CHAPTER IV

GEOCHEMICAL FACIES ANALYSIS OF THE ORDOVICIAN CARBONATE SEDIMENTS

The geochemical facies analysis is dependent upon many factors, notably, climatic influences, tectonic influences, provenance of the sediments, sedimentation rate, grain-size distribution, biological influences, geological age, and influences of diagenesis (Ernst, 1970). Opinions are divided as to the diagenetic information provided by trace elements for the genetic interpretation of carbonate rocks. Despite the fact that only very few studies have been done on this aspect, trace element analysis has been used in the following situations : (i) subdivision of shallow marine environment, (ii) differentiation of shallow-water and deep-water limestone, (iii) indication of the kind of sedimentation, (iv) support of interpretation of microfacies types with geochemical data, (v) explanation of early diagenetic and late diagenetic solution processes, and (vi) statements about ecological efficient environment factors (Flügel, 1978). However, the applications of trace elements in the genetic interpretation of carbonate rocks are limited and are not statistically supported at present.

4.1 Geochemical facies profiles.

In this investigation, altogether 122 samples of the Ordovician carbonate sediments from the three measured sections and the mineralized zone have been employed in the geochemical facies analysis. Among these, 57 samples are obtained from the Dewatering

Drift to Huai Chanee section, 18 samples are obtained from the drill-hole number 68, 22 samples are obtained from the drill-hole number 67, and 25 samples are obtained from the mineralized zone. It is noted that, samples obtained from the bottom part of the Dewatering Drift to Huai Chanee section and the drill-holes number 68, and 67 are also considered to be the upper part of the mineralized zone.

All of the 122 samples are quantitatively determined for the acid insoluble residue, calcium, magnesium, iron, strontium, manganese, barium, cobalt, lead, zinc, silver, arsenic, nickle, and mercury. However, the preliminary evaluation of silver, arsenic, nickle, and mercury contents of the Ordovician carbonate sediments samples reveal that they are too low to be detected by the atomic absorption spectrophotometric method. Therefore, the analyses of these four elemental compositions have to be given up. The measuring conditions, absorption sensitivities, and precision for these elements are presented in Table D-1 (Appendix D).

The geochemical facies profiles of the three measured sections are summarized and presented in Figures 4.1a, b, and c, and the analytical results are tabulated in Table 4.1a, and the graphic presentation of the analytical results are presented in Figure 4.1d. With respect to the concentrations of various geochemical parameters and different calcite/dolomite ratios in Figure 4.1d, their patterns are not well understood. The reliability of an adequate sample size has also been determined (Table 4.1b).

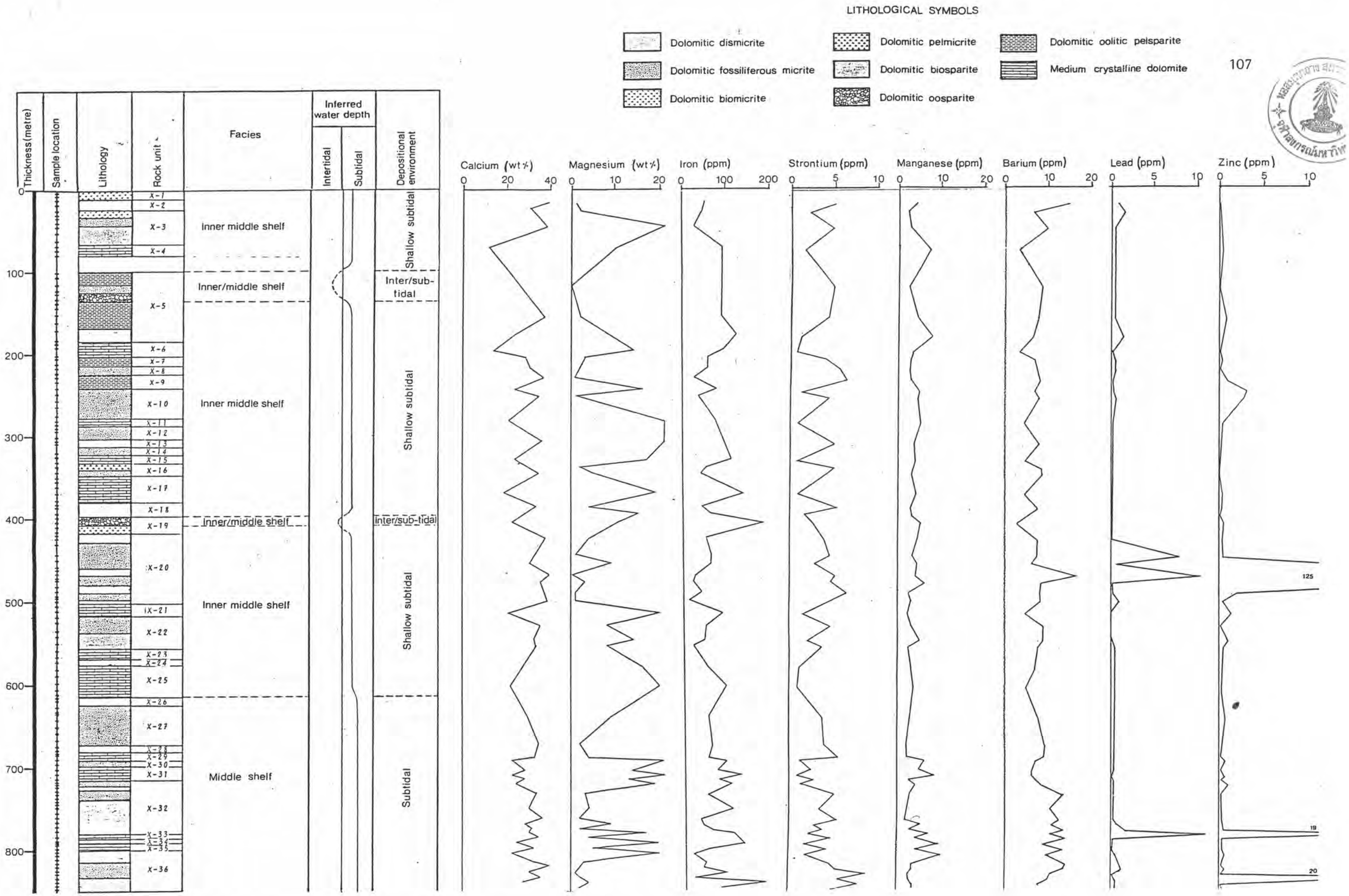

Figure 4.1a The graphic presentation of the distribution pattern of the geochemical parameters of the Dewatering Drift to Huai Chanee section.

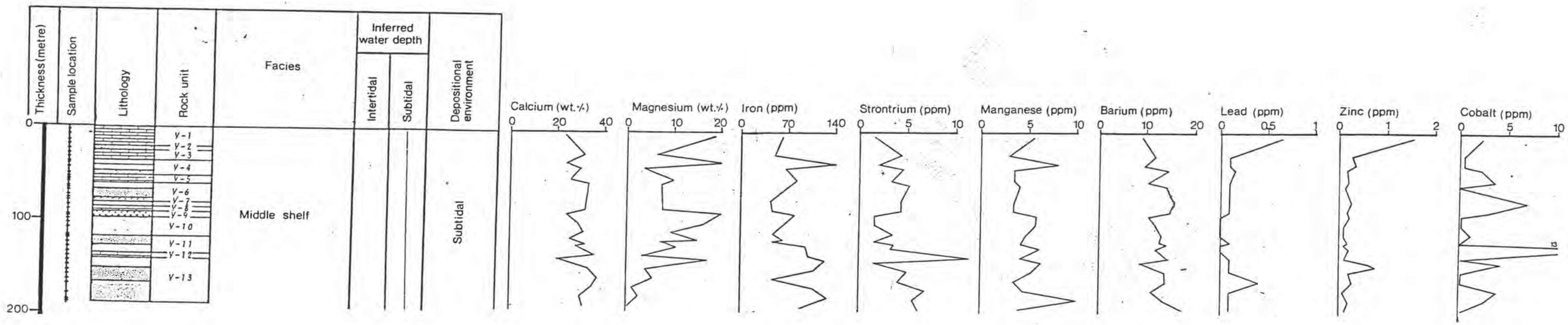

Figure 4.1b The graphic presentation of the distribution pattern of the geochemical parameters of the drill-hole number 68 section.

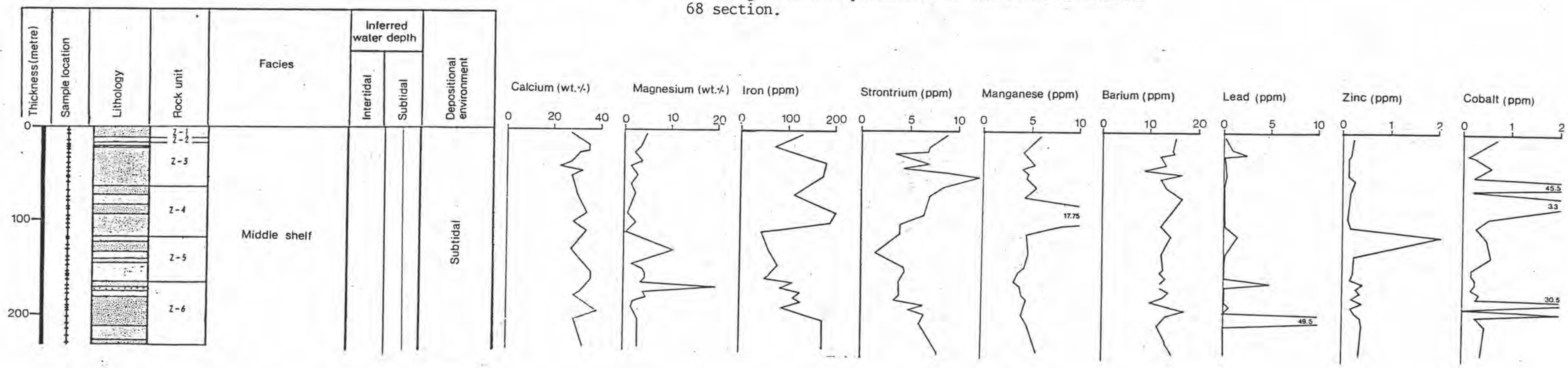

Figure 4.1c The graphic presentation of the distribution pattern of the geochemical parameters of the drill-hole number 67 section.

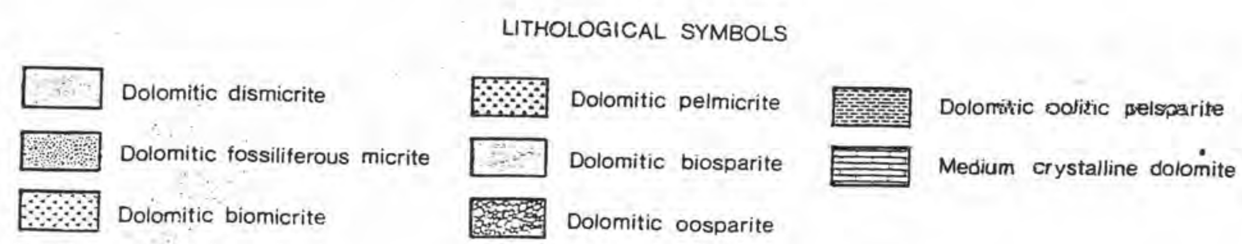

Table 4.1a The analytical results of the geochemical parameters.

Parameters	C/D<=0.1	C/D<=1.0	C/D<=9.0	C/D>9.0	Total
Calcium (wt.%)					
Range	11.63-38.75	23-31.25	22.5-37.5	29.4-65	11.63-38.75
Mean	23.71	27.58	32.07	36.32	30.91
Standard Deviation	6.4	2.69	2.95	6.95	6.35
Magnesium (wt.%)					
Range	10.6-21	8.8-16.5	1.55-9.5	0.08-2	0.08-21
Mean	18.96	13.39	4.21	1.18	7.38
Standard Deviation	2.67	2.61	2.04	0.56	6.77
Iron (ppm.)					
Range	17.6-158	46-109	2.8-190	11-203	2.8-109
Mean	92.29	83.5	85.02	70.87	83.07
Standard Deviation	35.98	34.43	49.89	42.90	44.9
Strontium (ppm.)					
Range	0.73-5.17	1.18-3.42	2.87-12.10	2.33-44.19	0.73-44.19
Mean	1.87	2.09	5.21	7.22	4.64
Standard Deviation	1.27	0.71	1.91	5.99	4.43
Lead (ppm.)					
Range	0-0.65	0-10.85	0-4.8	0-49.5	0-49.5
Mean	0.23	0.99	0.36	3.42	1.08
Standard Deviation	0.16	0.75	0.14	2.13	0.99
Zinc (ppm.)					
Range	0.1-1.53	0.12-19.1	0.08-20.20	0.09-124.5	0.08-124.5
Mean	0.52	1.90	0.69	8.91	2.58
Standard Deviation	0.37	0.82	0.27	7.06	0.24
Barium (ppm.)					
Range	3.33-13.94	2.83-12.72	6.11-16.78	6.67-17.39	2.83-17.39
Mean	7.43	8.65	11.89	11.16	10.52
Standard Deviation	2.8	2.97	2.79	3.23	3.41
Manganese (ppm.)					
Range	2.4-10.25	3.20-8.0	2.35-9.91	1.85-17.75	1.85-17.75
Mean	5.6	5.0	4.16	4.16	4.53
Standard Deviation	2.25	1.45	1.3	3.05	2.09
Cobalt (ppm.)					
Range	0-4.14	0-11.34	0-30.3	0-3.72	0-30.3
Mean	0.40	1.13	1.38	0.32	0.95
Standard Deviation	0.03	0.98	0.47	0.02	0.03
Acid insoluble residue (wt.%)					
Range	1.10-49.16	2.84-26.67	2.66-40.75	1.59-20.94	1.10-49.16
Mean	10.35	9.42	12.72	9.82	11.20
Standard Deviation	2.49	6.92	8.14	5.46	8.68

C/D = Calcite/Dolomite ratio. Number of sample = 122.

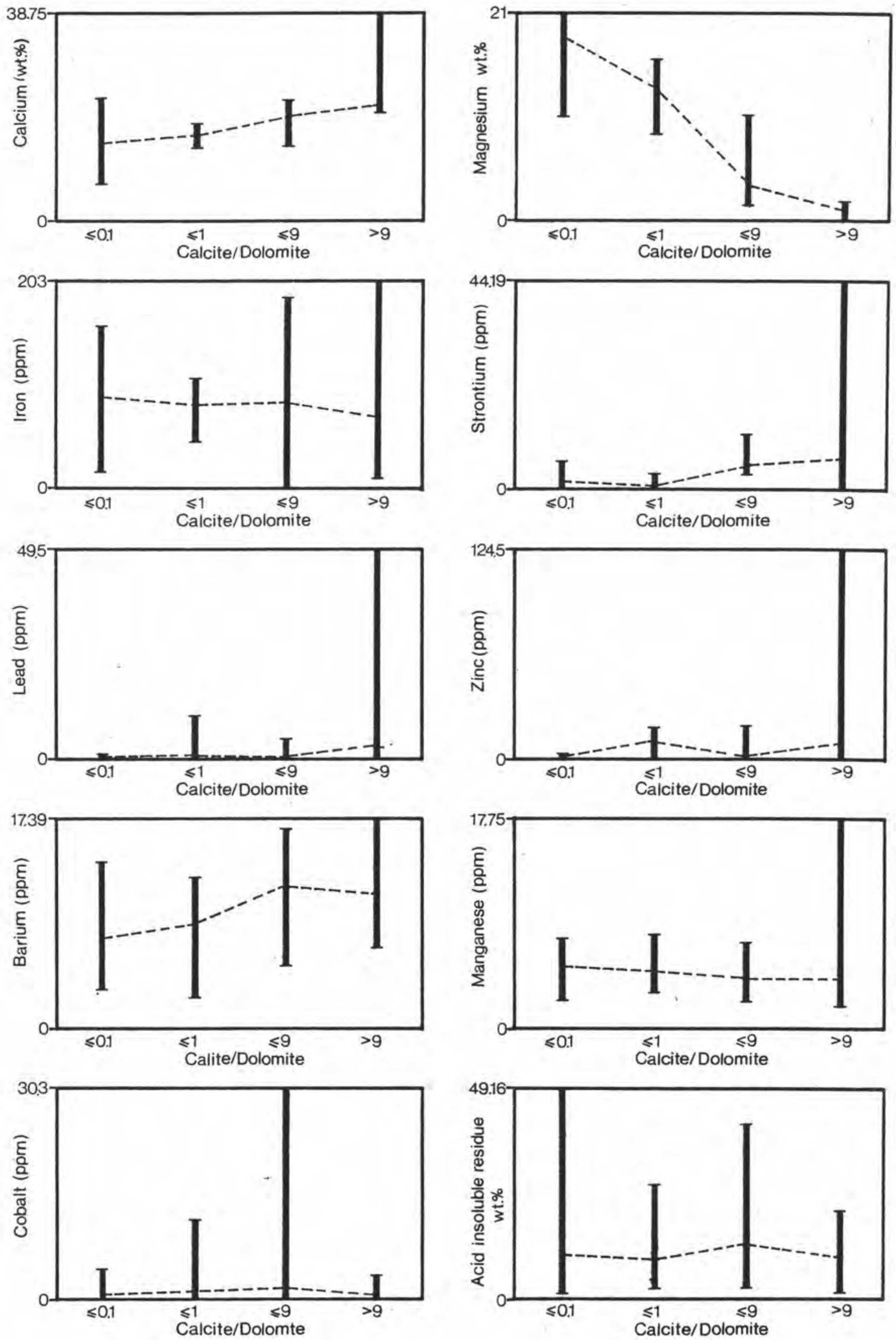

Figure 4.1d The graphic presentation of the analytical results of the geochemical parameters in Table 4.1a (dash line connecting the mean values).

Table 4.1b Sample size needed for 0.95 and 0.99 probability that population mean lies within 5 units of sample mean (Dennison, 1962).

Parameters	Initial Sample Standard Deviation	Number of initial Sample	Number of Needed sample	
			0.95 confidence limit	0.99 confidence limit
Calcium	6.35	122	7	9
Magnesium	6.77	122	10	22
Iron	44.90	122	325	560
Strontium	4.43	122	4	7
Lead	0.99	122	6	10
Zinc	3.24	122	33	51
Barium	3.41	122	3	4
Manganese	2.09	122	2	3

4.2 Relationships among the geochemical parameters.

Among the geochemical parameters in this study, calcium and magnesium are considered to be the major elements, iron, lead and zinc are considered to be the minor elements, and strontium, barium, manganese and cobalt are considered to be the trace elements. For lead and zinc, they are trace elements in the non-mineralized carbonate sediments, and minor elements in the mineralized zone.

The relationships among these geochemical parameters are determined using the correlation matrices (Table 4.2a), and the significance of the geochemical parameters has been determined (Table 4.2b). On the basis of the correlation matrices, the following conclusions can be drawn.

The correlation matrices of elemental composition of 122 samples of the Ordovician carbonate sediments both of non-mineralized and mineralized zones indicate that there is a very strong positive correlation ($r=+0.8144$) between lead and zinc. This indicates that they co-exist in carbonate sediments as well as in the mineralized zones. Besides, the strong positive correlations between lead and barium ($r=+0.6133$), zinc and acid insoluble residue ($r=+0.5315$), and barium and strontium ($r=+0.5204$) indicate that the lead, zinc, barium, strontium, and acid insoluble residue are predominantly present in relatively lower contents in the carbonate sediments. The strong positive correlation between barium and lead indicates that barium is presented both as trace element in carbonates (minor contribution) and barite in the mineralized zone (major contribution) and lead is related to the lead which is presented both as trace

Table 4.2a The correlation matrices of the geochemical parameters.

	Sr	Pb	Zn	Ba	Mn	Mg	Ca	Fe	Ca/Mg
Pb	0.1887								
Zn	0.1127	0.8144							
Ba	0.5204	0.6133	0.3578						
Mn	-0.1169	-0.0564	-0.1156	0.0275					
Mg	-0.5050	0.0922	-0.0181	-0.1835	0.2223				
Ca	0.3993	-0.2794	-0.3651	0.1369	-0.1656	-0.4402			
Fe	0.1831	-0.1000	-0.1305	-0.0280	0.4626	-0.0133	-0.2555		
Ca/Mg	0.1500	-0.0444	0.0440	0.0046	-0.0858	-0.3454	0.1894	-0.0208	
RS	0.1712	0.4854	0.5315	0.1817	-0.0346	-0.1520	-0.5405	0.3030	-0.1138

RS = Acid insoluble residue.

Number of sample = 122.

Table 4.2b The correlation coefficients and significance of the geochemical parameters.

Correlation coefficients		t	Significant 95%	99%	99.9%	Not significant
Pb-Zn	r = +0.8144	+14.9864			x	
Pb-Ba	r = +0.6133	+8.2906			x	
Zn-RS	r = +0.5315	+6.6999			x	
Ba-Sr	r = +0.5204	+6.5073			x	
Pb-RS	r = +0.4854	+5.9277			x	
Fe-Mn	r = +0.4626	+5.5708			x	
Ca-Sr	r = +0.3993	+4.6505			x	
Zn-Ba	r = +0.3578	+4.0909			x	
RS-Fe	r = +0.3030	+3.3950			x	
Mg-Mn	r = +0.2223	+2.4345	x			
Pb-Sr	r = +0.1887	+2.0511	x			
Fe-Sr	r = +0.1831	+1.9890	x			
RS-Ba	r = +0.1817	+1.9728				x
RS-Sr	r = +0.1712	+1.8554				x
Ca/Mg-Sr	r = +0.1500	+1.6198				x
Ca-Ba	r = +0.1369	+1.4758				x
Fe-Zn	r = -0.1305	-1.4055				x
RS-Mg	r = -0.1520	-1.6417				x
Ca-Mn	r = -0.1656	-1.7931				x
Mg-Ba	r = -0.1835	-1.9933	x			
Ca-Fe	r = -0.2555	-2.8212		x		
Ca-Pb	r = -0.2794	-3.1071		x		
Ca-Zn	r = -0.3651	-4.1879			x	
Mg-Sr	r = -0.5050	-6.2464			x	
Ca-RS	r = -0.5405	-6.8587			x	

r = correlation coefficient between parameters.

t = T-test values.

RS = Acid insoluble residue.

Number of sample = 122.

element in carbonates (minor contribution) and galena in the mineralized zone (major contribution). The strong positive correlation between barium and zinc is similar to that of for barium and lead except the zinc content is relatively lower. For relatively less positive correlation between barium and strontium (r=+0.5204) this indicates that they are both presented as trace element in the carbonate rocks. For the strongly negative correlation between calcium and acid insoluble residue (r=-0.5405), and magnesium and strontium (r=-0.5050) they probably indicate that the overall contents of acid insoluble residue in dolomite is generally higher than that of carbonates, and the strontium content in calcite is relatively higher than that of dolomite.

4.3 Geochemical characteristics of the mineralized and non-mineralized zones.

The determination of iron, strontium, barium, manganese, cobalt, and acid insoluble residue contents of the Ordovician carbonate sediments in the non-mineralized and mineralized zones has revealed that the strontium, barium, and acid insoluble residue contents of the mineralized zone are relatively higher than the non-mineralized zone, whereas the iron and cobalt contents are relatively lower than the non-mineralized zone. The manganese content of both mineralized and non-mineralized zones shows only slight different. The variation in this elemental composition is summarized in Table 4.3.

Table 4.3 The analytical results of some geochemical parameters in the mineralized, and non-mineralized zones.

Parameters	$\bar{X} \pm SD$	
	Mineralized zone	Non-mineralized zone
Iron (ppm.)	64.48 ± 39.85	85.99 ± 44.51
Strontium (ppm.)	4.60 ± 2.14	4.39 ± 2.30
Barium (ppm.)	12.81 ± 7.40	10.57 ± 3.46
Manganese (ppm.)	4.18 ± 3.13	4.40 ± 1.65
Cobalt (ppm.)	-	0.95 ± 0.06
RS (wt.%)	13.70 ± 6.60	11.96 ± 9.05

\- = Less than detection limit.

RS = acid insoluble residue.

Number of sample in mineralized zone = 25.

Number of sample in non-mineralized zone = 97.

It is important to note that, the Ordovician carbonate host rock of the mineralized zone is entirely characterized by dolomite. Therefore, an attempt has been made to compare these trace elemental compositions and acid insoluble residue of the mineralized zone with the non-mineralized zone. The results reveal that the strontium and barium contents of the mineralized zone are higher than those of the non-mineralized zone, whereas the iron, manganese, and cobalt are lower than the non-mineralized zone (Table 4.3).

The higher iron content in the non-mineralized carbonate sediments than that of the mineralized carbonate sediments is probably due to the presence of fine-grained pyrite. The lithological characteristics of the non-mineralized carbonate sediments is well-known to be the so-called "dark limestone series" (Diehl and Kern, 1981). Therefore, the dark coloration is mainly due to the presence of finely divided pyrite material. The relatively high barium content in the mineralized carbonate sediments is basically due to the presence of barite, as a gangue mineral, in the mineralized zone.

In conclusion, the contents of strontium, barium, and acid insoluble residue are relatively high in the mineralized zone which can be of significant in indicating the mineralized zone.