Annales de la Société géologique de Belgique, T. 110 - 1987, pp. 319-333 Août 1988

LITHOGEOCHEMISTRY OF THE PLATFORM SEDIMENTS DEPOSITED SOUTH OF THE BRABANT MASSIF (BELGIUM) DURING THE MESODEVONIAN AND FRASNIAN[1]

by

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(11 figures and 3 tables)

RESUME.- Dans le but de préciser l'évolution géochimique des sédiments de plate-forme déposés au S du Massif de Brabant pendant le Mésodévonien et le Frasnien, une prospection lithogéochimique stratégique a été entreprise au Service géologique de Belgique. Elle a été conduite de 1980 à 1984, principalement dans le Synclinorium de Verviers. Au total, 1 133 échantillons répartis sur 25 coupes (affleurements et sondages) ont été analysés par fluorescence X pour 27 éléments. Pour chaque coupe, les résultats des analyses ont été reportés en regard de la colonne lithostratigraphique correspondante, ce qui a permis la visualisation des tendances d'évolution du fond géochimique et la mise en évidence de niveaux stratigraphiques géochimiquement anomaux. En phase finale, toutes les données ont fait l'objet de traitements statistiques. Tout d'abord, l'établissement de diagrammes de corrélations binaires a confirmé le contrôle lithologique de certains éléments. Ensuite, dans les cas des échantillons de fond géochimique et pour certaines populations sélectionnées par l'âge et la nature des roches encaissantes, on a calculé divers paramètres de distribution et les coefficients de corrélation correspondants. Un traitement des données par analyse factorielle a aussi été utilisé en complément des autres traitements statistiques. Enfin, au sein de chaque formation lithostratigraphique et pour les types de roches les plus représentatifs, les fonds géochimiques (moyennes géométriques) ont été calculés en chaque localité et cartographiés en vue de la mise en évidence de gradients géochimiques régionaux éventuels.

ABSTRACT.- A lithogeochemical Survey was undertaken by the Belgian Geological Survey during 1980-1984 to determine the geochemical evolution of the platform sediments deposited south of the Brabant Massif during the Mesodevonian and Frasnian. Work was mainly concentrated in the Verviers Synclinorium.

1 133 samples from 25 localities (outcrops and drillholes) were analysed for 27 elements. For each section, the results were plotted in stratigraphic order to demonstrate the evolution of the geochemical background and to characterize anomalous stratigraphic levels. All the data were then treated statistically. Binary correlation diagrams were drawn to demonstrate the lithological control of some of the elements. Various distribution parameters and the relevant correlation matrices were determined for the background samples and for some populations selected on the basis of age and lithology. Factor analysis was carried out on all the data. Finally, the geochemical backgrounds (geometric means) of all the formations and the main rock types, calculated for each locality, were mapped to reveal possible regional geochemical gradients.

The study of the geochemical backgrounds of various sedimentary rocks underlines the passive role of the limestones as source of Ba, Fe, Mn, Pb, Zn and Cu. Most of the anomalies which have been detected concern Zn, either alone or with other elements. They are mainly related to sedimentological breaks such as zones of transgression - regression, important lithological changes or both together. Furthermore, the regional anomalous character of the time surface on which occurs a Ba, (Zn, Pb) sedimentary deposit (Chaudfontaine) recently discovered by drillhole (Dejonghe, 1979) is emphasized.

1. Manuscrit reçu le 1er décembre 1987.

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A.- INTRODUCTION

In Belgium, three major sedimentary structural units may be distinguished :

1. a basement of Cambrian, Ordovician and Silurian rocks, mainly phyllites and quartzites;
2. an old cover of Devonian and Carboniferous sandstones, shales and limestones; and,
3. a young cover including conglomerates, chalks, marls, sands and clays of Permian and younger age.

Units 1 and 2 are folded whereas the young cover is flat-lying. By removing the latter, the main tectonic units may be distinguished (Fig. 1). The basement, affected by the Caledonian orogeny, appears in three main massifs : Brabant, Rocroi and Stavelot. The Devono-Carboniferous cover rests on the flanks of these old massifs. On the northern side of the Brabant Massif (Kempen Basin) this cover is not folded. In contrast, on the southern side of the Massif it was strongly affected by the Variscan orogeny and subject to major thrusting, notably :

- in western and central Belgium where the Dinant Synclinorium overrides the Namur Synclinorium along the Midi-Eifel Thrust; and,
- to the east where the Verviers Synclinorium overrides the Liège Syncline along the Aguesses-Asse Thrust.

In Belgium, the first publications dealing with the geochemistry of Palaeozoic sedimentary rocks appeared less than ten years ago. Examples are :

- Dinantian : Van Orsmael *et al.* (1980), Swennen & Viaene (1981), Swennen *et al.* (1982a, b);
- Famennian : Dreesen & Thorez (1982);
- Frasnian : de Walque *et al.* (1977), Dejonghe & de Walque (1981); and,
- Givetian : Herbosch *et al.* (1983), Préat *et al.* (1983).

The present papers gives the results of a regional investigation, carried out between 1980 and 1984, to study the geochemical evolution of the platform sediments deposited south of the Brabant

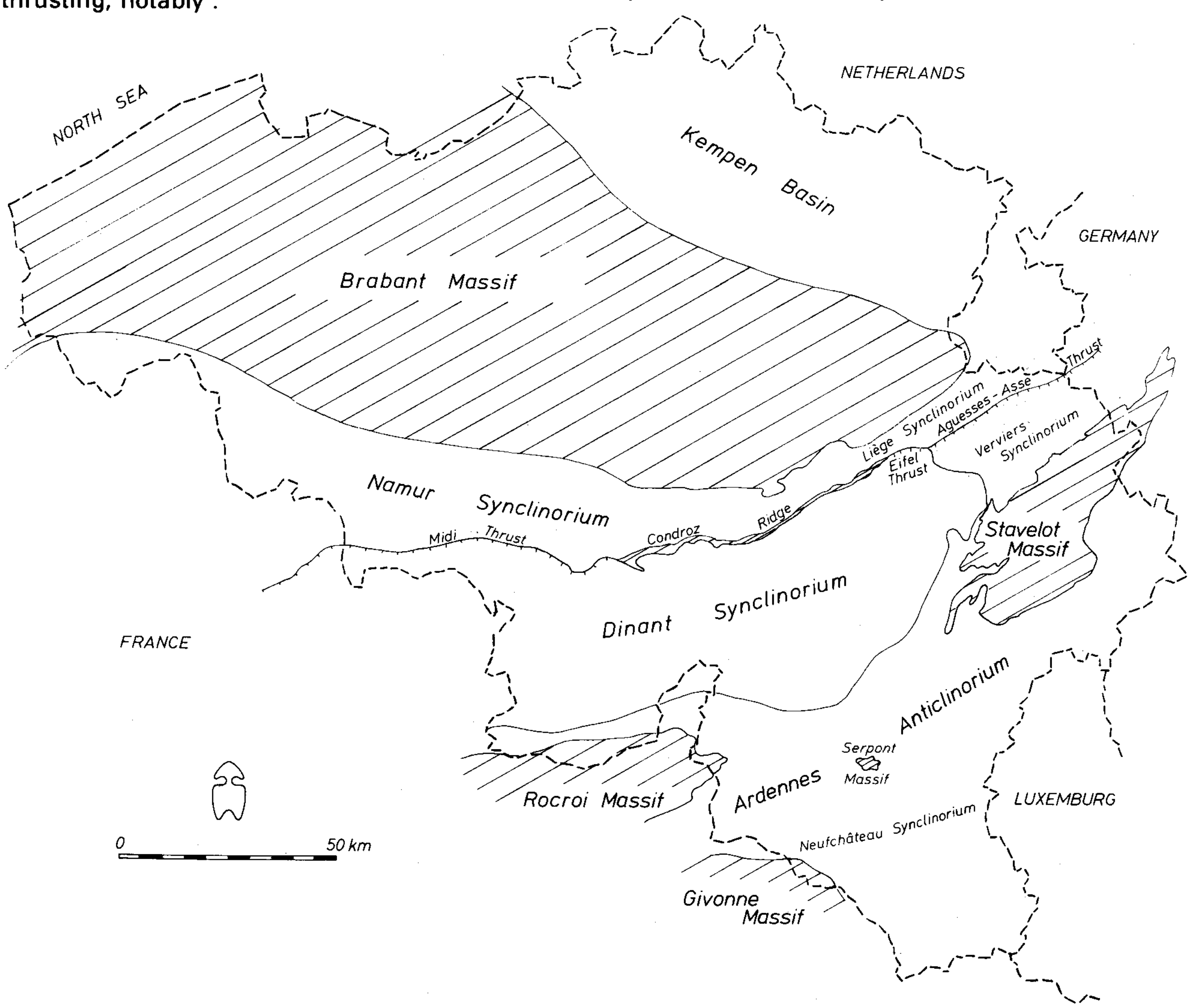

Figure 1.- Tectonic units of the Palaeozoic of Belgium.

Massif during the Mesodevonian and the Frasnian. The lithogeochemical study was carried out mainly in the Verviers Synclinorium where 20 sections, including outcrops and drillholes, were examined. In addition, 4 sections in the Namur Synclinorium and 1 section in the Dinant Synclinorium were studied.

Main past productions of lead and zinc in Belgium (around 1.500.000 tonnes of metals) were concentrated in the Verviers Synclinorium. All the mined ore came from vein or paleokarst - type deposits (Dejonghe & Jans, 1983; Dejonghe, 1985a, b). Recently, in this metallogenic district, a sedimentary Ba,(Zn,Pb) mineralisation hosted in Frasnian biostromal limestones was discovered at Chaudfontaine (Dejonghe, 1979). This discovery is important at least for two reasons :

1. it enlarges the scope of ore deposit's potential;
2. similar synsedimentary deposits may be regarded as source for the neighbouring vein and paleokarstic deposits.

The objectives of the study were thus to :

1. determine the geochemical backgrounds of rocks of various ages and lithologies;
2. search for geochemical gradients in the various formations;
3. determine whether the sedimentary mineralization of Chaudfontaine is reflected laterally by a geochemical anomaly; and,
4. detect anomalies at stratigraphic levels other than that of the Chaudfontaine mineralization.

B.- DESCRIPTION OF THE SAMPLED FORMATIONS

The formations which were sampled form part of a transgressive sequence which spread over the Brabant Massif during the Mesodevonian and Frasnian. An earlier, Eodevonian, transgression had deposited mainly coarse-grained detrital formations. The Mesodevonian and Frasnian stratigraphy of the Namur and Verviers synclinoria has been carefully studied by Lacroix (1972), Coen-Aubert (1974), and Coen-Aubert & Lacroix (1979, 1985). All the stratigraphic interpretations of sampled outcrops and drillcores are based on the work of these authors.

As the Chaudfontaine mineralization is situated in the Verviers Synclinorium, most of the prospecting effort was concentrated there. The lithostratigraphic and corresponding chronostratigraphic units in the area are as follows (Fig. 2) :

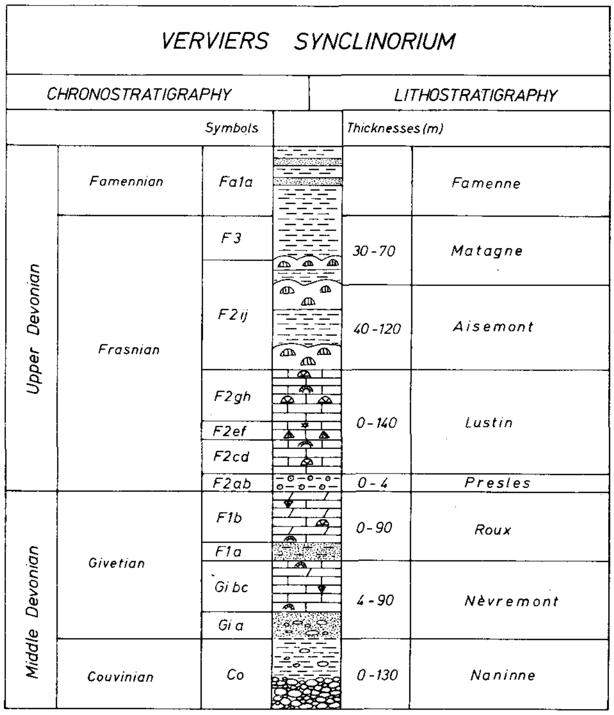

Figure 2.- Chronostratigraphic and lithostratigraphic units of the Verviers Synclinorium.

- **The Naninne Formation** comprises a basal conglomerate overlain by red, or sometimes green, shales.
- **The Nèvremont Formation** varies in lithology from west to east. In the west it is essentially terrigenous, but towards the east the terrigenous deposits are overlain by carbonate rocks.
- **The Roux Formation**, where well represented, comprises a lower terrigenous phase of micaceous and calcareous sandstones becoming more argillaceous eastwards, and an upper carbonate phase in which the proportions of limestone and dolomite vary from place to place.
- **The Presles Formation**, though relatively thin (max. 4 m), is lithologically very varied, ranging from shales, sometimes with seams of hematitic oolite, to dolomitic limestones with remains of calcareous oolites.
- **The Lustin Formation** is essentially calcareous. Biostromal levels, rich in debris of stromatoporoids and corals, alternate with nodular, organoclastic limestones and fine-grained limestones of lagoonal or sub-lagoonal facies.
- **The Aisemont Formation** is characterized by the coral *Phillipsastraea* which is concentrated in two biostromes, one at the bottom of the formation (abbreviated to «first biostrome»), the other at the top («second biostrome»). Normally, the biostromes are separated by shales. At

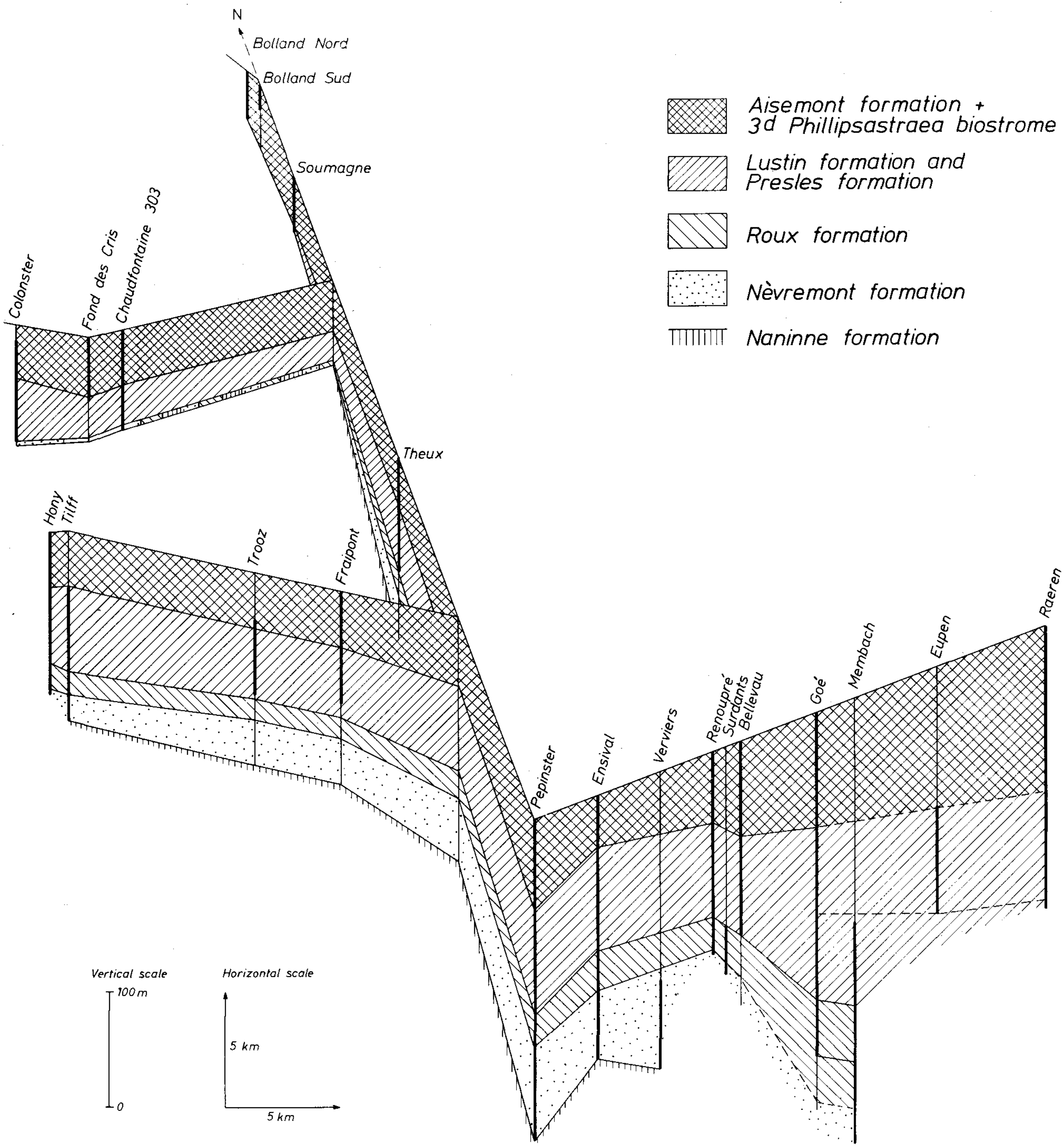

Figure 3.- Palinspastic reconstruction of the Giveto-Frasnian formations in the Verviers Synclinorium. Thickened vertical lines indicate sections observed in outcrop or drillholes. After Cnudde, *in* Dejonghe *et al.* (1982).

Chaudfontaine, however, the place of the shales is taken by a red bioherm. The Chaudfontaine mineralization is situated at the top of, and above, the second *Phillipsastraea* biostrome.

- **The Matagne Formation** terminates the Frasnian. It is mainly shale, but near or at the base there are red and green, nodular limestone rich in *Phillipsastraea* («third biostrome»). In some localities, they exhibit the typical facies of the «F2ij» red «marble» reefs which abound on the southern flank of the Dinant Synclinorium (Coen-Aubert, 1974, p. 128).

In the Soumagne drillcore, anhydrite is irregulary distributed through the three *Phillipsastraea* biostromes.

A palinspastic reconstruction of the Giveto-Frasnian formations of the Verviers Synclinorium (Fig. 3) was made by Cnudde (*in* Dejonghe *et al.,* 1982). This block-diagram shows that all the formations thin out to the north-west. This «bevelling», by condensation of the series, is due not to the proximity of the continent (Brabant Massif) but to the presence of a peripheral ridge named the «Booze - Le Val Dieu Ridge». During the Devonian and the Dinantian, this ridge functioned either as a positive area or as an island or, perhaps, as a real barrier blocking the connection between the Kempen and Ardennes basins (Kimpe *et al.,* 1978). During the Frasnian, the Chaudfontaine area was also a structural high situated on the flank of the «Booze - Le Val Dieu Ridge».

C.- PRESENTATION AND PROCESSING OF THE DATA

As details of sampling and analytical procedures are given by Dejonghe (1985a, 1987), only the main features will be indicated here.

On average, a sample was taken every metre of section, both in outcrop and drillcore. Simultaneous X.R.F. analyses of 27 elements were carried out at the Geological Survey of Sweden on a total of 1133 samples. Geochemical logs were drawn for every outcrop and drillhole. Since all are presented by Dejonghe (1985a, 1987), only one of the shortest of them is given here as an example (Figs. 4 and 5).

C.1.- TRENDS OF THE GEOCHEMICAL BACKGROUNDS

The main trends of the geochemical backgrounds, deduced directly from the geochemical logs are as follows :

The shales show an important increase in the content of Na_2O, K_2O, P, Y, Rb, Zr, V, Ti, Cr, Co, Fe and Ba. There is also an increase in Ni, Zn and Cu but it is less marked.

The dolomites and shales have markedly lower Sr contents than the limestones.

The dolomites shows an increase in the Cl and Mn contents.

The behaviour of S is enigmatic, whatever the lithology : the variations of S content can rarely be correlated with those of other elements.

C.2.- ANOMALIES

In general, stratigraphic levels corresponding to breaks in sedimentation or to marked lithological changes are anomalous as regards elements such as Zn, Pb and Ba. These levels, together with the localities (the latter plotted in Fig. 11) where anomalies were detected, are as follows.

The Presles Formation and the bottom of the Lustin Formation :

- Colonster : important anomalies in Zn (up to 890 ppm) and in Pb (up to 2434 ppm);
- Trooz : strong anomalies in Fe (up to 217600 ppm), Zn (up to 5335 ppm) and in Pb (up to 1260 ppm);
- Tilff : anomalies in Zn (709 ppm) and Ba (740 ppm);
- in most localities, an increase of the P content was noted.

The top of the Lustin Formation and the bottom of the first *Phillipsastraea* biostrome :

- Chaudfontaine (drillhole 134 E 303) : a small anomaly in Zn (190 ppm);
- Chaudfontaine (Fond des Cris quarries) : strong anomalies in Zn (up to 1360 ppm);
- Trooz : towards the top of the Lustin Formation a trend of increasing Zn and Pb content is observed. The first biostrome contains an anomaly in Zn (350 ppm). However, as the biostrome is very thin (here, less than 2 m), a distinction between its base an top is impossible at the sampling interval used;
- Huccorgne : anomalies in Zn (382 ppm);
- Engis : anomalies in Zn (469 ppm).

The top of the firts *Phillipsastraea* biostrome :

- Engis : anomalies in Ba (1085 ppm) and Zn (up to 568 ppm);
- Pépinster : anomalies in Zn (up to 1360 ppm);

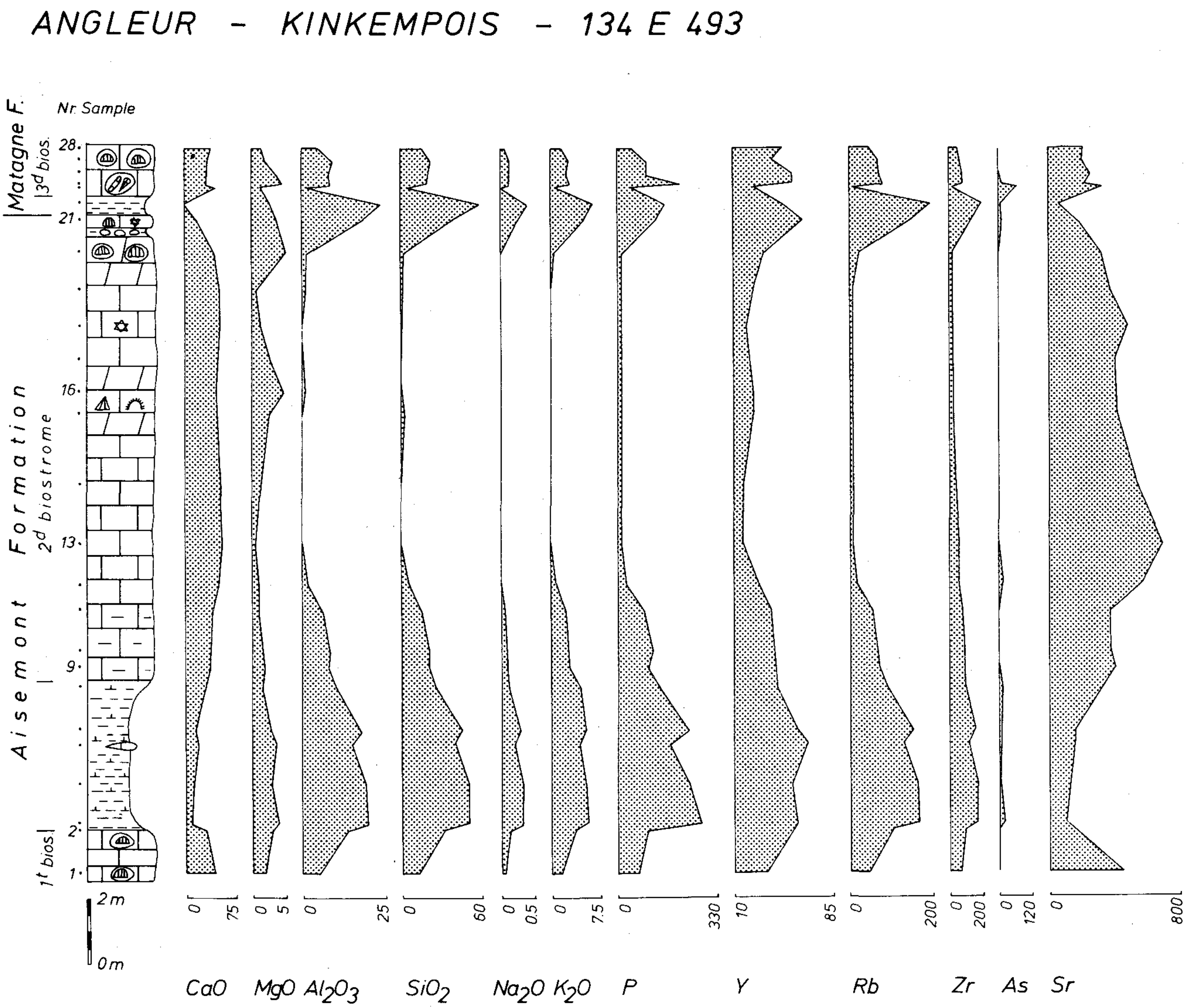

Figure 4.- Geochemical log of the Angleur-Kinkempois section. Oxides in %; monoelements in ppm. Sampling positions are indicated by dots to the left of the lithological log.

- Trooz : over a stratigraphic thickness of more than 10 m, all the shales which overlie the first biostrome are anomalous in Zn (up to 4683 ppm). The possibility of pollution was considered by Dejonghe (**1985a, 1987**) who, on the basis of various independent investigations (optical microscopy, microprobe analysis, selective chemical extraction, and short drillholes), concluded that the anomalies are probably natural. Significantly, Scheps and Friedrich (1983), working in the Inde Syncline (lateral equivalent in Germany of the Verviers Synclinorium), noted zinciferous anomalies up to 1000 ppm over a stratigraphic thickness of 4 m at exactly the same stratigraphic level;
- Fraipont : anomalies in Zn (1442 ppm), Pb (209 ppm) and Ba (750 ppm).

The top of the second *Phillipsastraea* biostrome and the base of the third *Phillipsastraea* biostrome where they are either in mutual contact or separated by a thin layer of shale. This is the level of the Chaudfontaine mineralization :

- Chaudfontaine (drillhole 134 E 769) : strong anomalies in Ba (up to 17183 ppm);
- Chaudfontaine (Les Thermes) : anomalies in Cu (90 ppm), As (45 ppm), Pb (690 ppm) and Zn (2434 ppm);
- Chaudfontaine (Fond des Cris quarries) : anomalies in Zn (up to 430 ppm) and Pb (up to 330 ppm);
- Kinkempois : anomalies in Ba (up to 2041 ppm) and Cu (110 ppm) as well as an increase in the Pb and Zn background values;
- Engis : anomaly in Zn (413 ppm);
- Colonster : anomaly in Zn (469 ppm);
- Prayon : weak *anomalies* in Pb (up to 120 ppm) and Zn (up to 333 ppm);
- Les Surdants, Renoupré : weak anomaly in Zn (320 ppm) 1 m above the second biostrome.

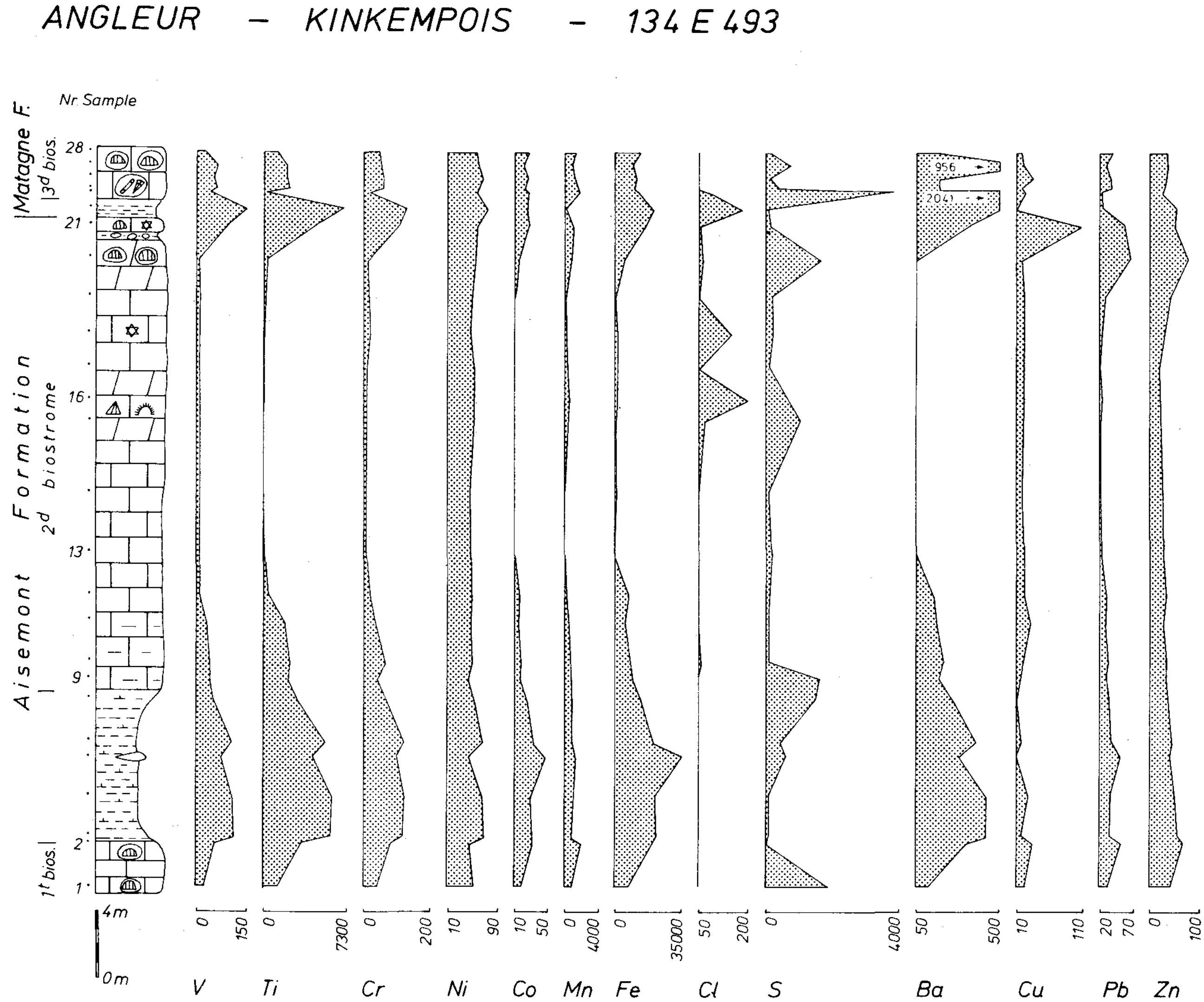

Figure 5.- Geochemical log of the Angleur-Kinkempois section (continued). Monoelements in ppm.

D.- TREATMENT OF THE DATA

All data have undergone various statistical treatments (1) to establish for each selected population :

1. diagrams of binary correlations;
2. distribution parameters of every chemical elements, including arithmetic and geometric means, standard and geometric deviations, variation coefficients and extrema;
3. matrices of correlation coefficients;
4. factors characterizing the variance of the system (factor analysis).

The populations were selected on the basis of the age and composition of the rock (e.g. dolomites of the Nèvremont Formation; limestones of the Lustin Formation). The following criteria were used to distinguish the compositional classes :

- sandstones : 75 % < SiO_2 < 100 %
- shales : 50 % < SiO_2 < 75 % and Al_2O_3 > 20 %
- «impure» (argillaceous and/or slightly dolomitic) limestones : 20 % < CaO < 40 % and MgO < 10 %
- «pure» limestones : CaO > 40 %; and,
- dolomites : mgO >10 %

D.1.- DIAGRAMS OF BINARY CORRELATIONS

The lithological control of some background elements, deduced from direct observation of the geochemical logs (section C.1), has been confir-

(1) Statistical studies 1 and 2 were carried out at the «Bureau de Recherches Géologiques et Minières - Orléans»; those of topics 2 and 3 at the «Centre de Traitement de l'Information» of the «Ministère des Affaires Economiques de Belgique».

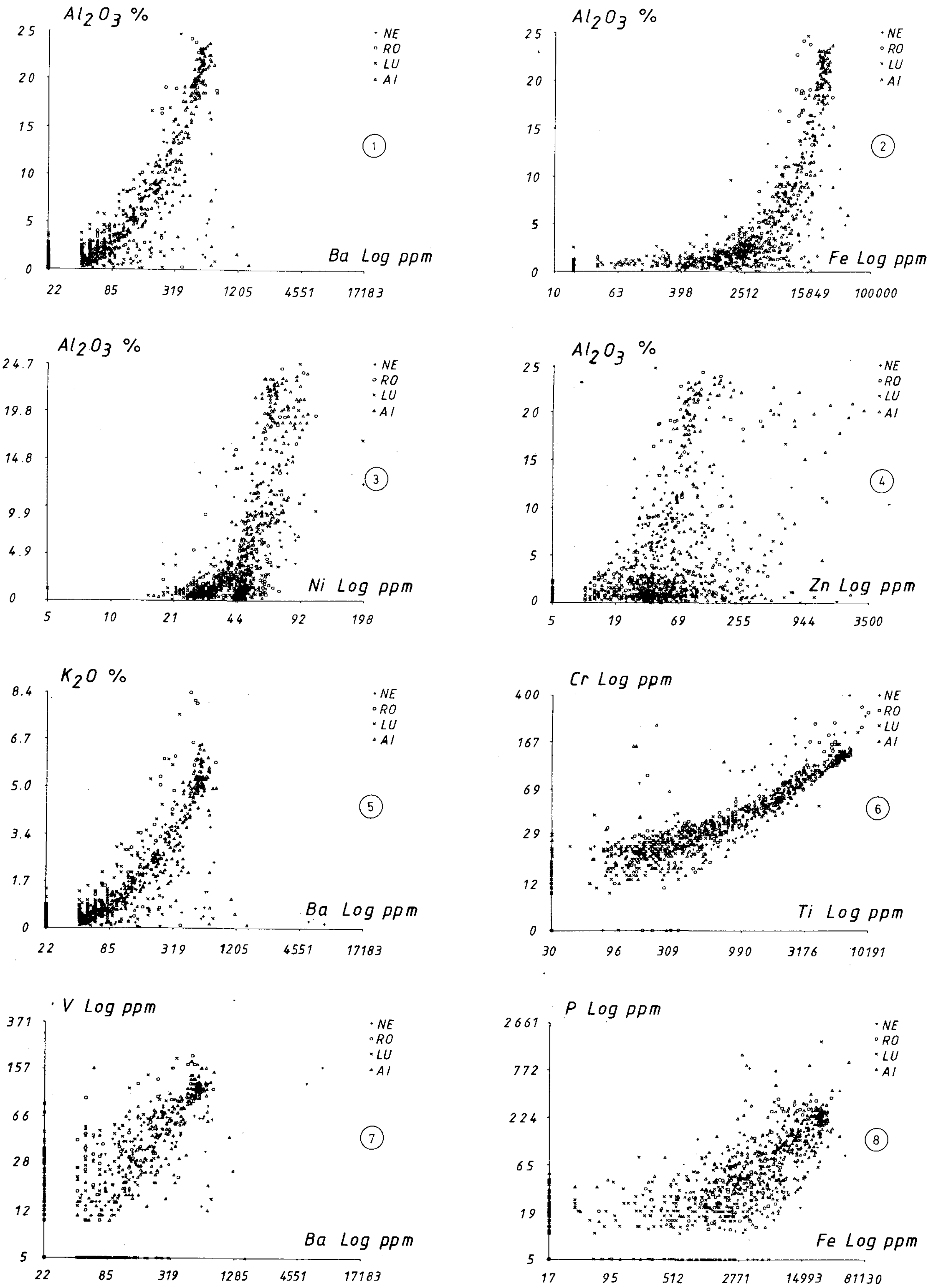

Figure 6.- Diagrams of binary correlations. Pinpoints representation. Correlations are positive and strong in most cases.

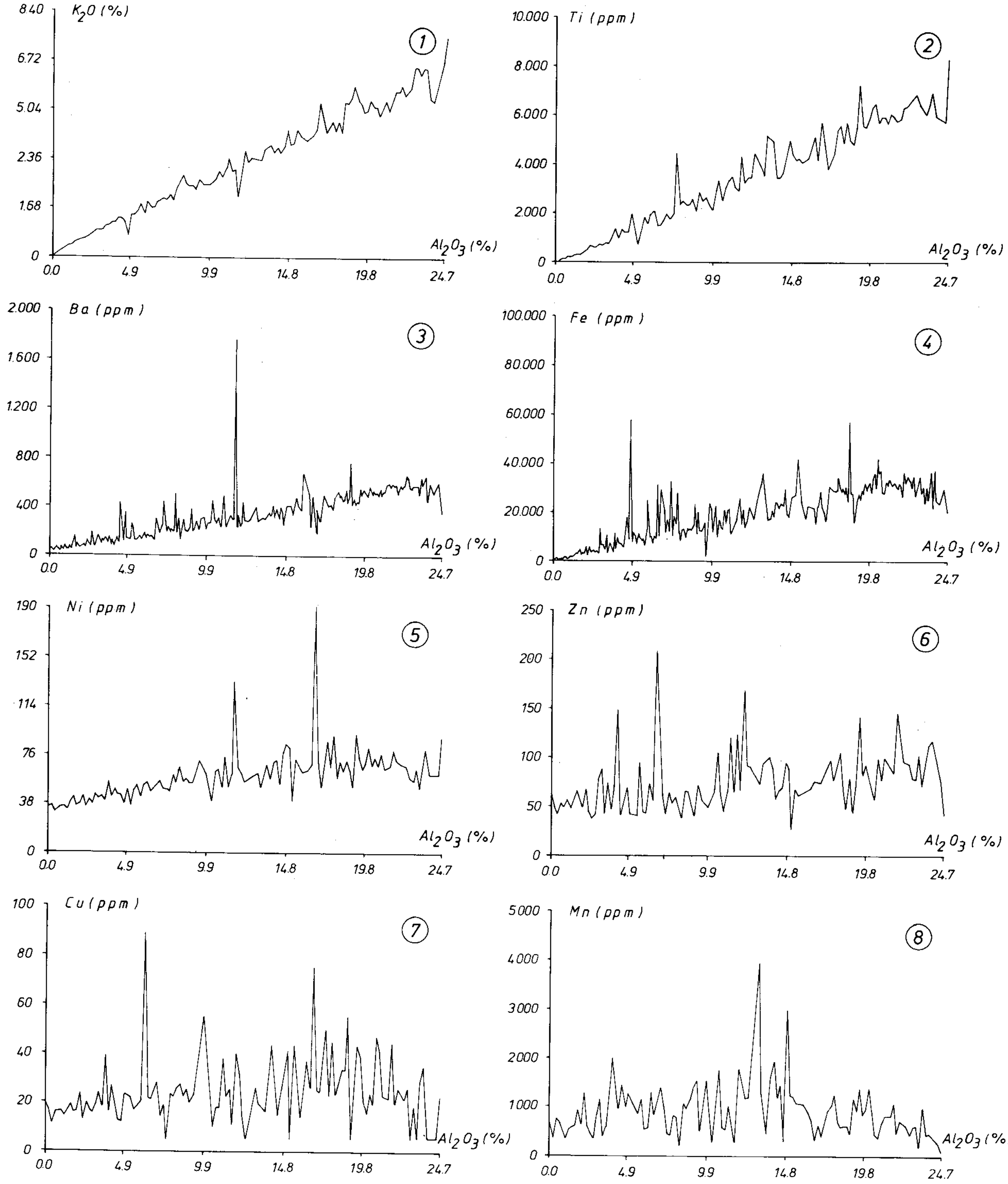

Figure 7.- Diagrams of binary correlations. Linear representation, smoothed.

med by binary correlation diagrams. Two types of representation have been used :

1. scatter plots in which samples from different formations are coded graphically (e.g. Fig. 6); and,

2. diagrams in which adjacent plotted points are joined to form a line plot. This representation is similar to that of well logging where the depth is replaced by the Al_2O_3 content (smoothed examples are show in Fig. 7).

Many of the elements show a strong positive correlation with Al_2O_3. This is very strong for SiO_2, K_2O (Fig. 7.1), Ba (Figs. 6.1 and 7.3), Fe (Figs. 6.2 and 7.4), Ti (Fig. 7.2), Cr and V. It is strong for Na_2O, MgO, P, Co, Y, Rb and Zr. The Ba - Al_2O_3 correlation is linear in natural values (65 ppm Ba at 0 % Al_2O_3; 600 ppm Ba at 25 % Al_2O_3). In the case of Fe (Fig. 7.4), it seems that saturation is reached at 20 % Al_2O_3 (30000 ppm Fe). Although Ni (Figs. 6.3 and 7.5) and Zn (Figs. 6.4 and 7.6) show a positive correlation with Al_2O_3, this is not as strongly marked as for the previous elements. However, the background values are doubled from 0 to 25 % Al_2O_3. For Cu (Fig. 7.7), a weak positive correlation appears between 15 % and 25 % Al_2O_3. There is no correlation with Al_2O_3 for Pb and Mn (Fig. 7.8). Cl and Sr show a strong negative correlation with Al_2O_3. The relationship between mineralogy and chemical data is thus clear. Most of the elements mentioned here above are bound to the clay minerals or eventually to S^{2-} or organic fraction correlated with clays.

All the binary correlation diagrams with MgO (see Dejonghe, 1987, p. 17) illustrate clearly that dolomitization is most intense in the Roux Formation. This agrees with field observations. In this study, it has been found that although the dolomites are sometimes anomalous in Zn, they are never anomalous in Pb. However, the strongest anomalies in Zn are encountered in the non-magnesian rocks of the Nèvremont and Lustin Formations. The Fe content of the dolomites is always high (generally between 2500 and 15000 ppm). Except for Sr (strongly negative), Mn and Cl (weakly positive), the other elements show no correlation with MgO. Sr is the only element which correlates positively with CaO.

Correlations between some pairs of minor and trace elements are positive and strong, notably for Cr-Ti (Fig. 6.6), V-Ba (Fig. 6.7), K_2O-Ba (Fig. 6.5), Y-Rb and Ni-Co. They are positive and moderate for Fe-P (Fig. 6.8), and positive and weak for Fe-Mn. There is no correlation between the following pairs of elements : Ba-S, Ba-Sr, Zn-Pb, Cu-Pb and Mn-Cl.

D.2.- DISTRIBUTION PARAMETERS AND MATRICES OF CORRELATION COEFFICIENTS

For various populations selected on the basis of the age and composition of the samples, tables of distribution parameters and matrices of correla-

Table 1.- Distribution parameters of the 25 analysed elements in pure limestones (n=591) of Givetian and Frasnian age (Nèvremont Formation through to Matagne Formation).
Oxides in %; monoelements in ppm. Elements below the detection limit have been taken into consideration for half the value of the detection limit.

Element	Detection limit	Arithmetic mean	Standard deviation	Coefficient of variation	Geometric mean	Geometric deviation	Minimum	Maximum
CaO	0.01	50.49	3.83	7.58	50.33	0.03	40.10	56.70
MgO	0.01	1.41	1.19	83.91	1.15	0.26	0.23	11.90
Al_2O_3	0.01	2.04	2.00	97.82	1.29	0.45	0.00	11.10
SiO_2	0.01	5.68	5.29	93.19	3.28	0.61	0.00	25.40
Na_2O	0.01	0.05	0.15	305.84	0.01	0.60	0.00	2.70
K_2O	0.01	0.63	0.59	93.97	0.43	0.40	0.01	3.50
P	10	55	124.70	225.67	28	0.45	6	1643
Y	10	16	9.99	60.96	13	0.31	5	61
Rb	10	16	19.38	121.97	10	0.39	5	130
Zr	10	37	27.84	74.78	27	0.39	5	150
As	20	12	9.29	75.78	11	0.15	10	170
Sr	20	315	133.05	42.21	290	0.17	45	797
V	10	12	12.75	110.30	8	0.33	5	83
Ti	60	539	592.40	109.85	307	0.49	30	4496
Cr	10	31	19.09	60.98	27	0.22	5	227
Ni	10	41	11.10	27.09	39	0.13	5	96
Co	10	11	7.98	75.75	9	0.27	5	72
Mn	80	503	592.06	117.72	314	0.43	39	5189
Fe	35	2429	3880.00	159.72	527	0.98	17	41614
Cl	50	91	51.16	56.05	79	0.24	25	490
S	50	750	2368.60	315.68	348	0.48	25	36289
Ba	45	63	60.96	96.78	45	0.34	22	7702
Cu	10	15	8.77	56.65	13	0.30	5	230
Pb	20	31	14.35	45.86	28	0.22	10	2698
Zn	10	50	39.12	77.81	37	0.37	5	5535

tion coefficients for 25 of the analysed elements (2) were determined. The large volume of the resulting data is a major obstacle to publication - which may well explain, in part at least, the rarity of this kind of information in the literature. Some of these tables, for all the formations studied, have been published (Dejonghe, 1985a, 1987). Table 1, concerning the pure limestones, is given here as an example.

In addition, a study was made of the behaviour of the backgrounds of 7 elements (Pb, Zn, Cu, Ba, Fe, Mn and Sr) relative to age and lithology. It was necessary to group some of the formations in order to constitute statistically representative populations. Only 2 of the elements, Ba and Pb, will be discussed here.

Barium

For every formation or group of formations, the evolution curves of Ba versus lithology have the same shape (Fig. 8). Furthermore, whatever the lithology, the backgrounds are always the highest in the Aisemont-Matagne Formations. Figure 8 clearly shows that Ba is roughly 10 times as abundant in the shales (500 < Ba < 600 ppm) as in the pure limestones and the dolomites (25 ppm < Ba < 75 ppm). The Ba content of the impure limestones is mid-way between those of the shales and those of the carbonates, suggesting that the Ba in the impure limestones is essentially bound to the argillaceous fraction. This is confirmed by the correlation coefficients (Table 2) of the pairs Ba-Al (0.89) and Ba-Si (0.49).

Lead

Figure 9 shows that the dolomites (36 ppm < Pb < 48 ppm) are nearly twice as rich in Pb as the shales (21 ppm < Pb < 28 ppm), while the limestones (24 ppm < Pb < 34 ppm) are only

(2) Mo and W, systematically below the detection limit of 10 ppm were omitted.

Table 2.- Correlation coefficients between Ba and some other elements. Extracted from matrices given by Dejonghe (1985a, 1987).

Populations	*Correlation coefficients*				*Significance level at 99 %*
	Ba-Al	Ba-Si	Ba-Mg	Ba-Ca	
all the shales (n = 74)	0.24	0.39	0.03	0.14	0.27
all the impure limestones (n = 108)	0.89	0.49	- 0.21	- 0.34	0.22
all the pure limestones (n = 591)	0.67	0.49	0.23	- 0.63	0.10
all the dolomites (n = 73)	0.70	0.35	- 0.35	- 0.47	0.22

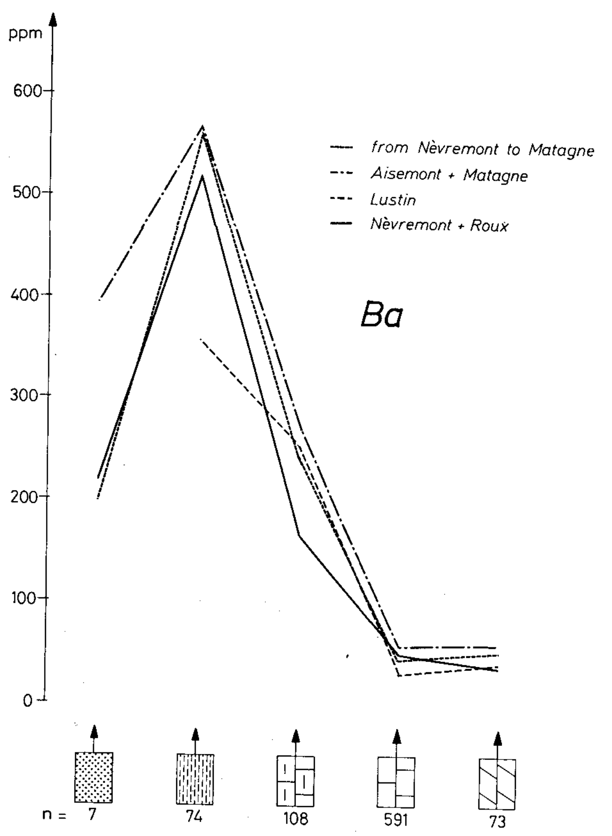

Figure 8.- Relationship between Ba content and lithology. From left to right : sandstone, shale, impure limestone, pure limestone, dolomite.

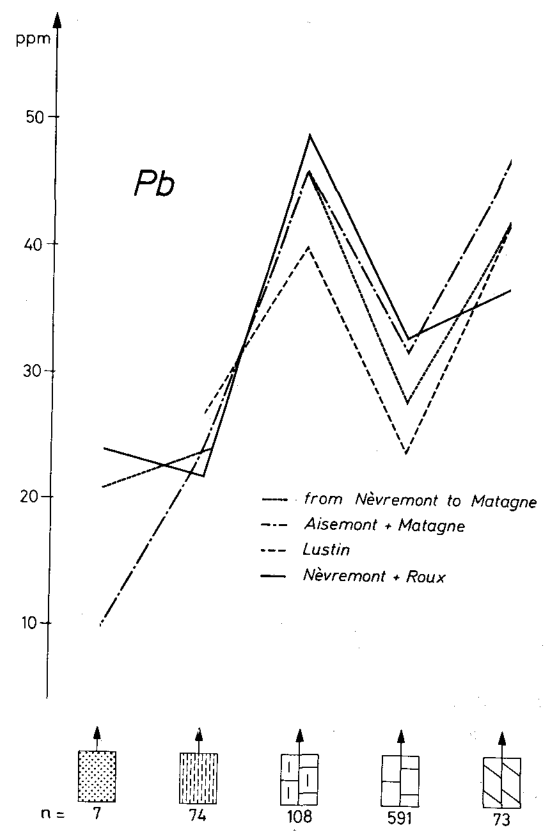

Figure 9.- Relationship between Pb content and lithology. From left to right : sandstone, shale, impure limestone, pure limestone, dolomite.

Table 3.- Correlation coefficients between Pb and some other elements. Extracted from matrices given by Dejonghe (1985a, 1987).

Populations	Correlation coefficients				Significance level at 99 %
	Pb-Al	Pb-Si	Pb-Mg	Pb-Ca	
all the shales (n = 74)	- 0.21	0.10	0.28	0.42	0.27
all the impure limestones (n = 108)	0.09	0.15	0.49	- 0.06	0.22
all the pure limestones (n = 591)	0.46	0.32	0.24	- 0.34	0.10
all the dolomites (n = 73)	0.44	0.40	- 0.22	- 0.21	0.27

slightly enriched in Pb. Thus, in this case, dolomitization of the limestones has led to their enrichment in Pb. Figure 9 also shows that the Pb content of the impure limestones (39 ppm < Pb < 50 ppm) is particularly high, suggesting that the Pb is bound to the dolomite present rather than to the argillaceous fraction. This is confirmed by the correlation coefficients (Table 3) : in the impure limestones, the coefficient Pb-Mg is relatively high (0.49) while those of the pairs Pb-Al (0.09) and Pb-Si (0.15) have no significance. In the pure limestones and the dolomites, however, the correlation coefficients Pb-Al (0.46 and 0.44 respectively) and Pb-Si (0.32 and 0.40 respectively) indicate that a certain linkage with the argillaceous fraction cannot be neglected. There are thus two possible Pb sources differing in strength. Their effect may be cumulative in the impure limestones.

D.3.- FACTOR ANALYSIS

Factor analysis was used to complement the other statistical techniques. Four populations of samples were considered : those from the Nèvremont and Roux Formations (n=207); those from the Lustin Formation (n=345); those from the Aisemont and Matagne Formations (n=491); and, at least, those from all Formations (Presles also included : n=1121 - Fig. 10).

The factor which accounts for most of the variance of the system has the same significance in all terrigenous rocks (group SiO_2, Al_2O_3, K_2O). Sr is the only element bound to CaO. In contrast, many elements are bound to the group SiO_2, Al_2O_3, K_2O, namely, Rb, Ti, Cr, Co, Fe, Ni, V and Zr. This first factor is most dominant (variance 48.93 %) in the Aisemont-Matagne population.

The nature of the second factor differs from population to population. In the Aisemont-Matagne population it is a dolomitization factor (8.56 % of variance, MgO, Mn and Cl opposed to Sr); in Lustin, a sulphide factor (12.17 % of variance; S, Pb, As and Zn); and in Nèvremont-Roux, a sandstone factor (11.78 % of variance; SiO_2, Cu, Pb, Zr and Cr opposed to CaO).

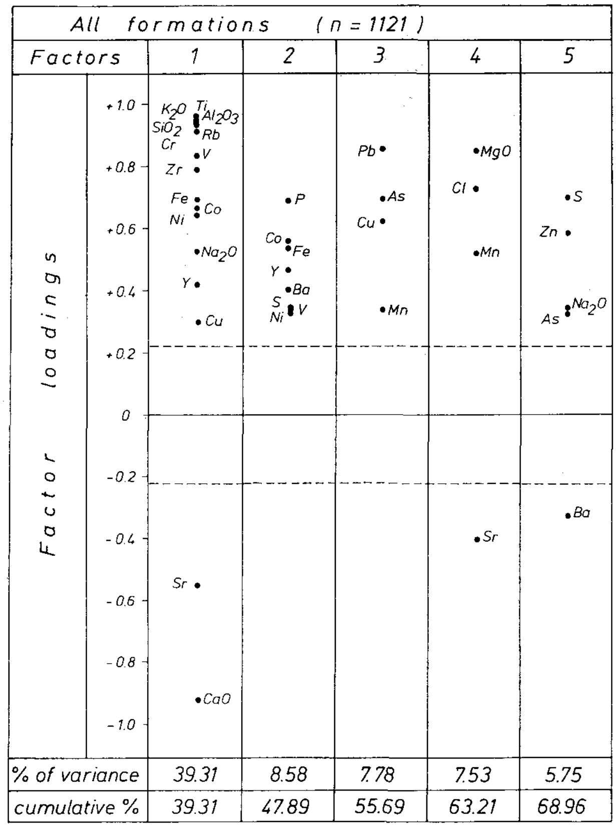

Figure 10.- Graphical representation of the results of principal component analysis applied to samples from all formations. Factor loadings below the significance level (0.22; Harman, 1967) are omitted.

It is difficult to interpret the factors which account for less than 10 % of the variance. Worthy of note, however, is factor 5 (5 % of variance; positively loaded with Ba and V) in the Aisemont-Matagne population. The barium-rich sedimentary mineralization of Chaudfontaine is located in the transition zone between these formations.

Factor analysis thus confirms all the trends previously detected but adds no new informations.

D.4.- IDENTIFICATION OF REGIONAL GEOCHEMICAL GRADIENTS

For every locality, the backgrounds (geometric means) in Pb, Zn, Cu, Ba and Mn were calculated for the various formations and the main lithologies.They were then mapped to determine possible regional geochemical gradients. As an example, the map of the backgrounds for the pure limestones of the Lustin Formation is presented in Figure 11.

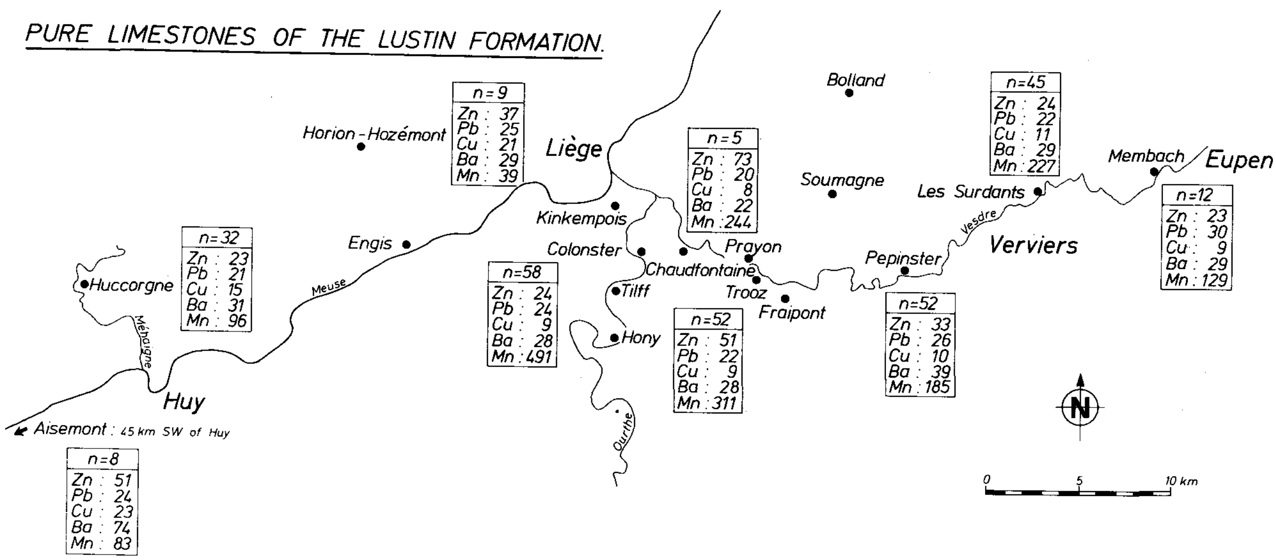

Figure 11.- Geographical variation of Zn, Pb, Cu, Ba and Mn (geometric means of the backgrounds) in the pure limestones of the Lustin Formation.

The main results of the study are as follows :

1. The pure limestones of the Nèvremont Formation show no significant gradient, but there are notably high Mn values at Tilff (1537 ppm) and Trooz (1084 ppm).
2. The pure limestones of the Lustin Formation (Fig. 11) show no gradient for Pb, Cu and Ba. The Zn content is, however, relatively high in the Chaudfontaine - Trooz area and at Aisemont. The same is true for Mn at Trooz, Tilff and Chaudfontaine. Thus, a discrete gradient seems to be present around the Chaudfontaine «high».
3. In the pure limestones of the Aisemont and Matagne Formations, the Bolland and Soumagne drillcore samples show relationships completely different from those of all the other localities. In the drillcores, the Zn grades are weak and the Pb grades high, while elsewhere this relationship is reversed. Apart from this, there is no significant gradient for any element. The Zn and Mn gradients which seem to exist in the pure limestones of the Lustin Formation around the Chaudfontaine «high» do not occur in the pure limestones of the Aisemont and Matagne Formations. However, compared with the limestones of the Lustin Formation, those of the Aisemont and Matagne Formations have consistently higher Mn contents, in particular at Hony (1258 ppm) and Soumagne (905 ppm).
4. The dolomites of the Roux Formation show no significant gradients, but they do have one peculiarity. While in other formations, whatever the lithology, the Zn background is commonly greater than the Pb background, this relationship is reversed in the dolomites of the Roux Formation.
5. In the dolomites of the Aisemont and Matagne Formations, the Bolland and Soumagne drillholes are again characterized by Zn values which are low (20 ppm and 5 ppm, respectively) compared with those of other localities. In contrast, at Aisemont, the Zn (93 ppm) and Ba (598 ppm) grades are high. In the case of Zn, an east-west positive gradient seems to exist but it is not confirmed by the other elements. Very high Mn values are found at Bolland (4078 ppm) and Colonster (4272 ppm).
6. No gradient was detected for any element in the shales of the Aisemont and Matagne Formations.

E.- CONCLUSIONS

The main conclusions for each of the objectives stated at the beginning of this study and their implication for exploration are as follows.

E.1.- GEOCHEMICAL BACKGROUNDS

Of the five lithologies which have been considered, the pure limestones are the poorest in Ba and Fe and are among the poorest in Mn, Pb, Cu and Zn. Moreover, most of the correlation coefficients between these elements and Ca are negative. The supply of these elements during carbonate sedimentation with no accompanying siliciclastic input was thus only accessory. Hence, if ore deposits are interbedded in carbonate rocks, they were formed by mineralizing solutions resulting from other processes superimposed on the carbonate depositional system.

In contrast, numerous elements are either tighly bound to clay minerals (e.g.: Ba, Fe and Zn) or are related to dolomitization (e.g.: Mn and Pb).

The shales are richest in Ba and Fe, and are among the richest in Zn and Cu. As these rocks have undergone important diagenetic transformations which resulted in the liberation of part of their adsorbed metals, it can be supposed that these trends were even more pronounced in the fresh sediments. Such muds were an important potential source of metals.

The role of dolomitization is also important. Facies and repartition of the Mesodevonian and Frasnian dolomites from the Verviers and Namur synclinoria have been precized by Dejonghe (1985a, ch. XI). All the dolomites encountered in this study are strata-bound and early diagenetic. They have undergone various transformations which overprinted the original structures. Some owe their origin to sabkha processes. Although the Sr and, to a lesser extent, the Zn were partially leached from the limestones by dolomitization, it seems that the Ba content was not affected. In contrast, substantial quantities of Mn and Pb, and moderate amounts of Fe were introduced by dolomitization.

This study of the geochemical backgrounds of various sedimentary rocks underlines the passive role of the limestones as a source of Ba, Fe, Mn, Pb, Zn and Cu. In the genesis of sedimentary ore deposits, the role of limestones is restricted to that of a trap.

The backgrounds of Ba, Fe, Zn, Mn and Sr are always highest in the Aisemont and Matagne Formations.

E.2.- GEOCHEMICAL GRADIENTS

No significant geochemical gradients have been identified either in the Verviers Synclinorium or in those parts of the Namur and Dinant synclinoria which have investigated. The only exception concerns the limestones of the Lustin Formation where the Zn grades increase in the vicinity of the Chaudfontaine «high».

E.3.- GEOCHEMICAL ANOMALIES

The sampling of the Naninne, Nèvremont and Roux Formations was insufficient for general conclusions to be drawn on the anomalies encountered. At Colonster and Tilff, however, the anomalous character of the Nèvremont Formation is clearly marked for Pb, Zn, Cu, Ni, Ba and As.

General conclusions may be presented for the Presles, Lustin, Aisemont and Matagne Formations which were examined at numerous localities in the Verviers, Namur and Dinant synclinoria. In these formations, anomalies are mainly related to sedimentological breaks such as zones of transgression-regression, important lithological changes, or both together. Minor anomalies within carbonate complexes often correspond to thin argillaceous partings which reflect minor sedimentological variations.

Most of the anomalies concern Zn, either alone or with other elements. Zn anomalies are abundant at the top of the Lustin Formation and at the bottom of the first *Phillipsastraea* biostrome. In the Aisemont and Matagne Formations, Ba is frequently associated with other metals. As is a good indicator of anomalies. Indeed, when As grades increase the grades of other metals also increase.

In the Presles Formation, where facies vary considerably from place to place, there are abundant anomalies involving various assemblages of elements. This thin formation (4 m max.) was deposited during a very rapid transgressive phase. In the vicinity of Les Mazures, it starts with a layer of hematitic oolite. At Les Surdants, it varies from carbonate oolites to hematitic and chamositic oolites associated with Fe sulphides. At Trooz, the main constituent of the formation is a dolomitic limestone with broken ooliths. At Colonster, where the formation starts with nodular limestones and ends with black shales containing carbonate nodules, spots of galena and sphalerite have been observed. In the Inde Syncline, in Germany, this formation (known as «Grenzschiefer») is 3 to 5 m thick and slightly enriched in Zn (300 ppm) and Cu (180 ppm) (Scheps & Friedrich, 1983). In all the localities in the Verviers Synclinorium, the Presles Formation is characterized by a P anomaly.

In the Lustin, Aisemont and Matagne Formations whatever the locality, the anomalies mainly occur at the bottom and top of carbonate units. However, important Zn anomalies (up to 4683 ppm) have been discovered at Trooz in the shales overlying the first *Phillipsastraea* biostrome. Scheps & Friedrich (1983) mention that at the same level in the Inde Syncline, Zn anomalies reach 1000 ppm and extend through a thickness of 4 m. They state the view that in the Aisemont and Matagne Formations «**the black shales and nodular limestones were deposited under euxinic conditions in a restricted environment of a swell and basin facies on top of an irregular**

subsiding shelf platform. This sedimentary environment is favourable for sulphide sedimentation» (Ibid, p. 420).

The Chaudfontaine mineralization is neither preceded nor followed by rocks with anomalous geochemical backgrounds. But, the time-surface on which this mineralization is developed is regionally anomalous. The anomalies vary from place to place in intensity as well as in the nature of the mineral assemblage. The situation is thus different from that occuring in the stratiform ore deposits of the southern side of the Massif Central in France (Barbier, 1979; Aubague *et al.,* 1982). The Chaudfontaine mineralization does not seem to be surrounded by a local geochemical halo and certainly no by a Mn halo as is the case for some exhalative sedimentary ore deposits such a those at Tynagh in Ireland (Russel, 1974) and Meggen in Germany (Gowsdz & Krebs, 1977).

ACKNOWLEDGEMENTS

Part of this work was supported by the Commission of the European Communities under contract n° 031-79 MPP-B. J. Boissonnas is particularly thanked for his help. X.R.F. analyses were performed at the Geological Survey of Sweden (Lulea) by J. Malmqvist and J.O. Burman. Access to the computer and statistical programs of the BRGM (France) was facilitated thanks to E. Wilhelm. I am also indebted to H. Martin and F. Sondag (University of Louvain), J.F. Sureau and P. Austrière (BRGM) and J.P. Goffaux (Ministry of Economic Affairs of Belgium) for stimulating discussion. a Lees (University of Louvain) is acknowledged for correcting the English text.

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