GEOCHEMISTRY OF BORON IN PELITIC SEDIMENTS

GEOCHEMISTRY OF BORON IN PELITIC SEDIMENTS

By

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SCOPE AND CONTENTS: A Geochemical study of the distribution of boron in shales has been made. One hundred and seventy four samples, comprising 17 Silurian, 17 Triassic, 40 Devonian, and 20 samples in each of the Precambrian, Ordovician, Mississippian, Jurassic and Cretaceous Periods were studied. Analytical data on major elements, CO_2 and relative boron concentrations have been used as an aid in environmental interpretation and in a general discussion of the geochemistry of boron.

The concentration of boron has been determined, using an emission spectrographic technique for all the samples. Major element analyses, obtained by rapid silicate methods, are presented for 14 samples. An additional 13 major element analyses have been incorporated from the literature. Seventy four CO_2 analyses were determined for shale samples containing a high carbonate fraction.

ACKNOWLEDGMENTS

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I am indebted to Dr. E.W. Mountjoy and Mr. W.S. MacKenzie for their assistance in collecting the samples for this study.

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ABSTRACT

One hundred and seventy four shale and argillaceous carbonate samples have been analyzed spectrographically for boron. The samples represent argillaceous sediments varying in age from the Proterozoic to the Cretaceous. A negative correlation between per cent CO_2 and boron suggests that boron is mainly distributed in the argillaceous fraction and in the silica fraction.

The B 2497.73Å line, because of an Fe coincidence at 2497.82Å, was found to be unsuitable for boron determinations in either the first or second orders of a Jarrel-Ash Wadsworth-mount spectrograph (Dispersion 5.2 and 2.6 A/mm. respectively). Consequently, an analytical method utilizing B 2496.78Å in the second order spectrum was used. The boron results of this method compared to a chemical method appear to be systematically lower at concentrations above 24 ppm. boron. For example, two samples analyzed chemically contained 24 and 117 ppm. boron whereas the same samples analyzed spectrographically contained 24 and 79 ppm. boron. Absolute boron values probably could be recalculated by adjusting the working curve.

Shales containing an apparent boron content above 75 ppm. appear to indicate a marine or hypersaline depositional environment. One section, Whitehorse Fm. (Triassic) has been misclassified into brackish or fresh water depositional environment based on low (below 75 ppm.) boron content. However, the mineralogy of this section is atypical

(very high carbonate content) and the results may be misleading. Samples from the Fernie, Banff, Mount Hawk, Thorold and Grimsby, and the sub-Devonian all contain more than 75 ppm. thus indicating marine depositional environments. A brackish water environment is suggested for shales from the Littleton and Kaskapau (Blackstone) Formations. One shale section, the Proterozoic (Miette Group), may have been deposited under a fresh water environment.

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INTRODUCTION

General

Within recent years the use of trace elements as criteria for depositional environments, has been proposed. Boron (Landergren 1945), boron and rubidium (Degens, Keith and Williams 1957, 1958), boron and lithium (Keith and Bystrom 1959), and boron and vanadium (Potter, Shimp and Witters 1963), have been reported to be measurably higher in marine shales than in comparable fresh water shales.

Investigations dealing specifically with the relative amounts of boron as a geochemical indicator of salinity and paleosalinity have appeared frequently. Frederickson and Reynolds (1959), Frederickson (1962), Walker and Price (1963), and Walker (1962, 1963, 1964) have reported a high boron content in marine illites. Experimental research carried out by Harder (1960), shows boron to be preferentially incorporated into the muscovite lattice. Conclusions reached by the above authors are, a) relative boron content in illitic shales is an indicator of sedimentation salinity, b) boron content can be used in geochemical prospecting for gas and oil bearing reefs through paleosalinity variations within specific paleogeographic locations, c) boron serves as a geochemical method for locating porosity.

Three models relating boron content in sea water have been proposed. The first, proposed by Landergren (1945) suggests that the boron concentration in sea water has gradually decreased from ancient to recent times. He attributes this decrease to a pronounced submarine volcanicity in the past, releasing abundant volatiles such as boron, and a subsequent continual depletion of boron from sea water resulting from co-precipitation with clay particles. The second model (Weber 1960) based on 33 shale analyses from formations of Ordovician, Devonian, and Cretaceous age which show an increase in boron content toward the present, suggests that boron was gradually added to the oceans by volcanism rather than by the condensation of volatile boron trichloride from a protoatmosphere. The third model (Reynolds, in press 1964) is based on the boron content of Precambrian illites obtained from relatively unmetamorphosed carbonate rocks. The boron contents for these samples, which range in age from Archaean to upper Proterozoic, are similar to reported normal marine post-Precambrian illites. Reynolds suggests that the boron content in sea water has remained constant for the past two to three billion years and supports the view that the oceans have grown throughout geologic time by the accumulation of degassing products of the earth's crust.

Purpose

The purpose of this study is to examine the claim that boron can be used as a geochemical paleosalinity indicator, to resolve the three boron models, to study the boron variance within and between stratigraphic sections of marine shales, and to elucidate the geochemistry of boron in marine shales. An additional purpose is to develop an accurate spectrographic method for boron, deemed necessary because of the large boron variation, 58 to 320 ppm. reported by different laboratories for a reference sample known as Syenite-1, a sample distributed by the Nonmetallic Standards Committee of the Canadian Association for Applied Spectroscopy.

METHODS

Sample Collection and Preparation

During the summer of 1962 the author was employed by the Geological Survey of Canada as a senior assistant studying Devonian reef structures, approximately thirty miles S.E. of Jasper. At that time six (shale) sections from Precambrian, Ordovician (sub-Devonian), Devonian, Mississippian, Triassic and Cretaceous lithologies (location map 1) were measured and samples collected (appendix 1). Additional shale samples from Jurassic[1], Devonian[2], and Silurian[3] periods were obtained from other sources. Samples were collected systematically at intervals varying from 25 ft. in relatively uniform shale sequences and at 5 ft. intervals where distinct differences in the shale could be recognized from one bed to another.

In planning this study it was obvious that variation in carbonate, quartz, and specific clay mineral content would create difficulties in obtaining a full understanding of B distribution. To elucidate the effects of these variables a large number of samples, approximately 20 from each period, were taken; CO_2[4] values were determined for carbonate rich shales; complete chemical analyses were made of two samples from each period, additional major element determinations were incorporated from the literature[2,5].

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[1] Mountjoy, E.W., Jurassic samples from Fernie fm. near Jasper.
[2] Shaw, D.M., (1954), Samples from the Littleton fm.
[3] Martini, I.P., Silurian samples from S. Ont. and N. New York State.
[4] Chemical analyses were done by J. Muysson, McMaster University.
[5] Candy, G., (1963), The geochemistry of some Ordovician and Silurian shales from S.W. Ont., (unpublished M.Sc. thesis, McMaster University).

Two hundred gm. of each sample were crushed to pea size; quartered manually to 50 gm.; fine crushed to 100 mesh in steel mortar and pestle, and ball mill; final 50 mgm. subsample was reduced to less than 200 mesh size in an agate mortar for spectrographic analysis.

Spectrographic Methods

Most B determinations in geochemistry have been made in the past by using the line B 2497.73 A[1]. Use of B 2496.78 A is limited because of a near coincidence by Fe 2496.53 A which can usually be partially resolved. The coincidence of Fe 2497.82 A and B 2497.73 A is also known, although the lines are too close in wavelength to be resolved in many spectra, but this coincidence has commonly been ignored because the iron line is believed to be very weak.

In the course of this study the author found that B 2497.73 A is unsuitable for B determination in either the first or second order of a Jarrell-Ash Wadsworth mount spectrograph (dispersion 5.2 and 2.6 A/m.m. respectively). Consequently an analytical method utilizing B 2496.78 A in the second order spectrum was developed and used.

The line Fe 2497.82 A has relative intensities of 15 and 50 (Harrison, op. cit.) for arc and spark respectively. It was decided to determine the relative sensitivities of Fe and B lines in an effort to correlate B determinations with Walker (1963). Two methods were used, one using the Stallwood jet with an argon-oxygen atmosphere and the other omitting the Stallwood jet and burning in air. Exposures of 120-140

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[1] Wavelengths are taken from Harrison (1939).

seconds were made at 8 amperes on Eastman-Kodak type S.A.1 plates. Samples containing 8% Fe_2O_3 in an artificial shale matrix, with varying B contents, were mixed with graphite in the ratio 1:2 before arcing.

Fig. 1 (taken from Bugry and Shaw, 1964) shows the relationship of boron and iron peak on a recording densitometer using an $A-O_2$ atmosphere, while fig. 2 shows the same relationship for samples burned in air. The results clearly demonstrate the iron interference on the higher wavelength boron line, which would require considerably better resolving power than 2.6 A/m.m. to separate distinctly. The results also show that in shales containing 8% Fe_2O_3, analyses made using B 2497.73 A would be considerably in error at B concentrations far above 32 ppm.

Spectrographic Method

A summary of spectrographic parameters of the analytical method is listed in(Table I).

Some variations from the standard spectrographic method were adopted. Corming ultraviolet filter #7-54 placed immediately behind the sector removed spectra of the first-order wavelengths around 4800 A. Although initially, use of the filter was deemed unnecessary because the sensitivity of the S.A.1 plates is greatest in the range 2400-3750 A, it was found that some first order lines were being recorded and so the filter was used.

Samples were burned in a random sequence, 25 samples and 3 standards on each plate, with each replicate on a different plate. To obtain 28 burns on each plate all unnecessary portions of the emulsion were masked off. By shifting the camera and rearranging the masks an unexposed strip of plate became available for exposure.

BURNED IN AN A-O_2 ATMOSPHERE

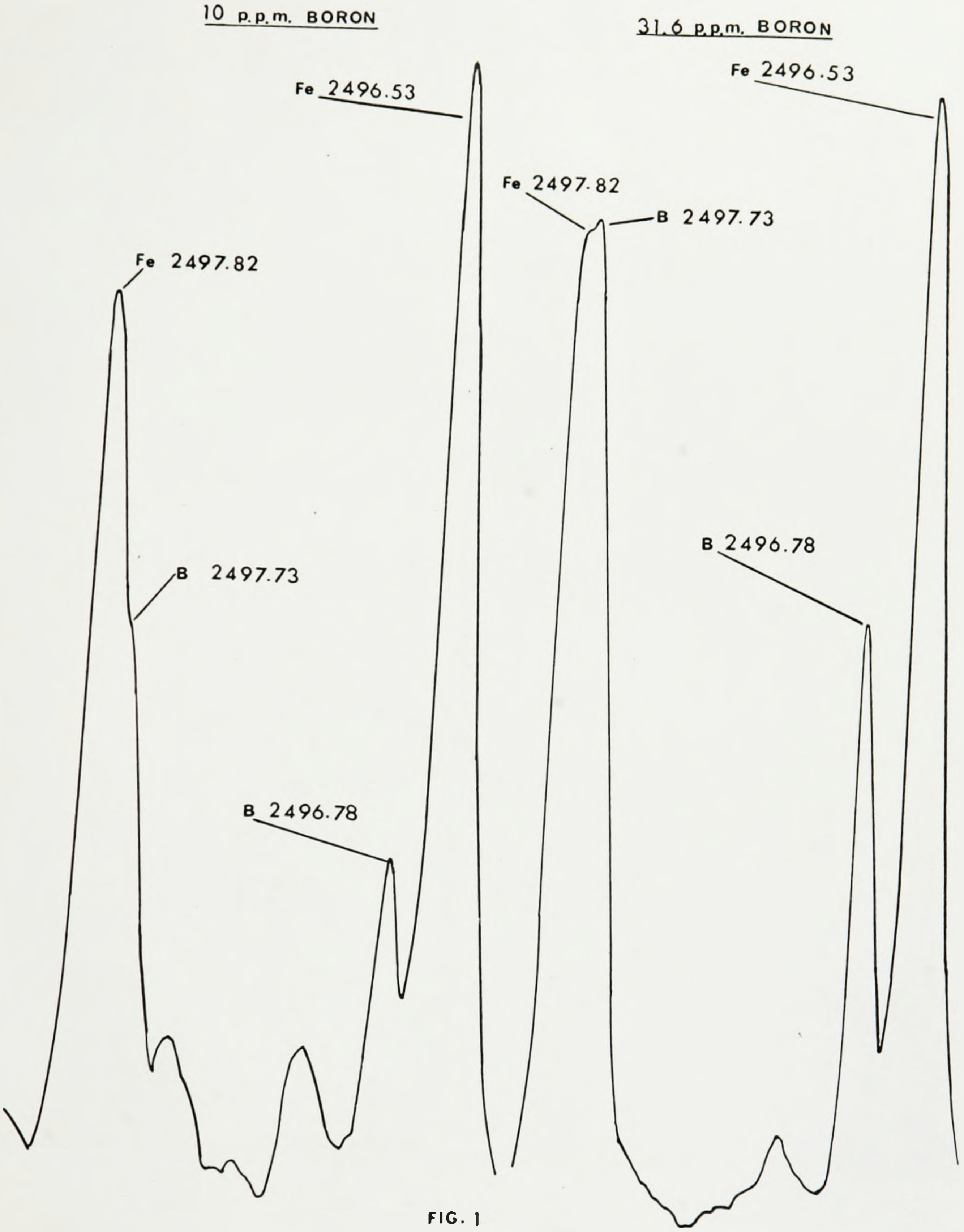


FIG. 1

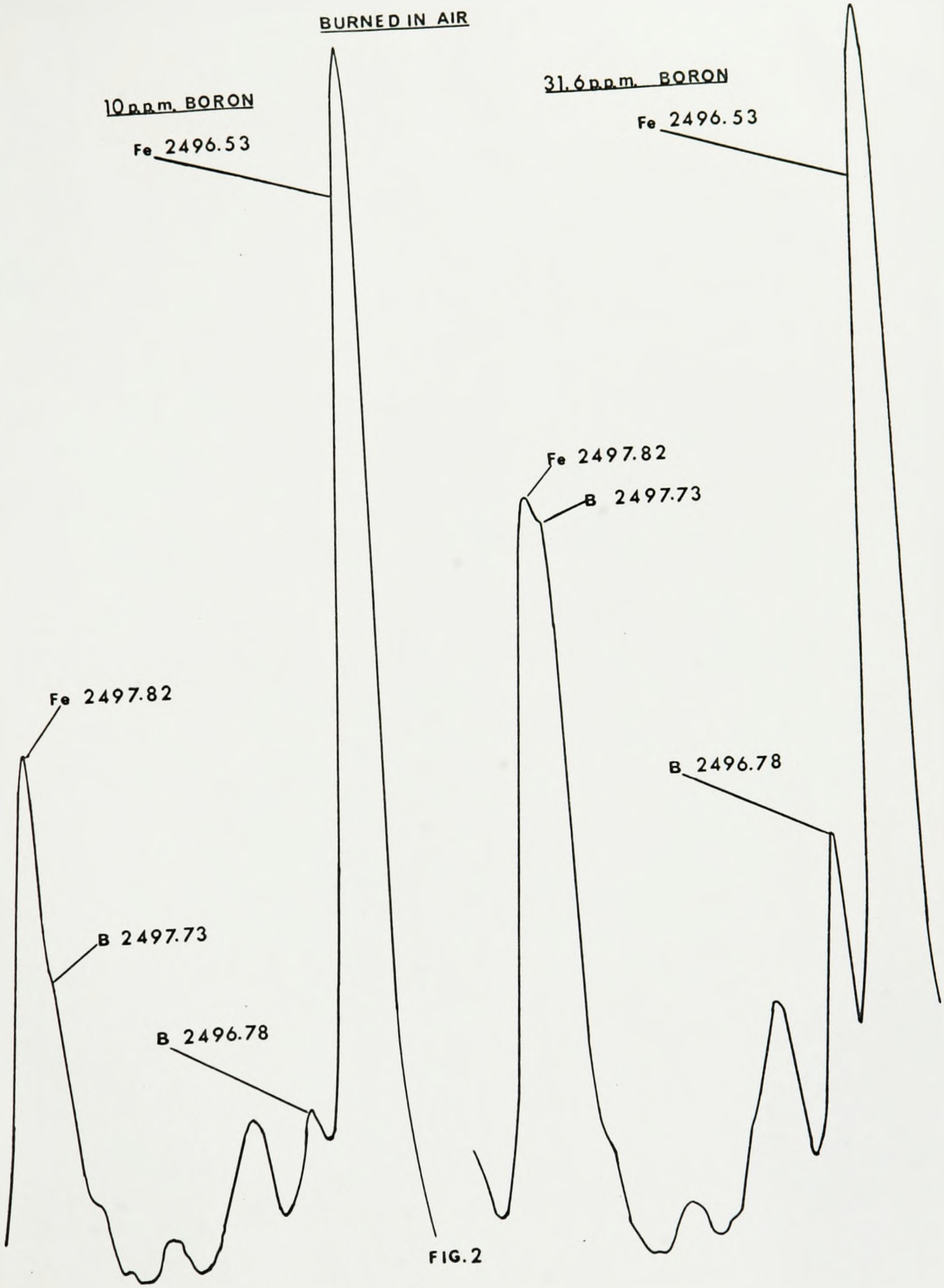

BURNED IN AIR
10 p.p.m. BORON
Fe 2496.53
Fe 2497.82
B 2497.73
B 2496.78
31.6 p.p.m. BORON
Fe 2496.53
Fe 2497.82
B 2497.73
B 2496.78

FIG. 2

Photographic Plate Calibration

A Jarrell-Ash densitometer was used to read percent light transmission of the analysis and internal standard lines from the photographic plates.

For basic plate calibration theory consult Ahrens and Taylor (1961). Essentially, a working curve, relating ppm. to log I_A/I_E where I_A is the corrected intensity of the analysis line; I_E is the corrected intensity of the internal standard line, was prepared using artificial standards. The log I_A/I_E ratios were determined for samples with an unknown concentration and from these ratio the B concentrations were read off directly from the working curve. An Intercom programme prepared by D.M. Shaw, for the Bendix G15D digital computer, obtained log I_A/I_E determinations from the transmission readings. Transmission readings from three successive steps for the analysis and internal standard lines together with a single reading of the "background" transmission opposite the darkest of the three successive readings were used. The programme computed a quadratic polynomial expressing the calibration of a narrow segment of the photographic plate, and calculated the intensity ratios, log I_A/I_E.

Working Curve

An artificial matrix (Table II) was prepared from Johnson-Matthey "Specpure" compounds, and was sintered for 10 hrs. at approximately 900°C. Standard samples for the construction of the working curves were prepared using this matrix with B added as borosilicate glass (12.7% B_2O_3). Standards containing from 0.0316% to 0.001% B were made up by dilution and

TABLE I: Details of Spectrographic Method

Instrument:	21 ft. Jarrell Ash Co. grating spectrograph Second Order dispersion = 2.6 A/m.m.
Condensing optics:	(distances are from the slit)
	- Cylindrical lens (horizontal axes) Focal length 25 cm.
	16.1 cm. Cylindrical lens (vertical axes) Focal length 6.7 cm.
	27.5 cm. Diaphragm with 5 m.m. aperture
	58.1 cm. Spherical lens. Focal length 10 cm.
	72.5 cm. Location of arc
Arc Gap:	4 m.m.
Slit Width:	30 microns
Slit Length:	8 m.m.
Intensity Reduction:	7 step rotating sector (log intensity ratio = 0.2) at the slit. One or no mesh screens at the diaphragm. Corning ultraviolet filter #7-54 placed immediately behind the sector.
Voltage:	225 volts D.C. open circuit
Current:	6.5 amps
Exposure:	to completion (120-140 seconds)

Electrodes: Anode: United Carbon Products Co. 1/8" diameter rod; plain crater 1/16" x 3/8"

Cathode: National Carbon Co. special graphite; 1/8" diameter rod

Gas Jet: A/O_2 = 80/20 mixture (Supplied in mixed tank by Canadian Liquid Air Co.) at 16 s.c.f.h. air.

Photographic Plates: Eastman Kodak Type SA-1 (2450-3750 A).

Processing: Kodak D-19 developer, 3 minutes at 20°C

Stop Bath 30 seconds

Acid Fix 4 minutes

Wash 20 minutes

Photometry: Jarrell Ash Co. Densitometer eighteen replicates of each were analysed (Fig. 3). Fig. 3a is an additional working curve, constructed for use on low B shales. The final working curve was determined by linear regression, using least squares method, log I_A/I_E on concentration (ppm).

Internal Standard

Samples were mixed in acetone 1:1 with a graphite and internal standard mix. The graphite used was supplied by United Carbon Products Inc. and the chemical reagents by Johnson-Matthey Co. Ltd. The internal standard was beryllium 0.025% added as BeO. The Be line used was 2494.58 A. Another Be line at 2494.56A is coincidental in the first orderspectra but is clearly resolved from the higher wavelength line in the second order.

Precision and Accuracy of Spectrographic Analyses

The syenite-1 sample distributed by the Nonmetallic Standards Committee of the Canadian Association for Applied Spectroscopy furnished an interlaboratory comparison between this method and a similar (same B line) method used by Ingamells and Suhr (1963). They obtained a value of 63 ppm. B, compared to 45 ppm. in this work. Other interlaboratory comparisons are listed in Table III. Chemical B determinations furnished by Gulf Research and Development Co. clearly indicate that values above 24 ppm. B reported in this work are systematically lower than the chemical values. However, the values compared relatively do not change the conclusion reached in this research.

Precision of replicate analyses was determined using a single variable analysis of variance (Dixon and Massey, 1957). This is the

TABLE II: Composition of Matrix in Wt. %

SiO_2	55
Al_2O_3	23
Fe_2O_3	8
NaCl	3
MgO	3
KCl	8

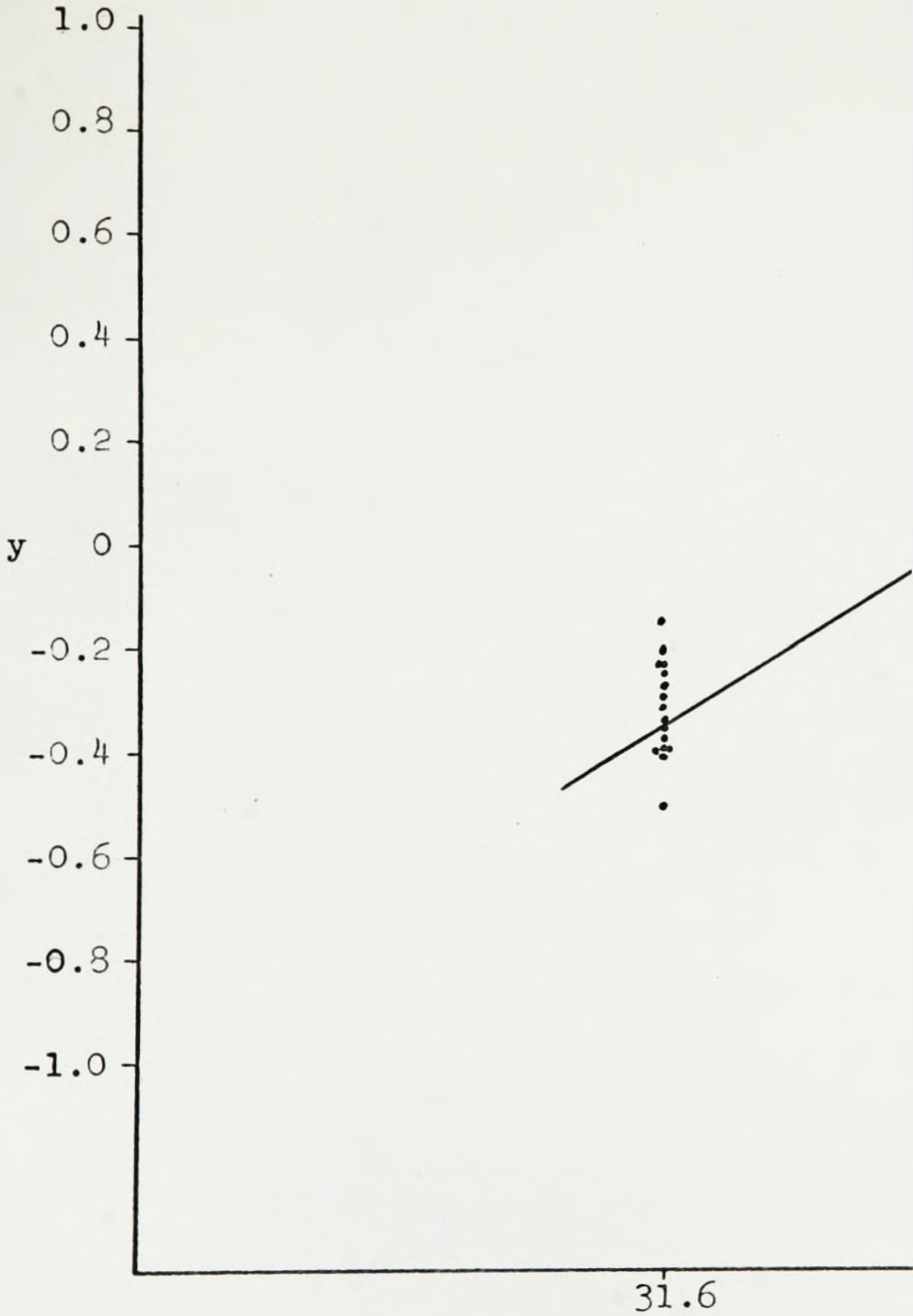
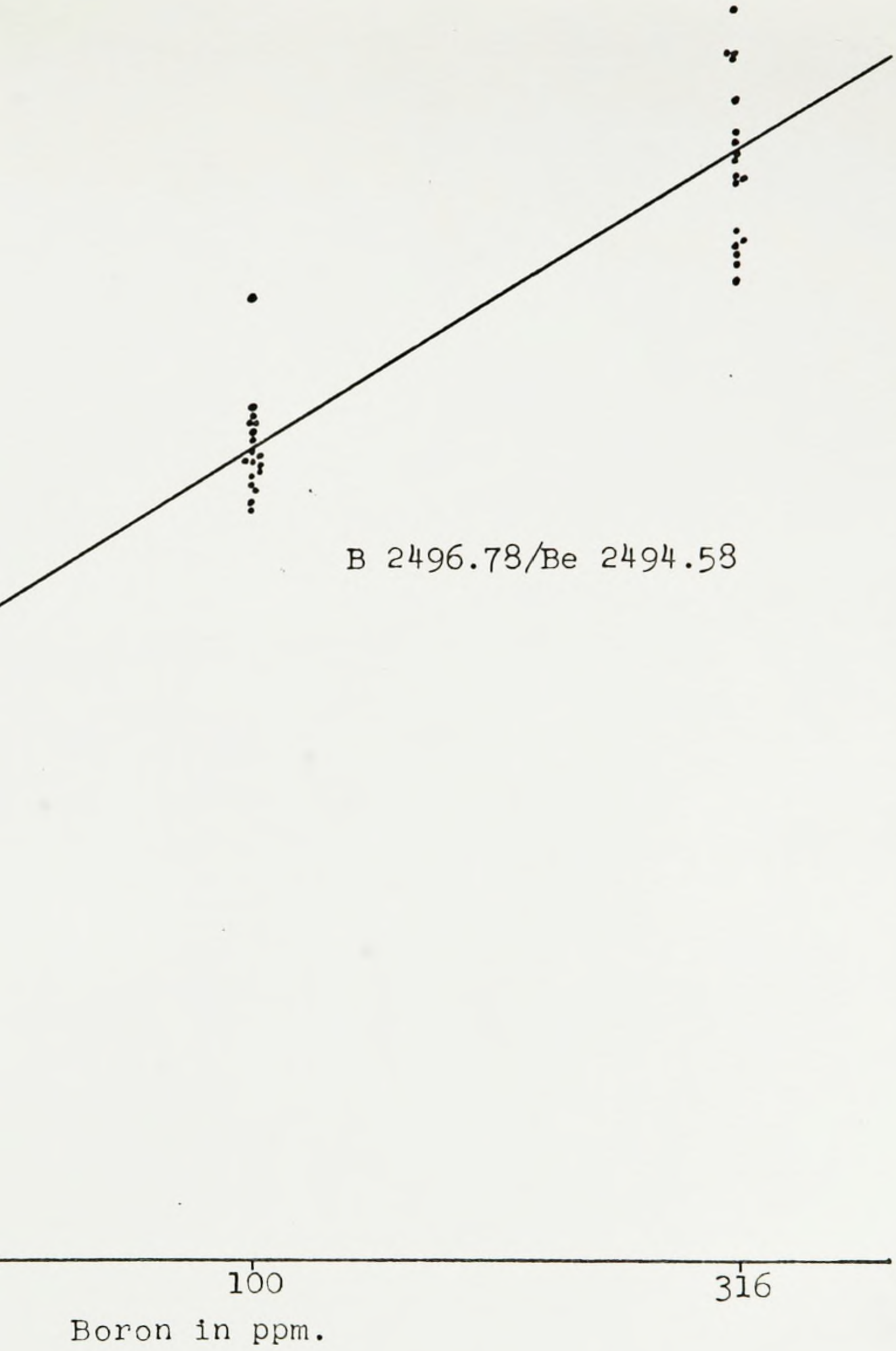


Fig. 3. Boron working curve,



slope = 1.18 from regression of y on x.

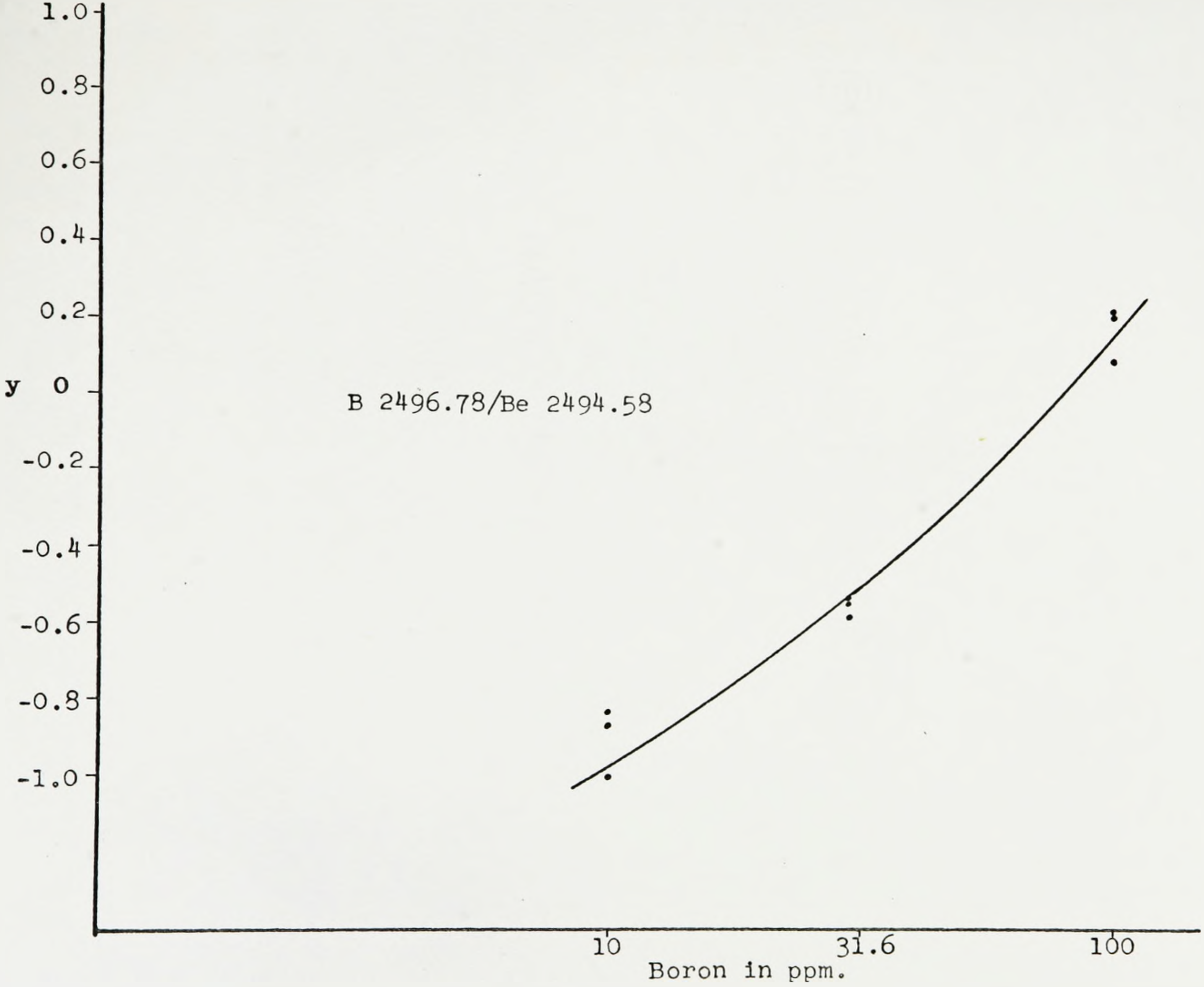


Fig. 3a. Boron working curve for low concentrations.

best estimate of the population error variance σ^2. A programme written by Dr. G.V. Middleton computed Sp^2, the pooled estimate of the error variance. A logarithmic transformation of the original data was used because of the greater dispersion about the arithmetic mean, for example the replicate burns of sample W-104 are 260, 255, 300 ppm. whereas in sample L-13 the replicates are 43, 42, 40 ppm.

Sp^2, the pooled variance (Table IV) was used to determine the analytical precision (estimated by the standard error, S, of the mean).

$$Sp^2 = nS^2$$

or, for triplicate analyses $S^2 = \frac{Sp^2}{3}$

The arithmetic coefficient of variation was approximated from S^2 as follows:

Let $\bar{x} + S = \log_{10}$ (upper limit) $= \log_{10}U$

and $\bar{x} - S = \log_{10}$ (lower limit) $= \log_{10}L$

Then $C\% = 100\,\frac{U-L}{2\bar{k}}$, where x is the grand mean in $\log_{10}$ units

and $\bar{k}$ = antilog x.

For the B method used C% = 9.8.

Discussion of Previous B Research

Many spectrographic determinations of B in clay and shale may be erroneous and represent Fe concentrations, because of a line coincidence at 2497 Å (Bugry and Shaw, 1964). This may explain an observed positive correlation between B and k_2O.

TABLE III

Summary of Analyses for Syenite Rock-$_{i}^{a}$ and Other Shale Samples

Participating Laboratories	Sample	B in ppm	Mean
Baker, 1961 (emission)	S-$_{i}$a	58,64,80,100,120	124
Ingamells and Suhr (1963) (emission)	S-$_{i}$a	63	
McMaster University (emission)	S-$_{i}$a	41,40,53	45
Potter, et al (1963) (emission)	951	96	
GR with DC* (chemical method)	951	98,98,97	98
McMaster University (emission)	951	58	
Potter, et al (1963) (emission)	1137	26	
GR with DC (chemical method)	1137	25,24,26	25
McMaster University (emission)	1137	24	
GR with DC (chemical method)	USGS-259571	118	
McMaster University (emission)	USGS-259571	79	
USGS (emission)	USGS-259571	150	

* Gulf Research and Development Company

TABLE III (continued)

Participating Laboratories	Sample	B in ppm	Mean
GR with DC (chemical method)	USGS-259600	80	
McMaster University (emission)	USGS-259600	50	
USGS (emission)	USGS-259600	100	

TABLE IV

Pooled Analysis of Variance table, determination of Sp^2

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares
Between Groups	1804.98556	173	10.41032
Within Groups	1.88667	348	$0.00542 = Sp^2$
Total	1806.87223	521	

Observed B variation in illite (Walker and Price, 1963) is in the range of 30-300 ppm. with a few values over 500 ppm. If these figures represent Fe, then Fe must vary within a similar range, that is over values x% to approximately 10x%. Since no data are available for B and Fe of individual illites, an indirect approach must be used. Table V presents K_2O and Fe_2O_3[1] for eleven fine fraction shales known to be (mainly) illite. The range for iron oxide is 1.33% to 10.15% which corresponds proportionately to that for boron values. The plot of K_2O against Fe_2O_3 in Fig. 4, shows a positive correlation between K_2O and Fe_2O_3. This relationship may result in spurious correlation between K_2O and B.

Figure 5 shows a plot of B and K_2O, taken from Walker and Price (op. cit.). The two major groups of points, for marine and non-marine clays respectively, each shows a positive correlation. It is the contention of the author that these correlations are considerably influenced by the potash-iron oxide correlation, resulting from the spectral line coincidence discussed previously. Further support is given by the stronger correlation in the non-marine samples, for which the apparent B values are lower and the effect of Fe consequently dominant.

[1] Total iron is expressed as ferric oxide

TABLE V

K_2O% and Fe_2O_3% values for 11 fine fraction shales known to be (mainly) illite

Source	K_2O%	Fe_2O_3%
Grim et al (1937)	6.93	6.81
"	6.09	6.48
Nagelschmidt and Hich (1943)	5.22	3.30
"	5.34	3.23
"	5.12	1.64
"	5.23	1.33
"	5.34	2.71
"	5.22	2.01
Mackenzie (1957)	6.31	3.85
Candy (1963)	6.91	10.15
"	7.42	6.23

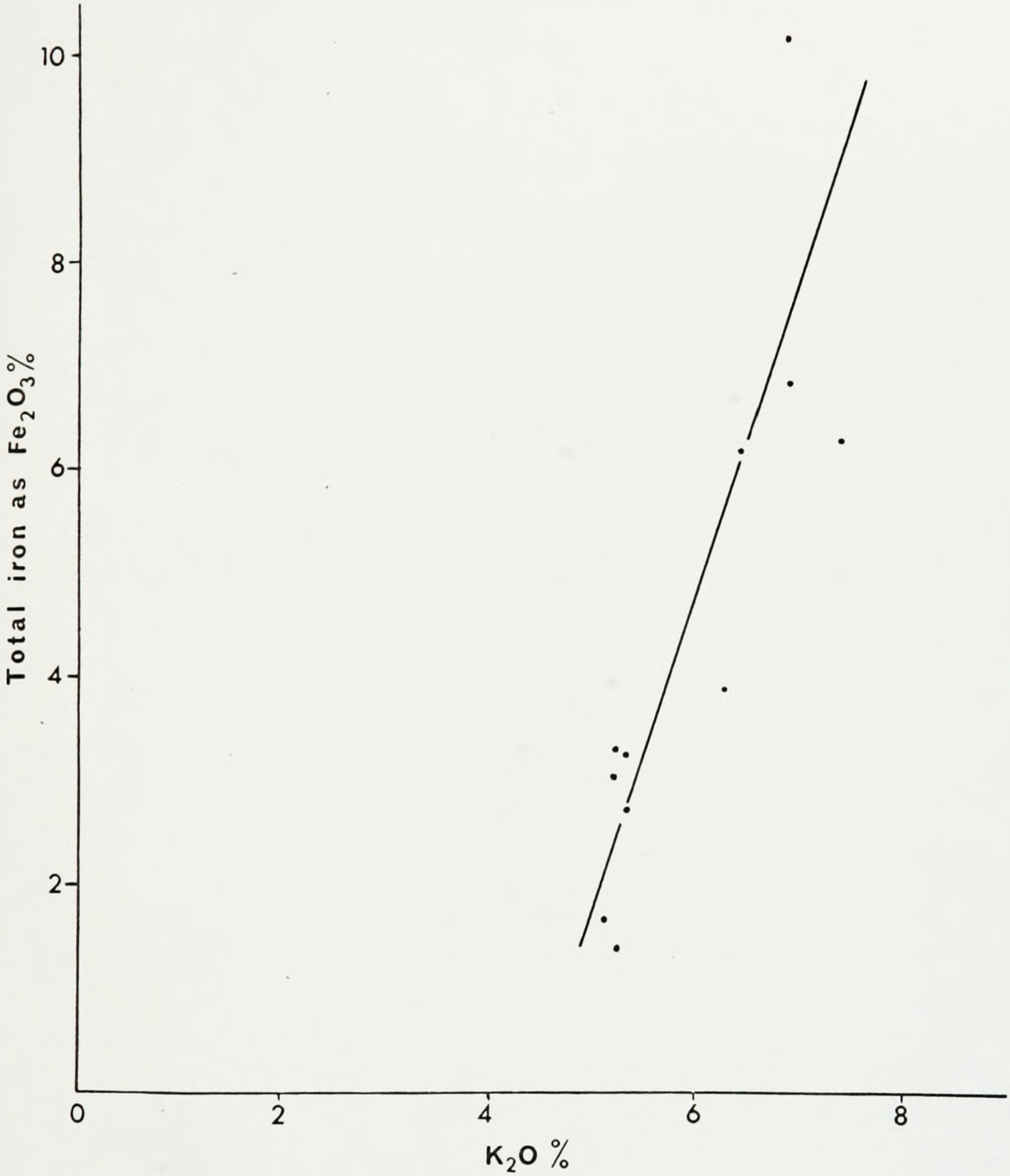


FIG. 4. Relationship between K_2O and iron from data on illites.

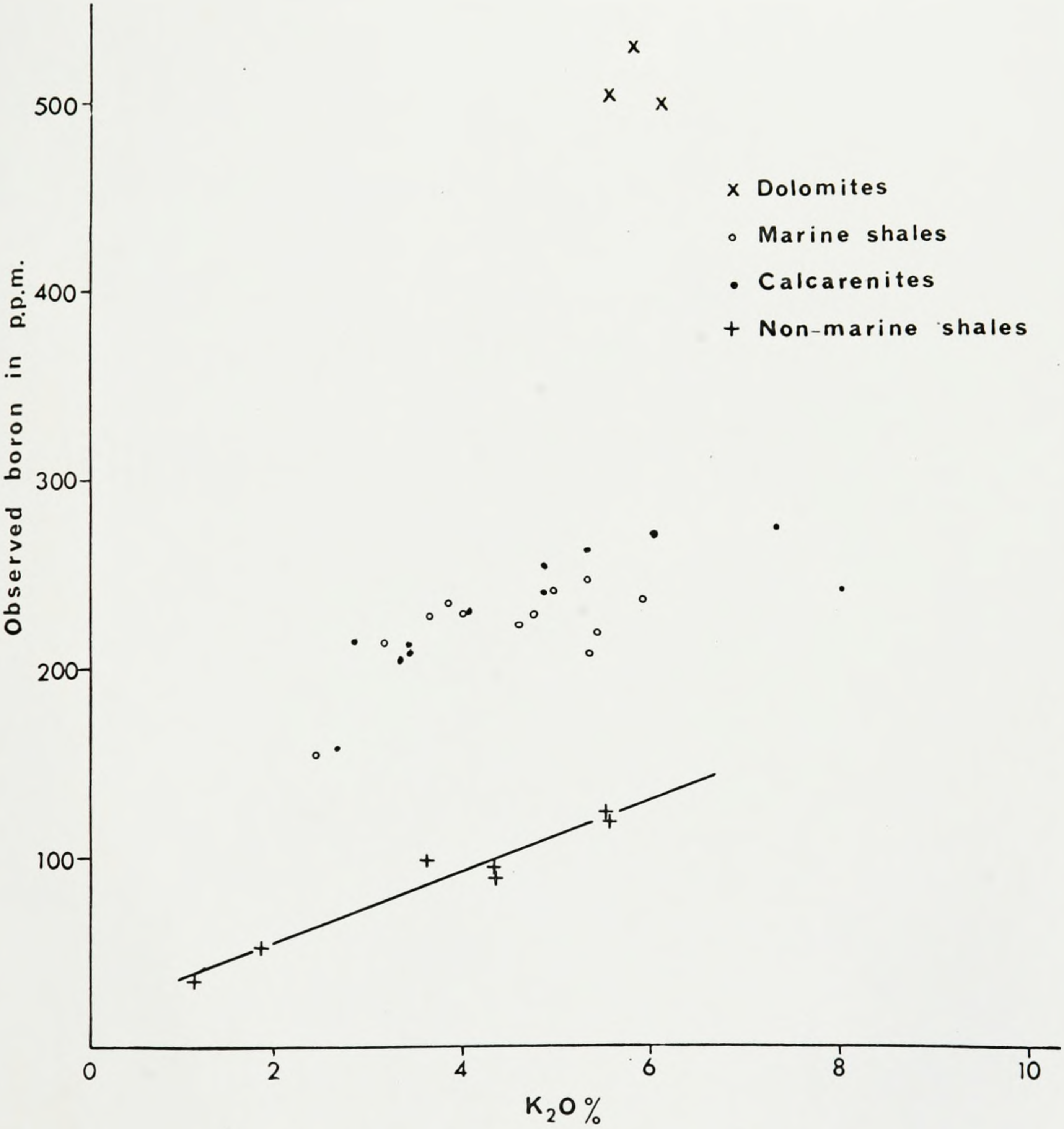


FIG. 5. Plot of B and K_2O data from Walker and Price (1963).

BORON GEOCHEMISTRY IN SHALES

One of the primary issues in the study of shales is their origin. Shales are composed of quartz, rock fragments, heavy minerals, clay minerals, finely divided silica and varying amounts of carbonates. Studies by Griffin (1962), Pryor and Glass (1961) have shown that a large portion of the clay minerals entering the Gulf of Mexico are detrital. On the other hand, Bien et al (1959) have clearly demonstrated that soluble silica entering the sea (Gulf of Mexico) from fresh waters (Mississippi River) is removed by co-precipitation with clay particles and by biological uptake. Thus a vexing problem is to distinguish the detrital fraction from the authigenic fraction in shales.

A common aim in trace and major element studies on sedimentary rocks is to obtain criteria which may reflect differences between depositional environments, that is, differences in the authigenic portion of a sediment. Unfortunately, the nature of the detrital component is dependent upon provenance and previous climatic conditions (Keller, 1956) rather than on specific conditions at the point of deposition. The chemical differences (Table VI) between marine and fresh water Pennsylvanian shales cannot be explained by a comparison of chemical differences present in aqueous environments (Table VII). For example, sea water contains more Cl, Na, and less CO_3, SO_4, Ca, and K than fresh water, yet comparing marine and fresh water shales only MnO, B and Li show promise of being different. Diagenesis, cation exchange, absorption, etc., have

TABLE VI

Comparison of Marine and Fresh Water Pennsylvanian Shales

(after Keith and Degens, 1959)

	Marine (N=15)		Fresh water (N=15)	
	$\bar{x}$	S	$\bar{x}$	S
per cent				
SiO_2	54.53	3.33	57.29	3.30
TiO_2	0.92	0.05	0.94	0.10
Al_2O_3	20.89	1.54	21.24	1.43
MnO	0.80	0.05	0.12	0.07
CaO	0.54	0.49	0.31	0.16
MgO	1.65	0.29	1.73	0.15
Na_2O	0.22	0.03	0.21	0.04
K_2O	3.71	0.37	3.53	0.34
P_2O_5	0.23	0.12	0.17	0.06
Fe	6.67	3.34	5.82	2.13
S	0.92	0.68	0.15	0.13
Wt. Loss (750°C)	8.73	1.46	7.27	1.53
p.p.m.				
B	115	34	44	28
Ga	8	7	17	4
Li	159	26	92	24
F	817	182	642	121
Sr	250	52	205	52

$\bar{x}$ = mean

S = standard deviation

TABLE VII

Average composition of dissolved solids in Lake and River Waters and in Sea Water (from Rankama and Sahama, 1950)

Constituent	Lake and River Water	River Water less cyclic salts	Sea Water
	per cent		
CO_3	35.15	35.13	0.41*
SO_4	12.14	11.35	7.68
Cl	5.68	0.00	55.04
NO_3	0.90	0.90	
Ca	20.39	20.27	1.15
Mg	3.41	3.03	3.69
Na	5.79	2.63	30.62
K	2.12	2.02	1.10
Fe_2O_3, Al_2O_3	2.75	2.75	
SiO_2	11.67	11.67	
H_3BO_3, Sr, Br	-	-	0.31

* As HCO_3^-

been employed in an effort to interpret the data. The results are somewhat disheartening. The content of major and minor element distribution in shales is governed by the fact that different environments do not appear to be sufficiently distinctive in chemical factors to appreciably change the principal clay components. The cations which are absorbed on the surface of the clay minerals are only loosely held and are readily exchanged for other cations as the clay passes from one chemical environment into another.

The best diagnostic element would thus be one which, owing to its chemical behaviour, can modify the basic clay lattice in the environment in which the element is concentrated. It is also desirable that such an element would not later be removed by complicating stages of diagenesis and weathering.

Boron content in marine sediments was assumed by Landergren (1945) to be due to adsorption of the borate ion on detrital clay minerals. Arrhenius (1954), however, attributes only a minor fraction of the B to be adsorbed on the surface and less than 10% to be in ion exchange positions. The results of EDTA experiments (Table VIII) by Goldberg and Arrhenius (1958) on a S. Pacific pelagic sediment indicate that the main concentration of B remaining after treatment is incorporated in the fine, 1-3µ size, fraction and is not in the ion exchange site. The B in the fine fraction resists dissolution when boiled in 0.1 N hydrochloric acid, but is released by boiling in strong alkali. These results suggest that B is proxying for silicon in the tetrahedral sheets of the clay minerals because silica is more soluble at higher pH. Arrhenius (op. cit.) sug-

TABLE VIII

(After Goldberg and Arrhenius, 1958); Percentage loss of the total amount of individual elements at treatment with EDTA of fractions of sample Cap.33 BG. The original percentage concentrations of the elements in the sample fractions are shown in the column marked "Orig."

Oxide	Grain size fraction							
	32µ		10-32µ		3-10µ		1-3µ	
	Loss	Orig.	Loss	Orig.	Loss	Orig.	Loss	Orig.
MgO	100	0.8	45	0.9	35	2.2	30	4.6
SrO	100	0.14	100	0.11	83	0.08	57	0.08
B_2O_3	100	0.022	43	0.028	33	0.021	6	0.080
CuO	66	0.068	58	0.077	20	0.120	19	0.310
V_2O_5	50	0.026	25	0.015	15	0.020	7	0.054
					Amorphous ferric iron-silicates, and clay minerals			
Most frequent minerals	Apatite Phillipsite (MnO_2)		Phillipsite Apatite (MnO_2)		Phillipsite Apatite (MnO_2)		Phillipsite (MnO_2)	

gests that at least a portion of these clays appear to have formed by precipitation from an ionic solution of B, Si, and Al in sea water.

Harder (1961) treated clays low in B with solutions containing H_3BO_3, H_3BO_3 and NH_4OH, $Na_2B_4O_7$ and HCl, and $Na_2B_4O_7$ and HCl, and $Na_2B_4O_7$. The results (Table IX) indicate that clays can take B from such solutions. The quantities of B incorporated depend on the duration of treatment, temperature, concentration of B, pH of the solution and mineralogical composition of the clays.

Frederickson and Reynolds (1959, 1962 patent no. 3,022,140) have outlined a method for treating shales for paleosalinity studies. Their method is:

1. to separate the 2 micron size particles from a shale by sedimentation and centrifugation.
2. to chemically treat the clay solids and remove all the clay minerals, except illite, by boiling for 4 hrs. in 6N NaOH, subsequent boiling for 1 hr. in HCl and washing the residue in distilled water to remove all soluble products of the chemical treatment.

This treatment slowly dissolves kaolinite, chlorite, montmorillonite mixed-layer illite-montmorillonite and other clay minerals in minor amounts. Frederickson and Reynolds claim that although illite is attacked by the alkali solution the residue remaining is dominantly illite. Table X shows the amount of B before treatment and after treatment. Their conclusions are a) that B is not removed from the illite by this process, b) that once the B has been incorporated into the illite structure it stays there in substantially the same quantity regardless of processes normally occurring in sedimentary rocks.

TABLE IX

Data compiled from Harder (1960) showing uptake of B from solutions by different clay minerals

Clay Mineral	Treatment	g B/t
Montmorillonite	$H_3BO_3 + Na_2B_4O_7$ (10 g/$\ell \cdot H_2O$)	6.0 original
Polkville, Miss., U.S.A.	pH = 7, 30 days	9.3 after treatment
		3.3 increase
Kaolinite	$H_3BO_3 + Na_2B_4O_7$ (10 g/$\ell \cdot H_2O$)	10.5 original
Westerwald, Germany	pH = 7, 30 days	15.0 after treatment
		4.5 increase
Muscovite	$H_3BO_3 + NH_4OH$ (10 g/$\ell \cdot H_2O$)	21.0 original
Tjurkil, Sweden	pH = 7.15, 30 days	65.0 after treatment
	T = 18 C	44.0 increase

Walker and Price (1963), Walker (1962, 1963, and 1964) have concluded that the 0.5μ shale fraction, supplemented by X-ray analyses for illite identification, produces the best results for B as a paleosalinity indicator. Their curves (the method will be amplified later) relate K_2O and B in the 0.5μ fraction to known salinity environments.

There is an obvious contradiction between Goldberg and Arrhenius (op. cit.) and Frederickson and Reynolds (op. cit.) as to whether or not strong alkali solutions will dissolve B in clays. Part of the discrepancy probably lies in the duration of treatment used in each of the two cases. Apart from this discrepancy there is the B-illite-Fe problem. It was clearly shown in the method (Fig. 1, 2, 4 and 5) of this research that the B line 2497.73 used by most of the previous investigators is subject to an iron interference. It is the contention of the author that some of the data (Table X) reflects the iron content in the illite and not the B content. Removal of other clay minerals and increasing the content of illite would increase the amount of Fe_2O_3 giving rise to an erroneous increase in B.

The assumption made in paleosalinity studies is that all or most of the B is incorporated into the structure of illite. The only feasible place of incorporation is at the edge of the clay particles, B substituting for silicon. Why this incorporation should take place only in illite is unexplained. The similarities between the clay lattice structure of illite, montmorillonite and chlorite suggests that incorporation should be similar in all three. In any event, the rigorous alkali treat-

TABLE X

(After Frederickson and Reynolds, 1959)

Boron and Illite Content of Some Shales Before and After Chemical Treatment

	Before Treatment		After Treatment	
Sample[1]	% Illite	ppm. B	% Illite	ppm. B
Shale 1	50	193	73	217
Shale 2	62	70	81	88
Shale 3	64	160	70	192
Shale 4	64	153	62	154
Shale 5	47	90	53	150

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[1] All samples are Cretaceous shales from New Mexico

ment, 6N NaOH, should remove the B incorporated at the edge of the clays. These inconsistencies coupled with the B-Fe interference leads the author to be skeptical concerning the validity of previous B research.

REVIEW AND AMPLIFICATION OF VARIABLES CONCERNING BORON

Although some of the B research may be erroneous various aspects will be developed for comparative purposes. For clarity and heuristic development the author proposes a model to relate the measured B concentration and the relevant variables.

$$B\ (\text{conc.}) = f\ (x_1 \ldots\ldots x_6)$$

where x_1 = distribution of illite

x_2 = degree of salinity in depositional environment

x_3 = B in parent material from which the detrital clay particles were derived

x_4 = grain size

x_5 = biological effect

x_6 = location of B within the shale.

Boron as a function of illite distribution

If B concentration is a function of the clay mineral illite, as claimed by previous workers, then the distribution of B should be governed by illite content. Generally the clay minerals kaolinite, chlorite, illite and montmorillonite are found in Archean (Frederickson, in press) to recent (Griffin, 1962) shales. The pre-Middle Mississippian clay suites are usually less complex and tend to be nearly monomineralic with illite constituting the major clay mineral.

> "Montmorillonite is relatively less abundant in the older Paleozoic than in Tertiary sediments but this may be due to differences in weathering conditions rather than time diagenesis. The older Paleozoic basin sediments are largely carbonate rocks and the Tertiary clastic rocks. This suggests a general difference in the determining background. As illite is by far the dominant clay mineral in the older Paleozoic carbonates, it is apparent that the weathering and diagenetic conditions prevalent at the time (chemical deposition) favoured the formation and preservation of illite. Where as conditions during Tertiary time (clastic deposition) favoured the formation of montmorillonite from volcanic material, it is likely that conditions during the older Paleozoic favoured the development of a more illite like clay from volcanic material. Examination indicates that most of the altered Cambrian and Ordovician volcanic material is in the form of a mixed layer illite-montmorillonite"(Weaver, 1958).

The black shales (Exshaw, Banff, and Fernie), rich in organic matter and pyrite, are abundant in illite and mixed layer illite-montmorillonite and seldom contain kaolinite (Weaver, 1958).

If the B content is solely dependent on illite content then the expected B content should be higher in pre-Mississippian shales relative to shales containing montmorillonite. It will be shown later that this is not the case.

Boron as a function of salinity

Landergren (1945) studied B in two profiles of Swedish Pleistocene sediments. The depositional environment of the sediments, classified by diatoms, was sea water, brackish water, and fresh water. He showed:

1) that B content and grain size vary antipathetically in the profile of sediments of various types accumulated under conditions of constant salinity.

2) that B content varies regularly with salinity in a profile of "relatively uniform composition".

Salinity and related B were calculated by Landergren from the mean value of B in the top fifty cm. of a sediment profile in contact with water having a salinity of 35 p.p.t. (parts per thousand). The mean B value calculated from ten analyses was 0.015%. The co-ordinates (Landergren, op. cit.) of this profile are plotted (Fig. 6) and a straight line drawn through them and the origin. To check the value of this relationship the salinity of a second profile, B content 0.0025%, was interpolated and found to be 5.83 p.p.t. Independent information, that the second profile was deposited under salinity condition of 5.9 ± 0.4 p.p.t., indicated an excellent agreement in the data.

Further verification of relationship between B and salinity (see Table XI, Fig. 7) has been furnished by Frederickson and Reynolds (1959).

Other papers which present evidence of the relationship between B and salinity include Degens, Keith and Williams (1958) and Potter et al (1963). An antipathetic relationship between "adjusted" B and per cent K_2O in sedimentary illites has been furnished by Walker and Price (1963). Analyses of the 0.5 or less clay fraction from dominantly illitic shales show a strong positive correlation between B and % K_2O. The "adjusted" B is obtained as follows: a theoretical value of 8.5% K_2O (pure illite) divided by the % K_2O x observed B. The result is an antipathetic relationship between "adjusted" B and % K_2O (observed). The computation recalculates the total amount of B that would exist in 100% non-degraded illite. The justification for this recalculation is not clear but it has been sug-

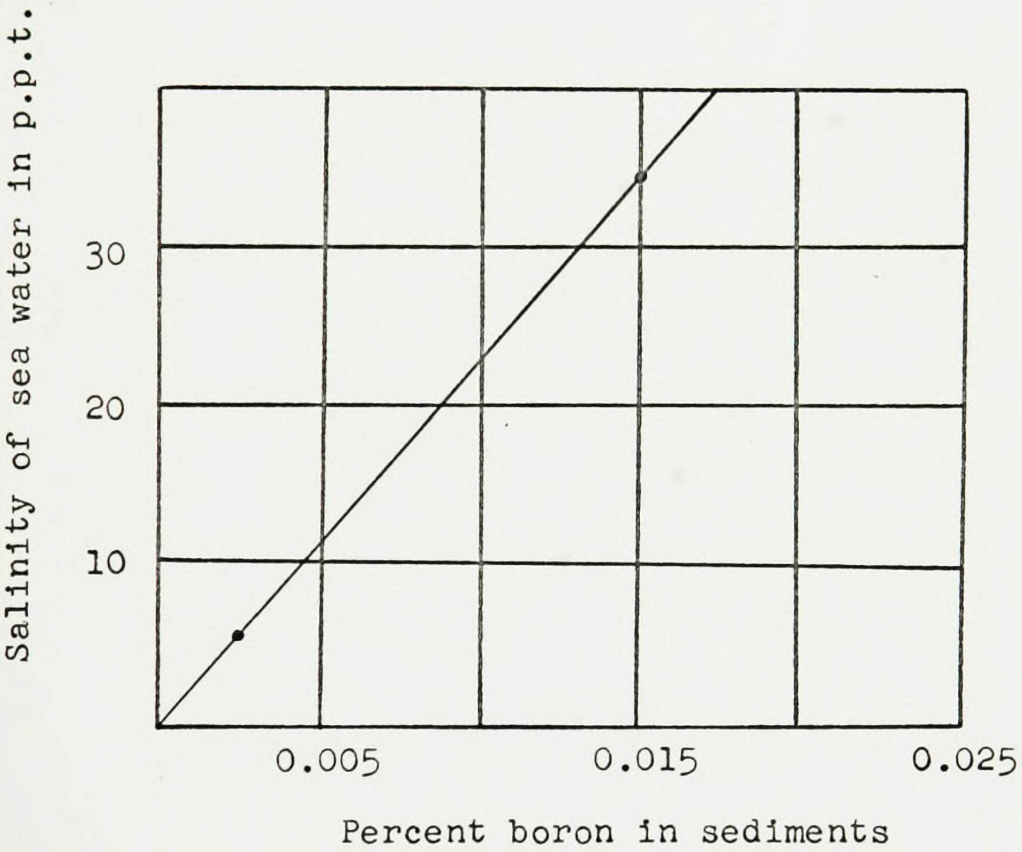

Fig. 6. The relationship between boron content of a marine clay sediment and the salinity of the water (after Landergren, 1945).

TABLE XI

(After Frederickson and Reynolds, 1959) Results of B in Gulf Coast Bottom Waters

Total Dissolved Solids (Salinity) in Parts Per Thousand (0/00)	B Content in Parts Per Million (ppm.)	Environment
46.5	6.0	Shallow bay, not over six feet deep well aerated
46.0	6.4	
46.0	6.2	
46.5	5.8	
46.5	6.2	
48.0	6.5	
6.0	1.0	Bayou, euxinic
5.0	0.86	
8.5	1.3	
7.5	1.0	
6.5	1.1	
38.5	5.0	
26.5	3.3	
29.0	3.6	
27.0	3.3	
21.0	3.0	
22.5	2.8	
50.0	6.5	Shallow bay grading to euxinic bayou
51.0	6.6	
53.0	6.2	
56.0	7.0	
55.0	7.8	
58.0	7.5	
62.0	8.1	
63.5	7.8	
67.5	8.8	
270.0 (saturated)	88.0	Tidal pool: salt bottom
2.0	0.20	Colo. River 10 mi. from Coast
22.0	2.9	Euxinic bayou
19.5	2.8	
18.5	2.7	
16.5	2.4	
11.5	1.8	
38.0	5.2	Surf zone of the open Gulf of Mexico

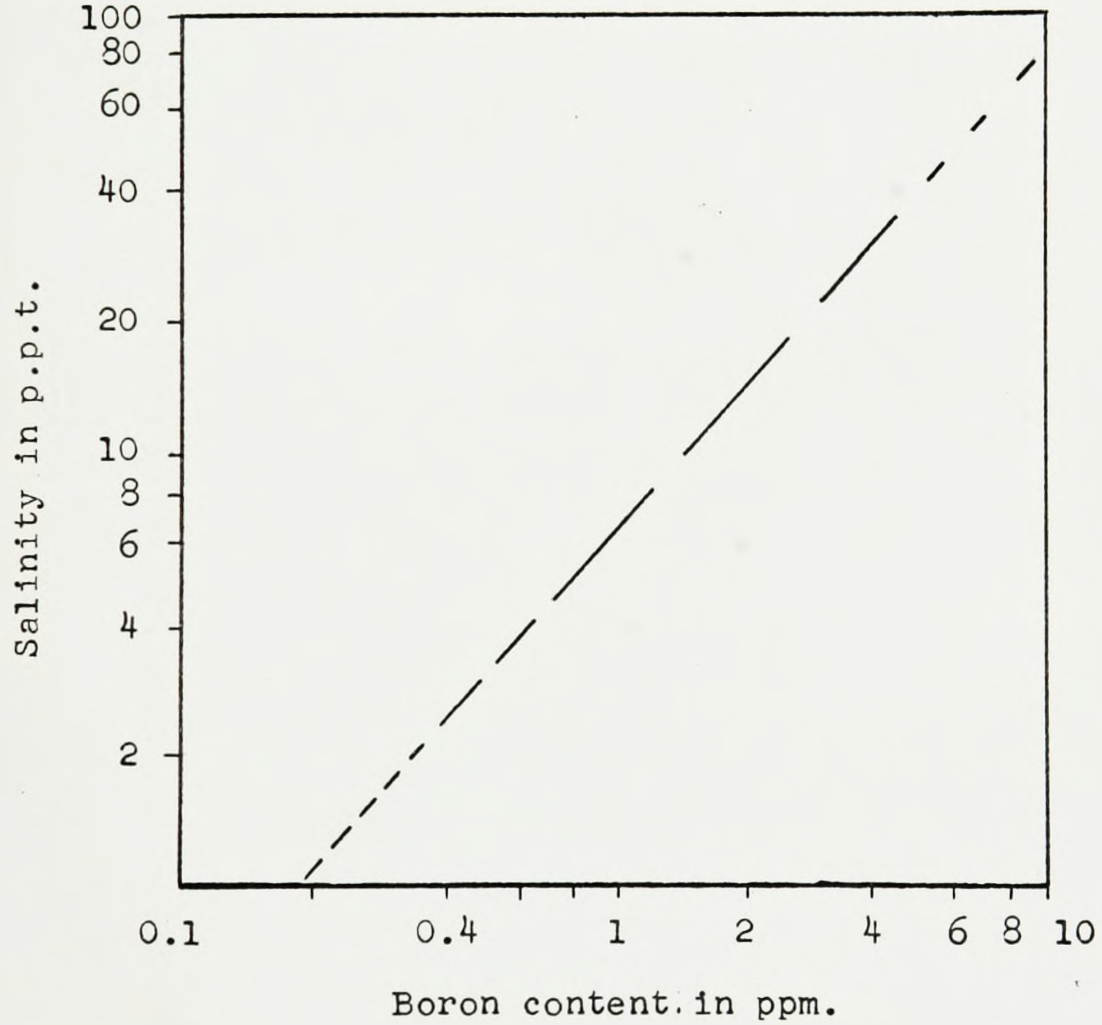

Fig. 7. The relationship between boron content and salinity of the Gulf of Mexico bottom waters (after Frederickson and Reynolds, 1959).

gested by Walker (1963) that the charge deficiency resulting from B^{+3} and Al^{+3} intering the Si^{+4} tetrahedral site would be balanced by K^{+}.

By plotting % K_2O against adjusted B from four contrasted salinity environments, a number of quadratic functions approximating straight lines have been constructed (Fig. 8). From this evidence, Walker and Price proposed that the slope and position of these lines are a true measure of paleosalinity. Subsequently, "departure curves" were constructed (Fig. 9). These "departure curves" were then used to convert "adjusted" B concentrations to "equivalent" B concentrations. These authors believe that "equivalent" B values less than 200 ppm. would indicate that the water was too fresh for normal marine faunas, but not necessarily completely fresh water. Values between 300 and 400 ppm. and between 800 and 1000 ppm. would suggest a normal marine environment and a hypersaline environment respectively.

Walker and Price conclude that whole rock analyses for K_2O and B can be applied directly on the curves to obtain paleosalinity determinations. It was, however, demonstrated earlier that the data are probably unreliable, and their conclusions partly invalid.

Boron in Parent Material

Until recently B was generally believed to accumulate in the end-products of magmatic differentiation in granites and pegmatites. Boro-silicate minerals reedmergnerite[1], $NaBSi_3O_8$, and danburite[2],

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[1] Reedmergnerite, discovered by Charles Milton of the U.S.G.S. in evaporite deposits of the Tertiary Green River fm., Green River, Wyoming.

[2] Danburite, Harder (1959, 1961a) and Stubican and Roy (1962, p. 1166).

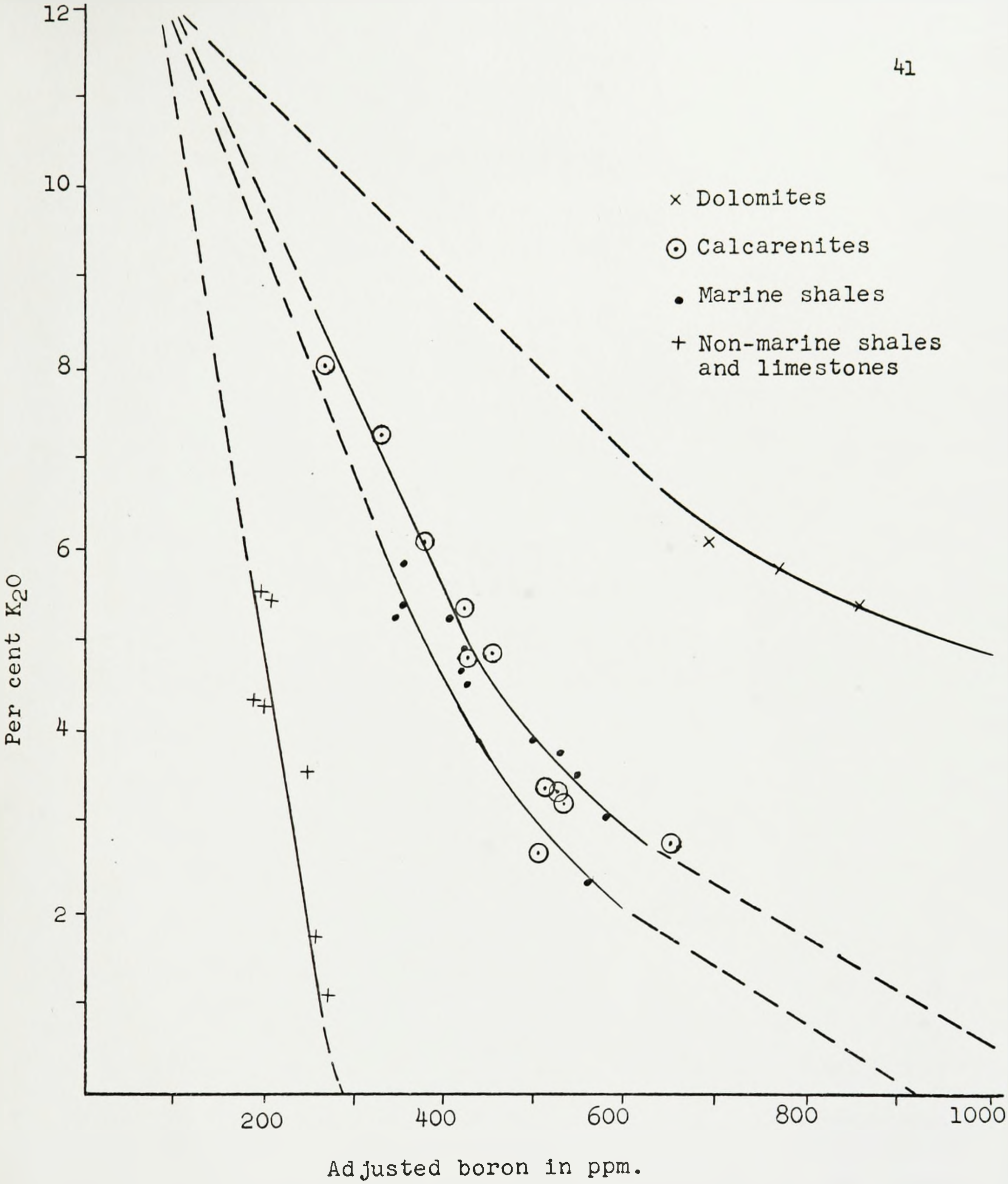

Fig. 8. After Walker and Price (1963), relationships between adjusted boron and per cent K_2O for four different salinity environments.

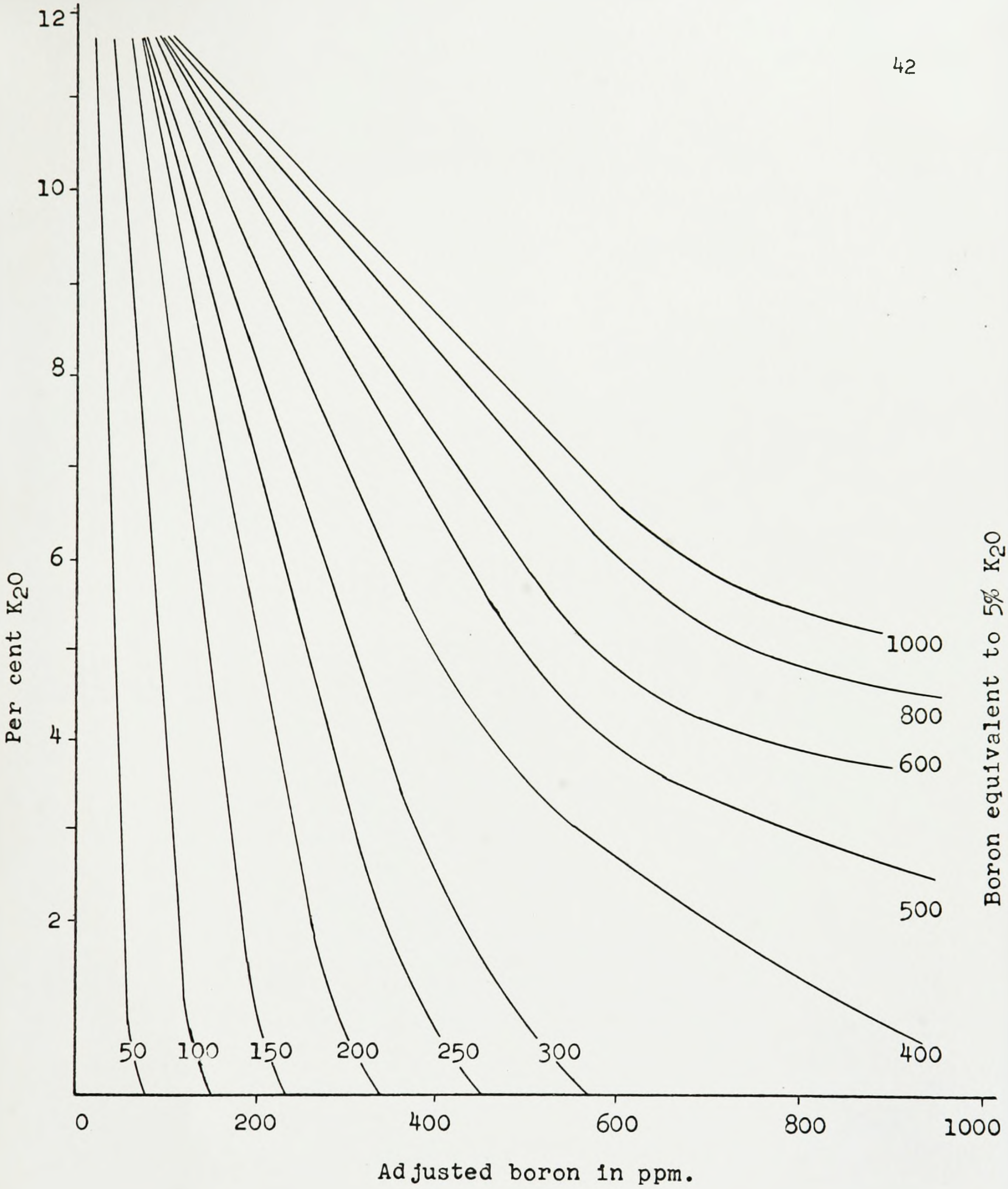

Fig. 9. After Walker and Price (1963), departure curves for computing equivalent boron.

$CaB_2Si_2O_8$, analogues of albite and anorthite respectively have been recognized. Other investigators, Getling and Savinova (1958), claim that some of the B is concentrated in ultramafic, mafic, and intermediate rock types. Fig. 10 represents a compilation (after Getling and Savinova, op. cit.) of available analyses from the literature of these rock types. Some of the rocks containing high iron content may not be reliable from iron interference on the B line, but the granite and intermediate rock analyses probably are reliable because of low iron content.

Assuming that the B measured in granites is contained in the feldspars, that the mineral tourmaline is absent and that the feldspars weather to clay minerals, a quantitative calculation of expected B content in clay minerals can be determined. The factors conducive to the formation of clay minerals are summarized in Table XII. Chemical equations may be written to describe reactions of the feldspars with water to produce clay minerals (Keller, 1956). Microcline and water may be calculated to give rise to kaolinite, or muscovite (high K-sericite), respectively as follows:

1) $2KAlSi_3O_8 + 3HOH \quad H_4Al_2Si_2O_9 + 2KOH + 4SiO_2$

2) $3KAlSi_3O_8 + 2HOH \quad KAl_2(OH)_2Si_3AlO_{10} + 2KOH + 6SiO_2$

In a similar way, microcline and oligoclase ($Ab_{80}An_{20}$) may be balanced to place all the potassium in muscovite (sericite).

3) $3KAlSi_3O_8 + 4NaAlSi_3O_8 + CaAl_2Si_2O_8 + 6HOH$

$3KAl_2(OH)_2Si_3Al_{10} + 12SiO_2 + 4NaOH + Ca(OH)_2$

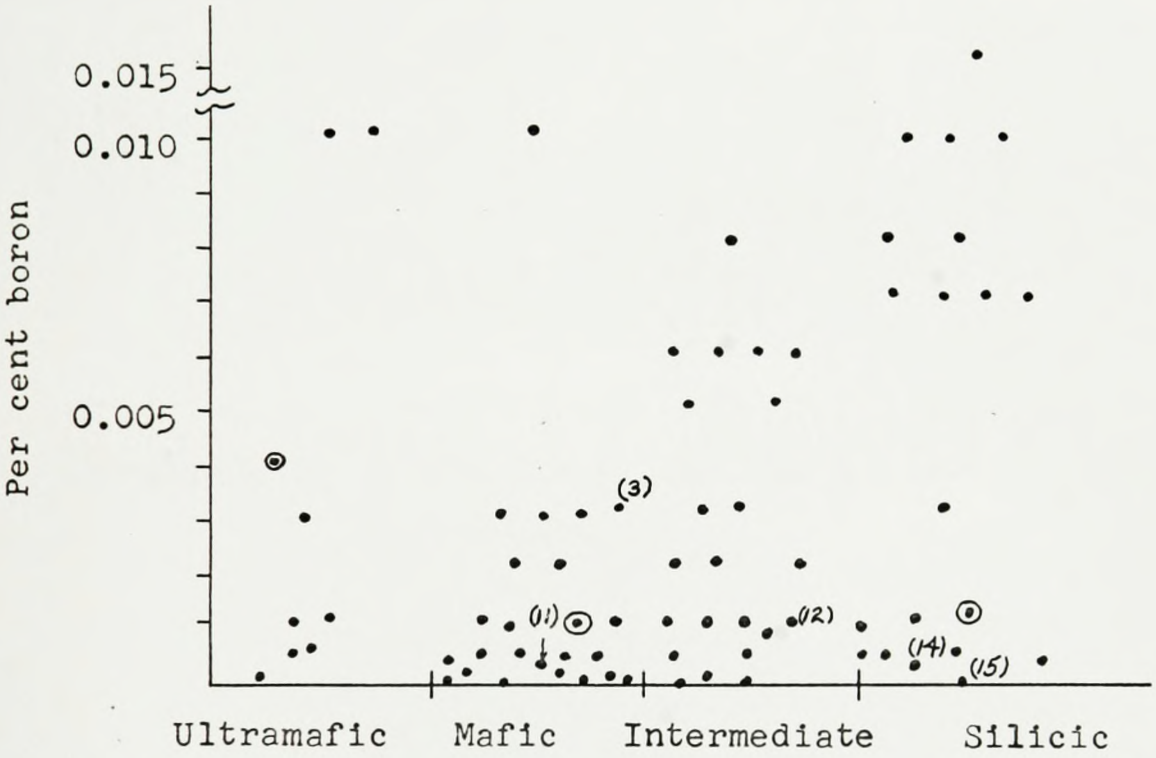

Fig. 10. Boron content of igneous rocks of different compositions, after Getling and Savinova (1958, p. 476), figures in parenthese show the number of analyses, ⦿ - averages.

TABLE XII

After Keller, 1956

Kaolin Group

Excess of H^+ and removal of Ca, Mg, Fe, Na, K.

a) Precipitation exceeds evaporation (as in humid climate of southeastern U.S.
b) Intense leaching. Not stagnant water. Permeable rocks.
c) Oxidation of Fe to Fe_2O_3 or to FeS_2 (removal of Fe from system).

High Al:Si ratio. Removal of silica.

d) Silica stabilized in solution by Na^+, K (granite and other Na, K rocks).

Montmorillonite Group

Retention of Mg, Ca, Fe. No excess H^+.

a) Evaporation exceeds precipitation (semi-aridity, soils of western U.S.).
b) Stagnant water
    Poor leaching
    Standing water (ash, tuff inlakes and oceans).
c) Alkaline conditions.
d) Fe remaining in system.
e) Silicates highly susceptible to alteration, like ash.

High Si:Al ratio. Retention of silica.

a) Flocculated by Ca^{++}, Mg^{++}.
b) Inefficient leaching.

Illite Group

Retention of M ions, especially K and Ca.

No excess H^+.

a) Moderate rain. Wetting and drying.
b) $CaCO_3$ present.
c) Marine conditions.

High Si:Al ratio

N plus 1 cycle sedimentary illite is abundant.

The significance of this is that silica appears as an end product. The lost wt. % in 1, 2, 3 is 46%, 48% and 53% respectively as clay minerals are produced from the feldspars. Granites contain approximately 55 to 80% feldspar, therefore the weight lost on weathering would be 28 to 40%. The quartz in granite varies from 20 to 45 wt. % and shale contains about 20% quartz. Therefore, total weight loss in granite weathering to shale is possibly 50%.

If this approach is correct, granites containing 10 ppm. B would generate approximately 20 ppm. in the shale end-product. Similarly, a granite containing 50 ppm. would give rise to 100 ppm. B in clays. This variation in B could be solely attributed to provenance.

The measurement of B content in fresh water shales probably reflects variation resulting from provenance because little or no B is available for incorporation in fresh water environments. Values reported by Potter et al. (1963) are 11 to 99 ppm. B and 8 to 83 ppm. B for modern fresh water and ancient fresh water argillaceous sediments respectively.

Boron Content as a Function of Grain Size

Studies by Landergren (1958), Walker (1963) reveal an antipathetic relationship between grain size and B content in clay sediments. Therefore in shales, apart from occurrences of tourmaline, it is assumed that quartz fraction, both detrital and finely divided authigenic silica, contains little or no B. This suggests that B incorporation into clay particles is proportional to the reacting surface available. However, two aspects of this relationship are generally overlooked, 1) actual clay mineral grain size, 2) distribution of specific clay minerals. Quantitative determination of the clay mineral suite entering the Upper Mississippi

Embayment (Pryor and Glass, 1961) indicate an environmental distribution of the clay minerals. Table XIII shows the clay mineral content in fluviatile (dominantly kaolinite), inner neritic (mixtures of the three clays), and outer neritic (dominantly montmorillonite) environments. The segregation is a function of a) differential settling of the clay particles owing to differences in particle size, b) differences in flocculation rate, c) differences in floccule size.

The grain sizes of the clay minerals are kaolinite 2µ to 4µ, illite 0.1µ to 0.3µ and montmorillonite in smaller particles. Montmorillonite therefore would be expected to be found in the outer neritic environment, and because of its size should incorporate more B. From previous research this is apparently not the case. It is inconceivable that one mechanism which apparently incorporates B into illite would not affect structurally similar minerals such as chlorite and montmorillonite clearly, until some mechanical method is developed by which separation of clay minerals becomes feasible, conclusions pertaining to the genetic relationship of B and clay minerals will be misleading. In many cases X-ray identification of clay minerals is helpful but the errors may approach 20% (Griffin, 1962); this may obscure the true picture.

B as a Function of Biological Variation

Conflicting evidence pertaining to correlations between B and salinity in shells has been reported. Rucker and Valentine (1961) found no correlation between B and salinity on 71 recent Grassostrea virginica shells. Neither growth, rate, age, nor intraspecific racial differences

TABLE XIII

Average clay mineral composition of clays from the three environments (after Pryor and Glass, 1961)

Environment	No. of Samples	Clay Minerals (parts in ten) Kaolinite	 Illite	 Montmorillonite
Fluviatile	112	6.9	1.9	1.2
Inner Neritic	19	3.1	3.1	3.8
Outer Neritic	68	0.9	1.3	7.8

of the oysters appeared to affect B content. On the other hand, Leutwein and Waskowiak (1962) have reported a positive correlation between B and salinity from recent marine mollusks. Further study may resolve the question as to whether marine fauna can remove B from sea water.

An important aspect concerning availability and nature of B concentration in Gulf of Mexico waters has been carried out by Noakes and Hood (1961). Inorganic and organic forms of B have been identified. The organic B complex studied by Gast et al. (1958) is believed to consist of B linked through hydroxyl groups to soluble organic compounds. Inorganic B is probably in the form of H_3BO_3 or other borate ions.

Several conclusions resulting from this research are 1) positive correlation between inorganic B and chlorinity, 2) organic or complex B increases with increases in dissolved oxygen. The low content of organic B (Fig. 11) in the oxygen deficient zone, postulated by Richards (1957), is a result of high aerobic action consuming O_2 and thereby causing an O_2 minimum layer and an increase of inorganic B. If this is the case sediments deposited in a reducing environment may have more available inorganic B to be adsorbed to clay particles. An underlying assumption is that B in organic complexes would not tend to be incorporated into the clay minerals.

Location of Boron in Shales

Research carried out by Frederickson and Reynolds (1959) and Goldberg and Arrhenius (1958) has shown that B can not be removed from the 2μ clay size sediment by applying acids or organic (EDTA) reagents. This indicates that the B is in a lattice position. Stubican and Roy (1962), have

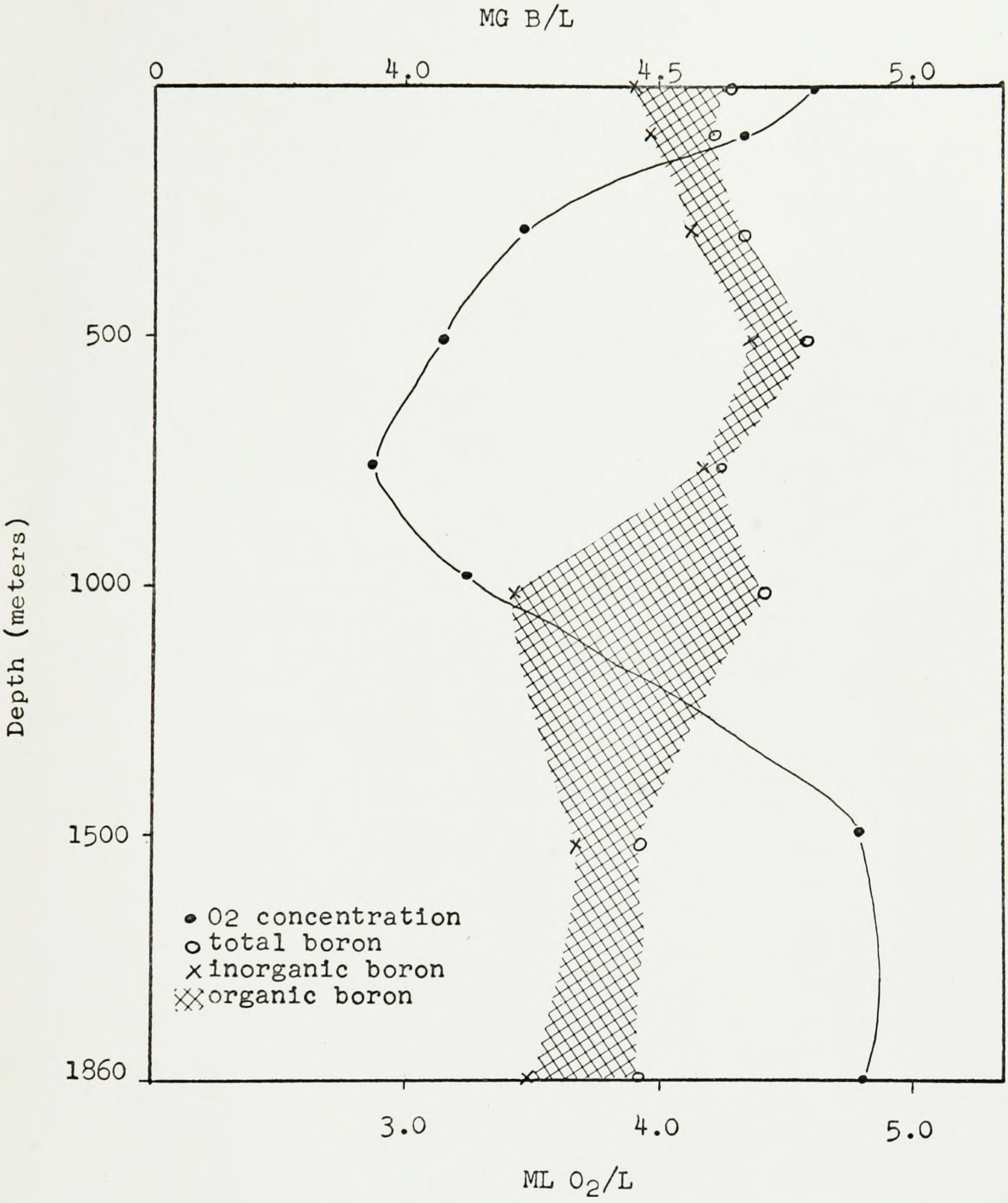

Fig. 11. Distribution of boron (organic and inorganic) with depth (after Noakes and Hood, 1961).

confirmed the presence of B in the tetrahedral layer in synthetic saponites by infrared spectroscopy.

In general there are two physio-chemical aspects that have generally been overlooked. The first is the diagonal properties of the elements and the second the limited electronic configuration of B.

The diagonal properties of the elements are expressed by electronegativity values (Table XIV) which increase from left to right on the periodic table and decrease from top to bottom. The resultant similarity in diagonal electronegativity values gives rise to similar properties for elements rather than the anticipated similar vertical properties. Thus B and Si diadochy would be expected.

The electronic configuration of B^{+3} is $2(1s^2)$ electrons, this allows coordination bonding to take place in 4 locations, $2s^2$ and $2p^6$, therefore the resulting structure should be a tetrahedron BO_4 or BO_3 planar triangular but not octahedral (lack of 3-d orbitals).

TABLE XIV

All values taken from Green (1959), and are expressed in kilocalories/gram-atom

Li	Be	B	C	N	O	F
125	210	290	370	450	530	605
Na	Mg	Al	Si	P	S	Cl
118	174	220	270	320	385	460

GENERAL DESCRIPTION OF THE SHALES STUDIED

In the previous review the author has attempted to evaluate some of the inherent problems confronting boron studies. At present it is difficult to quantitatively assess the effect of these variables. However, it is possible to quantitatively compare the B content in argillaceous rocks with other depositional criteria and evaluate the use of B as an indicator of depositional environment (i.e. paleosalinity).

Nine shale sequences (Appendix 1), ranging in age from the Proterozoic (Miette Group) to the Upper Cretaceous (Kaskapau or Blackstone Fm.) were studied. Seven sequences were sampled from the Rocky Mts., Table XV, and two additional sequences were incorporated from the Silurian (S. Ont. and N. New York State) and Littleton Fms.

Precambrian (Miette Group)

The Proterozoic (Miette Group) rocks located near Jasper consist of shale and phyllite, sandstone, conglomerate, and carbonates with a few poorly preserved algal (?) markings. Lack of fossils within this group restrict any attempt to classify these rocks into marine and non-marine depositional environments. In addition, the post depositional metamorphism may invalidate any attempt to accurately classify the sedimentary environment based on B determinations.

Ordovician and/or Cambrian

These shales and carbonates are generally referred to as sub-Devonian and lie unconformably beneath the well-defined Devonian lithology. Three mappable units consist of Lower Ordovician (Chushina Fm.) limestone and calcareous shale, the Upper Cambrian (Lynx Fm.) carbonates and the Upper and/or Middle Cambrian (Arctomys Fm.) green and red shales. The samples were obtained from both the Chushina and Arctomys Fm.

Brachiopod and trilobite fragments including Bellefontia cf. nonius (Walcott) have been described by McLaren (1955) in the Medicine Lake section which is approximately 30 miles northwest of section B. Based on the association of limestone and the occurrence of trilobites it was concluded that the shales are of marine origin.

Silurian (mainly Thorold and Grimsby Fms.)

Two sections of Silurian lithology were measured in 1963 by I.P. Martini (McMaster University). Nine samples were collected from a section at De Cew Falls, South Ontario and 8 samples from a similar lithologic section at Lockport (N. New York State).

These shales are red, grey, in part slightly calcareous, and of uncertain depositional environment.

Devonian (Littleton Fm.)

Samples of the Littleton Fm. were acquired from Shaw (1954) from the Appalachian region of New Hampshire. The Littleton Fm. has been traced from fossiliferous shales near the Connecticut River to sillimanite gneisses in the White Mountains and is generally thought to have

TABLE XV

Table of Formations (compiled after Mountjoy, 1962)

ERA	PERIOD OR EPOCH	GROUP OR FORMATION (map-unit)		LITHOLOGY	THICKNESS (feet)
MESOZOIC	Upper Cretaceous	Brazeau Formation		Sandstone, arkosic, conglomeratic sandstone	500+
		Smoky Group	Wapiabi Fm.	Shale, black, with thin siltstone beds	1,600±
			Cardium Fm.	Sandstone, fine-grained, quartzose	300
			Kaskapau Fm.	Shale, black, concretionary	1,700±
	Upper and Lower Cretaceous	Dunvegan and Shaftesbury Fms.		Sandstone, coarse-grained, crossbedded; shale, dark grey, silty	600
		Disconformity			
	Lower Cretaceous	Luscar Formation		Sandstone, fine-grained, greenish grey; siltstone, shale, coal	2,000±
		Cadomin Formation		Conglomerate, chert and quartzite	10 to 30
		Disconformity ?			
	Lower Cretaceous and Jurassic	Nikanassin Fm.		Sandstone, siltstone, silty mudstone, dark grey	1,000 to 2,000
	Jurassic	Fernie Group		Shale, black and dark grey, concretionary; all members present	700 to 900
		Disconformity			
	Triassic	Whitehorse Fm.		Carbonate, light grey, silty; breccias, red mudstone, gypsum	100 to 1,500
		Sulphur Mountain Fm.		Siltstone, dark brownish grey, thin-bedded, silty mudstone	600 to 1,000
		Disconformity			
	Permian and/or Pennsylvanian	Rocky Mountain Fm.		Chert, grey, massive; sandstone, cherty, brown	0 to 220
		Disconformity			
	Mississippian	Rundle Group	Formation D	Dolomite, cherty, dense, medium-bedded	250 to 400
			Formation C	Dolomite, brown, coarse-grained, porous	150 to 400
			Formation B	Limestone, dark grey, fine-grained, thin-bedded	200 to 360
			Formation A	Limestone, crinoidal, light grey, coarse-grained, thick-bedded	115 to 300
		Banff Formation		Limestone and calcareous shale, dark brown, thin-bedded	500 to 760
		Disconformity			
		Palliser Formation		Limestone, dolomitic, dark grey, fine-crystalline, massive	700 to 900
		Sassenach Fm.		Sandstone, calcareous, fine-grained, siltstone; silty shale, silty carbonates	0 to 600

been deposited under conditions of a normal marine environment. Samples L-1 to L-10 are shales, argillite and slate whereas L-11 to L-70 consist of slate, schist and gneisses.

Devonian (Mount Hawk and Perdrix Fms.)

The Devonian lithology of the Rocky Mountains near Jasper consists of a carbonate reef (Cairn and Southest Fms.) and off-reef shale (Mount Hawk and Perdrix Fms.) sequences.

The Perdrix Fm. shales, in transitional areas, are commonly overlain by the Mount Hawk Fm. limestones and shales. Nudirostra athabascensis (kindle) and N. insculpta McLaren occur in the lower beds of the Perdrix, whereas the Mount Hawk is highly fossiliferous and contains abundant corals and brachiopods (McLaren, 1955). The associated carbonates in addition to the fossil fauna present strongly suggest a marine sedimentation environment.

Mississippian (Banff)

The Banff (Exshaw and Banff) consists of black commonly calcareous and fossiliferous shales. The Exshaw, black fissile shale, underlies the black and grey calcareous shales of the Banff and varies in thickness from 0 feet to 20 feet. The presence of rugose corals, brachiopods, blastoids, and crinoids within the Banff indicates a marine depositional environment.

Triassic (Whitehorse)

The Triassic is subdivided into the Whitehorse Fm. (carbonates) and the Sulphur Mountain Fm. (clastic sandstone and siltstone). The Whitehorse contains in part an evaporitic facies of gypsum and anhydrite.

The shales are not typical but comprise an argillaceous fraction in the carbonate lithology. The argillaceous carbonates weather red, green, yellow and buff. Wherever the argillaceous component exceeds the carbonate content there is a pronounced lack of bedding giving rise to mudstones.

The Whitehorse lithology probably represents a highly evaporitic facies and thus a higher salinity depositional environment would be expected rather than a normal marine environment.

Jurassic (Fernie Group)

Essentially the Fernie Group comprises six divisible units, Upper Fernie shales, Green Beds (shale), Grey Beds (shale), Rock Cr. member (clastics), Toarcian shales, and Nordegg (carbonates). The shales are abundant in marine fauna, pelecypods and ammonites (Frebold, 1957) which strongly suggest a marine depositional environment.

Cretaceous (Kaskapau or Blackstone Fms.)

The Blackstone Fm. varies in thickness (1,700 ft. ±) and is divided into four zones, Transition, Rusty Shale, *Inoceramus labiatus*, and the Barren zone.

The samples in this study were collected from the Barren zone and the underlying Dunvegan (Mountain Park) Fm. both void of fossils. However, the Upper Cretaceous Fms. overlying the Blackstone are represented by non-marine Molluscan faunas (Tozer, 1956) which could suggest a similar non-marine environment for the Blackstone shale deposition.

DISTRIBUTION OF BORON IN SHALES

The results of B determinations on shales are listed in Table XVI. Average values, grand mean, standard deviation, and the variance both for arithmetic and logarithmic data are given. In all there are 174 samples, comprising 17 Silurian, 17 Triassic, 40 Devonian, and 20 samples in each of the Precambrian, Ordovician, Mississippian, Jurassic and Cretaceous.

This study does not provide a basis for empirically identifying the distribution function of B because the samples do not come from restricted geological environments. However, the data are sufficiently numerous to suggest that B distribution is skewed toward the smaller concentrations (Fig. 12).

The a priori boron model suggested by previous works is that boron is incorporated into the clay mineral illite and the incorporation is a function of the salinity and grain size. If this model is correct then it is conceivable that there are limited available sites for boron incorporation and as boron is absorbed the number of sites diminish resulting in a log. normal distribution for incorporated boron content. Similarly, a generally limited supply of boron in normal sea water with infrequent greater boron reserves in hypersaline waters would tend to produce a log. normal distribution of boron in shales. The causal relationship demonstrated by a log. normal distribution therefore can not be resolved.

TABLE XVI

Uncorrected B (ppm.) Data (oldest sample at the bottom)

Precambrian Sample No.	B	Ordovician Sample No.	B	Silurian Sample No.	B	Devonian (Western) Sample No.	B	Devonian (Littleton) Sample No.	B
I- 1	47	B- 5	10	A-100	403	28-4$_1$	101	L- 1	29
I- 2	89	B- 6	14	W-100	273	28-4^1	35	L- 2	55
I- 3	38	B- 7	26	W-101	141	28-3	125	L- 3	90
I- 4	17	B- 8	21	A-101	343	28-2	56	L- 8	63
I- 5	43	B- 9	55	A-102	328	28-1	72	L- 9	43
I- 6	46	B-10	33	A-103	335	46-1	115	L-10	71
I- 7	34	B-11	6	W-102	145	46-2	25	L-11	55
I- 8	41	B-12	83	W-103	278	46-3	83	L-12	50
I- 9	46	B-13	53	A-104	235	46-4	77	L-13	42
I-10	39	B-14	25	W-104	272	46-5	133	L-14	27
I-11	42	B-15	72	W-105	325	46-6	65	L-28	66
I-12	43	B-16	65	A-105	352	46-7	60	L-61	36
I-13	42	B-17	64	A-106	360	46-8	76	L-62	53
I-14	43	B-18	125	K-106	393	46-9	60	L-63	55
I-15	45	B-18$_A$	48	K-107	333	46-10	72	L-64	59
I-16	39	B-19	37	A-107	272	27-3	101	L-65	25
I-17	41	B-20	252	A-108	178	27-2	229	L-66	45
I-18	44	B-21	98			27-1	114	L-67	50
I-19	43	B-22	104			30-34	39	L-69	66
I-20	41	B-23	140			30-33	44	L-70	45
$\bar{k}$ = Grand mean (90 ppm.)									
$\bar{x}$ = (mean)	43.2		66.6		292.1		84.1		51.3
s = (standard deviation)	12.5		58.0		79.5		45.8		15.9
s^2 = variance	156.98		3349.21		6329.1		2092.2		253.31
s_1^2 = (variance log transformation)	0.015		0.164		0.0195		0.051		0.020

TABLE XVI (continued)

Uncorrected B (ppm.) Data (oldest sample at the bottom)

Mississippian		Triassic		Jurassic		Cretaceous	
Sample No.	B	Sample No.	B	Sample No.	B	Sample No.	B
C-18	144	D-17	40	M-18	107	H-20	48
C-17	110	D-16	35	M-17	174	H-19	44
C-16	107	D-15	11	M-16	119	H-18	90
C-15	114	D-14	25	M-15	153	H-17	60
C-14	72	D-13	1	M-14	84	H-16	78
C-13	94	D-12	16	M-20	105	H-15	79
C-12	114	D-11	1	M-25	87	H-14	54
C-11	45	D-10	18	M-27	114	H-13	69
C-10	88	D- 9	19	M-11	110	H-12	70
C- 9	108	D- 8	12	M-28	174	H-11	66
C- 8	139	D- 7	11	M-10	75	H-10	72
C- 7	151	D- 6	40	M- 9	110	H- 9	77
C- 6	56	D- 5	7	M- 8	148	H- 8	51
C- 5	62	D- 4	49	M- 7	171	H- 7	37
C- 4	60	D- 3	37	M- 6	79	H- 6	41
C- 3	74	D- 2	36	M- 5	159	H- 5	67
C- 2	66	D- 1	51	M-29	221	H- 4	77
C- 1	58			M-30	20	H- 3	37
RA-2	42			M- 4	67	H- 2	37
RA-1	50			M- 3	178	H- 1	48

$\bar{k}$ = Grand mean (90 ppm.)

	Mississippian	Triassic	Jurassic	Cretaceous
$\bar{x}$ = (mean)	87.7	24.1	122.7	60.1
s = (standard deviation)	34.0	16.3	48.6	16.5
s^2 = (variance)	1161.38	265.9	2356.05	272.06
s_1^2 = (variance log transformation)	0.030	0.27	0.052	0.016

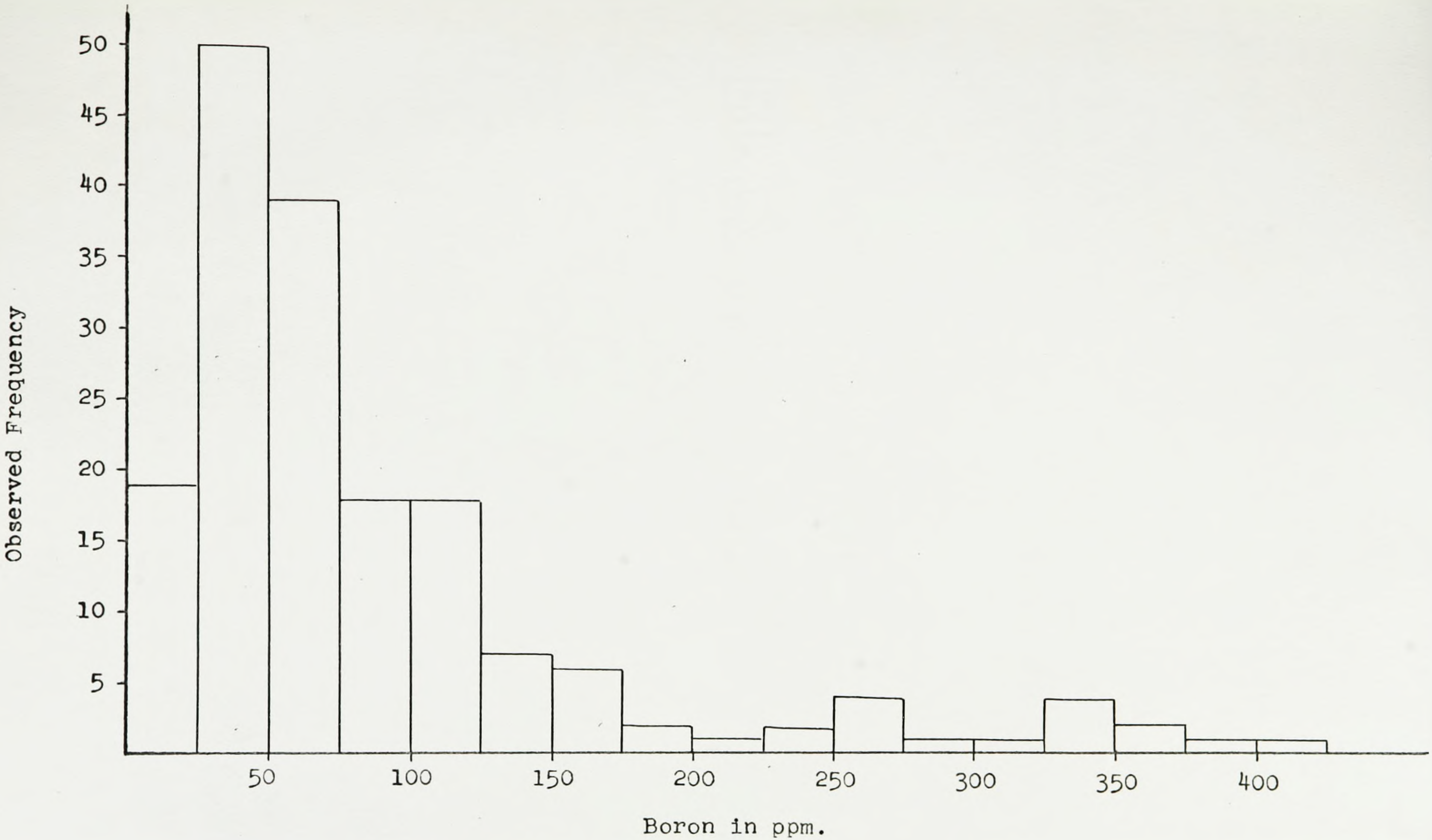

Fig. 12. Histogram illustrating the skewed nature of boron in shales.

RELATIONSHIP BETWEEN B AND CO_2

Four sections, Ordovician, Devonian, Mississippian and the Triassic are calcareous. The Triassic, in part, has a high CO_2 content and samples D-7 to D-15 inclusive are actually argillaceous dolomites and/or limestones.

CO_2 content was determined for 74 samples (17 for each calcareous section) and 6 (2 from each section) additional determinations were obtained from sections I, M, and H. The correlation coefficient (arithmetic data) between CO_2 and B is -0.281, where r_{ij} is significant at the 95% level if the value falls outside the range of +0.194 to -0.194 (N=74). The correlation coefficient for logarithmic data is -0.156 which is not significant at the 95% level.

Fig. 13 shows a plot of % CO_2 and B content. Although there is a low negative correlation using all the data, within each section there is a definite negative correlation between CO_2 and B. However, the individual negative correlations within each period are not the same. The expected correlation if no B was allocated to the carbonates would be a single line. The differences between CO_2 content in calcite and dolomite are insufficient to produce such an aberrant variation. What this correlation does imply is that other variables within the system are superimposed on the carbonate and B content and are affecting the results.

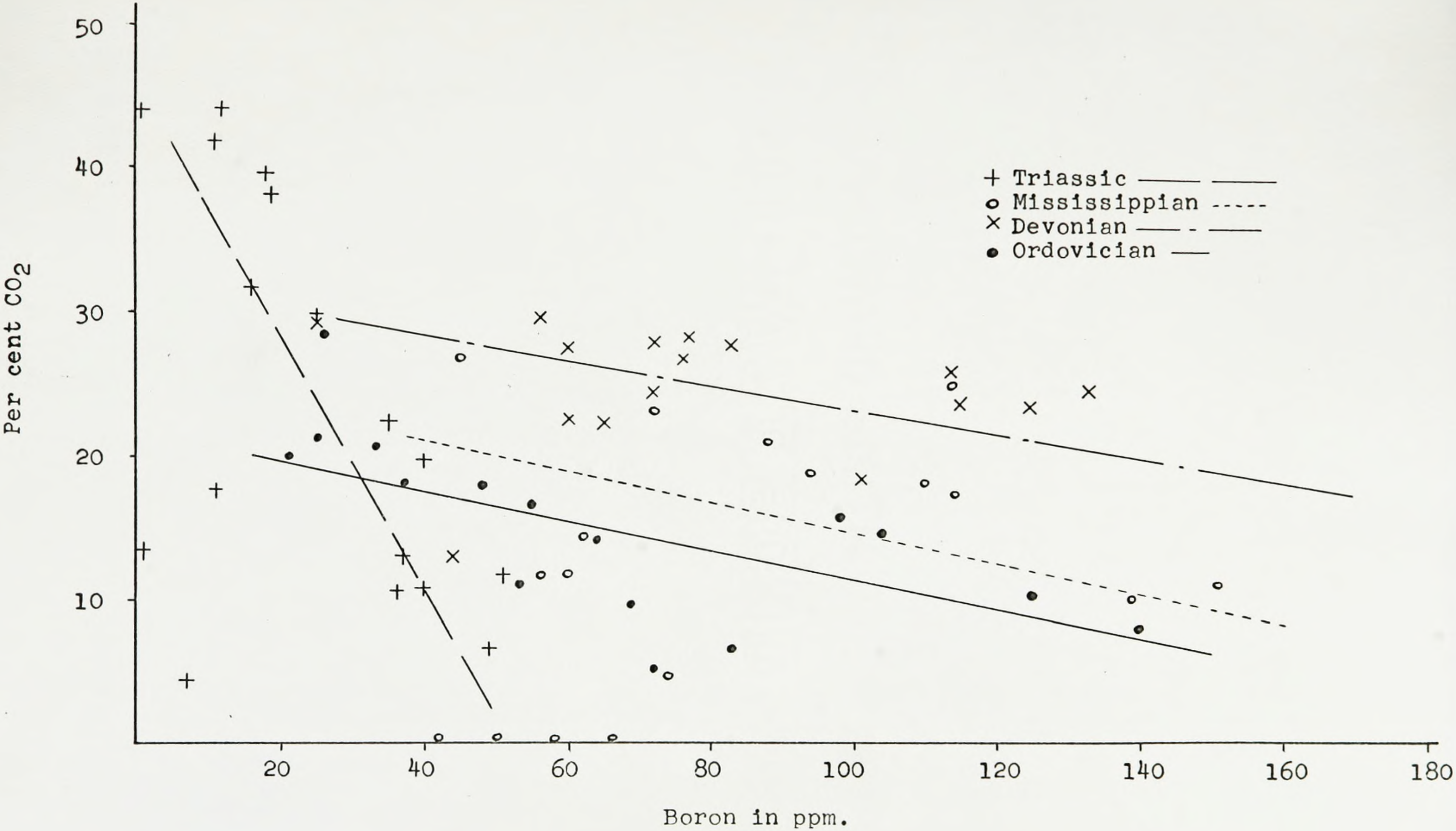

Fig. 13. Plot of per cent CO_2 against boron (ppm.).

For purposes of comparing calcareous shales with non-calcareous shales, all the B in calcareous shales was corrected for the carbonate fraction. A graphical method was employed (Fig. 14). Per cent CO_2 was plotted against % shale material. Two lines representing 0% to 100% calcite and dolomite were drawn and the % shale material was obtained from the abscissa. The uncorrected B content (Table XVI) for the four calcareous sections was then assigned to the clay material and recalculated to 100% (Table XVII). The error caused by a misclassification as to whether the carbonate fraction is calcite or dolomite ranges from approximately ±8% in shale material at very high CO_2 values to less than 1% for very low CO_2 values.

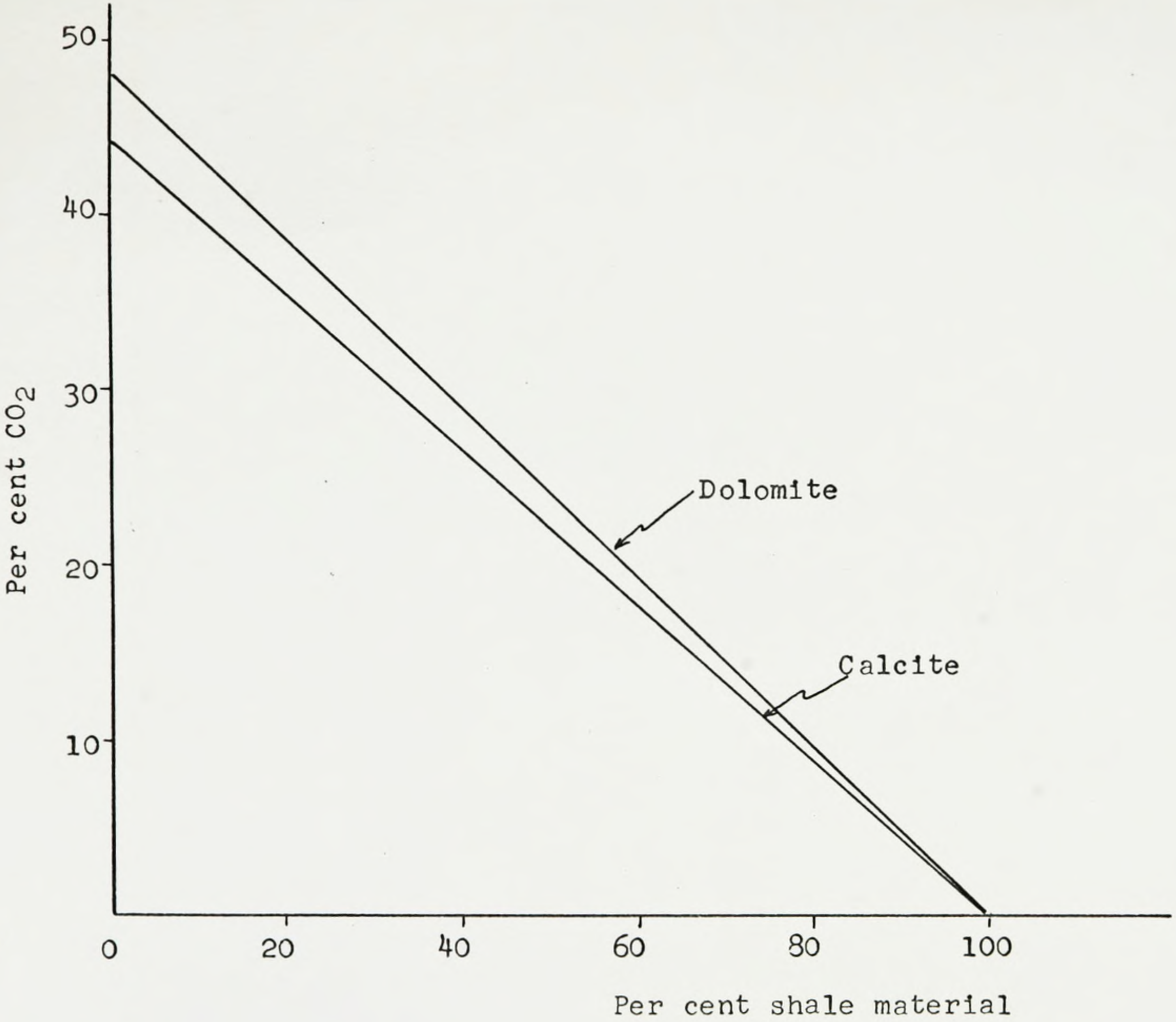

Fig. 14. Plot of per cent CO_2 in theoretical calcite and dolomite against shale material.

TABLE XVII

B (ppm.) Data Corrected for Carbonate Fraction (oldest sample at the bottom)

Ordovician			Devonian			Mississippi			Triassic		
Sample No.	CO_2%	B	Sample No.	CO_2%	B	Sample No.	CO_2%	B	Sample No.	CO_2%	B
B- 7	28.5	63	28-3	23.5	264	C-17	18.4	188	D-17	19.6	68
B- 8	20.0	36	28-2	29.7	170	C-15	25.3	265	D-16	22.5	64
B- 9	16.7	84	28-1	28.3	200	C-14	23.3	151	D-15	17.7	17
B-10	20.7	54	46-1	23.8	248	C-13	18.9	165	D-14	29.9	66
B-12	6.7	97	46-2	29.8	77	C-12	17.3	187	D-13	13.5	1.5
B-13	11.1	68	46-3	27.8	223	C-11	26.9	115	D-12	31.6	46
B-14	21.4	45	46-4	28.4	218	C-10	21.0	166	D-11	44.7	14
B-15	5.3	81	46-5	24.8	302	C- 8	10.0	180	D-10	39.6	100
B-16	9.7	86	46-6	22.4	131	C- 7	11.0	201	D- 9	38.2	90
B-17	14.3	90	46-7	27.5	158	C- 6	11.6	61	D- 8	44.4	150
B-18	10.4	158	46-8	27.0	193	C- 5	14.4	92	D- 7	41.8	85
B-18A	18.1	76	46-9	22.6	122	C- 4	11.8	82	D- 6	10.8	52
B-19	18.2	59	46-10	24.5	161	C- 3	4.6	83	D- 5	4.4	8
B-20	2.3	262	27-3	18.5	174	C- 2	0.02	66	D- 4	6.60	58
B-21	15.9	146	27-2	22.5	467	C- 1	0.02	58	D- 3	13.0	50
B-22	14.8	150	27-1	25.8	274	RA- 2	0.2	50	D- 2	10.6	46
B-23	8.0	167	30-33	12.9	62	RA- 1	0.1	42	D- 1	11.7	67
$\bar{x}$ = (mean)		101.3			202.6			126.6			57.8
s = (standard deviation)		57.8			95.1			65.9			37.0
s^2 = (variance)		3343.3			9014.7			4344.4			1372.4
s_1^2 = (variance log transformation)		0.051			0.045			0.061			0.239

RELATIONSHIP BETWEEN CALCULATED MINERAL COMPOSITIONS AND BORON

Several difficulties are usually encountered in comparing shales. Particularly vexing is the difficulty of distinguishing fine grained chert from clay. Acid leaching may alter both the amount and nature of the residual clay, and any attempt to separate clay from chert (silica) mechanically leaves an unknown amount of fine grained silica with the clay. For purposes of comparing the B content with four shale fractions (carbonate, minor mineral constituent, clay, chert or silica) hypothetical mineral compositions (norms) were calculated from the chemical analyses (Appendix II).

A modified form of a method proposed by Imbrie and Poldervaart (1959) was used. The minor chemical oxides, in terms of molecular ratios, TiO_2, Na_2O and P_2O_5 were recalculated as rutile, albite, and apatite. All the CaO and CO_2 and as much MgO as required was used to form calcite and dolomite. The balance of the MgO and all K_2O was used to form illite and either sericite, chlorite, and montmorillonite depending on the relative amounts of MgO and K_2O. Residual Fe_2O_3 and Al_2O_3 were computed as montmorillonite and residual SiO_2 was regarded as chert or silica.

During the calculation it was apparent the samples B-10, DC-3, and C-2 were deficient in Al_2O_3 in comparison to MgO and K_2O, therefore the total Al_2O_3 and Fe_2O_3 were used to form illite and sericite and remaining K_2O not used was reported as excess K_2O. The excess K_2O was 4.7%, 0.35%, and 1.58% for samples B-10, DC-3, and C-2 respectively. The excess K_2O

could possibly be in a feldspar rock fragment, unfortunately it was impossible to distinguish the K_2O in the clay minerals and in the feldspars.

Other inconsistencies involved a negative computation in hematite and silica, this was not considered serious as the values did not exceed 1.95%. These values were entered (Table XIX) as negative values and not computed into the total minerals calculated. The assumed mineral assemblage and ideal compositions used in the calculation are listed in Table XVIII.

The method as tested by X-ray technique (Imbrie and Poldervaart, op. cit.) was unreliable for specific clay mineral calculation but was found to compute the carbonate, total clay, and silica within an accuracy of 5%.

The 27 total shale analyses have been divided into two groups, one consisting of only the Littleton Fm. samples and the other composed of 16 analyses (2 from each Period). The correlation coefficients between B, minor constituents, carbonate, clay minerals (total), and silica are listed in Table XX. The results indicate a significant negative correlation between B and the minor mineral constituents for 27 shales (both arithmetic and logarithmic data). However, this correlation was not significant when the 16 non-metamorphic shales and the 11 Littleton Fm. samples were separated. Boron was also found to be positively correlated with the carbonate fraction in the Littleton Fm. samples. Other significant correlations obtained were

1) negative correlations between the clay minerals and the carbonate fraction and between clay fraction and the silica for 27 samples (both arithmetic and logarithmic data),
2) for the 16 shales, negative correlation between a) carbonate and clay fractions, b) carbonate and silica fraction (arithmetic data), c) negative correlation between the carbonate and clay fractions and between clay and silica fractions (logarithmic data),
3) for the 11 Littleton Fm. samples, a negative correlation between clay and silica fractions (both logarithmic and arithmetic data).

The conclusions are that B does not appear to be a function of the total clay minerals, and appears to be dependent on both the clay and silica fractions. This does not exclude the possibility that the B could be directly related to a specific clay mineral or other mineral which is not included in the calculated groups. However, it does suggest that the total B content in shale is dependent on more than one variable.

The carbonate fraction because of the negative correlation between CO_2 and B probably does not contain the bulk of the B. The clay and silica fractions are the most probable B containing fractions. To determine whether or not authigenic silica (chert) contains B, three samples of Ancaster Chert were analysed for B. These samples were white and crypto-crystalline, occurring as lenses and nodules within a carbonate lithology. Boron content for the chert was 36, 25, and 32 ppm. which

TABLE XVIII

After Imbrie and Poldervaart (1959)

Minerals Assumed	Ideal Composition
Apatite	$3CaO.P_2O_5$
Albite	$Na_2O.Al_2O_3.6SiO_2$
Rutile	TiO_2
Hematite	Fe_2O_3
Calcite	$CaO.CO_2$
Dolomite	$CaO.MgO.2CO_2$
Illite	$2K_2O.3MgO.(Al_2O_3,Fe_2O_3)_8.24SiO_2.12H_2O$
Sericite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
Montmorillonite	$(Al_2O_3,Fe_2O_3)_2.8SiO_2.2H_2O$
Chlorite	$4MgO.2Al_2O_3.2SiO_2$
Silica	SiO_2

	Precambrian	
Sample No.	I-2	I-12
B%	0.0089	0.0043
Minor Constituents %	4.07	5.88
Apatite	0.22	0.22
Albite	2.96	4.90
Rutile	0.89	0.76
Hematite	-	-
Carbonates %	0.04	2.35
Calcite	-	-
Dolomite	0.04	2.35
Clays %	99.01	75.82
Illite	51.67	39.79
Montmorillonite	23.73	12.78
Sericite	23.61	23.25
Chlorite	-	-
Silica or Chert %	0.01	12.60
Total	103.12	96.65

* After Candy (1963)

x Excess K_2O remaining after the calculation

TABLE XIX

Ordovician		Silurian		Devonian	
B-10^x	B-18	DC2* (A103)	DC3*^{x} (A101)	RB-46-1	RB-28-3
0.0033	0.0125	0.0335	0.0343	0.0115	0.0125
0.50	4.68	2.33	2.60	2.02	3.61
0.13	0.24	0.30	0.24	0.15	0.26
-	3.97	0.76	1.01	1.52	3.04
0.37	0.47	1.27	1.35	0.35	0.31
-	-	-	-	-1.95	-
43.40	23.48	0.07	0.02	53.61	53.46
1.21	21.64	0.07	0.02	48.07	52.82
42.19	1.84	-	-	5.54	0.64
29.72	50.30	71.48	54.45	42.08	28.72
15.40	39.40	53.97	42.89	41.07	-
-	-	5.51	-	-	1.07
14.32	10.90	12.00	11.56	1.01	21.60
-	-	-	-	-	6.05
22.48	19.83	25.92	41.51	4.71	12.60
96.10	98.29	99.80	98.58	102.42	98.39

TABLE XIX (Continued)

Sample No.	Mississippian		Triassic		Jurassic		Cretaceous	
	C-2[x]	C-17	D-4	D-16	M-9	M-15	H-8	H-18
B%	0.0066	0.0110	0.0049	0.0035	0.0110	0.0153	0.0051	0.0090
Minor Constituents								
Apatite	0.07	0.37	1.77	0.17	0.30	0.50	0.39	0.37
Albite	2.20	2.28	9.56	18.35	5.58	7.70	7.10	4.06
Rutile	0.41	0.41	0.51	0.31	0.67	0.75	0.70	0.84
Hematite	-	-	-0.68	-	-	-	-	-
Carbonates								
Calcite	0.05	30.54	4.88	51.12	0.07	1.45	0.07	-
Dolomite	-	10.35	9.34	-	-	3.63	-	-
Clays								
Illite	21.96	-	25.88	-	19.45	36.81	33.15	30.25
Montmorillonite	-	2.31	-	-	18.11	18.86	19.64	24.25
Sericite	7.69	28.77	15.13	18.64	7.42	7.42	-	7.89
Chlorite	-	9.01	-	3.68	-	-	0.35	-
Silica or Chert	62.59	17.53	41.11	16.08	46.49	19.75	36.03	29.02
Total	94.97	101.57	108.18	108.35	98.09	96.87	97.43	96.68

[x] Excess K_2O remaining after the calculation

TABLE XIX (Continued)

Samples from the Littleton Formation, Devonian, Shaw (1956)

Sample No.	L-1	L-2	L-3	L-8	L-9	L-10	L-11	L-12	L-62	L-66	L-69
B%	0.0029	0.0055	0.0090	0.0063	0.0043	0.0071	0.0055	0.0050	0.0053	0.0045	0.0066
Minor Constituents											
Apatite	0.20	-	0.24	0.26	0.30	0.15	0.39	0.39	0.33	0.26	0.35
Albite	1.35	9.30	4.57	5.75	6.51	6.68	13.53	21.82	7.86	12.35	11.42
Rutile	0.80	0.65	1.06	0.99	1.00	0.97	0.60	1.04	1.10	1.00	1.03
Hematite	6.45	-	-	-	5.65	-	7.57	-	-	-	-
Carbonates											
Calcite	-	-	-	-	0.11	-	-	0.07	-	0.23	0.11
Dolomite	0.14	-	0.66	0.06	-	0.23	0.17	-	0.32	-	-
Clays											
Illite	55.65	58.06	24.57	30.70	66.12	23.46	51.74	42.01	42.24	49.23	51.53
Montmorillonite	-	26.76	31.74	32.45	-	31.81	-	13.03	51.64	21.97	20.83
Sericite	4.17	-	15.72	11.87	-	10.60	-	10.34	0.66	7.81	1.03
Chlorite	-	0.20	-	-	0.87	-	1.61	-	-	-	-
Silica (Chert)	33.39	5.42	22.61	17.57	20.53	25.99	25.18	13.13	-1.48	8.71	15.27
Total	102.15	100.39	100.61	99.64	101.09	99.89	100.79	101.83	104.15	101.56	101.57

TABLE XX

Correlation Coefficient Matrix for 27 Shales (Arithmetic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	-0.432	-0.039	-0.007	0.189
Minor Constituents		1.000	-0.217	0.107	-0.163
Carbonate Fraction			1.000	-0.685	-0.239
Clay Fraction				1.000	-0.503
Silica					1.000

Correlation Coefficient Matrix for 27 Shales (Logarithmic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	-0.388	-0.060	0.054	0.066
Minor Constituents		1.000	-0.269	0.310	-0.020
Carbonate Fraction			1.000	-0.614	0.070
Clay				1.000	-0.458
Silica					1.000

r_{ij} is significant at the 95% level if the value falls outside the range +0.323 to -0.323.

TABLE XX (Continued)

Correlation Coefficient Matrix for 16 Shales (Arithmetic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	-0.364	-0.272	0.276	0.097
Minor Constituents		1.000	0.072	-0.196	0.016
Carbonate Fraction			1.000	-0.648	-0.491
Clay				1.000	-0.331
Silica					1.000

Correlation Coefficient Matrix for 16 Shales (Logarithmic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	-0.179	-0.329	0.389	0.021
Minor Constituents		1.000	-0.032	0.060	0.051
Carbonate Fraction			1.000	-0.543	0.065
Clay				1.000	-0.459
Silica					1.000

r_{ij} is significant at the 95% level if the value falls outside the range +0.426 and -0.426

TABLE XX (Continued)

Correlation Coefficient Matrix for 11 Littleton Fm. shales (Arithmetic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	0.340	0.602	0.128	-0.005
Minor Constituents		1.000	-0.376	-0.442	-0.050
Carbonate Fraction			1.000	0.112	0.102
Clay				1.000	-0.869
Silica					1.000

Correlation Coefficient Matrix for 11 Littleton Fm. shales (Logarithmic Data)

	Boron	Minor Constituents	Carbonate Fraction	Clay	Silica
Boron	1.000	-0.339	0.221	0.213	0.012
Minor Constituents		1.000	-0.205	-0.397	0.089
Carbonate Fraction			1.000	-0.137	-0.135
Clay				1.000	-0.719
Silica					1.000

r_{ij} is significant at the 95% level if the value falls outside the range +0.521 and -0.521

is slightly lower than the averages, 43 ppm. and 51 ppm. B, of the shales from the Precambrian (Miette Group), Littleton Fm. respectively.

Clearly, some of the B may be attributed to the presence of detrital tourmaline. The remainder is probably incorporated in both the clay and silica fractions. However, the lack of correlation between B and clay mineral content may be a result of multivariable effects which are not being measured but are assumed constant. These variable taken together constitute the total environment and include salinity (availability of B), temperature, pH, detrital B and biological effects. The basic assumption is that these variables are constant within the shales studied. This assumption is necessary if relative B content in shale is to be meaningful. It appears as if this assumption is not realistic and the actual measurements of B represent the end product of the action of a large number of variables in a multivariable component system.

BORON AS A SALINITY INDICATOR

The average B content (Potter et al., 1963) for modern argillaceous sediments is 89.6 ppm. and 123.6 ppm. B for ancient marine sediments. Corresponding averages of 45.6 ppm. and 39.7 ppm. B are reported for modern fresh water and ancient fresh water argillaceous sediments respectively.

For purposes of classification based on these values a brackish water environment is postulated for shales with average B content between the values for fresh and marine water environments (Table XXI). The Precambrian (Miette Group) based on the average value of 43.2 ppm. B appears to have been deposited under fresh water conditions. The Devonian (Littleton Fm.), Triassic and the Cretaceous fall inbetween the values for fresh and marine water environments and could be considered to be deposited in a brackish environment. The remainder of the shales could be classified as marine. These results are acceptable to the author. Both the Precambrian and the Littleton shales have undergone different degrees of metamorphism and the depositional environments are in doubt. The only misclassified group of shales appears to be the shales from the Triassic (Whitehorse Fm.). However, the results for this section may be invalid because the shales are highly calcareous and can not be compared to less calcareous shales.

The spectrographic method employed by Potter et al. (op. cit.) is different from that of Walker and Price (1963), and Frederickson and Reynolds (1959). Although the B line used by Potter et al. (op. cit.) was probably 2497.73 (the line used was not mentioned in the paper), a buffer composed of 2 parts graphite powder and one part $CaCO_3$ was used. This would suppress the iron line at 2497Å resulting in little or no interference.

A further comparison of B research is furnished by recalculating B content to "adjusted" B (method previously outlined, after Walker and Price (op. cit.)). Both the B content and K_2O values were recomputed to 100% (eliminating the carbonate fraction) clay material and then the "adjusted" B content was calculated and plotted against K_2O (Fig. 15).

The results indicate that by this calculation only the Devonian (Mount Hawk and Perdrix) and the Silurian plot within normal marine or hypersaline environments. However, it was previously established that part of Walker and Price's data are erroneous.

TABLE XXI

	Marine	S	Brackish	S	Fresh Water	S
Modern Sediments[1]	89.6[2]	18.9			45.6	25.4
Ancient Sediments[1]	123.6	46.2			39.7	24.2
Precambrian					43.2	12.5
Ordovician*	101.3	57.8				
Silurian	292.1	79.5				
Devonian*	202.6	95.1				
Littleton Fm.			51.3	15.9		
Mississippian*	126.6	65.9				
Triassic*			57.8	37.0		
Jurassic	122.7	60.1				
Cretaceous			60.1	16.5		

[1] Potter et al. (1963)

[2] Boron content in ppm.

* Boron data corrected for carbonate content

S (standard deviation)

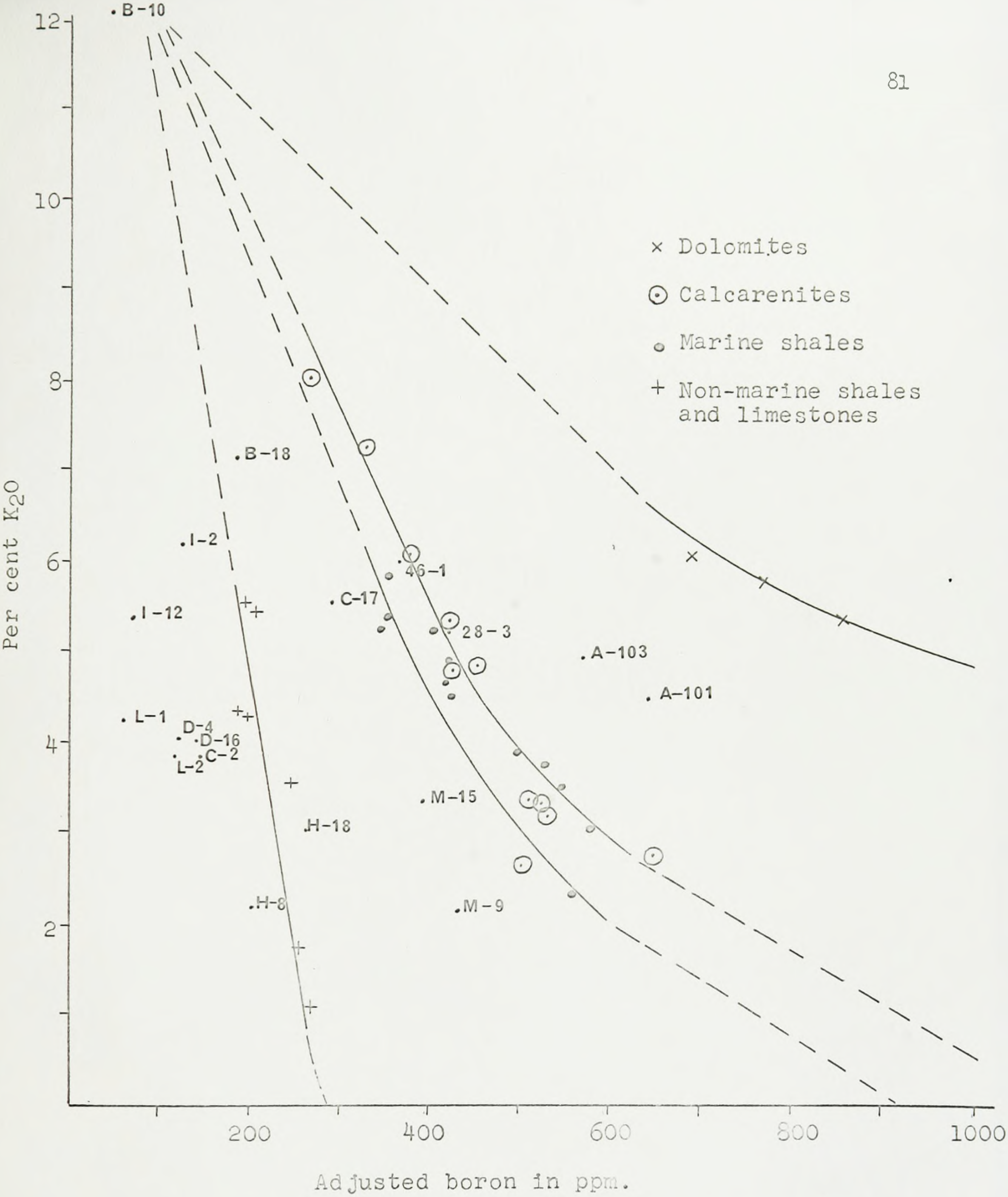

Fig. 15. Relationship between adjusted boron and K_2O for illites (four salinity environments) from Walker and Price (1963). Plot of 18 values from this study.

BORON AND PALEOSALINITY

The distribution of B in shales throughout geological time (Proterozoic to Cretaceous) Fig. 16 is variable. No attempt can be validly made as to the B content in sea water from the past to the present, as it is apparent that the samples collected for this study do not come from restricted environments and have different mineralogical compositions. However, the data are sufficiently numerous in shales previously identified by fossil evidence to be marine (Ordovician, Devonian, Mississippian, and Jurassic) to suggest that a B content greater than 75 ppm. represents a marine depositional environment. Values below 75 ppm. B probably indicate brackish and fresh water deposition.

Unfortunately the only reliable B determinations below the suggested 75 ppm. B come from the Cretaceous shales, and the depositional environment for these shales has not been established. The B averages for the Miette Group, Littleton Fm. and the Triassic argillaceous rocks are subject to question, as both the Precambrian and Littleton shales have been metamorphosed and the Triassic rocks are atypical (highly calcareous) shales.

The B distribution between sections studied is highly varied, but within each section the B content appears to be characteristic of that section. The variances between sections are not equal (both arithmetic and logarithmic), and appear to be a function of different depositional environments and different mineralogical make-up. The number of variables acting to produce the B concentration are numerous and for this reason causal relationships can not be determined.

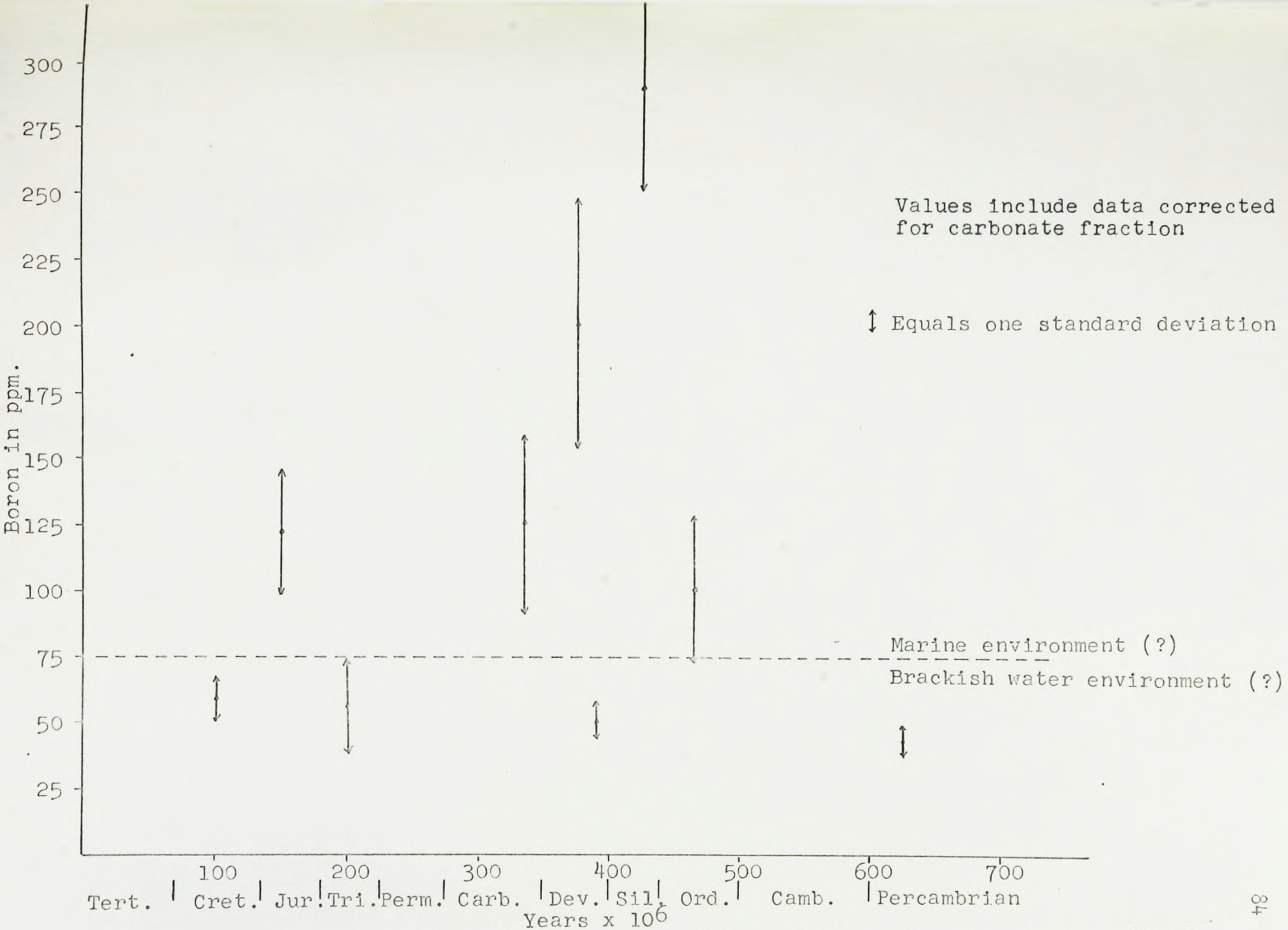

Fig. 16. Plot of boron content against time (time scale after Holmes, 1959).

CONCLUSIONS

1. Shale samples from the Fernie, Banff, Devonian (Western Canada), and Ordovician marine lithologies (based on marine fauna) generally contain B values in excess of 75 ppm.

2. The Blackstone Cretaceous shales, depositional environment unknown, contain a low B content (average 60.1 ppm. B) which suggests a brackish or fresh water depositional environment.

3. The high B content, average of 292.1 ppm. B, of the Silurian (Thorold and Grimsby) suggests a marine depositional environment.

4. Boron content in shales is negatively correlated with the carbonate fraction.

5. The conclusion that most of the B is concentrated in the illite fraction is erroneous and is a result of an iron coincidence on the B 2497Å spectral line.

6. Boron is contained in both the clay and authigenic silica fraction of the shale.

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APPENDIX I

DESCRIPTION OF STRATIGRAPHIC SECTIONS

LEGEND

▱	Dolomite
▱	Silty dolomite
▤	Limestone
▤	Silty limestone
▱	Argillaceous dolomite and dolomitic mudstones
▤	Limestone and calcareous shale
░	Sandstone and siltstone
▭	Argillite and shale
░	Argillaceous sandstone and siltstone
▤	Shale
▒	Covered interval
▒	Conglomerate

Section I (Proterozoic, Miette Group)

Location:	Longitude 118 16' W.
	Latitude 52 52' N.

The east-west route, highway and C.N.R., from Jasper to Yellowhead pass parallels the trend of major anticlinal folds which are transverse to the common northwest regional strike of the Rocky Mountain Main Ranges. The roadcuts expose abundant green and purple argillites, shales, sandstones and quartzites of probably Proterozoic age.

Section I was measured on the south side of the highway southwest of Geikie near the junction of Meadow Cr. and Miette River.

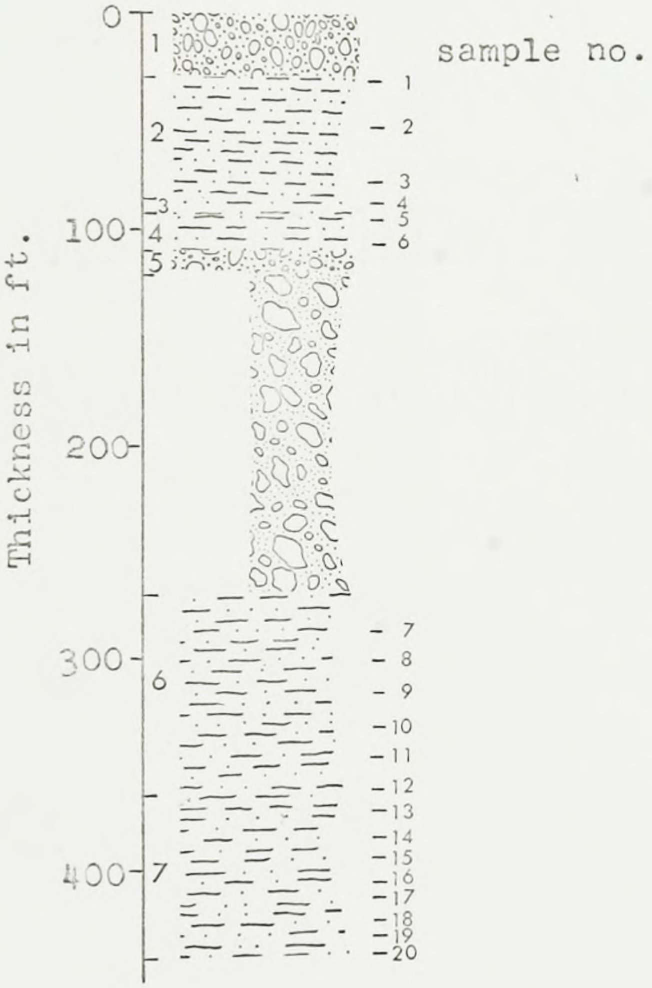
Description of Section I (Proterozoic, Miette Group)

Unit	Lithology	Unit Thickness (ft.)	Total Thickness (ft.)
1	Conglomerate, stratified, pebbles composed of quartzite, 1/4" to 1/2", few feldspar pebbles: matrix consists of light blue to light grey pebbles, fine to very coarse grain; weathers resistant in beds 3' thick, few interbeds of sandstone.	30'	
2	Shale and argillite, non-calcareous, very slightly silty, fine to very fine grained, medium grey to greenish grey, thin bedded, prominent slaty cleavage; weathers buff to rusty grey, few interbeds of more competent argillites, somewhat recessive.	53'	83'
3	Argillite, non-calcareous, silty, medium grained, medium grey; weathers rusty and buff, competent and resistant.	7'	90'
4	Interbedded, argillite, non-calcareous, papery, medium greenish grey; weathers rusty buff in beds 2' thick recessive: conglomerate, white quartz and feldspar, pebbles 1/8" to 1/2"; weathers medium grey green, resistant.	20'	110'

Unit	Lithology	Unit Thickness (ft.)	Total Thickness (ft.)
5	Conglomerate and sandstone, few shaly partings, pebbles 1/8" to 1/2", white quartz and feldspar, medium grey green; weathers grey green in beds 2' to 3', resistant.	14'	124'
	Measurement discontinued, beds highly contorted - measurement continued after approximately 150' of partially convered interval.	150'	274'
6	Argillite, non-calcareous, very fine grained, medium grey and light green, slaty, in part fissile; weathers buff to grey in part purple, recessive.	95'	369'
7	Argillite, non-calcareous, very fine grained medium grey and green, slaty cleavage somewhat papery; weathers buff to light green, in part purplish.	70'	439'

Proterozic (Miette Group)

Section I, showing sample locations.



Section B (Ordovician and/or Cambrian)

Location: Longitude 117° 68' W.

Latitude 52° 34' N.

Approximately 6 miles S.W. from the junction of the Cairn and Southesk Rivers, a small tributary flowing N.E. joins the Southesk River. Section B was measured 4.5 miles upstream on the N.W. side of the tributary.

Section B, view from gravel terrace looking N.W. across a ridge exposure of Devonian, Ordovician and Cambrian lithology.

Description of Section B (Ordovician and/or Cambrian)

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Cairn		
	Dolomite, very dark brown, fetid, medium crystalline; weathers very dark brown in beds 1' to 6" thick and resistant.		
	Ordovician 130/35 S.W.		
1	Dolomite, very light grey, very coarsely crystalline, slightly calcareous, porous; weathers light grey to light brown in beds 2" to 1' ave. = 6", few argillaceous partings.	20'	
	Covered interval	30'	50'
2	Interbedded limestone, very light grey, tinge of green, micro-crystalline to finely crystalline, in part darker grey, argillaceous, highly mottled, in part looks brecciated; weathers medium grey and in part very deep maroon and orange buff for the mottled limestone, in beds 2" to 6": shales very fine grained, slightly silty, very calcareous, dense, light to medium grey with tinge of green, very thin bedded; weathers grey green, platy, in beds up to 3' thick.	55'	105'

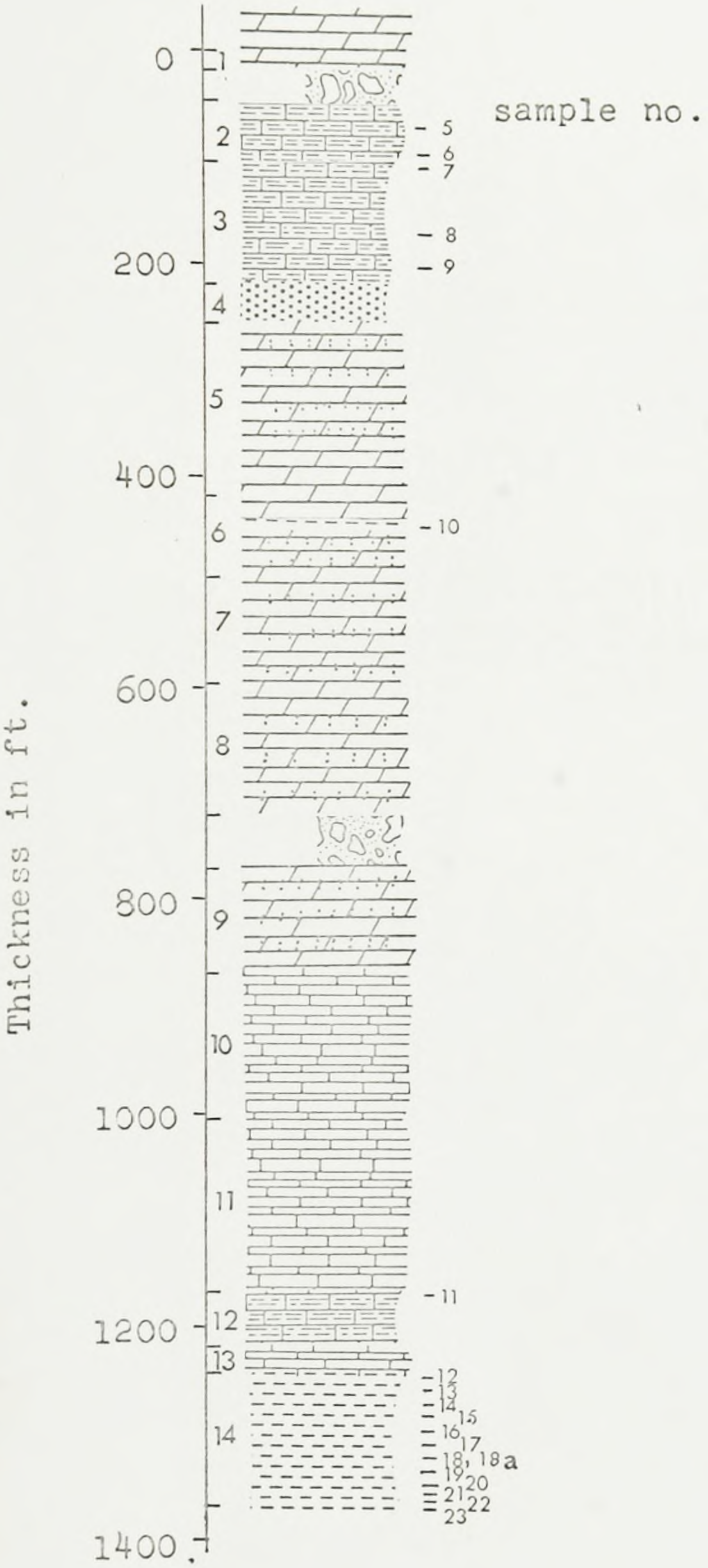
Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
3	Partially covered; shales fine grained, very calcareous, very light grey, fissile in part, few light maroon to grey limestone interbeds with orange mottling, few trilobite fragments, bottom 25' contain more limestone interbeds.	115'	220'
4	Sandstone and siltstone, non-calcareous, light grey to orange buff; weathers bright orange to yellow red in beds approximately 2' thick, lower part of unit contains very prominent silt laminae, thinly bedded, flagstone weathering, recessive. 130/40 S.W.	60'	280'
5	Dolomite, very silty, fine crystalline, in part argillaceous; weathers yellow orange buff to light grey, in beds 1' to 6", forms cliff.	144'	424'
6	Dolomite, fine crystalline and coarse crystalline, very silty, red to maroon, commonly light sandy brown, in part changes to siltstone; weathers maroon to buff, blocky, resistant. at 31', 1' bed of green shales.	75'	499'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	135/42 S.W.		
7	Dolomite, very silty, silty laminations very prominent, very coarse crystalline to medium crystalline, grey maroon to light grey; weathers yellow orange, blocky, in part flagstone weathering, very resistant.	100'	599'
8	Dolomite, very silty, medium grey, micro-crystalline with few very coarse crystalline patches, prominent silt laminations, slightly cherty, lenses and blebs of chert parallel to bedding plane; weathers grey buff, in part medium grey, resistant.	139'	738'
	Covered interval	40'	778'
9	Dolomite, slightly calcareous, medium grey, medium crystalline, silty, slightly cherty; weathers dark grey and buff in beds 6" to 3' somewhat massive, resistant.	93'	871'
	130/40 S.W.		
10	Limestone, few interbeds of dolomite, dark to medium grey, fine crystalline, very silty, argillaceous mottling; weathers medium grey, thin bedded to 2', bottom of unit very dolomitic and silty.	145'	1016'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Partially covered.		
11	Limestone, dolomitic, fine crystalline, prominent silt laminations, argillaceous and dolomitic mottlings; weathers grey to buff recessive.	165'	1181'
12	Shale, calcareous, fine grained, medium grey, in part interbedded with medium grey nodular limestone beds; weathers rusty brown, somewhat recessive.	43'	1224'
13	Limestone, orange mottling, looks brecciated, medium grey, fine to microcrystalline, in part very coarse crystalline; weathers orange buff.	20'	1244'
14	Shale, fine grained, calcareous, upper 60 ft. slightly silty, greenish grey to green, in part fissile, few interbeds of more competent limestone similar to unit 13; weathers green to brown-grey, recessive.	120'	1364'

Ordovician and/or Cambrian

Section B, showing sample locations.



Section A, W, and K (Silurian, mainly Thorold and Grimsby)

The Silurian sections were measured at two localities by Mr. I.P. Martini.

De Cew Falls Section (A)

Location:	Longitude	78° 16' W.
	Latitude	43° 07' N.

Twelve Mile Creek flows approximately north through the city of St. Catharines. A Power House situated on the creek south of St. Catharines and directly east of Power Glen has been built on the east bank of the creek. On the north-east side of the Power House the Silurian section including De Cew to Whirlpool Fms. has been exposed by excavation. Samples were obtained from the Neahga, Thorold, Grimsby and Power Glen Fms.

Lockport Section (W and K)

Location:	Longitude	78° 42' W.
	Latitude	43° 11' N.

North west of the town of Lockport two sections of Silurian lithologies are exposed. One section (Neahga, Thorold and Grimsby Fms.) is located along the Erie Railroad which runs approximately west-east, north of St. Patricks Cemetery. The section is exposed 1/4 mile to the west of the cemetery. The second section (Grimsby Fm.) is located 1/4 mile N.N.W. from the Erie Railroad section at the Lower Whitemore Quarry.

Samples were collected from the two exposures a) Neahga, Thorold and upper Grimsby at Erie Railroad (W-samples), b) the Whitemore Quarry (K-samples).

Description of De Cew Section (A)

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Neahga		
1	Shale, greenish grey to dark grey.	1.25'	
	Thorold		
2	Sandstone, white to light grey, fine grained massive; weathers buff with grey shale partings.	9'	10.25'
	Grimsby		
3	Sandstone, argillaceous, red, fine grained, massive, green and yellow mottled, cross-bedded, varying thickness of red shale to siltstone.	31'	41.25'
4	Shale, red and green, minor bands of red sandstone.	11'	52.25'
	Power Glen		
5	Shale, calcareous, dark grey to green, fissile, comprises nearly three-quarters of the total section, remainder arenaceous shale and thin beds of light grey, calcareous sandstone and shale.	48'	100.25'
	Whirlpool		
6	Sandstone, quartzose, white to light grey, fine to medium grained, massive, thick bedded; weathers buff.	12'	112.25'

Description of the Lockport (W and K) Sections

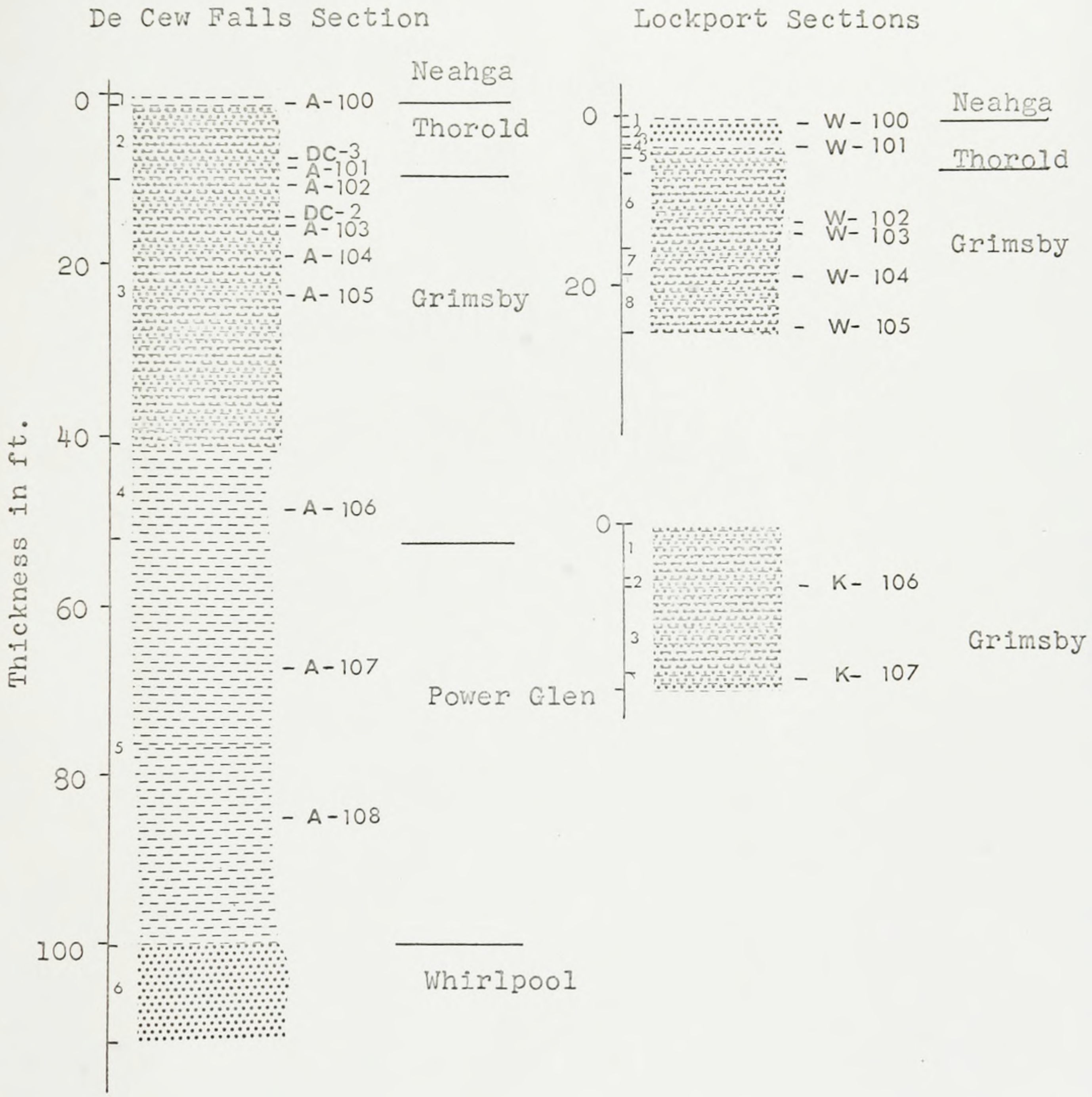
Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Eire Railroad Section		
	Neahga		
1	Shale, blue and grey green, interbedded with limestone.	1.5'	
	Thorold		
2	Sandstone, calcareous, slightly argillaceous, medium grey, few shale pebbles, brownish light grey, in part fine grained to silty, very hard, blocky, massive, slightly laminated; weathers grey brown.	2'	3.5'
3	Shale, grey, soft, fissile; weathers grey, occurs as argillaceous partings.	0.5'	4.0'
4	Sandstone, slightly argillaceous, increasing in argillaceous content towards the bottom.	1.0'	5.0'
	Grimsby		
5	Sandstone, argillaceous, calcareous, medium red, greenish grey mottling; weathers light brown grey.	3'	8.0'
6	Interbedded sandstone and siltstone, argillaceous, in part shale, medium red, weathers medium red, sandstone slightly calcareous, few sub-angular to sub-rounded grains; weathers brown grey, extremely hard, blocky, massive.	7.5'	15.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
7	Sandstone, argillaceous, medium-red to light brown grey, very fine to fine grained, well sorted, medium to very hard; weathers orange to greenish brown, blocky, massive, few more argillaceous interbeds.	2.5'	18.0'
8	Sandstone, medium red, fine grained, in part very argillaceous, well sorted; weathers brownish grey to light grey, in part blocky, massive.	7.5'	25.5'
	<u>Lower Whitemore Quarry</u> Beginning of measurement within lower portion of the Grimsby.		
1	Sandstone, red to greenish grey, fine grained, good sorting, sub-angular grains, mottled in patches; weathers red to greenish grey, in part blocky, massive.	7'	
2	Shale, silty and fine grained, red, soft, sub-fissile; weathers greyish red.	0.5'	7.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
3	Sandstone, in part few shale pebbles, red to brownish grey, light grey, well sorted, mottled in patches, very fine to fine grained; weathers buff to medium grey, blocky, massive.	11.5'	18.0'

Silurian

Sections A, W and K, showing sample locations.



Chemical analyses of samples DC-2 and DC-3 were obtained from Candy (1963).

Section 28, 27, 46, and 30 (Devonian, Mount Hawk Samples)

Section 28 and 27

Location:	Longitude	117° 21' W.
	Latitude	52' 51' N.

Deception Creek flows approximately south, joining the Medicine-tent River 1.5 miles S.E. of the junction of Rocky and Medicine-tent Rivers.

<u>Section 28</u> was measured 1.5 miles upstream, on the west side of Deception Creek. A small tributary cuts through the core of an anticline exposing Cairn, Perdrix, etc., lithology on the S.W. limb.

<u>Section 27</u> was measured on the east side of Deception Creek.

Section 28, showing offreef shale section of the Alexo, Mount Hawk and Perdrix.

Section 27, showing three Cairn reef structures.

Description of Section 28 (Devonian)

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Palliser limestone		
1	Limestone, dark grey, massive, micro-crystalline to crypto-crystalline, in beds up to 5' to 8', in part bedding indistinct weathers medium to dark grey, very resistant		
	Alexo		
2	Limestone, dolomitic, fine-crystalline, dark brown to dark grey, numerous sparny calcite blotches and stringers; weathers dark to medium grey brown.	9.5'	
3	Dolomite, in part silty, calcareous, fine-crystalline to micro-crystalline; weathers light to medium grey in beds 5' to 3'.	10'	19.5'
4	Limestone, dark grey, micro-crystalline; weathers dark to medium grey in beds 2" to 4", slightly recessive, cf. units 3 and 5.	10'	29.5'
5	Dolomite, dark grey, slightly silty, micro-crystalline to crypto-crystalline; weathers medium to dark greyish brown.	13'	42.5'
6	Dolomite, calcareous, silty, fine-crystalline, medium brown to grey, numerous white sparny calcite specks; weathers rusty grey, bedding indistinct.	18.5'	61.0'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
7	Siltstone, calcareous, dark brown; weathers medium brown, flagstone, slightly recessive.	22'	83.0'
8	Limestone, dark grey, fine-crystalline to coarse-crystalline; weathers medium to light grey.	3.5'	86.5'
9	Siltstone, slightly calcareous, light grey, prominent cross-bedding, in part a sandstone; weathers medium brown, very finely laminated, resistant.	123.5'	210.0'
10	Limestone, dark grey, very silty, fine-crystalline, few silty laminations in beds 2' thick; weathers yellow brown, resistant, at top of unit few shaly interbeds.	13'	223.0'
11	Shale, very calcareous, fossiliferous, numerous brachiopods, dark brown; weathers rusty orange brown, recessive.	141'	364.0'
12	Partly covered, shale same as unit 11.	58'	432.0'
13	Siltstone, highly calcareous, dark grey brown, fine-grained; weathers brown, flagstone, resistant.	20'	452.0'
14	Limestone, argillaceous, dark brown, fine-crystalline; weathers dark grey and tan brown, recessive.	31.5'	483.5'

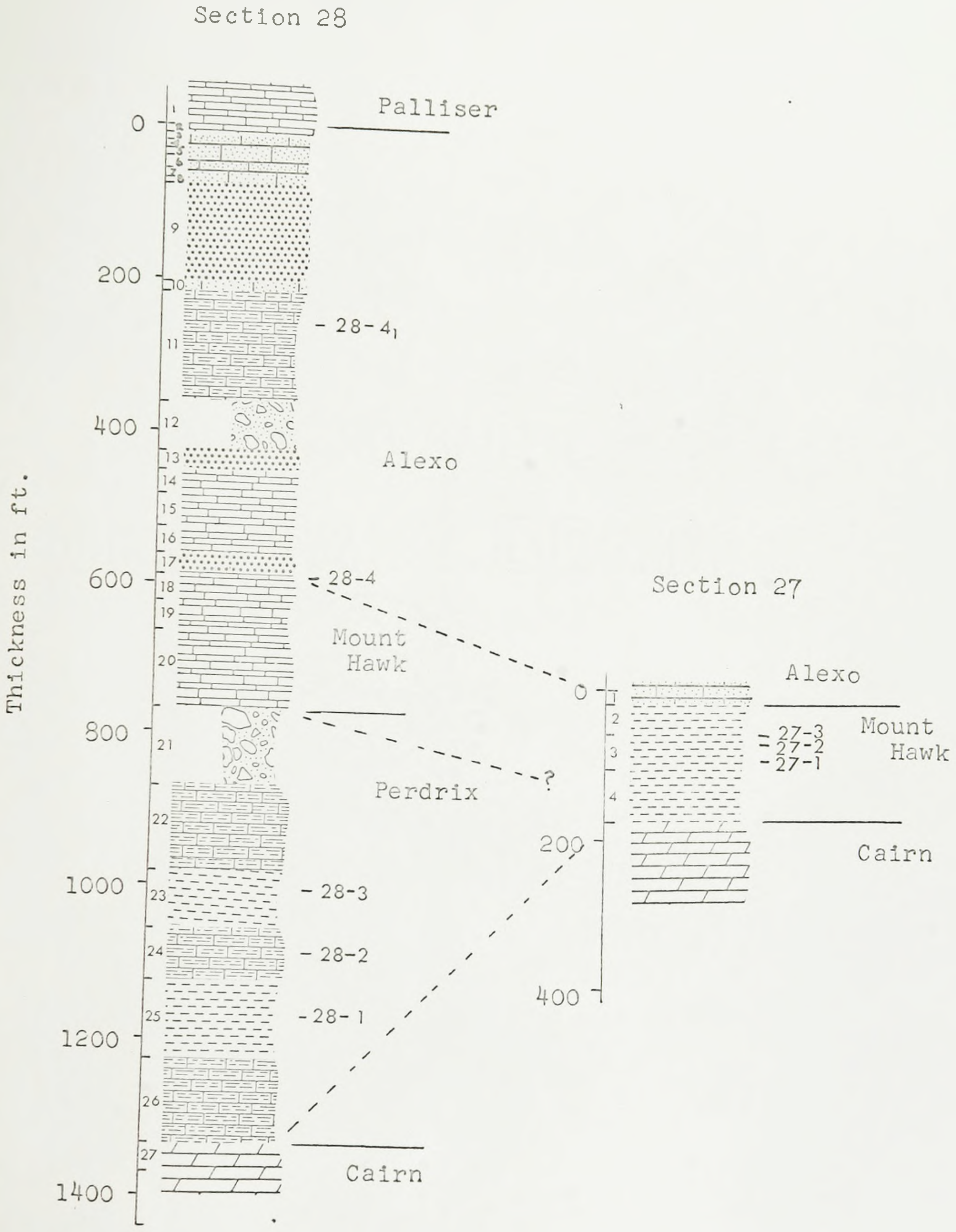
Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
15	Limestone, argillaceous and silty, dark grey and dark brown, fine-crystalline to micro-crystalline; weathers yellowish brown.	53.5'	537.0'
16	Limestone, argillaceous, slightly silty, dark grey, bedding indistinct; weathers dark to medium grey, recessive.	32'	569.0'
17	Siltstone, very calcareous, dark grey, in beds 1' to 2' thick; weathers buff, resistant.	23'	592.0'
	Mount Hawk 123/45 S.W.		
18	Limestone, dark grey, argillaceous, contains numerous shaly interbeds, shale intervals 6" to 1' thick; limestone weathers dark grey to light brown.	33.5'	625.5'
19	Partially covered. Limestone, dark grey, micro- to crypto-crystalline, in beds 4" to 6"; weathers dark grey to buff, recessive cf. unit 20 and contains more argillaceous and shaly interbeds.	42'	667.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
20	Limestone, fine-crystalline, dark grey, in beds 1' to 3'; weathers yellowish grey, few argillaceous interbeds, recessive, main feature is the irregular weathering, crumbly and nodular, in part has numerous sparny calcite stringers and lenses, brecciated.	103'	770.5'
21	Perdrix Covered interval, recessive Perdrix shales.	97.5'	868.0'
22	Interbedded limestone, argillaceous, dark grey, micro-crystalline to very coarse-crystalline, in beds up to 2' thick, in part folding has produced slaty cleavage: shale, calcareous, fine-grained, dark brown, fissile; weathers dark to medium brown, recessive.	116.5'	984.5'
23	Shale, calcareous, dark brown, fine-grained, thin bedded to fissile, in part appears to be a mudstone; weathers light grey to tan brown, recessive.	69'	1053.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
24	Interbedded shale, calcareous, dark brown, fissile; weathers dark brown to light grey: limestone, micro-crystalline, dark grey in beds up to 1' thick with numerous shaly and argillaceous partings.	83'	1136.5'
25	Shale, calcareous, in part a mudstone, dark brown, fissile, few limestone interbeds; weathers light brown, recessive.	87.5'	1224.0'
26	Partially covered.		
	Interbedded limestone, cherty, chert in 1" beds, black, limestone, dark grey, micro-crystalline; weathers dark grey to light brown 2" to 6".	115.5'	1339.5'
	Shale, calcareous, dark grey to brown, weathers medium brown, limestone and shale sequences appear to be cyclic.	115.5'	1339.5'
	Cairn		
27	Dolomite, very calcareous, in part cherty, chert finely disseminated in small nodules, very light grey, dolomite medium-crystalline, in part argillaceous; weathers light grey, recessive, in beds 2' to 4', numerous white sparny calcite blebs.	30.5'	1370.0'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
Description of Section 27 East side Deception Creek			
1	Alexo		
	Limestone, argillaceous, silty, dark grey, micro-crystalline; weathers yellow grey in moderately resistant beds 2" to 4", brittle, numerous white sparny infillings.	21.0'	
	Mount Hawk		
2	Shale, calcareous, fissile, fine-grained, grey; weathers yellow green, at base contains few beds of more resistant limestone, nodular.	44.0'	65.0'
3	Shale, very dark brown, calcareous, fissile, in part concretionary, few argillaceous limestone interbeds; weathers light brown, few pyrite inclusions.	41.0'	106.0'
4	Shale, calcareous, fissile, frequently conchoided fracture; weathers buff and light green, recessive.	76.0'	182.0'
	Cairn reef		
5	Dolomite, calcareous, medium to coarse-crystalline, green-grey, numerous white calcite (sparny) infilled vugs and veins.	100.0'	282.0'

Sections 28 and 27, showing sample locations.



Section 30 (Devonian)

Location:	Longitude	117° 22' W.
	Latitude	52° 49' N.

Section 30 was measured on Mt. Balcarres immediately up slope, west of the junction of Rocky and Restless Rivers.

Faulting has exposed several hundred ft. of sub-Devonian strata in addition to the entire Devonian section. The Mount Hawk and the Maligne are exposed and accessible.

Description of Section 30

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
1	Interbedded Limestone, dark grey, fine-grained, at base of unit very few limestone beds 6" to 1' thick; weathering buff brown: shale dark grey with a slightly greenish tinge, calcareous, in part fissile; weathers brown, shale makes up major component of unit, recessive.	69.0'	
2	Covered interval. Shale, weathers dark grey to brown.	89.5'	158.5'
3	Partially covered interval. Interbedded limestone, very slightly silty, dark grey brown, fine-grained, in beds 1/2" to 1', containing numerous hematitic stains; weathers grey to buff: shale, dark grey to brown, calcareous, in horizons 3' thick, fine-grained; weathers dark grey to dark brown, above 29' shale interbands increase in thickness up to 10'.	74.0'	232.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
4	Interbedded *limestone*, dark grey to black, fine-grained in beds, ave. 6", in part finely laminated: *shale*, calcareous, dark grey to brown, few specks of rusty iron blebs, in beds up to 1'; weathers medium brown, recessive.	50.0'	282.5'
	Perdrix		
5	Limestone, dark grey, fine-grained, very thinly bedded and finely laminated, numerous argillaceous partings, in beds 1/8" to 4"; weathers grey to buff, incompetent, uneven weathering, recessive.	40.0'	322.5'
6	Covered interval, probably maligne.	22.0'	344.5'
	Maligne		
7	Dolomite, medium-crystalline, cherty, contains few *Amphipora*, few *Stromatoporaidea*, numerous amoeboid-shaped white sparny calcite blebs up to 4" in diameter; weathers dark brown grey, in part fragmental and highly broken up, resistant.	30.5'	375'

Section 46 (Devonian)

Location: Longitude 117° 05' W.

Latitude 52° 29' N.

Section 46 was measured on the north side of Chocolate Mt. approximately 1.5 miles upstream from the junction of the north and south forks of Isaac Creek. The entire Devonian is easily accessible and totally exposed.

Section 46, view looking S.E. onto the north side of Chocolate Mt.

Description of Section 46

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
1	Dolomite, medium to dark brown, fine-crystalline, corals and Amphipora, porous, contains numerous white dolomite blebs (probably weathered out Stromatoporoids), bedding indistinct in beds 3' thick; weathers medium to light brown, more argillaceous beds weathering buff, moderately resistant.	55'	
	Alexo		
	Mount Hawk 115/45 S.W.		
2	Limestone, dark brown to black, micro-crystalline, brachiopod fragments numerous, few argillaceous partings, in beds 4" to 6"; weathers light grey tan, moderately resistant.	52'	107.0'
3	Limestone, dark brown to black, very argillaceous bedding indistinct; weathers light brown grey.	30'	137.0'
4	Interbedded limestone, dark brown, fine-crystalline; weathers light rusty brown: shale, dark brown, sheared, thin-bedded, bottom of unit forms base of rubbly weathering cliff.	29'	166.0'

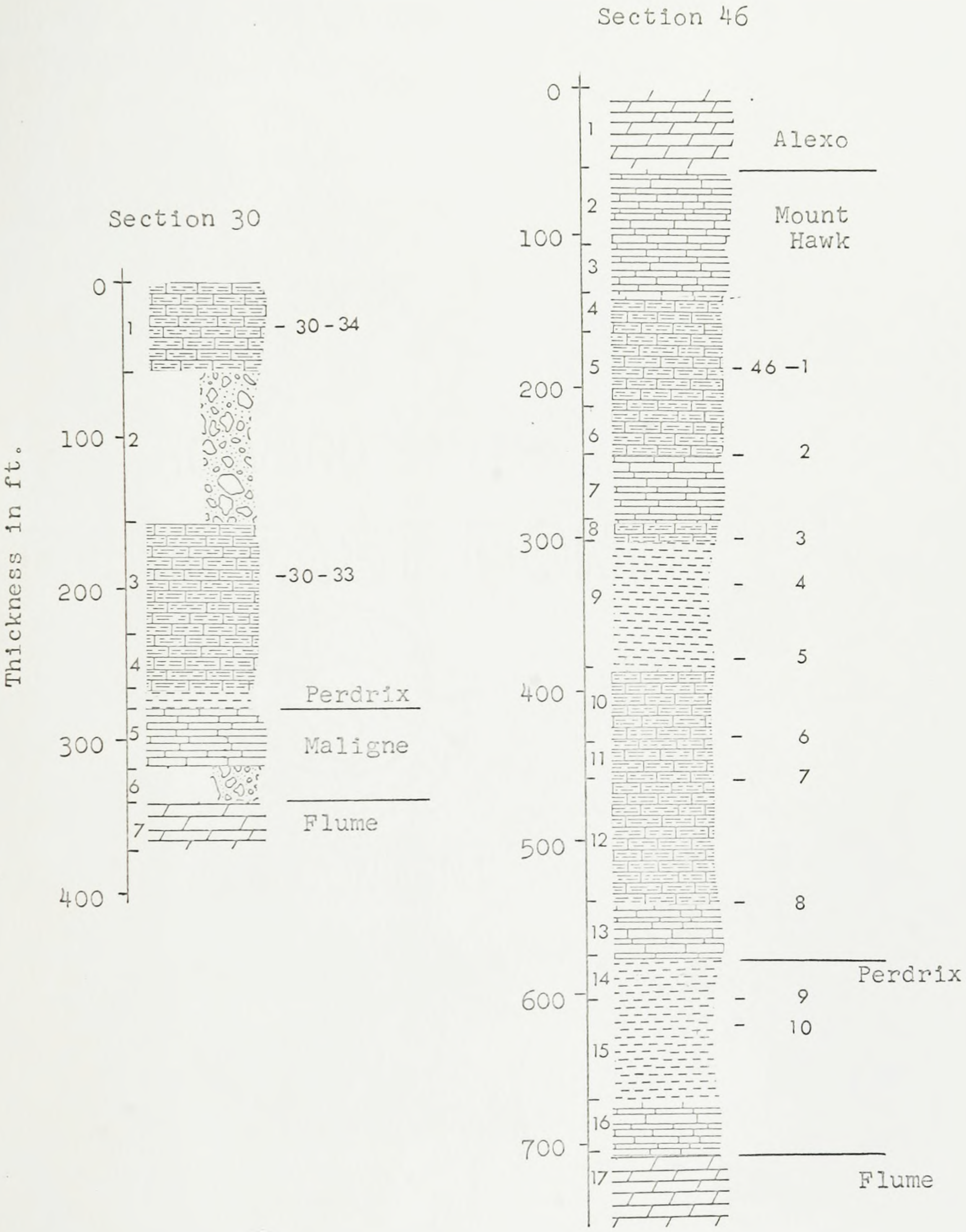
Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
5	Interbedded shale, beds 6" thick, very dark brown, sheared, calcareous, fine-grained; weathers light brown: limestone, micro-crystalline, nodular; weathers light grey in beds 1" to 2" thick, recessive.	49'	215.0'
6	Interbedded shale, dark brown, fine-grained calcareous, sheared, in part fissile; weathers medium brown: limestone in beds up to 6" thick, weathers medium grey in part nodular, moderately resistant.	30'	245.0'
7	Limestone, fine-crystalline, argillaceous, very dark brown black, numerous very calcareous shaly partings commonly 1" wide; weathers very irregularly or rubbly, in part blocky, medium grey to buff, moderately resistant.	44'	289.0'
8	Interbedded limestone, very argillaceous, dark brown to black, nodular, in beds 3' to 6" thick, numerous shaly partings; weathers brown to buff: shale dark to medium brown, sheared in beds 1" to 2" thick, calcareous, fine-grained; weathers light brown.	12'	301.0'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
9	Shale, fine-grained, medium brown, thin-bedded, in part fissile, few interbeds of nodular limestone; weathers very light brown, flecky, recessive.	86'	387.0'
10	Interbedded shale, calcareous, dark brown, very fine-grained, thin-bedded; weathers medium to dark brown, partially covered: limestone, argillaceous, dark brown to black, micro-crystalline, in beds 2" to 6", recessive.	47'	434.0'
11	Interbedded shale, dark brown, calcareous, fine-grained, in part thin-bedded to platy; weathers dark grey and medium brown: limestone dark brown and black, cleaves easily, argillaceous, fine-crystalline, in beds 4" to 6", resistant.	25'	459.0'
12	Interbedded shale, very calcareous, fine-grained, black, very platy; weathers dark grey to black: limestone, thin-bedded, argillaceous, dark grey to black, numerous argillaceous partings, cleaves in the plates, in beds 4" to 6", resistant.	84'	543.0'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
13	Limestone, argillaceous, dark grey black, argillaceous and shaly partings, few elongated chert blebs, in beds 6" to 1'; weathers rusty brown, moderately resistant.	32'	575.0'
	Mount Hawk		
	Perdrix		
14	Partially covered. Shale, black, calcareous, fissile, few more competent limestone beds; weathers black, very recessive.	30'	605.0'
15	Interbedded limestone dark grey to black, argillaceous, fine-crystalline to microcrystalline, in beds 2" to 6"; weathers light to medium grey brown: shale, calcareous, black, fissile, in bands up to 6" thick; weathers black, platy, recessive.	66'	671.0'
	Maligne		
16	Limestone, dark grey to black, few sparny calcite blotches, few argillaceous partings, microcrystalline, in very regular beds of 2" to 4", weathers medium grey to light grey brown, resistant.	36.5'	707.5'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Flume		
17	Dolomite, fine crystalline, dark brown, fetid, argillaceous, contains lenses of black cherty along bedding planes, uniform bedding 2" to 4"; weathers medium brown to buff, moderately resistant.		

Sections 30 and 46, showing sample locations.



Section C (Mississippian, Banff and Exshaw)

Location: Longitude 117° 58' W.

Latitude 52° 32' N.

A small creek draining the water from the valley north west of Arete and Valley Head Mountains flows south east of Mount Isaac and eventually into the Brazeau River.

Section C was measured on the south west side of Valley Head Mountain approximately 1.75 miles upstream from where the River changes direction to north east from north west. The entire Exshaw and Banff are exposed and accessible.

Section C, looking east toward Valley Head Mountain.

Description of Section C

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Rundle (A) limestone.		
	Banff		
1	Shale, calcareous, dark grey green, finely grained, in part fissile; weathers grey to black, slaty, recessive.	134'	
2	Shale, calcareous, dark grey to black, finely grained, numerous limestone interbeds 1/2" thick; weathers platy, black, recessive. Lower 4' composed of limestone, argillaceous, micro-crystalline, fossiliferous, in beds 1/2" thick; weathers platy, very dark grey.	10'	144'
3	Shale, calcareous, dark brown, finely grained, in part fissile; weathers light to medium grey.	12'	156'
4	Shale, calcareous, light green grey, finely grained, platy, in part fissile; weathers very light green grey.	12'	168'
5	Interbedded limestone, coarse to finely crystalline, mostly fossil hash; weathers light grey, thin bedded, resistant: shale, calcareous, green grey, in part fissile; weathers very light grey.	13'	181'

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
6	Shale, calcareous, fissile, medium grey to light green, bottom 5' contain few 2" limestone beds spaced 6" apart; shale weathers medium grey green.	31'	212'
7	Shale, calcareous, dark grey to near black, finely grained, fissile: weathers black slightly rusty.	33'	245'
8	Shale, calcareous, medium grey slightly greenish, numerous brachiopods, indurated, dense; weathers greenish brown contains numerous iron stains, few concretions.	14'	259'
9	Exshaw (?) Shale, non-calcareous, fissile, silty, jet black, in part very dark brown; weathers dark grey to dark brown, recessive.	4'	263'
10	Shale, non-calcareous, silty, jet black to dark grey, in part fissile; weathers dark grey with tinge of rusty orange.	12'	275'
11	Costigan Limestone, finely crystalline, dark grey to black in beds 1' to 6", argillaceous, few brachiopods; weathers		

Section RA (Mississippian, Exshaw)

Location:	Longitude 117° 00' W.
	Latitude 52° 39' N.

Section RA, comprising the Exshaw Fm., was measured on the southeast side of the mountain that rises immediately to the west of the junction between Cairn and Southesk Rivers.

The Exshaw Fm. studied lies on top of the more resistant Costigan Fm. and Palliser cliff. Section RA was measured at the top of a talus slope which rises from the terrace above the west bank of the Southesk River approximately two miles upstream from the forks.

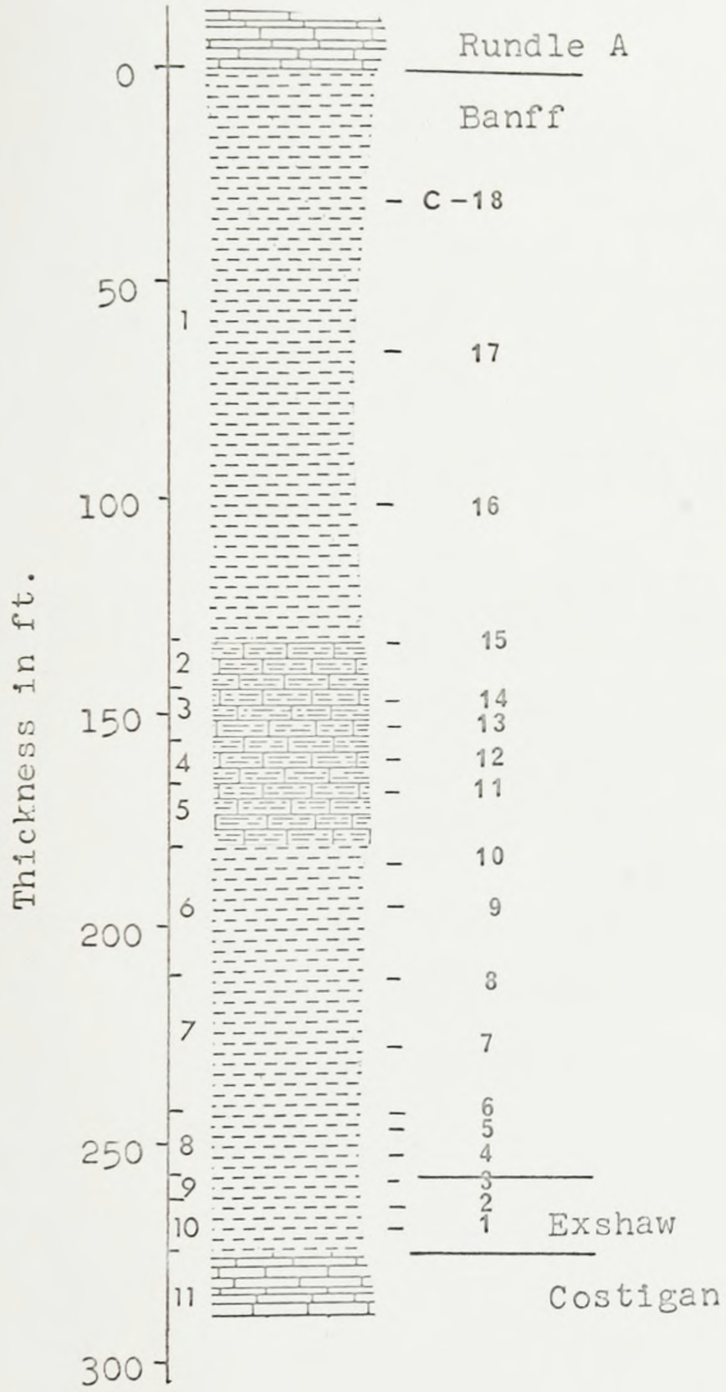
Description of Section RA

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Banff		
1	Interbedded shale, finely grained, fissile, black, in part dark brown, in beds up to 15' thick, shale makes up 90% of unit; weathers dark grey to black: limestone, dark grey, finely crystalline, in beds 4" to 6" thick; weathers dark grey to buff.		
	Exshaw		
2	Shale, black, fissile, slightly calcareous, silty, finely grained, papery, several more competent interbeds; weathers buff-brown and rusty.	15'	
3	Shale, grey to black, slightly calcareous, silty, fine grained, in part fissile; weathers buff and rusty.	1.5'	
4	Costigan limestone.		

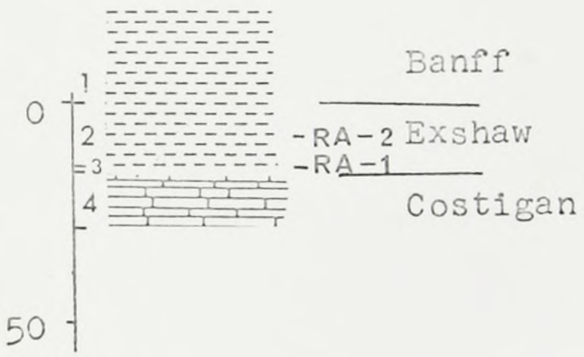
Mississippian

Sections C and RA, showing sample locations.

Section C



Section RA



Section D (Triassic, Whitehorse)

Location:	Longitude	116° 56' W.
	Latitude	52° 31' N.

A small creek draining the waters from the valley N.W. of Arete and Valley Head Mountains flows S.E. of Mt. Isaac and eventually into the Brazeau River.

Section D was measured approximately 1.5 miles on the west bank downstream from a lake which feeds the creek at its head.

The lower contact between Sulphur Mt. and Whitehorse Fms. is exposed but the upper part of the Whitehorse Fm. is faulted and covered.

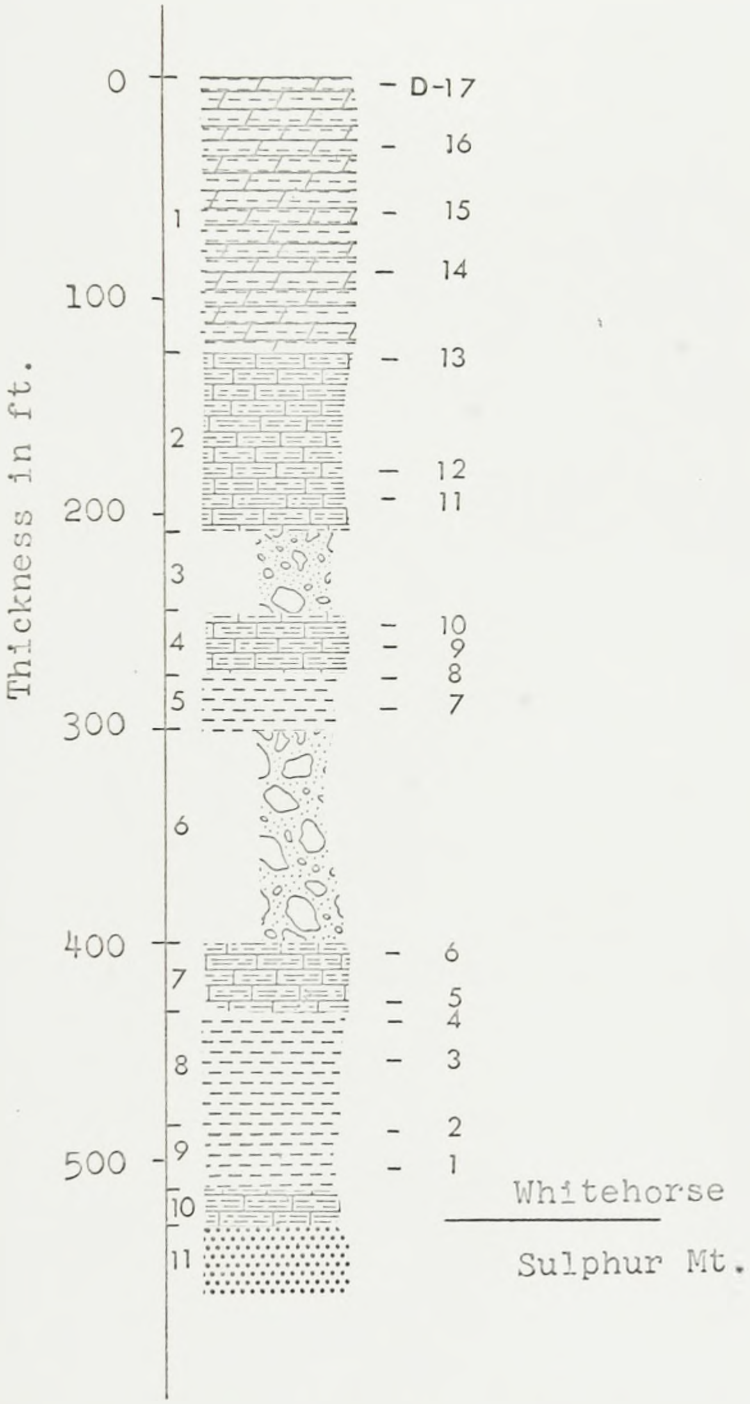
Section D, looking directly west toward a ridge which forms part of Sawtooth Mountain.

Description of Section D (Triassic)

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Beginning of measurement near top of Whitehorse. Fault zone highly contorted.		
1	Mudstone and argillaceous dolomite, in part silty, fine grained, red, pink and buff; weathers buff to pink, in part brecciated.	125'	
2	Dolomite and limestone, in part mudstone, very argillaceous, maroon to green, lacks bedding, brecciated, finely grained; weathers maroon, and buff.	85'	210.0'
3	Covered interval, probably green and red mudstone.	35'	245.0'
4	Dolomite and very argillaceous limestone, fine grained, red, maroon, and green, bedding indistinct; weathers green and maroon, recessive.	30'	275.0'
5	Shale, or argillacecus limestone, very light grey to white, bedding indistinct, porous, crumbly; weathers orange-yellow, very recessive.	25'	300.0'
6	Covered, same as unit 5.	100'	400.0'

Triassic

Section D, showing sample locations.



Section M (Jurassic, Fernie)

Section M was measured at two localities by Dr. E.W. Mountjoy. For description of the sections see Frebold (1957, p. 108).

Morris Creek Section

Location:	Longitude	117° 49' W.
	Latitude	53° 09' N.

Morris Creek flows N.E. into the Fiddle River. Samples M-2 to M-13 were taken at the Morris bridge situated on the highway about half-way between Pocahontas and Miette Hot Springs.

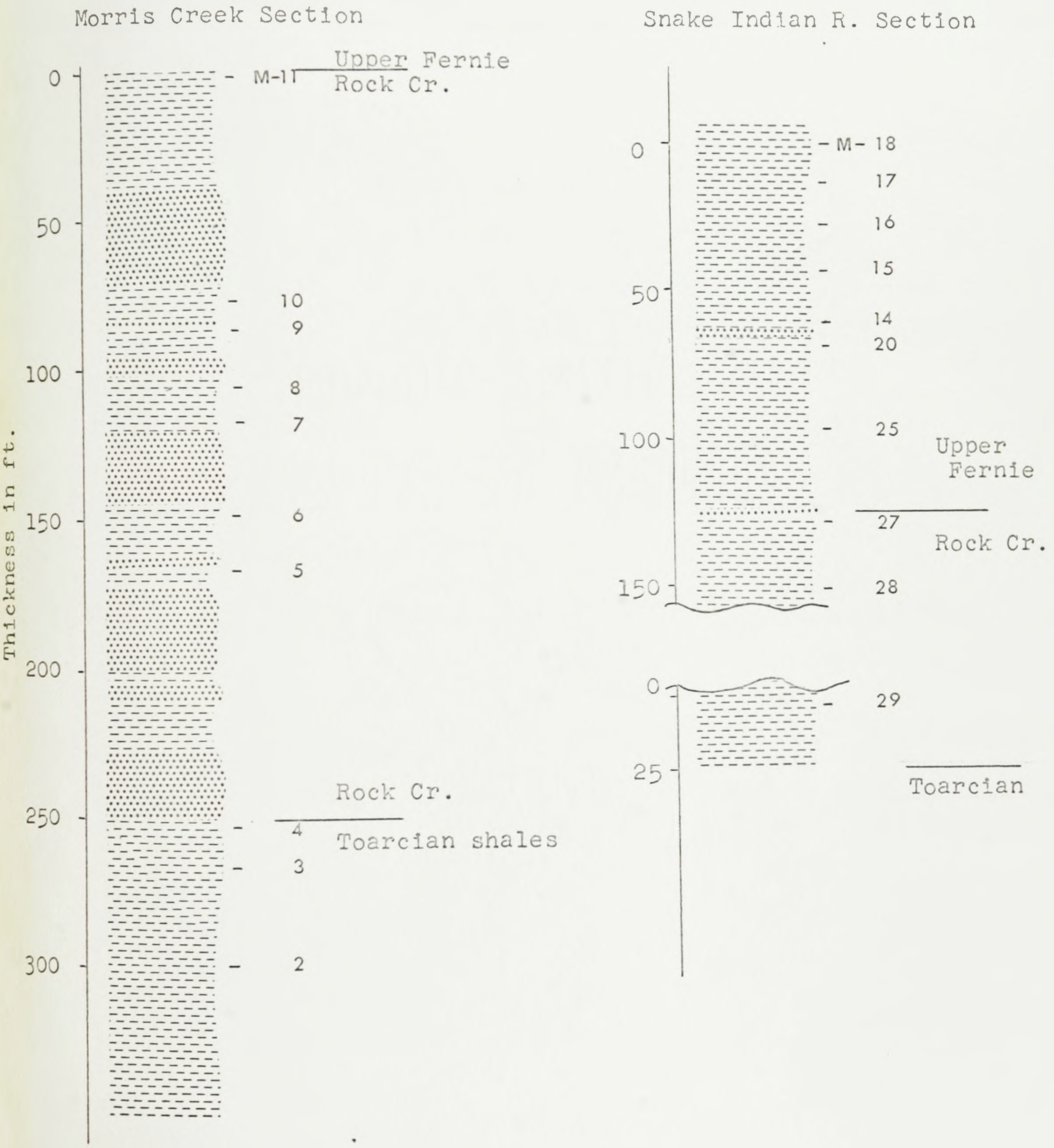
Snake Indian River Section

Location:	Longitude	118° 15' W.
	Latitude	53° 18' N.

Samples M-14 to M-30 were taken from a section of the Fernie Fm. on the N.E. bank of the Snake Indian River approximately one mile below the Snake Indian Falls.

Jurassic

Sections M, showing sample locations.



Section H (Kaskapau or Blackstone Fm.)

Location:	Longitude	117° 19' W.
	Latitude	53° 02' N.

The C.N.R. runs approximately north and south through the Town of Cadomin. The railway track has been cut perpendicular to strike and exposes the Lower Cretaceous Mountain Park or Dunvegan Fm. and the overlying Kaskapau (Blackstone) Fm.

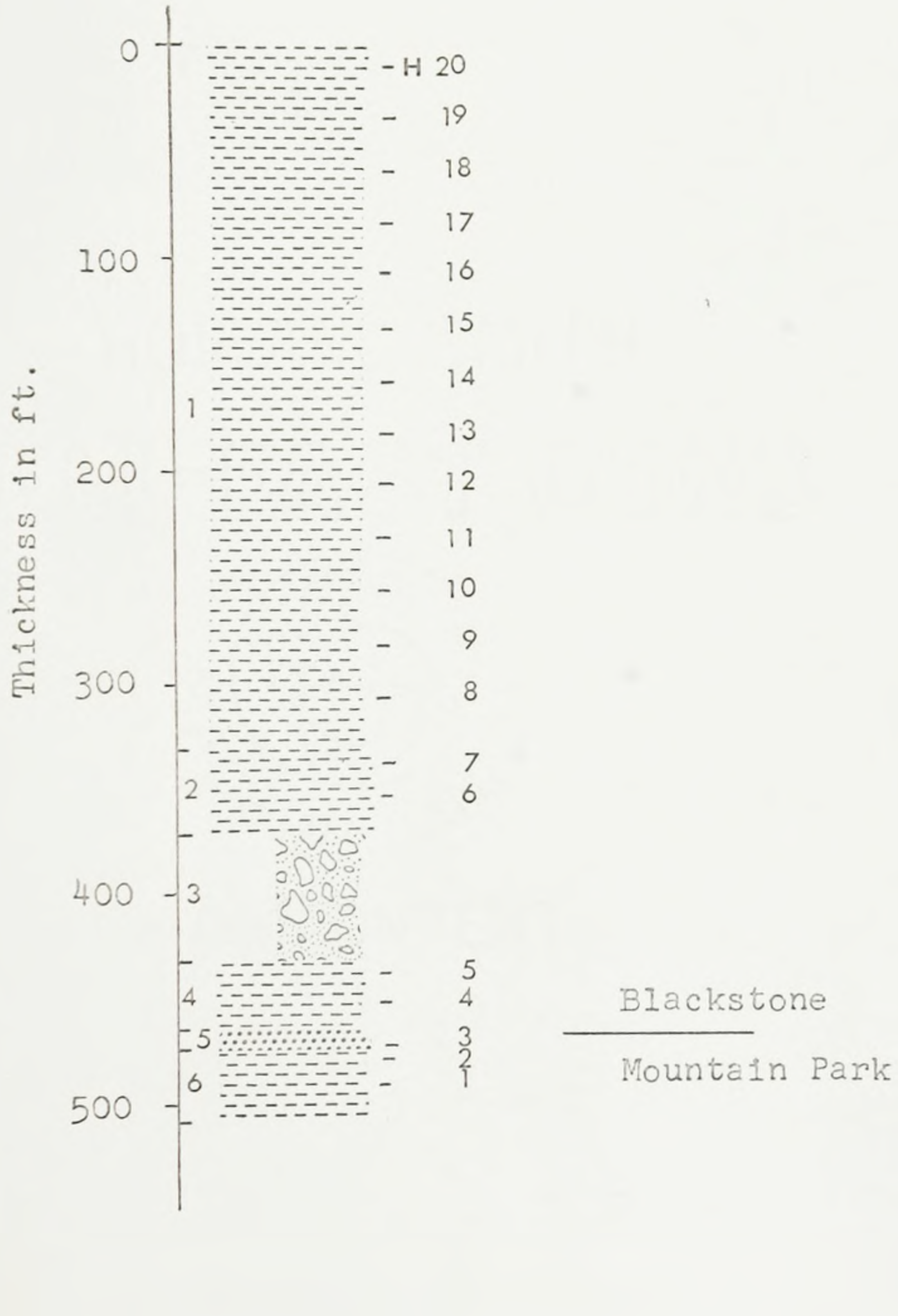
Section H was measured on the west bank of the railroad cut. The section dips vertically and is totally exposed.

Description of Section H

Unit	Lithology	Thickness (ft.)	Total Thickness (ft.)
	Beginning of section within Blackstone Fm.		
1	Shale, black, fine grained, fissile, very thin bedded, numerous silt stringers and concretions; weathers black to dark grey, platy-concretions up to 6" thick.	332'	
2	Shale, in part silty, very finely laminated, papery, dark grey to black, fine grained; weathers medium grey to black in part few very dark maroon beds, somewhat resistant.	72'	374'
3	Covered interval, probably black shale as in unit 4.	55'	429'
4	Shales, fine grained, black, very uniform; weathers black to deep maroon, platy, recessive.	36'	465'
5	Siltstone, very argillaceous, grey, in part appears to be concretionary, bedding indistinct, few interbeds of green shale, both dark green and light green; weathers maroon to green, in part rusty.	9'	474'
6	Shale, fine grained, medium to dark green, glauconitic ?, in part fissile and in part a mudstone, in beds 1/4" to 2", few silty beds; weathers green grey, platy, recessive.	34'	508'

Cretaceous

Section H, showing sample locations.



APPENDIX II

CHEMICAL ANALYSES

Major Element Analyses (Wt. Percent)

	I-2	I-12	B-10	B-18	C-2	C-17	D-4	D-16	H-8	H-18	M-9	M-15	28-3	46-1
SiO_2	52.25	54.14	36.77	47.49	78.72	34.93	67.61	37.79	70.35	66.26	75.05	58.24	26.99	26.57
Al_2O_3	25.00	23.45	9.15	12.55	8.68	9.65	8.19	4.75	13.66	16.31	12.14	16.24	8.36	8.67
Fe_2O_3	1.03	.53	.84	3.31	.74	1.11	.62	.70	1.79	2.82	2.70	1.72	1.31	1.06
FeO	5.71	5.49	.33	1.29	.76	2.67	.35	.12	2.17	1.39	.76	3.27	1.68	1.72
CaO	.04	.74	13.58	12.94	.11	20.46	6.53	28.86	.35	.21	.37	2.19	29.93	28.70
MgO	2.21	2.21	9.88	2.08	.91	4.87	3.14	.98	1.44	1.30	.71	2.36	1.89	2.92
Na_2O	.35	.58	.00	.47	.26	.27	1.13	.52	.84	.48	.66	.91	.36	0.18
K_2O	6.22	5.39	6.89	5.54	3.85	3.23	3.50	2.17	2.20	2.94	2.17	3.32	2.50	2.78
TiO_2	.89	.76	.37	.47	.41	.41	.51	.31	.70	.84	.67	.75	.31	.35
P_2O_5	.10	.10	.06	.11	.03	.17	.81	.08	.18	.17	.14	.23	.12	.07
C	.12	.07			2.31	.26		.10	.87	1.17	.38	1.05	.35	.22
MnO	.03	.11	.00	.12	.01	.05	.01	.01	.02	.00	.01	.02	.07	.04
H_2O^{+140}	4.61	4.15	.66	2.25	1.90	2.62	.86	.63	4.06	4.40	2.88	4.00	2.03	2.09
H_2O^{-140}	.32	.29	.35	1.09	.79	.96	.43	.20	1.51	2.10	1.58	2.21	.46	.51
CO_2	.01	1.05	20.67	10.39	.02	18.37	6.60	22.48	.03	.02	.03	2.37	23.53	23.78
Total	98.89	99.06	99.55	100.10	99.50	100.03	99.60	99.70	100.17	100.41	100.25	98.88	99.89	99.66