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LITHOGEOCHEMISTRY OF THE DINANTIAN STRATA OF THE CAMPINE-BRABANT BASIN (NORTHERN BELGIUM)[1]

by

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(9 figures and 14 tables)

ABSTRACT.- The geochemical distribution patterns of Mg, Sr, Na, Zn, Pb, Fe, Mn, organic carbon and K in the Dinantian carbonates of the Campine-Brabant Basin have been investigated. The distribution is influenced by the mineral content of clays, organic material, sulphides and oxides and by the processes of dolomitization, calcite cementation, neomorphism and karstification. Mg, Na, Fe and K are enriched in clayey limestones. During dolomitization Mg, Na, Mn, Fe and Zn were supplied and Sr was removed. The concentration of Fe and Mn is high in the strata with an important terrigenous component. They are mainly related to Fe- and Mn- oxyhydroxides. However, their contents are also high in veins, which formed as a result of stress periods, and in late diagenetic cemented, recrystallized and karstified limestones.

Numerous factors which influence the geochemical distribution in carbonate rocks, have been distinguished and interpreted by a combination of sediment petrographical and diagenetic investigations and a statistical treatment of geochemical data.

RESUME.- Les modèles de distribution géochimique de Mg, Sr, Na, Zn, Pb, Fe, Mn, carbone organique et K dans les carbonates du Dinantien dans le bassin de la Campine, ont été examinés. Cette distribution est influencée par le contenu minéralogique des argiles, de la matière organique, des sulfures et des oxydes, et par les processus de dolomitisation, de néomorphisme et de karstification. Mn, Na, Fe et K sont enrichis dans les calcaires argileux. Durant la dolomitisation, Mg, Na, Mn, Fe et Zn furent apportés et Sr fut emporté. Les teneurs en Fe et Mn sont élevées dans les couches à apport terrigène appréciable. Cependant, ces teneurs sont également importantes dans les veines, formées au cours de périodes de haute tension, et dans les calcaires recristallisés, karstifiés et cimentés tardivement.

De nombreux facteurs qui influencent la distribution géochimique dans les carbonates, ont été distingués et interprétés par combinaison d'approches différentes: pétrographie sédimentaire, investigation diagénétique et traitement statistique des analyses géochimiques.

1.- INTRODUCTION

The last fifteen years, lithogeochemistry of carbonates has been extensively used in paleoenvironmental studies (Veizer & Demovic, 1974; Kranz, 1976; Veizer *et al.*, 1977, 1978; Pascal, 1979; Coulon, 1979; Swennen, 1986; Swennen, *et al.*, 1986) and in geochemical prospections (Russell, 1974; Gwosdz & Krebs, 1977; Swennen & Viaene, 1981; Herbosch *et al.*, 1983; Préat *et al.*, 1983; Erickson *et al.*, 1983; Dejonghe, 1985, 1987a,b; Swennen, 1986; Van Oyen & Viaene, 1988; Clifford *et al.*, 1988). High Sr concentrations have been interpreted as an indication for hypersaline and deep sea rock types (Veizer & Demovic, 1974). However, although high concentrations of Fe and Mn have been used as an indication of the proximity of the continent (Pascal, 1979; Coulon, 1979), the study of Parker *et al.* (1985) showed that diagenetic alteration can destroy the primary signature. One of the most obvious results of the lithogeochemical investigations was the recognition of the large influence

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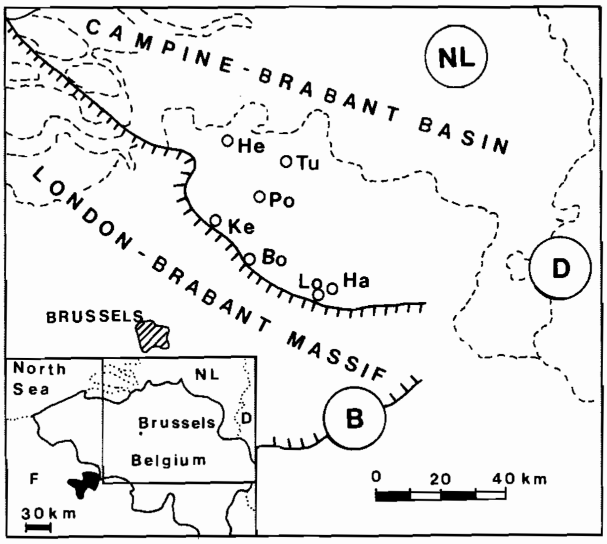

Fig. 1.- Location of the borehole which are geochemically investigated. The barbed lines mark the northern and southern border of the Dinantian strata

(Bo: Booischot; Ha: Halen; He: Heibaart; Ke: Kessel; Lo: Loksbergen; Po: Poederlee; Tu: Turnhout).

Table 1.- Sedimentation environment of the different Visean stages and sub-stages in the Campine-Brabant Basin.

Stage or substage and borehole	Sedimentation environment
Lower Moliniacian	
Booischot	Evolution of open marine subtidal to restricted, intertidal and supratidal
Kessel	Restricted and supratidal
Loksbergen	Open marine subtidal
Halen	Shallow, open marine subtidal
Turnhout	Lower part: intertidal to very shallow subtidal Upper part: shallow, open marine subtidal
Heibaart	No or very limited sedimentation
Upper Moliniacian	
Booischot	Lower part: restricted, intertidal and supratidal Upper part: restricted and open marine subtidal
Kessel	Lower part: evolution from open marine subtidal to intertidal Upper part: shallow, open marine subtidal
Halen	Cyclic sedimentation: from open marine subtidal to restricted
Turnhout	Subtidal sedimentation, but mostly eroded
Heibaart	Shallow, open marine subtidal
Reworked sequence	
Halen	Open marine subtidal, conglomerates and breccias
Turnhout	Cryptalgal sediments in subtidal environment (above wave base)
Livian	
Heibaart	Open marine subtidal (below wave base)
Lower Warnantian	
Halen	Cyclic sedimentation: from open marine subtidal to restricted
Turnhout	Cryptalgal sediments in subtidal environment (above wave base)
Heibaart	Lower part: subtidal at or just below wave base Upper part: development of a reef mound
Poederlee	Cyclic sedimentation: core, flank and top facies of reef mounds
Upper Warnantian	
Halen	Open marine subtidal and restricted
Turnhout	Open marine subtidal

of the non-carbonate phase on the distribution of trace elements in carbonate rocks (e.g. Barber, 1974; Pascal, 1979; Swennen *et al.,* 1986; Dejonghe, 1987a).

The aim of this study is to discuss the geochemical distribution patterns in the Dinantian carbonates of the Campine-Brabant Basin. The importance of a petrographical knowledge of the analysed samples and of the selection of the samples, which are statistically treated, will be illustrated.

The Dinantian carbonates of the Campine-Brabant Basin are known from several boreholes. Seven boreholes have been investigated (fig. 1). The sedimentology and the facies description of the Dinantian of the Campine-Brabant Basin have been discussed by Muchez *et al.* (1987a) and Muchez (1988). The results are summarized in table 1. Details of the analysed samples are given in the discussion of the geochemical distribution patterns.

2. METHODS

Each five meter, a representative sample of the rocks has been taken. When important lithological variations occurred, a more detailed sampling was carried out.

Rock analyses for Mg, Sr, Na, Zn, Pb, Fe, Mn and K were made by a Varian Techtron atomic absorption spectrometer. The insoluble residue (IR) was determined gravimetrically after a HCl (12.5N) attack. The organic carbon (C_{org}) content was measured by the Walkley and Black method (Allison, 1965). This method has the disadvantage of also oxidizing partly or completely other constituents such as sulphides within the carbonate rocks. The analytical procedure has been described by Van Orsmael *et. al.* (1980), Van Orsmael (1982) and Swennen *et al.,* (1986). Analytical precision at the 95 % confidence level, determined by 50 replicate analyses, is better than 10 percent for most of the analysed elements (Van Orsmael *et al.,* 1980).

The lithogeochemistry of the Dinantian strata of the Campine-Brabant Basin was also studied by Op de Beeck (Swennen *et al.,* 1982a). The results of that study have been used and processed with the new data.

In several geochemical studies (Veizer *et al.,* 1978; Parker *et al.,* 1985; Swennen, 1986; Dejonghe, 1987a; Van Oyen & Viaene, 1988), the data have been logarithmically transformed, because lithogeochemical distributions often display a lognormal distribution (Ahrens, 1954). The choice of logarithmic or non-transformed data is based on the Shapiro-Wilk ($n<51$) and the Kolmogorov D ($n>50$) tests. In this study the logarithmically transformed variables are preceeded by a capital letter L (e.g. LMn).

Zonations in dolomite crystals visible under cathodoluminescence were analysed on an Applied Research Laboratories model 'AMX' electron microprobe for calcium, magnesium, iron and manganese. The detection limit for $CaCO_3$, $MgCO_3$ and $FeCO_3$ is 0,08 mol%, 0,08 mol%, 0,09

Table 2.- Median (m) and range (5%-95%) of the variables in different units of the Campine Basin.

Stage, lithology, borehole	Mg (%)		Sr (ppm)		Na (ppm)		Zn (ppm)		Pb (ppm)		Fe (ppm)		Mn (ppm)		C (%)		IR (%)		K (ppm)	
	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range	m	5%-95% range
Lower Moliniacian IR-rich limest.																				
Booischot (n=21)	0.30	0.05- 2.12	304	20-1106	149	86-364	17	3- 50	2	2- 13	1637	229-20885	453	37-1184	0.11	0.01-0.65	11.9	1.8-94.0	392	15-2302
Kessel (n=24)	0.32	0.09- 0.83	193	45- 294	141	47-593	27	5- 100	2	2- 13	4392	269-34284	1316	205-3778	0.07	0.03-0.57	21.9	2.9-79.5	799	19-4200
Lower Moliniacian limestones																				
Loksbergen (n=21)	0.16	0.07- 0.35	286	165- 765	61	40-140	19	7- 43	6	2- 56	205	111- 3554	153	85-2053	0.04	0.02-0.56	1.9	1.5- 6.0	16	6- 91
Turnhout (n=52)	0.19	0.12- 0.28	210	147- 251	88	54-117	3	1- 28	2	2- 29	66	38- 147	53	27- 100	0.03	0.01-0.05	1.5	0.0- 2.2	16	8- 28
Dinantian dolostones																				
Booischot (n=14)	12.42	11.53-13.25	108	86- 160	208	112-291	15	3- 90	2	2- 9	3872	2175- 7347	988	594-1763	0.10	0.05-0.37	1.4	0.2-12.8	67	18- 503
Halen (n=35)	11.30	10.13-12.46	98	55- 123	329	205-657	54	6- 637	2	2- 21	11315	4448-26830	2096	977-6623	0.12	0.05-0.32	1.1	0.1- 1.8	28	15- 97
Upper Moliniacian limestones																				
Booischot (n=23)	0.13	0.02- 0.23	192	27- 457	61	33-184	70	12-5278	111	17-4936	554	170- 3656	381	136-4116	0.04	0.01-0.64	1.9	0.5-17.0	36	6- 336
Halen (n=23)	0.41	0.03- 1.56	258	43- 462	112	79-157	15	2- 131	2	2- 68	512	176- 3090	338	105-5170	0.10	0.03-0.68	1.3	0.5- 2.8	23	8- 90
Lower Warnantian limestones																				
Heibaart (n=33)	0.15	0.10- 0.22	184	104- 528	76	40-106	8	2- 26	4	2- 7	226	140- 284	213	139- 445	0.04	0.02-0.07	2.0	1.4-20.0	11	4- 42
Poederlee (n=40)	0.16	0.11- 1.01	200	139- 321	85	49-266	4	1- 318	2	2- 19	227	84- 2415	175	92- 751	0.04	0.02-0.27	2.9	1.5- 8.2	17	9- 54

mol% and 0,11 mol% respectively. Their standards are respectively calcite, magnesite, rhodochrosite and siderite.

3.- RESULTS AND INTERPRETATION

The geochemical data of each borehole are given in a geochemical profile. Furthermore, the data are subdivided according to lithostratigraphical units,and carbonate mineralogy (limestone versus dolomite). Often the lithostratigraphical units correspond with the biostratigraphical units. A dolomite contains more than 10% Mg. Of selected groups of samples a histogram, the median (m) and the range (5-95 %) of the variables, correlation matrix and a factor analysis (Varimax rotated) were calculated. In most of the selected groups, the anomalous samples have been omitted. The correlations were evaluated by bivariate plots. The results of the correlation matrix are presented by the element associations.

Legend

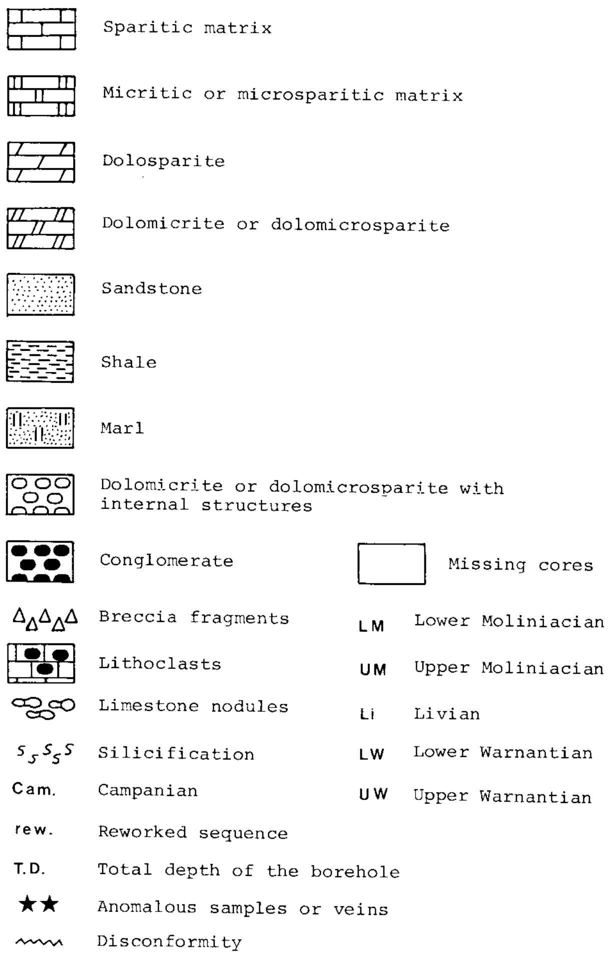

Fig. 2.- Legend of the lithological logs in the geochemical profiles.

Table 3.- Factor analysis of the IR-rich Moliniacian carbonates ($Mg < 3$ %) in the Booischot boreole ($n = 21$).
——— $\geqslant$ 0,65 ---- $\geqslant$ 0,45 and $<$ 0,65

Variable	Factor 1	Factor 2	Factor 3	Communalities
LMg	- 0.01	0.87	0.22	0.80
LSr	- 0.86	0.28	- 0.22	0.84
LNa	0.82	- 0.11	- 0.37	0.81
LZn	- 0.34	0.08	0.80	0.76
LFe	0.88	0.25	- 0.19	0.87
Mn	- 0.12	0.80	- 0.37	0.79
LC_{org}	0.52	0.23	0.70	0.82
LIR	0.92	- 0.16	0.10	0.89
LK	0.91	- 0.01	0.03	0.83
explained variance (%)	48	18	17	

The element associations are not given in this paper. They can be obtained from the authors on request. The calculations were carried out by SAS computer programs. The statistical treatment of the geochemical data has been carried out on the thick units with a large availability of core samples.

3.1.- LOWER MOLINIACIAN STRATA

3.1.1.- IR-rich limestones

a.- Booischot borehole

Within the lithogeochemical profile of the Booischot borehole (fig. 3), three important lithological units can be distinguished: a dolostone unit, a clay-rich carbonate unit with sandstone layers and a limestone unit. In this paragraph we focus on the clay- and sandstone-rich unit. The geochemical profile is very irregular. High Sr, Fe, Mn, IR and K contents occur compared with those in other units (table 2). The Mg distribution shows two populations; a first with a Mg content lower than 0,6% and a second with a Mg content between 1,6% and 2,1 %. LNa (+), LFe(+), LIR (+), LK (+) and LSr (-) are present in factor 1 of the factor analysis (table 3). This association explains 48% of the total variance. The elements in the second and third factors are LMg(+), Mn(+) and LZn(+), LC_{org}(+) respectively. Each of them explains more than 16% of the total variance.

Na, Fe and K are associated with the clays, which form an important part of the insoluble residue (IR). Furthermore, the clayey horizons contain hematite nodules. Sr is negatively correlated with IR and thus more incorporated in the calcite lattice than adsorbed on clays (Barber, 1974; Dejonghe, 1987a). In the correlation matrix, no relationship exists between Mg and Mn. This illustrates that the factor analysis can group elements without a clear explanation. The relation between Zn and C_{org} in factor 3 can be explained by the oxidation of sulphides in the analytical procedure and by the preferential adsorption of Zn on organic material (Vine & Tourtelot, 1970).

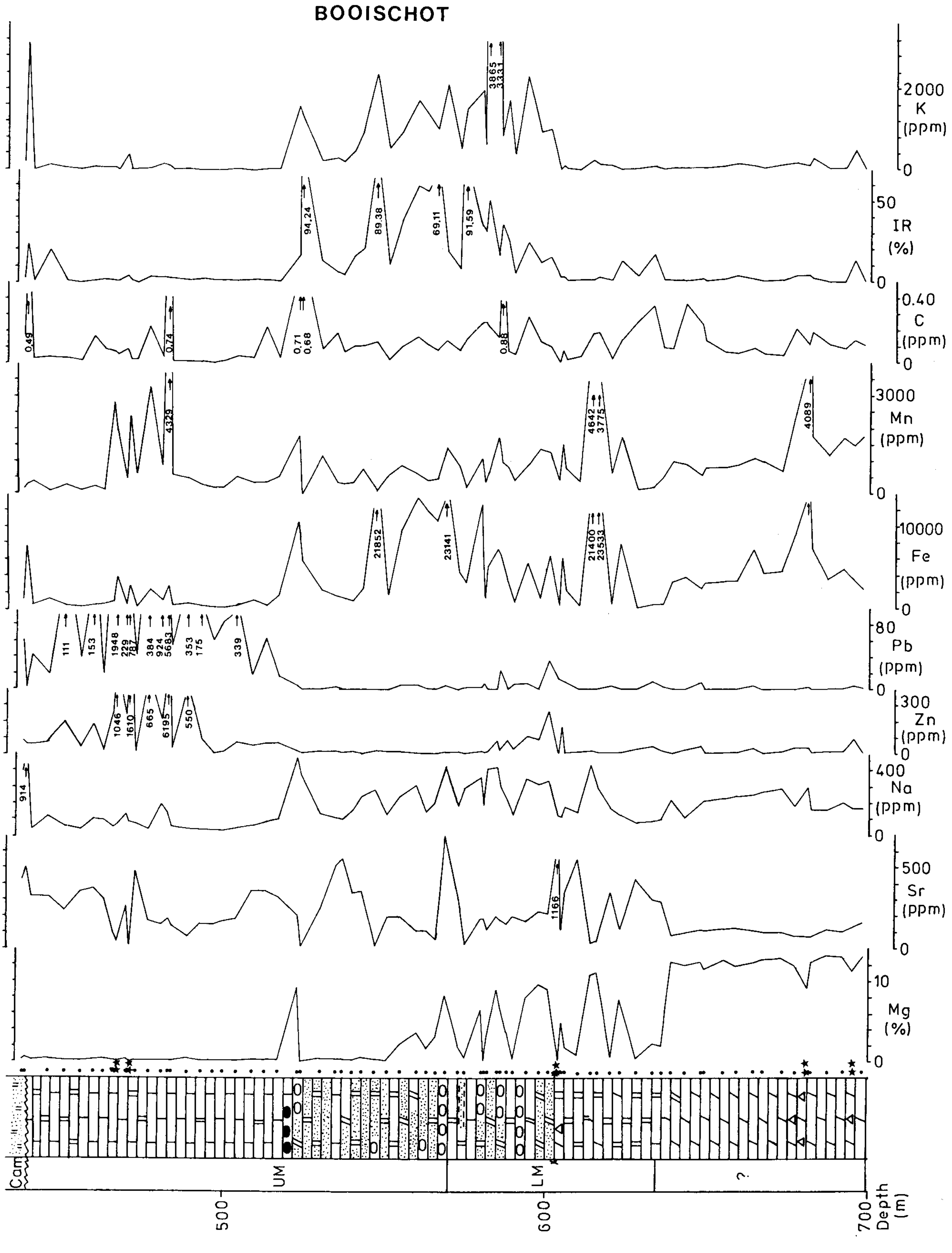

Fig. 3.- Geochemical profile of the Dinantian in the Booischot borehole (legend see fig. 2).

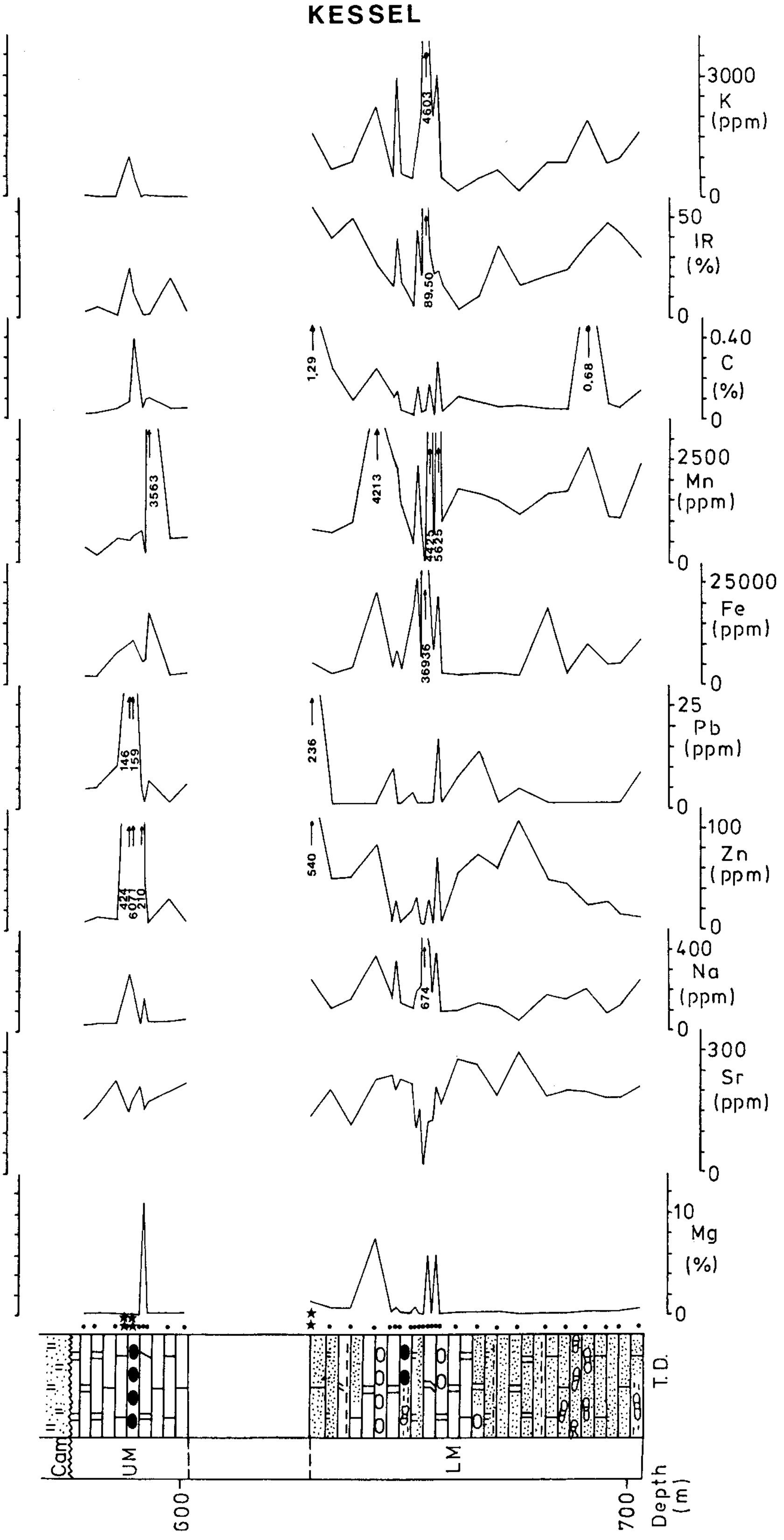

Fig. 4.- Geochemical profile of the Visean in the Kessel borehole (legend see fig. 2).

Table 4.- Factor analysis of the Moliniacian strata (Mg < 1%) in the Kessel borehole (n = 24).

Variable	Factor 1	Factor 2	Factor 3	Communalities
LMg	0.49	0.36	0.62	0.76
Sr	- 0.67	0.29	0.39	0.68
LNa	0.92	0.07	- 0.09	0.85
LZn	- 0.16	0.02	0.88	0.81
LFe	0.89	0.23	- 0.06	0.85
Mn	- 0.05	0.95	- 0.07	0.91
LCorg	0.12	0.76	0.42	0.77
LIR	0.84	- 0.16	0.36	0.85
LK	0.94	0.07	0.06	0.88
explained variance (%)	44	20	18	

However, recent studies indicate that Zn is mainly associated whit Fe-oxyhydroxides (Robinson, 1981; Scott, 1986). It should be noticed that one sample (a sandstone) whith a low Zn and a high Corg content prevents a positive correlation in the correlation matrix.

b.- Kessel borehole

A few samples are anomalous in Zn and Pb (fig. 4; 622 m and 588-587 m). The anomalous Zn and Pb contents are associated with an organic-rich horizon (622 m) and with a conglomerate at 588-587 m. In both horizons pyrite and sphalerite have been recognized. In the conglomerate, sphalerite occurs in the pores of the recrystallized matrix. These anomalous samples and those with a Mg concentration higher than 1 % have not been used in the statistical treatment.

The Fe, Mn, IR and K concentrations are often very high (fig. 4). Sr(-), LNa(+), LFe(+), LIR(+), LK(+) and to a lesser extent Mg(+) contribute to the 44 % of the variance of the first factor (table 4). The second factor indicates a correlation between LCorg and Mn, and the third factor between LZn and LMg.

The very high Fe, Mn, IR and K contents indicate an important continental influence. This is also attested by petrographic observations. The association of Na, Fe and K with IR is interpreted as adsorption and incorporation of the three elements in the structure of clay minerals. Furthermore, hematite nodules are present in the clayey horizons. Also Mg can be adsorded on clay (Pascal, 1979). Mn is partially transported in water as an organic complex (Yariv & Croos, 1979); this explain the association of Mn and Corg in factor 2. Van Orsmael (1982) concluded from his study that the Corg content in limestones is useful as a measure for the reducing conditions of the sedimentation environment. In mildly reducing conditions, Mn-oxyhydroxides break down and Mn (II) is adsorbed to calcite in carbonate rocks (Thompson *et al.*, 1986). These reducing conditions are an alternative explanation for the association of Mn and Corg. The weak association of Zn and Mg in factor 3 can not be interpreted with the present data.

3.1.2.- Limestones

a.- Loksbergen borehole

The concentrations of Mg, Na, Zn, Fe, Mn, IR and K in Lower Moliniacian limestones (fig. 5) are much lower than those in the boreholes of Kessel and Booischot. Two factors are apparent in the factor analysis (table 5). The first factor includes LMg, LSr, LCorg, LIR, LK and to a lesser extent LNa and LZn, and the second LNa, LFe and LMn.

The Mg, Sr, Corg, K, IR, Na, Zn association can be explained by the difference in lithology. An alternation of micritic and coarse-grained limestones exists in the Lower Moliniacian strata of the Loksbergen borehole. Micritic limestones are richer in Mg, Sr, clays and organic matter than the coarse-grained limestones, which can contain up to 40 volume percent Sr-poor cements. Furthermore, the exchange of ions in micrites is less efficient than in grainstones (Pingitore, 1982). The first element association will be defined as the micrite association factor. A similar element association has been interpreted as a shielding effect of organic material (Swennen, *et al.*, 1982b; Swennen, 1986). Because the micrites contain more organic material than the coarse-grained limestones, the leaching of Sr and Mg during diagenesis is less effective. However, the Corg content in the Loksbergen borehole is very low and can not explain the observed differences in concentration.

During diagenesis, Mn and Fe concentrations increase. The distribution coefficients of Mn and Fe are larger than 1 (Michard, 1968; Veizer, 1974). These elements have been used to characterize the textural maturity of limestones. The removal of Sr and Na is associated with this process (Brand & Veizer, 1980). Especially Sr and Mn are useful diagenetic indicators, because of their widely divergent partition coefficients, their association with the carbonate lattice, and their large compositional differences in marine and meteoric water (Kinsman, 1969). The association of Na with Fe seems peculiar. However, Brand & Veizer (1980) found in their factor analysis of originally high Mg-calcites, Na in their diagenetic equilibration factor. Three processes can contribute to the association of Na, Fe and Mn: concentration of Na by membrane filtration (Hitchon *et al.*, 1971), increase of the Mn and Fe concentration in pore waters due to the admixture of meteoric waters (Brand & Veizer, 1980) or due to the change of redox potential in the subsurface (Evamy, 1969; Moore & Druckman, 1981). These processes influence the concentrations of the elements in the pore water in the subsurface.

From the geochemical profile and the petrography of the samples, a relation between the

Table 5.- Factor analysis of the Lower Moliniacian strata in the Loksbergen borehole (n = 21).

Variable	Factor 1	Factor 2	Communalities
LMg	0.87	- 0.36	0.88
LSr	0.86	0.06	0.75
LNa	0.50	0.69	0.73
LZn	0.55	0.39	0.45
LFe	0.02	0.97	0.94
LMn	- 0.18	0.95	0.93
LC$_{org}$	0.91	- 0.02	0.83
LIR	0.75	0.09	0.56
LK	0.76	0.14	0.60
explained variance (%)	45	29	

Table 6.- Factor analysis of the Lower Moliniacian limestones in the Turnhout borehole (n = 52).

Variable	Factor 1	Factor 2	Factor 3	Communaiities
Mg	0.62	- 0.20	0.21	0.47
Sr	0.43	- 0.65	- 0.09	0.62
Na	0.78	0.05	0.32	0.71
LZn	0.02	0.68	- 0.33	0.57
LFe	0.77	0.29	0.02	0.68
LMn	0.70	0.23	- 0.25	0.61
C$_{org}$	0.23	0.65	0.25	0.54
IR	0.24	0.65	- 0.18	0.51
LK	0.13	- 0.06	0.91	0.85
explained variance (%)	27	21	14	

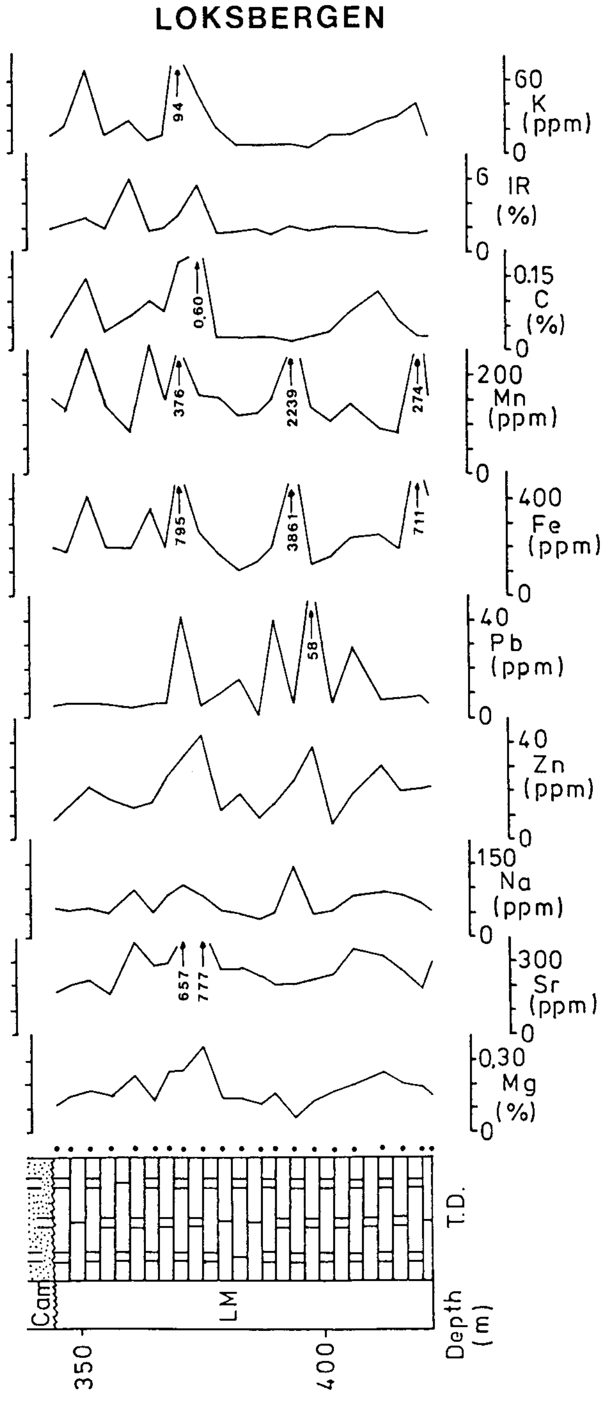

Fig. 5.- Geochemical profile of the Visean in the Loksbergen borehole (legend see fig. 2)

samples with a high Fe, Mn and Na content and the presence of small Fe-rich veins in these limestone cores is apparent. So, the second factor probably represents the equilibration of the subsurface fluids with the existing geochemical conditions. Moreover, the geochemistry of the fluids is probably the result of a long interaction between the rocks and the pore waters. When the samples with a high Na, Fe and Mn content are omitted from the statistical treatement, Fe and Na occur in the first micrite association factor.

b.- Turnhout borehole

The trace element concentrations in the Lower Moliniacian pure limestones are low (table 2 and fig. 6). The homogeneous pattern is disturbed at 2662-2663 m by high Mg, Na, Zn, Pb, Fe, Mn and C$_{org}$ contents. These samples have not been used in the processing of the data. The high trace element concentrations are associated with a dolomite vein, rich in sphalerite, pyrite and galena. The high C$_{org}$ content is probably due to the oxidation of the sulphides in the analytical method.

In the factor analysis an association of Mg, Na, LMn and LFe is apparent (table 6). Factor 2 groups Sr(-), LZn(+), C$_{org}$(+) and IR(+). Factor 3 mainly contains IR.

The association of Mg, Na, Fe and Mn in one factor can not be explained unequivocally. The fact that Mn is not correlated with Mg possibly suggests that two processes played a role in the association. A first process groups Na, Fe, Mn and a second Mg, Na and Fe. The association of Mg, Na, Fe can be interpreted as a diagenetic equilibration factor sensu strictu (see paragraph 3.1.2.a).

The distribution of Mg in limestones, which underwent an intensive diagenesis does not represent the original Mg distribution, but the result of dissolution and precipitation processes (Videtich, 1985). If the original Na and Fe concentration follow this redistribution pattern, their association with Mg can be explained. Notice also that these three trace elements are often associated in dolomite crystals. Dolomite rhombohedrons are present as small inclusions in the

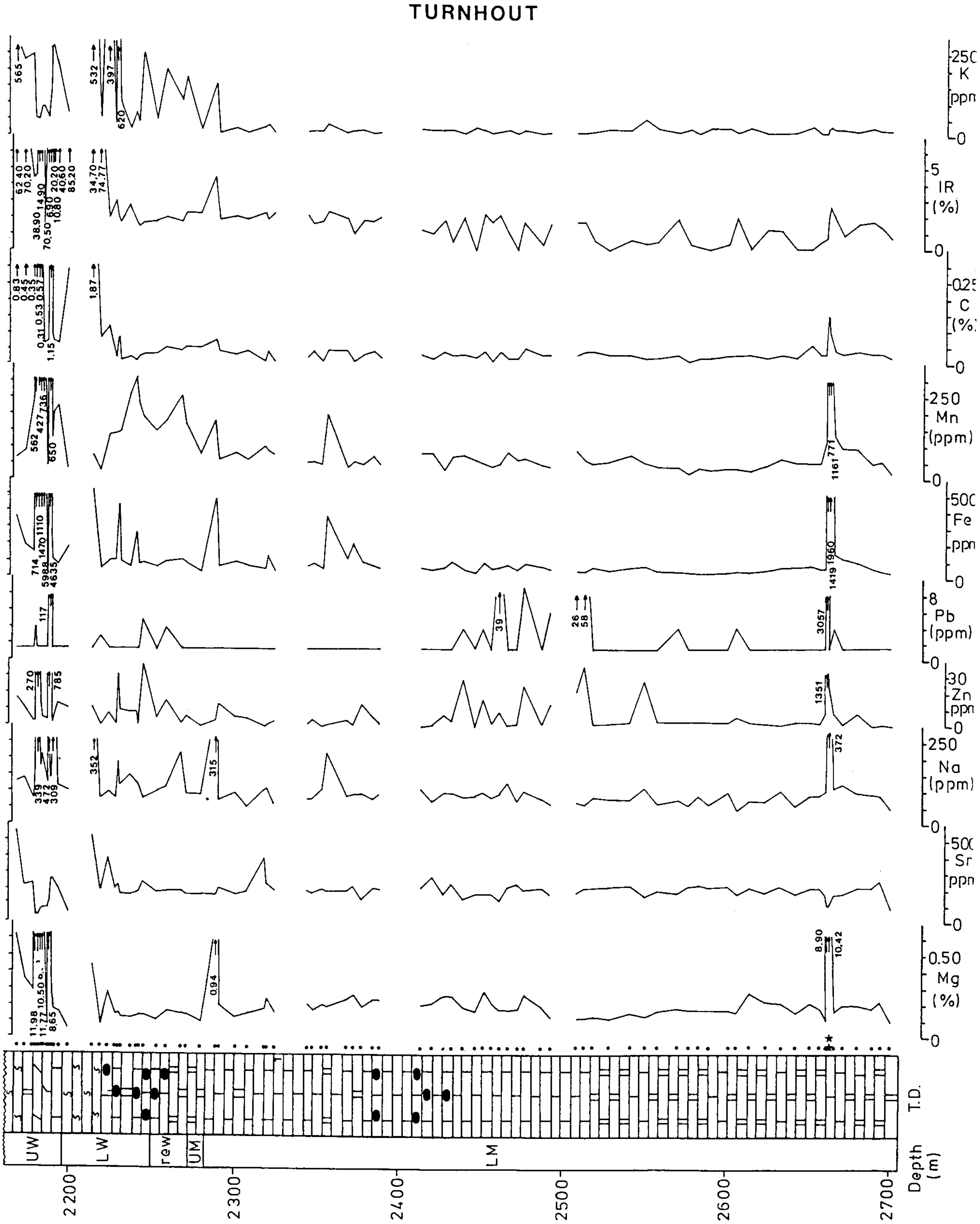

Fig. 6.- Geochemical profile of the Visean in the Turnhout borehole (legend see fig. 2).

Table 7.- Factor analysis of the dolomites in the Booischot borehole (n = 14).

Variable	Factor 1	Factor 2	Factor 3	Communalities
Mg	- 0.86	- 0.16	0.01	0.76
Sr	- 0.51	- 0.01	- 0.67	0.71
Na	0.20	- 0.93	- 0.07	0.91
LZn	0.53	0.43	0.16	0.49
LFe	0.37	0.00	0.89	0.94
LMn	- 0.40	0.30	- 0.76	0.83
LC_{org}	0.24	0.95	0.05	0.97
LIR	0.91	- 0.02	0.09	0.84
LK	0.84	- 0.20	0.38	0.88
explained variance (%)	36	23	22	

Table 8.- Factor analysis of the dolomites in the Halen borehole (n = 35).

Variable	Factor 1	Factor 2	Factor 3	Communalities
Mg	- 0.80	- 0.33	0.38	0.88
Sr	- 0.06	0.85	- 0.11	0.74
LNa	0.51	- 0.18	0.58	0.62
LZn	0.75	- 0.43	0.12	0.76
LFe	0.96	- 0.11	0.01	0.93
LMn	0.98	0.01	- 0.04	0.96
LC_{org}	0.88	0.09	0.21	0.82
IR	0.18	0.86	0.19	0.81
LK	- 0.12	0.13	0.89	0.83
explained variance (%)	46	20	15	

bladed calcite cements in the Lower Moliniacian strata. Their presence may cause this Mg, Na, Fe association.

The concentrations of Zn, IR and C_{org} are very low; therefore an interpretation of their distribution pattern has not been worked out.

3.1.3.- Dolostones

a.- Booischot borehole

The thick dolostone unit contains two anomalous samples (fig. 3): a breccia at 682 m with a low Mg content and the sample at 695 m with an IR content of 12,8%. These two samples were not further treated. The Mn and Fe concentrations are high and the Sr content low (table 2). The factor analysis (table 7) groups Mg(-), LIR(+) and LK(+) and to a lesser extent Sr (-) and LZn(+) in factor 1, NA(-) and LC_{org}(+) in factor 2 and LFe(-), LMn(-) and Sr (-) in factor 3.

Low Sr concentrations in dolomites can be explained by the influence of subsurface meteoric water flow during the dolomitization process (Choquette & Steinen, 1980; Dunham & Olson, 1980; Tucker, 1983; Baum *et al.*, 1985). Land (1980) and Hardie (1987) however, showed that the interpretation of the composition of the dolomitizing fluids based on the Sr concentration is not valid.

High Mn concentrations in carbonates are not the result of a normal marine diagenesis. Churnet *et al.* (1982) interpreted high Mn and Fe contents as an indication for a mixing zone dolomitization. High Mn and Fe contents also occur in dolomites, which did not underwent meteoric influences (Taylor & Sibley, 1986; Burns & Baker, 1987). Anomalous Fe and Mn values are derived from Mn- and Fe-oxyhydroxides and coatings on detrital minerals (Caroll, 1958; Berner, 1970). The Fe and Mn are released during diagenesis (Caroll, 1958; Curtis, 1967; Burns & Baker, 1987) and incorporated in the dolomite lattice. Geochemically, no argument is in favour for one of these processes.

The negative correlation between IR, K and Mg simply indicates that the strata rich in insoluble residue, contain less dolomite. The association of Na and C_{org} in factor 2 can not be explained. Notice that a limited number of samples has been analysed. Factor 3 indicates that the enrichment of Fe and Mn in the dolomite is associated with a decrease in the Sr content.

Table 9.- Microprobe analysis of zoned dolomite crystals in the Halen borehole.
b.d. = below detection limit.

Depth and occurrence	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$
	mol%	mol%	mol%	mol%
1331 m				
core	52.82	45.01	0.15	0.09
	52.18	44.73	0.40	0.44
1st brown-yellow zone	56.03	38.97	1.24	1.00
	56.72	39.06	0.62	1.77
dark zone	54.83	39.33	1.92	0.62
	55.48	38.91	1.86	0.85
2nd brown-yellow zone	53.22	42.04	0.86	0.42
	55.30	40.99	1.21	0.56
1167 m				
core	52.73	45.52	b.d.	0.17
	52.52	44.97	b.d.	b.d.
1st brown-yellow zone	56.78	40.09	0.37	0.27
	57.28	39.93	0.37	0.30
dark zone	55.58	39.14	3.29	0.61
2nd brown-yellow zone	56.70	39.70	0.48	0.26

b.- Halen borehole

In the geochemical profile of the Halen borehole (fig. 7), several samples of the dolosparites between 1366 and 1185 m have a Mg content lower than 10%. These samples contain Fe-rich calcite veins or are breccias with an Fe-rich matrix. They were omitted from the processing of the geochemical data of the dolostone unit.

The median of Na, Zn, Fe and Mn (table 2) is high. One important group appears in the factor analysis (table 8): LFe(+), LMn +), LZn(+), LNa(+), LC_{org} (+) and LMg(-).

The high Fe and Mn values can be explained by a mixing zone dolomitization or by the release of Fe and Mn from terrigenous components during diagenesis (see paragraph 3.1.3a). Under cathodoluminescence, the dolomite crystals show a complex zoning around a uniform orange luminescent core (Muchez, 1988). The zones are less stoichiometric than the core and are richer in Mn and Fe (table 9). The association of Fe, Mn, Zn and

HALEN

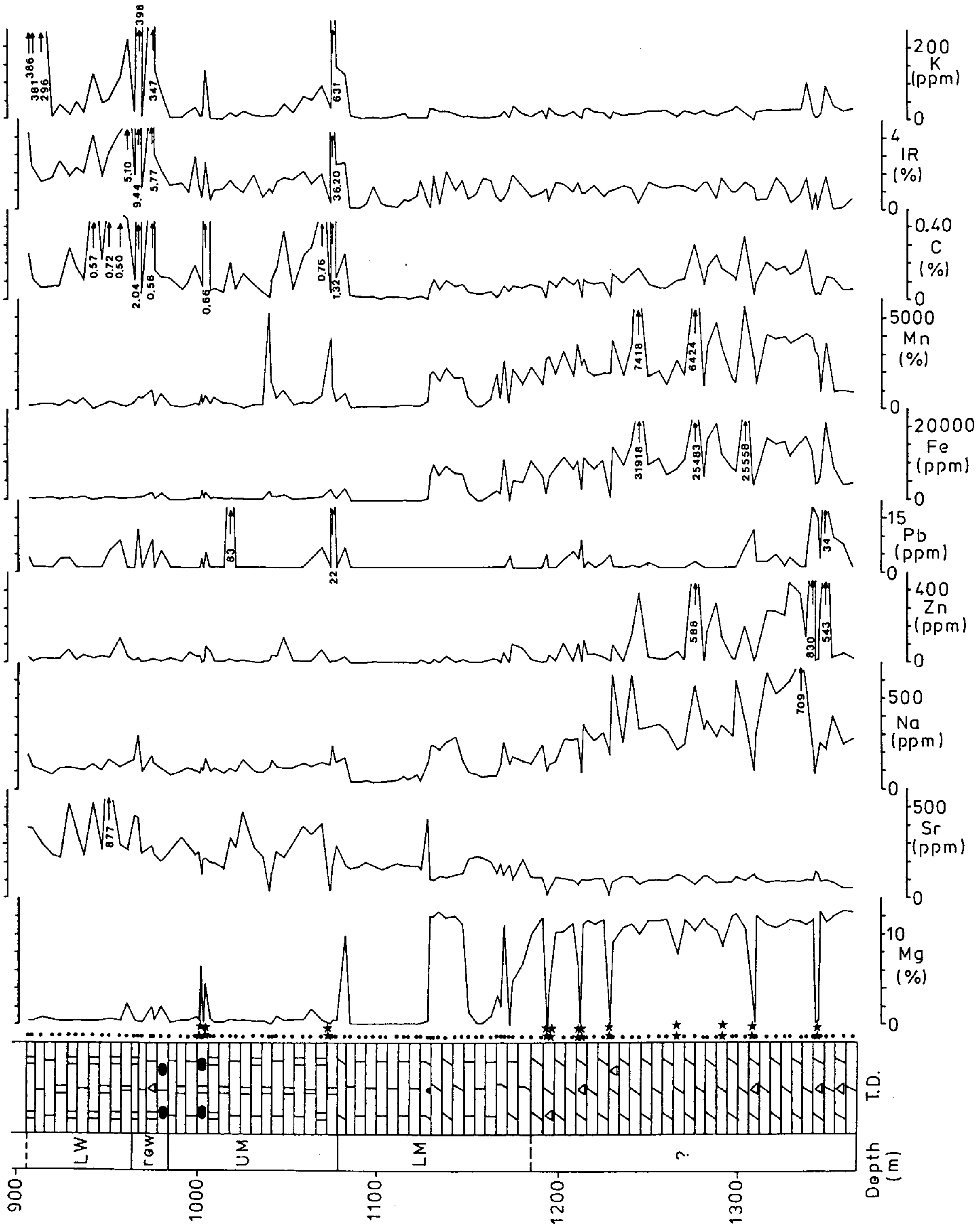

Fig. 7.- Geochemical profile of the Dinantian in the Halen borehole (legend see fig. 2).

Na in factor 1 could indicate that their concentrations increase during the growth of the dolomite crystals. The most evolved dolomites have an idiotopic habit and form a porous framework. In these pores, organic material is present. This explains the positive correlation between the organic material and Fe, Na, Mn and Zn. Na however, is not only associated with the dolomites, it also occurs in association with the clays (factor 3). It should be remarked that an association of Na with dolomite not necessarily implies an incorporation of this element in the dolomite lattice. Important quantities of Na occur in fluid inclusions in dolomites (Weber, 1964). Fluid inclusions are abundant in the dolomites of the Halen borehole.

The association of Sr and IR in factor 2 is not clear. However, the IR content is low and hence also the accuracy.

3.2.- UPPER MOLINIACIAN STRATA

a.- Booischot borehole

The geochemical profile of Upper Moliniacian strata in the Booischot berehole is very irregular and shows unusually high Zn, Pb, Mn, Mn, C_{org}, Fe contents and low Mg and Sr concentrations (fig. 3). The Zn and Pb anomaly occurs over a larger interval than the Fe and Mn anomaly. Three factors occur in the factor analysis (table 10). The first factor contains Mg(-), Sr(-), LZn, LPb, LFe, LMn, and the second LNa, LK and LC_{org} and to a lesser extent Mg and LFe, and the third LIR.

The high Zn, Pb, Mn, Fe, C_{org} and the low Mg and Sr concentrations are associated with intense recrystallized and karstified horizons in the Upper Moliniacian strata. Zn, Pb and Fe occur as sulphides in veins and pores. The difference in the extent of the anomalous intervals can be explained by the fact that the very high Fe and Mn values are associated with the karstified horizons and high Pb and Zn concentrations with the karstified and recrystallized limestones. The recrystallization occurs over a larger interval than the karstification. The second factor is characterized by Na, C_{org} K, Mg and Fe which probably represent the micrite association factor (see paragraph 3.1.2.a).

b.- Halen borehole

The geochemical profile shows an irregular distribution of, Fe, Mn, C_{org}, IR and K (fig. 7). Two samples with a high Mg content occur at 1002 and 1004 m. These samples have been left out from the processing of data, as well as the sample with an IR content of 36.20%. Three factors are differentiated in the factor analysis (table 11). Factor 1 groups LMg(-), Sr(-), LFe(+), LMn(+), factor 2 LC_{org}(+), LK(+), Sr(+) and factor 3 LZn(+), LC_{org}(+) and IR(+).

Table 10.- Factor analysis of the Upper Moliniacian strata in the Booischot borehole (n = 23).

Variable	Factor 1	Factor 2	Factor 3	Communalities
Mg	- 0.84	0.47	0.04	0.93
Sr	- 0.84	0.39	- 0.27	0.94
LNa	0.00	0.82	0.34	0.79
LZn	0.85	0.42	- 0.07	0.90
LPb	0.89	0.19	- 0.09	0.84
LFe	0.68	0.45	0.17	0.69
LMn	0.91	0.21	- 0.08	0.87
LC_{org}	0.27	0.84	- 0.23	0.83
LIR	- 0.00	0.21	0.93	0.91
LK	0.04	0.82	0.27	0.75
explained variance (%)	43	29	12	

Table 11.- Factor analysis of the Upper Moliniacian strata in the Halen borehole (n = 23).

Variable	Factor 1	Factor 2	Factor 3	Communalities
LMg	- 0.73	0.27	0.43	0.79
Sr	- 0.83	0.46	0.14	0.91
LNa	0.28	0.82	- 0.11	0.76
LZn	0.03	- 0.04	0.93	0.86
LFe	0.92	0.34	0.05	0.96
LMn	0.96	0.24	- 0.05	0.98
LC_{org}	- 0.30	0.68	0.58	0.88
IR	- 0.28	0.42	0.46	0.47
LK	0.01	0.91	0.17	0.86
explained variance (%)	36	29	18	

The samples at 1004 and 1002 m are partially dolomitized limestones. The irregular distribution pattern of Sr, Fe, Mn, C_{org} IR and K can be explained by the presence of an Fe-rich matrix and allochems in some packstones and grainstones and of clayey horizons. Factor 1 contains the elements Fe and Mn, which increase during diagenesis, and Sr and Mg, which are removed. High Mn and Fe concentrations suggest that diagenetic equilibration (recrystallization) occurred in meteoric waters (Hutcheon *et al.*, 1985; Machel, 1986) or in a fluid enriched in Mn and Fe, due to the reduction of Mn- and Fe-oxyhydroxides (Caroll, 1958; Burns & Baker, 1987).

The Na, C_{org}, K association is a clay-organic carbon factor. Shielding by organic matter and the contrast in ion exchange and initial Sr concentration between fine- and coarse-grained rocks explains the presence of Sr in second factor. The association of Zn and C_{org} can be explained by oxidation of sulphides during the analytical procedure. Their limited association with IR can not explained.

3.3.- LOWER WARNANTIAN STRATA

a.- Heibaart borehole

For the geochemical distribution of the Lower Warnantian limestones, special attention has been given to the distribution patterns of the elements in the reef mound between 1225 m and 1102 m (Muchez *et al.*, 1987b).

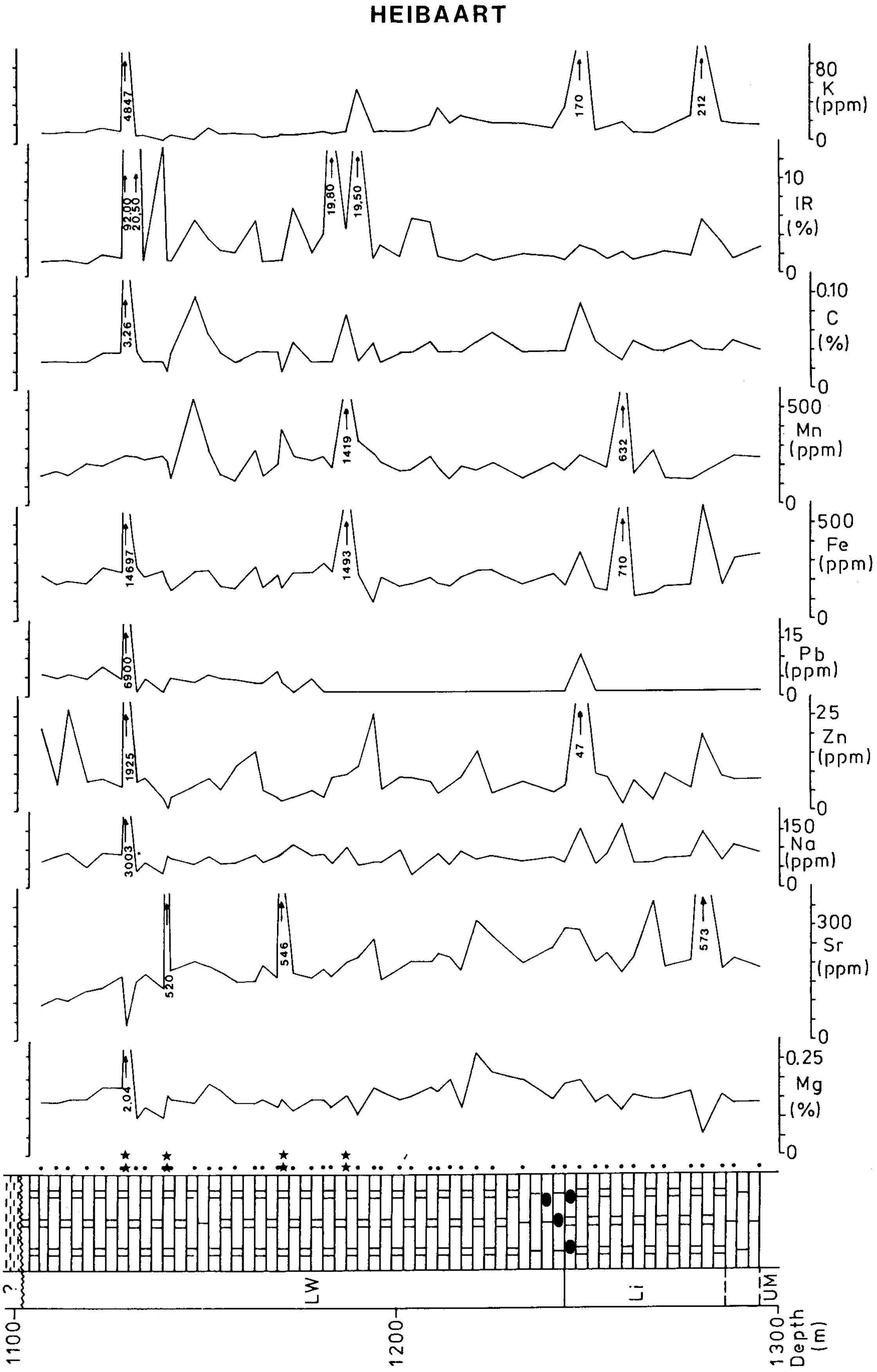

Fig. 8.- Geochemical profile of the Visean in the Heibaart borehole (legend see fig. 2).

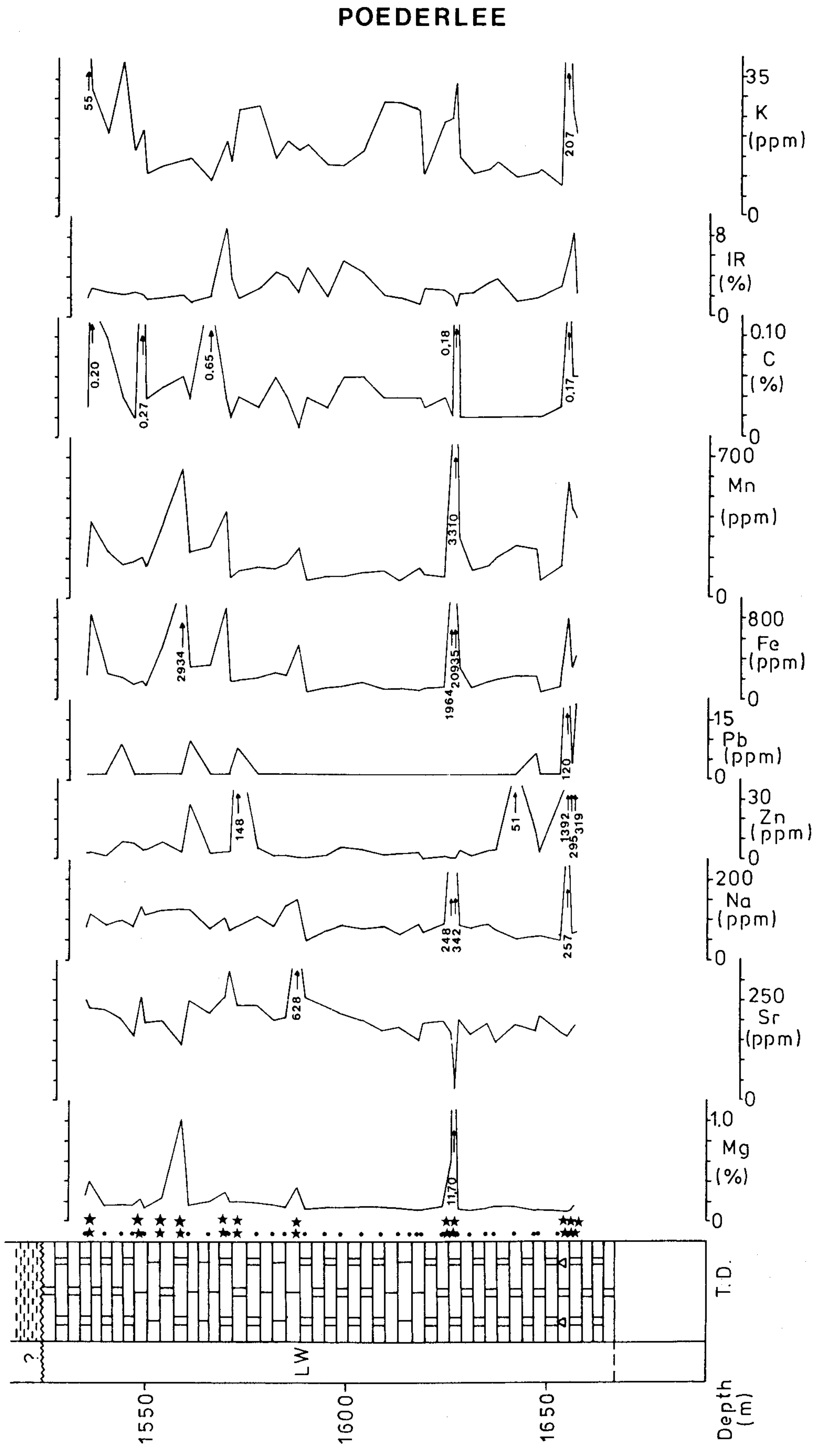

Fig. 9.- Geochemical profile of the Visean in the Poederlee borehole (legend see fig. 2).

Table 12.- Factor analysis of the Lower Warnantian limestones in the Heibaart borehole (n = 33).

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communalities
LMg	- 0.41	0.67	0.30	0.24	0.76
LSr	- 0.08	0.05	0.95	0.04	0.91
Na	0.04	0.07	0.07	0.94	0.89
LZn	- 0.06	0.61	- 0.60	- 0.20	0.78
Fe	0.82	- 0.03	- 0.23	0.19	0.76
LMn	0.75	0.05	0.46	- 0.05	0.78
LC_{org}	0.36	0.67	0.02	- 0.13	0.59
LIR	0.69	- 0.12	- 0.08	- 0.54	0.79
LK	- 0.10	0.63	- 0.07	0.17	0.45
explained variance (%)	23	19	18	15	

Two samples with anomalous concentrations are obvious in the geochemical profile (fig. 8). The first sample at 1187 m is a calcite vein with high Fe and Mn contents. High Fe and Mn concentrations in veins indicate the importance of meteoric water and/or modified formation waters under reducing conditions in the precipitation of calcite (Hutcheon *et al.*, 1985; Moore, 1985). The second at 1126 m is a clay-rich karst infilling with a very high Na, Zn, Pb, Fe, C_{org}, IR and K value. In the further treatment of the data these two samples are omitted. Due to the omnipresence of very small calcite veins in the limestones, veins also have been analysed with the bulk rock. Fe, Mn and IR occur together in factor 1 of the factor analysis (table 12), explaining 23 % of the total variance. Factor 2 contains LMg, LC_{org}, LZn and LK. LZn(-); LMn(+) and especially LSr(+) are associated in factor 3. Factor 4 comprises Na (+) and IR(-).

The association of Fe and Mn in factor 1 is interpreted to represent the equilibration of basinal fluids with existing geochemical conditions and the interaction between rocks and pore waters (for discussion see paragraph 3.1.2a). The petrographic study showed the occurrence of authigenic quartz crystals in the micritic limestone and in Fe-rich calcite veins. This propably causes the association of insoluble residue (authigenic quartz) within this factor 1. Factor 2 is the micrite association factor. When a factor analysis is carried out without the two samples with high Sr values (calcite veins with a Sr content > 500 ppm), Sr occurs in factor 2. This is in agreement with the micrite association interpretation. This illustrates the usefulness to carry out petrographical research. These data are a necessity to unravel the variability in the geochemical distribution pattern. Factor 3 is determined by two Sr-rich calcite veins at 1170 m and 1140 m. These veins have a low Zn concentration explaining the negative correlation between Sr and Zn. If the two samples are left out (which should be done), factor 3 does not develop in the factor analysis. The high Sr content in the veins indicates higher Sr concentrations in the fluids precipitating the calcite. This can be the result of the neomorphism and the removal of Sr from the limestones. High Sr concentrations can also occur during deep burial diagenesis, when basinal fluids migrate upwards along faults (Prezbindowski, 1985). The negative association of Na and IR in factor 4 is not clear. The diagenetic overprint on the reef mounds largely influences the geochemical distribution pattern in these limestones.

Table 13.- Factor analysis of the Lower Warnantian limesones in the Poederlee borehole (n = 40).

Variable	Factor 1	Factor 2	Factor 3	Communalities
LMg	0.90	- 0.26	- 0.15	0.90
LSr	- 0.62	- 0.10	0.34	0.50
LNa	0.83	0.10	0.15	0.72
LZn	- 0.04	0.92	- 0.03	0.85
LPb	0.07	0.94	0.06	0.90
LFe	0.95	0.05	- 0.01	0.91
LMn	0.90	0.19	- 0.07	0.86
LC_{org}	0.47	0.20	0.27	0.34
LIR	- 0.12	0.06	0.86	0.77
LK	0.36	0.57	0.41	0.62
explained variance (%)	40	22	12	

b.- Poederlee borehole

The geochemical profile shows several horizons with anomalous concentrations (fig. 9). Anomalous high Mg, Na, Fe, Mn, C_{org} and low Sr values occur in dolomite veins. Furthermore, two types of calcite veins can be distinguished:

- a first type with high Sr values and enriched in Fe and Mn;
- a second type with very high Fe and Mn concentrations.

High Na, Zn, Pb, Fe, Mn, IR and K content appear in the clayey breccia at 1657-1655 m. Due to the omnipresence of veins in the host limestone, veins were not excluded from the processed data set. In the element association and the factor analysis (table 13), the same variables are associated. A first factor mainly includes LMg(+), LSr(-), LNa(+), LFe(+), LMn(+), C_{org}(+), a second LZn(+), LPb(+), LK(+) and a third LIR(+).

The variables in the first factor are interpreted as the enrichment of Na, Fe and Mn in dolomite veins. Petrographically, organic material (impsonite) is associated with these veins. The second factor is caused by the exceptional concentrations of Pb and Zn in the clayey breccia at 1657-1655 m. Authigenic quartz forms the major constituent of the insoluble residue. The occurrence of the IR in a separate factor suggests that the silicification occurred independently from the other two diagenetic processes (dolomitization and brecciation).

From the discussions it can be concluded that the main variability in the geochemical distribution is caused by anomalous values.

4.- DISCUSSION AND CONCLUSIONS

4.1.- INFLUENCE OF THE MINERALOGY ON THE GEOCHEMICAL DISTRIBUTION PATTERN

Veizer & Demovic(1974) concluded from their geochemical study of Mesozoic limestones that the original $CaCO_3$ mineralogy has an important influence on the distribution pattern of Sr. Aragonite has a much higher Sr concentration than Mg-calcite and this difference remains after diagenesis. From our study of mainly subtidal deposits, this conclusion can not be confirmed. This can be due to an original uniform mineralogical composition of the limestones (e.g. high magnesium calcites).

The studied dolomites are enriched in Na, Mn, Fe, Zn and depleted in Sr compared with equivalent non-dolomitized limestones. A similar distribution has been recognized by Dejonghe (1987c) in Devonian dolomites of southern Belgium. Clays in limestones influence the distribution pattern of Mg, Na, Fe and K. The Fe, Zn and Pb distribution is influenced by the presence of sulphides or Fe-oxyhydroxides,

4.2.- TRACE ELEMENTS AS ENVIRONMENTAL AND DIAGENETIC INDICATORS IN LIMESTONES

Na and Sr have been frequently used as paleosalinity indicators (Veizer & Demovic, 1974; Kranz, 1976; Veizer,1977; Veizer *et al.*, 1977, 1978). In this study, Sr and Na can not be used as paleosalinity indicators. The distribution pattern of the trace elements is too much influenced by other factors such as the micrite association, the enrichment of Na in cements and veinlets, the adsorption and the incorporation on and in clay minerals and the removal of Sr during neomorphism.

The concentration of Fe and Mn has been applied to deduce the continental influence in the sedimentation environment (Friedman, 1969; Coulon, 1979; Pascal, 1979). The concentration of these two elements is very high in strata with an important terrigenous supply (Lower Moliniacian in the Booischot and Kessel borehole).However, other processes also can enrich carbonate rocks in Fe and Mn: dolomitization, karstification, neomorphism and early to late calcite cementation. We conclude that Fe and Mn can not be used as environmental indicators without a sediment petrographical analysis of samples.

Parker *et al.* (1985) concluded that the Mn/Fe ratio is not useful as a paleoenvironmental indicator, because diagenesis influences this ratio too much. In our study, high Mn/Fe ratios (>0,80) in limestones are the result of an extensive diagenesis under slightly reducing conclusions (Muchez, 1988).

Mg, which is present in relatively high concentrations in the primary sediment, can be removed (neomorphism) or supplied (dolomitization) during diagenesis.

A summary of the most important recognized influences on the geochemical distribution pattern of the elements in the carbonate rocks of the Campine-Brabant Basin is given in table 14.

Table 14.- Summary of factors influencing the distribution of the elements in the carbonates of the Campine-Brabant Basin.

Mineralogy	Occurrence and/or process	Influence on
Calcite: - sedimentary	- original mineralogy	?
	- sedimentation environment	Mg, Sr, Na, Fe, Mn
- diagenetic	- neomorphism	Mg, Sr, Fe, Mn
	- cementation	Mn, Fe, Na
	- veins	Mn, Fe, Sr
Dolomite	- completely dolomitized limestones	Mg, Mn, Fe, Zn, Na, Sr
	- veins	Mg, Mn, Fe, Na, Sr
Clays	- sedimentation environment/ diagenesis	on most elements
Organic material	- sedimentation environment/ diagenesis	Mg?, Sr?
Quartz	- sedimentation environment/ diagenesis	Dilution
Sulphides	- diagenesis/mineralization	Fe, Zn, Pb

A comparison of the distribution of the trace elements in the Visean carbonates south and north of the Brabant Massif has been published by Muchez (1989).

4.3.- IMPLICATIONS

The geochemical distribution of trace elements in limestones is influenced by the sedimentation environments, small amounts of non-carbonate mineral (clays, organic matter, ...), diagenetic and epigenetic processes such as dolomitization, neomorphism, cementation, karstification, mineralization and fracturing with calcite precipitation. These numerous factors restrict the interpretation of trace element concentrations in sediment petrographical and diagenetic studies and in lithogeochemical prospections in carbonates. A combination of petrographical and statistically processed geochemical data, is necessary for a better understanding of rock geochemistry.

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BIBLIOGRAPHY

ALLISON, L., 1965. Organic carbon. *In:* Methods of soil analysis, part 2. *Am. Soc. of agron. Inc.,* Madison: 1367-1378.

AHRENS, L., 1954. The lognormal distribution of elements. *Geochim. Cosmochim. Acta,* 5: 49-73.

BARBER, C., 1974. Major and trace element associations in limestones and dolomites. *Chem. Geol.,* 14: 273-280.

BAUM, G.R., HARRIS, W. B. & DREZ, P. E. 1985. Origin of dolomite in the Eocene Castle Hayne Limestone, North Carolina. *J. Sediment. Petrology,* 55: 506-517.

BERNER, R.A. 1970. Sedimentary pyrite formation. *Am. J. Sc.,* 268: 1-23.

BRAND, U. & VEIZER, J., 1980. Chemical diagenesis of a multicomponent carbonate system - 1 : Trace elements. *J. Sediment. Petrology,* 50: 1219-1236.

BURNS, S.J. & BAKER, P.A., 1987. A geochemical study of dolomite in the Monterey Formation, California. *J. Sediment. Petrology,* 57: 128-139.

CARROLL, D., 1958. Role of clay minerals in the transportation of iron. *Geochim. Cosmochim. Acta,* 14: 1-28.

CHOQUETTE, P.W. & STEINEN, R.P., 1980. Mississippian non-supratidal dolomite, Ste. Geneviève Limestones, Illinois basin : evidence for mixed-water dolomitization. *In:* Zenger, D.H., Dunham, J.B. & Ethington, R.L. (eds.): Concepts and models of dolomitization. *Soc. Econ. Paleont. Min. Spec. Publ.,* 28: 163-196.

CHURNET, H.G., MISRA, K.C. & WALKER, K.R., 1982. Deposition and dolomitization of upper Knox carbonate sediments, Copper Ridge district, East Tennessee. *Geol. Soc. Am. Bull.,* 93: 76-86.

CLIFFORD, J.A., KUCHA, H. & MELDRUM, A.H., 1988. Lithogeochemistry, its applicability to base metal exploration in a carbonate environment. *In:* Boissonnas, J. & Omenetto, P. (eds.): Mineral deposits within the European community. Springer-Verlag Berlin: 391-405.

COULON, M., 1979. Milieux de sédimentation, strontium et manganèse dans les calcaires à entroques de Bourgogne. *Bull. Soc. géol. France,* 21 : 681-685.

CURTIS, C.D., 1967. Diagenetic iron minerals in some British carboniferous sediments. *Geochim. Cosmochim. Acta,* 31 : 2109-2123.

DEJONGHE, L., 1985. Contribution à l'étude métallogénique du synclinorium de Verviers (Belgique). Thèse de doctorat d'état et sciences naturelles. Université Pierre et Marie Curie, Paris 6. *Mém. Sc. Terre,* 85-23: 389 pp.

DEJONGHE, L., 1987a. Lithogéochimie de sédiments de plate-forme déposés au sud du Massif de Brabant (Belgique) pendant le Mésodévonien et le Frasnien. *Mém. Expl. Cartes Géol. Min. Belg.,* 23: 147 pp.

DEJONGHE, L., 1987b. Lithogeochemistry of the platform sediments deposited south of the Brabant Massif (Belgium) during the Mesodevonian and Frasnian. *Ann. Soc. géol. Belg.,* 110: 319-333.

DEJONGHE, L., 1987c. Contribution à l'étude des dolomies mésodévoniennes et frasniennes dans les synclinoria de Verviers et de Namur: répartition, pétrographie et géochimie. *Bull. Soc. belge Géol.,* 96: 107-119.

DUNHAM, J.B. & OLSON, E.R., 1980. Shallow subsurface dolomitization of of subtidally deposited carbonate sediments in the Hanson Creek Formation (Ordovician-Silurian of central Nevada). *In:* Zenger, D.H., Dunham, J.B. & Ethington, R.L. (eds.): Concepts and models of dolomitization. *Soc. Econ. Paleont. Min. Spec. Publ.,* 28: 139-161.

ERICKSON, R.L., MOSIER, E.L., VIETS, J.G., ODLAND, S.K. & ERICKSON, M.S., 1983. Subsurface geochemical exploration in carbonate Terrane-midcontinent, USA. *In:* Kisvarsanyi, G. *et al.* (eds.). *Proc. Int. Conf. Mississippi Valley Type lead-zinc deposits,* Rolla, Missouri, 1983: 575-583.

EVAMY, B.D., 1969. The precipitational environment and correlation of calcite cements deduced from artificial staining. *J. Sediment. Petrology,* 39: 787-793.

FRIEDMAN, G.M., 1969. Trace elements as possible environmental indicators in carbonate sediments. *Soc. Econ. Paleont. Min. Spec. Publ.,* 14: 193-198.

GWOSDZ, W. & KREBS, W., 1977. Manganese halo surrounding Meggen ore deposit, Germany. *Trans. Inst. Miner. Metal. (Sect. B. Appl. Earth Sci.),* 86: 73-77.

HARDIE, L.A., 1987. Perspectives, dolomitization: a critical view of some current views. *J. Sediment. Petrology,* 57: 166-183.

HERBOSCH, A., CAUET, S. & PREAT, A., 1983. Recherche de métallotectes de nature géochimique pour la prospection des gîtes Pb-Zn belges. Partie I: Géochimie isotopique du Pb et du S. Partie II: Sédimentologie et lithogéochimie : exemple du Givétien du bord sud du synclinorium de Dinant. *Prof. paper Serv. géol. Belg.,* 197: 123 p.

HITCHON, B., BILLINGS, G.K. & KLOVAN, J.E., 1971. Geochemistry and origin of formation waters in the western Canada sedimentary basin - III Factors controlling chemical composition. *Geochim. Cosmochim. Acta,* 35: 567-598.

HUTCHEON, I., NAHNYBIDA, C. & KROUSE, H.R., 1985. The geochemistry of carbonate cements in the Avalon sand, Grand Banks of Newfoundland. *Mineral. Magaz.,* 49: 457-467.

KINSMAN, D.J.J., 1969. Interpretation of Sr^{2+} concentrations in carbonate minerals and rocks. *J. Sediment. Petrology,* 39: 486-508.

KRANZ, J.R., 1976. Strontium - ein Fazies-Diagenese-Indikator im Oberen Wettersteinkalk (Mittel-Trias) der Ostalpen. *Geol.Rundschau.*, 65: 593-615.

LAND, L.S., 1980. The isopotic and trace element geochemistry of dolomite: the state of the art. *In:* Zenger, D.H., Dunham, J.B. & Ethington, R.L. (eds.): Concepts and models of dolomitization. *Soc. Econ. Paleont. Min. Spec. Publ.*, 28: 87-110.

MACHEL, H.G., 1986. Limestone diagenesis of Upper Devonian Nisku carbonates in the subsurface of central Alberta. *Can. J. Earth Sci.*, 23: 1804-1822.

MICHARD, C.R., 1968. Coprécipitation de l'ion manganeux avec le carbonate de calcium. *Comptes Rendus Acad. Sci. Paris*. sér. D, 267: 1685-1688.

MOORE, C.H.,1985. Upper Jurassic subsurface cements: a case history. *In:* Schneidermann, N. & Harris, P.M. (eds.): Carbonate cements. *Soc. Econ. Paleont. Min. Publ.*, 36: 291-308.

MOORE, C.H. & DRUCKMAN, Y., 1981. Burial diagenesis and porosity evolution, Upper Jurassic Smackover, Arkansas and Louisiana. *Bull. Am. Assoc. Petrol. Geol.*, 65: 597-628.

MUCHEZ, Ph., 1988. Sedimentologische, diagenetische en geochemische studie van de Dinantiaan strata ten noorden van het Brabant Massief (Bekken van de Kempen). Unpublished Ph. D. thesis, Katholieke Universiteit Leuven, Belgium, 311 p.

MUCHEZ, Ph., 1989. Comparison of the Visean strata north and south of the London-Brabant Massif. *Bull. Soc. belge Géol.*, 98: 155-162.

MUCHEZ, Ph., VIAENE, W., WOLF & M. BOUCKAERT, J., 1987a. Sedimentology, coalification pattern and paleogeography of the Campine-Brabant Basin during the Visean. *Geol Mijnbouw*, 66: 313-326.

MUCHEZ, Ph., CONIL, R., VIAENE, W., BOUCKAERT, J. & POTY, E., 1987b. Sedimentology and biostratigraphy of the Visean carbonates of the Heibaart (DzH1) borehole (northern Belgium). *Ann. Soc. géol. Belg.*, 110: 199-208.

PARKER, W.C., RAGLAND, P.C. & TEXTORIS, D.A., 1985. Controls on trace elements in the Ordovician Black River Group, New York, U.S.A. *Chem. Geol.*, 53: 83-94.

PASCAL, A., 1979. Utilisation des éléments traces dans la caractérisation des paléomilieux sédimentaires Urgoniens basco-cantabriques (Espagne). *Géobios, Mémoire Spécial*, 3: 331-345.

PINGITORE, N.E., 1982. The role of diffusion during carbonate diagenesis. *J. Sediment. Petrology*, 52: 27-39.

PREAT, A., CAUET, S. & HERBOSCH, A., 1983. Caractère épigénétique-étranger des gîtes filoniens Pb-Zn (Ba-F) du district du bord sud du synclinorium de Dinant (Belgique). *Mineral. Deposita*, 18: 349-363.

PREZBINDOWSKI, D.R., 1985. Burial cementation - Is it important? A case study, Stuart City Trend, South Central Texas. *In:* Schneidermann, N. & Harris, P.M. (eds.): Carbonate cements. *Soc. Econ. Paleont. Min. Spec. Publ.*, 36: 241-264.

ROBINSON, G.D., 1981. Adsorption of Cu, Zn and Pb near sulfide deposits by hydrous manganese-iron oxide coatings on stream alluviums. *Chem. Geol.*, 33: 65-79.

RUSSELL, M.J., 1974. Manganese halo surrounding the Tynagh ore deposit, Ireland: a preliminary note. *Trans. Inst. Miner. Metal.(Sect. B, Appl. Earth Sci.)*, 83: 65-66.

SCOTT, K.M., 1986. Elemental partitioning into Mn- and Fe-oxides derived from dolomitic shale-hosted Pb-Zn deposits, northwest Queensland, Autralia. *Chem. Geol.*, 57: 395-414.

SWENNEN, R., 1986. Lithogeochemistry of Dinantian carbonates in the Vesdre Basin (Verviers synclinorium: E-Belgium) and its relations to paleogeography, lithology, diagenesis and Pb-Zn mineralizations. *Meded. Kon. Acad. Wet., & Schone Kunsten België. Klasse Wet.*, 48(2): 66-108.

SWENNEN, R. & VIAENE, W.,1981. Lithogeochemistry of some carbonate sections of the Dinantian in the Vesder region (Belgium). *Bull. Soc. belge Géol.*, 90: 65-80.

SWENNEN, R., VAN ORSMAEL, J., JACOBS, L., OP DE BEECK, K., BOUCKAERT, J. & VIAENE, W., 1982a. Dinantian sedimentation around the Brabant Massif; sedimentology and geochemistry. *Public. Natuurh. Gen. Limburg*, 32: 16-23.

SWENNEN, R., BOONEN, P. & VIAENE, W.,1982b. Stratigraphy and lithogeochemistry of the Walhorn section (Lower Visean; Vesder Basin, E-Belgium) and its implications. *Bull. Soc. belge Géol.*, 91: 239-258.

SWENNEN, R., VIAENE, W., BOUCKAERT, J., SIMAKOV, K.V. & VAN OYEN, P., 1986. Lithogeochemistry of Upper Famennian-Tournaisian strata in the Omolon area (NE-USSR) and its implications. *Ann. Soc. géol. Belg.*, 109: 249-261.

TAYLOR, T.R. & SIBLEY, D.F., 1986. Petrographic and geochemical characteristics of dolomite types and the origin of ferroan dolomite in the Trenton Formation, Ordovician, Michigan Basin, U.S.A. *Sedimentology*, 33: 61-86.

THOMSON, J., HIGGS, N. C., JARVIS, I., HYDES, D. J., COLLEY, S. & WILSON, T.R.S., 1986. The behaviour of manganese in Atlantic carbonate sediments. *Geochim. Cosmochim. Acta*, 50: 1807-1818.

TUCKER, M.E., 1983. Diagenesis, geochemistry and origin of a Precambrian dolomite: the Beck Spring dolomite of eastern California. *J. Sediment. Petrology*, 53: 1097-1119.

VAN ORSMAEL, J., 1982. Lithogeochemie van de Dinantiaan karbonaatgesteenten in het synclinorium van Dinant. Unpublished Ph. D. thesis, Katholieke Universiteit Leuven, Belgium, 128 pp.

VAN ORSMAEL, J., VIAENE, W. & BOUCKAERT, J., 1980. Lithogeochemistry of Upper Tournaisian and Lower Visean carbonate rocks in the Dinant basin, Belgium: a preliminary study. *Meded. Rijks Geol. Dienst*, 32: 96-100.

VAN OYEN, P. & VIAENE, W., 1988. Lithogeochemical investigations in the Navan area, Ireland. *In:* Boissonnas, J. & Omenetto, P. (eds.): Mineral deposits within the European Community. Springer-Verlag Berlin: 378-389.

VEIZER, J., 1974. Cheminal diagenesis of Belemnite shells and possible consequences for paleotemperature determination. *N. Jb. Geol. Palaönt. Abh.*, 145: 279-305.

VEIZER, J., 1977. Diagenesis of Pre-Quaternary carbonates as indicated by tracer studies. *J. Sediment. Petrology*, 47: 565-581.

VEIZER, J. & DEMOVIC, R., 1974. Strontium as a tool in facies analysis. *J. Sediment. Petrol.*, 44: 93-115.

VEIZER, J., LEMIEUX, J., JONES, B., GIBLING, M.R. & SAVELLE, J., 1977. Sodium: paleosalinity indicator in ancient carbonate rocks. *Geology*, 5: 177-179.

VEIZER, J., LEMIEUX, J., BRIAN, J., GIBLING, M.R. & SAVELLE, J., 1978. Paleosalinity and dolomitization of a Lower Paleozoic carbonate sequence; Somerset and Prince of the Wales Islands Arctic, Canada. *Can. J. Earth Sci.*, 15: 1448-1461.

VIDETICH, P.E., 1985. Electron microprobe study of Mg distribution in recent Mg calcites and recrystallized equivalents from the Pleistocene and Tertiary. *J. Sediment. Petrology*, 55: 421-429.

VINE, J.D. & TOURTELOT, E.B., 1970. Geochemistry of black shale deposits. A summary report. *Econ. Geol.*, 65: 253-272.

WEBER, J.N., 1964. Trace element composition of dolostones and dolomites and its bearing on the dolomite problem. *Geochim. Cosmochim. Acta*, 28: 1817-1868.

YARIV, S. & CROSS, H., 1979. Geochemistry of colloid systems. Springer-Verlag, Berlin: 450 p.