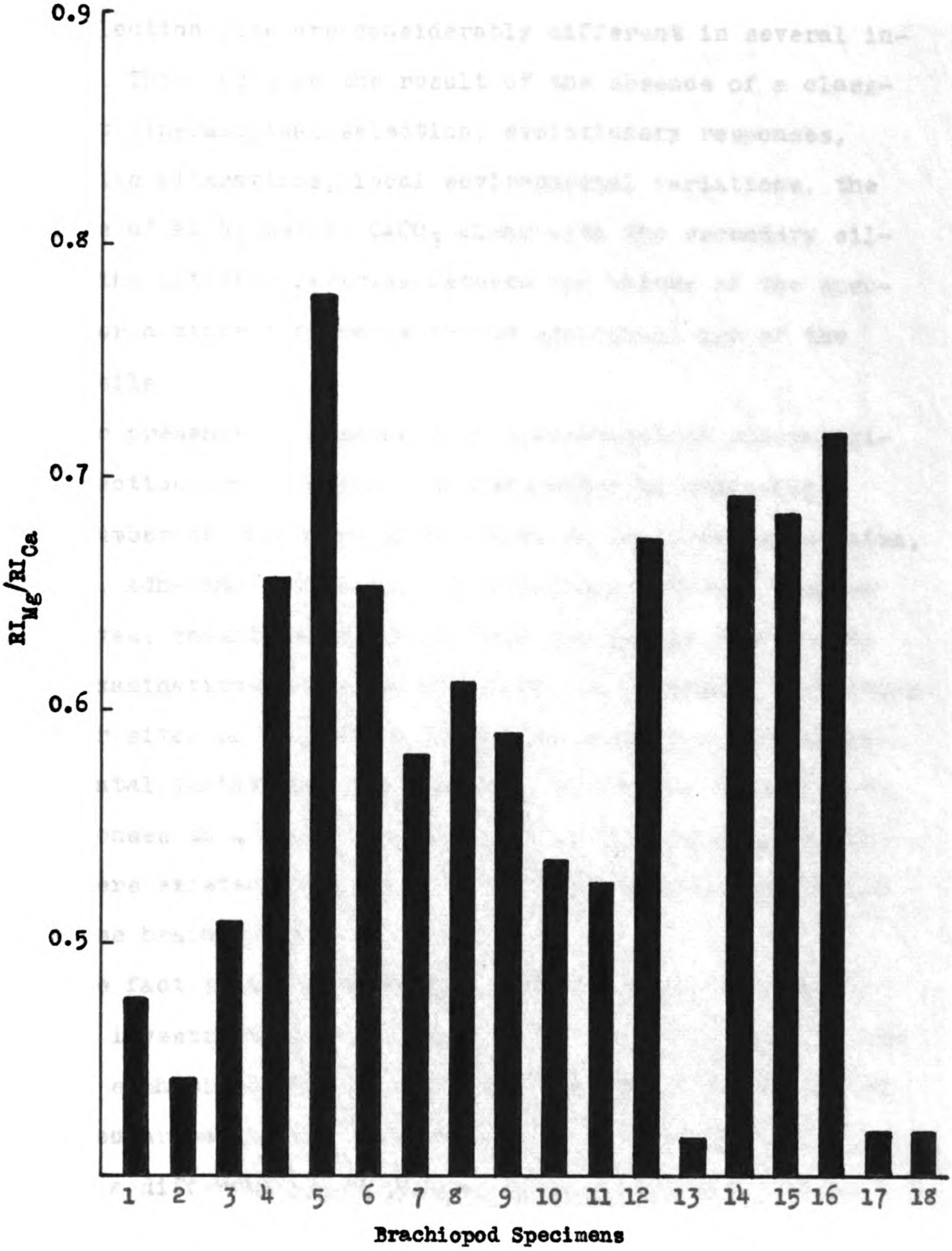

Fig. 11. RI_{Mg}/RI_{Ca} bar graph composite for plates 4, 5, and 6

and collection site are considerably different in several instances. This could be the result of the absence of a class-distinct mineralogical selection, evolutionary responses, diagenetic alterations, local environmental variations, the presence of $MgCO_3$ and/or $CaCO_3$ along with the secondary silica in the interior cavities between the valves of the specimens, or a minor difference in the geological age of the two fossils.

The presence or absence of a class-distinct mineralogical selection could possibly be determined by analyzing a large number of specimens of the same genus, species, stratum, and age. Adhering sediments, including any material between the valves, should be separated from the shells previous to these examinations and sediments from the immediate vicinities of their sites of collection should be checked for local environmental variations. If, however, variations were caused by responses to a rapid evolutionary change, it would appear that there existed no class-distinct mineralogical selection for these brachiopods.

The fact that the specimens used for mineralogical-selection investigations must be of the same age can not be too greatly emphasized. It must be remembered that the bottom of a particular bed in one locality can represent either the same or a different age than the bottom of the same bed at another locality. This situation is shown in Figure 12, which

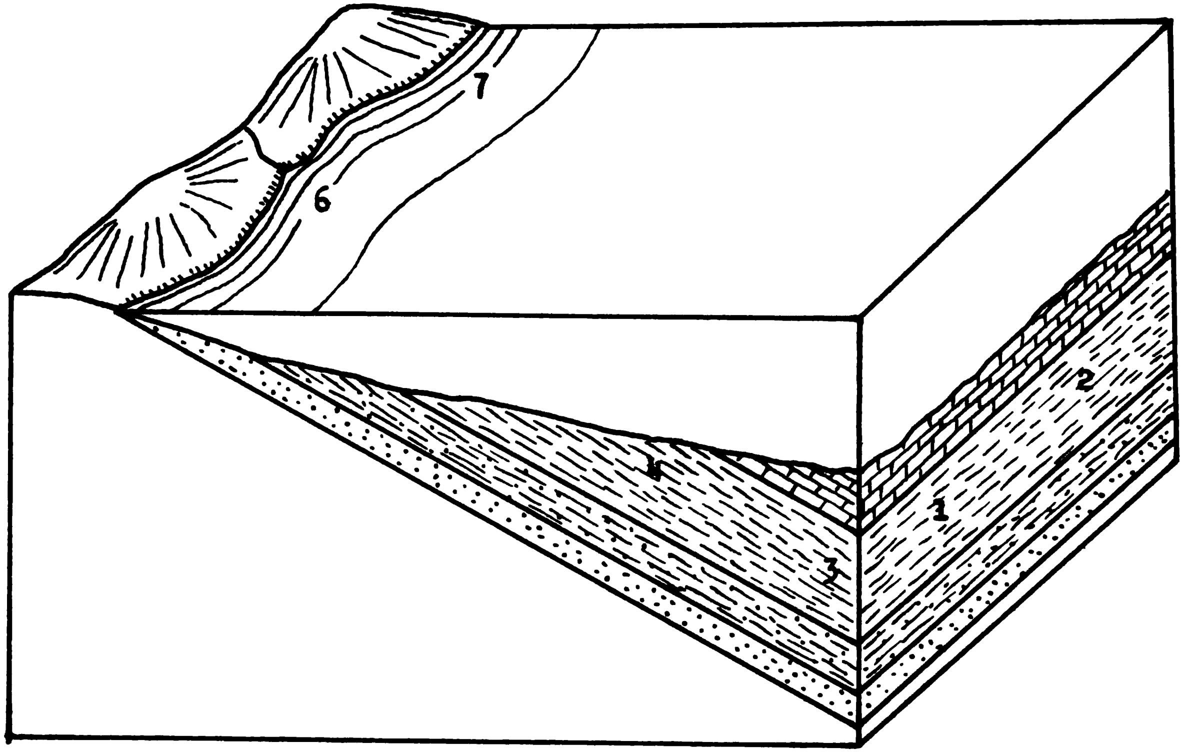

Fig. 12. Block diagram illustrating on-lap of sediments

is a block diagram of on-lapping sediments with numbered marine organisms. Assuming that there was no relocation of the organisms before their burial, organisms #1 and #2 should be of the same age and organism #4 should be younger than organism #3 even though all four organisms are to be found in the same bed.

A check on the compositions of the sediments should show indications of environmental variations. If two organisms were located as #6 and #7 in the diagram, where a fresh-water stream enters the sea in the vicinity of #6, it seems not improbable that the dilution of marine-water constituents would be detectable in the sediments as well as in organism #6 and should result in an analysis which would differ from that of #7 and its associated sediments.

If one were to assume that, in the case of the specimens examined, there were a class-distinct mineralogical selection and no variations due to evolutionary responses or local environmental fluctuations, an interpretation of the $MgCO_3/CaCO_3$ data might be made on the basis of major environmental and time changes. As stated earlier, many geologists believe that the formations from the Greendale through the Arnheim in southwestern Ohio were deposited by a southern invasion of the sea and those immediately above the Arnheim by a northern arm of the sea. Since there was little relief in this locality during Ordovician time, such a change in seas could have been accomplished by a gentle warping of the land surface.

If, with the progression of time, the temperatures of these seas were rising toward the overall higher temperatures of Silurian time, the associated calcareous marine organisms should reflect this in higher magnesium contents.[10] The fossilized specimens should, therefore, show increases in magnesium contents from the Greendale up through and including the Arnheim formations. The specimens in the formations immediately above the Arnheim should show the same trend but have slightly lower magnesium concentrations during the first part of this northern sea deposition than the same genera and species in the southern sea deposits due to the somewhat cooler waters of the northern sea.

The various strata from which the specimens were collected are diagrammed in Figure 13 and the fossils are represented by the same reference numbers as in Table I. The dashed lines are time-lines and the solid lines separate different formations. On the basis of the data in Figure 11, the specimens are located in the diagram with the idea of increasing magnesium content with time. Therefore, since #1 has more $MgCO_3$ than #2, #1 must be younger than #2 and, according to the law of superposition, be above the time-line for #2. Specimen #4 is younger than #3 and both have greater

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[10] It has been found that, for many calcareous marine skeletons, the magnesium content increases with the temperature of the organism's environment.

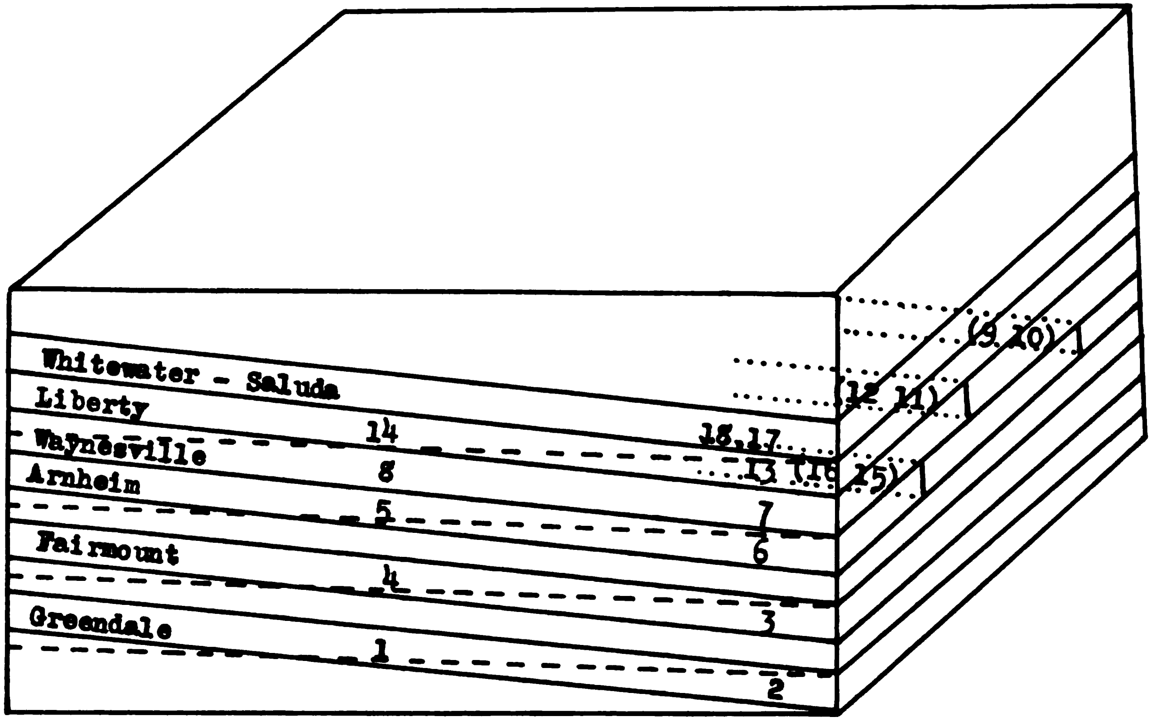

Fig. 13. Ordovician strata and associated brachiopods

magnesium contents than #1 or #2. Specimen #5 is younger than #6, etc.

If a change in seas occurred, the time of this change might be established by noting where there is a decrease in magnesium contents of fossils of the same genus and species. Specimens #5 and #6 in the Arnheim formation drop in magnesium content to the lower values for #7 and #8 in the Waynesville formation. Fossils #17 and #18 in the Whitewater have much less magnesium than #15 and #16 in the Arnheim. This leads to the support of the theory that the deposits above the Arnheim were deposited in a different arm of the sea than those below the Arnheim.

However, specimens #9, #10, #11, #12, #13, and #14 seem to vary greatly in magnesium content. On the basis of #13 and #14, one would believe that no class-distinct mineralogical selection existed for this species or that local variations in their environment had a profound effect. Diagenesis might be a factor of concern, but no alterations were observable megascopically.

SUMMARY AND CONCLUSIONS

Several facts which were established by means of the preceding investigations are: 1) the major and trace elements in all the brachiopod specimens were similar; 2) the quantities of certain elements varied between different specimens; 3) all the brachiopods examined belonged to the calcareous group; 4) the specimens contained less than 1.5 % Mg^{++} by weight; and 5) the ratios of $MgCO_3/CaCO_3$ differed between the same species as well as between different genera and species.

The analyses of certain specimens seem to support the theory that, in the vicinity of southwestern Ohio, the formations from the Greendale through the Arnheim were deposited during a southern invasion of the sea and those immediately above the Arnheim in a northern arm of the sea. Other fossil analyses gave rise to much uncertainty in such an interpretation.

In order that a solution to the Cincinnati Arch problem may be obtained, investigations should be made along various lines. It should be determined whether or not a class-distinct mineralogical selection exists between the same brachiopod species. Complete removal of all the sediment from the interiors and exteriors of the shells might yield better results. Local environmental changes might be detected

in analyses of the sediments associated with the fossils. A consideration of these and other factors should lead to more conclusive results.

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