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STRATIGRAPHY AND LITHOGEOCHEMISTRY OF THE WALHORN SECTION (LOWER VISEAN; VESDER BASIN, E.-BELGIUM) AND ITS IMPLICATIONS

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ABSTRACT. - The lithostratigraphy, biostratigraphy, sedimentpetrography and lithogeochemistry of the Walhorn quarry (123E-224; Vesder basin, Belgium) has been studied.

The Vesder Dolostone Formation consists of thin bedded brown to brown-grey dolostones, banded palisade calcite beds and a dolostone breccia. Features indicating evaporitic sedimentation environments are presents in all three units. An eogenetic relationship between primary (dolostone breccia) and secondary (brown to brown-grey dolostones) dolostones, was recognized. Dolomitization is explained by refluxing hypersaline solutions. The upper part of this formation is of Visean age (Moliniacian).

The Ourthe Breccia Formation is an evaporitic collapse breccia of Lower Visean age (Moliniacian).

In the Neffe Formation, 4 successive transgressive limestone sequences of Lower Visean age (Moliniacian : VI or V2a) were recognized below the Banc d'Or de Bachant. The sedimentation environment changed from supra- to inter- and from inter- to subtidal. Correlations are possible with the eastern part of the Dinant basin, but are untill yet less clear with the Namur basin and the Aachen area.

The lithogeochemistry revealed different characteristic distribution patterns for the different lithologies. Most trace elements, except Sr, are higher in the dolostones than in the limestones. The distribution in the secondary dolostones and primary dolostone breccias is controlled by lithological and paleoenvironmental features. High Zn, Pb, Fe, Mn and Ni concentrations and low Sr, Na concentrations were detected in the dedolomitized zones, which are present in the dolostone breccia. They are related to weathering processes. In the limestone breccias and overlying limestones higher trace element concentrations are related to micritic strata with birdseyes, corresponding to supra- to intertidal sediments, and possibly to adsorption phenomena on Fe Mn oxides/hydroxides and clays. The geochemical and geological data suggest an absence of nearby mineralizations in the Walhorn area. The use of Sr as a hypersalinity indicator in limestones and dolostones, and as a diagenetic indicator in dolostones is confirmed. The Na content in dolostones, is related to the dolomitizing solutions; its use as hypersaline indicator in limestones is confirmed. However, the present data suggest that the proposed approximate boundary between normal marine and hypersaline environments of 230 ppm (VEIZER et al., 1978) must be lowered for the Dinant-Namur basin.

RESUME.- Les sédiments carbonatés de la carrière de Walhorn (123E-224, bassin de la Vesdre) font l'objet de la présente étude.

La Formation des Dolomies de la Vesdre consiste en dolomies brunes à gris-brunes, surmontés de bancs de calcite en forme de palisade et d'une brèche dolomitique. Divers phénomènes indiquent une sédimentation évaporitique. Le sommet de cette formation est d'âge Viséen inférieur (Moliniacien). Une relation éogénétique existe entre la dolomie primaire (brèche dolomitique) et la dolomie secondaire (dolomies brunes à gris-brunes). La dolomitisation s'est effectuée par l'intermédiaire des solutions hypersalines refluxantes.

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La Formation de la Brèche de l'Ourthe est une brèche calcaire d'origine évaporitique et d'âge Viséen inférieur (Moliniacien).

Sous le Banc d'or de Bachant, la Formation de Neffe est composée de 4 séquences calcareuses transgressives. Ces calcaires sont d'âge Viséen inférieur (Moliniacien : VI ou V2a). Ils se sont déposés dans des milieux supra- à intertidaux et inter- à subtidaux. De bonnes corrélations sont possibles avec le bassin de Dinant tandis qu'elles sont moins évidentes avec le bassin de Namur ou la région d'Aix-la-Chapelle.

L'étude lithogéochimique a révélée des distributions caractéristiques pour les différentes lithologies. A l'exception du Sr, tous les éléments en traces sont enrichis dans les dolomies. La distribution géochimique dans les dolomies (primaires et secondaires) est contrôlée par la lithologie et le milieu de sédimentation original. Les zones de dédolomitisation à l'intérieur et au sommet de la brèche dolomitique révèlent des concentrations en Zn, Pb, Fe et Mn et des faibles teneurs en Sr et Na, expliqués par des phénomènes d'altération superficielle. Dans la brèche calcaire et dans les calcaires, les concentrations d'éléments en trace sont en relation avec la présence de micrites avec "birds-eyes" du faciès supra- à intertidal et avec des phénomènes d'adsorption (Fe Mn oxides/hydroxides et argiles). Les données géologiques et géochimiques suggèrent l'absence de minéralisations Pb-Zn dans les environs de Walhorn. L'intérêt de Sr comme indicateur de hypersalinité dans les calcaires et les dolomies et comme indicateur diagénétique dans les dolomies a été confirmé. Na est, dans les dolomies, en relation avec les solutions dolomitisantes. Son intérêt comme indicateur de hypersalinité dans les calcaires a été confirmé. Le contenu en Na limitant les zones hypersalines des zones de salinité normale (230 ppm, VEIZER et al. 1978) doit être abaissé dans les bassins de Dinant et Namur.

INTRODUCTION.

The recent interest in the Dinantian around the Brabant Massif was initiated by new stimulating facts with regard to evaporites and related phenomena (BLESS et al. 1980) and by the renewed interest for potential Pb-Zn deposits related to these strata.

The development of correct paleogeographic and metallogenetic models has to be based on a detailed knowledge of geological data. Recent data, however, are very scarce for the Vesder basin (E-Belgium).

The present paper presents the results of a litho- and biostratigraphic study of the Walhorn quarry (123E-224). This quarry shows the most representative succession for the Lower Visean in the E-Vesder basin. Furthermore, recent investigations revealed the presence of different evaporitic sequences and different types of dolostones (SWENNEN et al. 1981, JACOBS et al. 1982). The lithogeochemical study will allow us to compare data from this area, which is barren of known mineralizations, with data from the mineralized part of the E-Vesder basin (SWENNEN and VIAENE, 1981). Also, the use of lithogeochemical variables as diagenetic and/or paleosalinity indicators, as proposed by several authors will be checked.

The results of more general investigations of litho- and biostratigraphic correlations and of the lithogeochemistry of the Dinantian in the Vesder basin are also summarized and will be compared with the data of the Walhorn section. Therefore, the present study may contribute to a better understanding of the stratigraphy and the lithogeochemical distribution in the Dinantian carbonates of the Vesder basin (E-Belgium).

I. GEOLOGICAL SETTING.

Figure 1A shows the geographical position of the Walhorn quarry (123E-224). The studied section lies about 500 m S of the Walhorn village, which is situated about 6 km W of the Belgian-German boundary at Eynatten. The exploitation consists of two quarries, a small one in the N and a large one in the S.

In a schematic cross-section (fig. 1B and C) five lithological units can be distinguished in the main Walhorn quarry :

1. Dolostones.
2. Banded palisade calcite beds.
3. Dolostone breccia with rusty coloured dedolomitization zones within and on top of this unit. The presence of a limestone breccia intercalation is explained by a small fault (JACOBS et al. 1982, fig. 3).
4. Limestone breccia.
5. Micritic, pelletic, intraclastic, oolitic and algal limestones.

A gradual transition exists between 4 and 5.

The limestones of the first, smaller quarry are described together with the limestones of unit 5, since they display similar features. These limestones are separated from the dolostones of the main quarry by an important fault.

II. LITHOLOGICAL AND SEDIMENTPETROGRAPHICAL FEATURES.

The different units show variable lithological and sedimentpetrographical features, which allow us to define their different sedimentary environments.

Unit 1 : The dolostones.

This unit is exposed over 35 m, the lower part being cut off by a fault. It consists of thin-bedded (average bed thickness : ± 40 cm), brown to brown-grey dolostones with a homogeneous and porous aspect. Weathering turns them into a brown friable rock. Very thin-bedded dolostones enriched in clay occur.

Crinoid ossicles (up to 30%) occur in the lower part of the unit. Some relicts of brachiopods and of plants were found. In thin sections, few foraminifer and ostracod

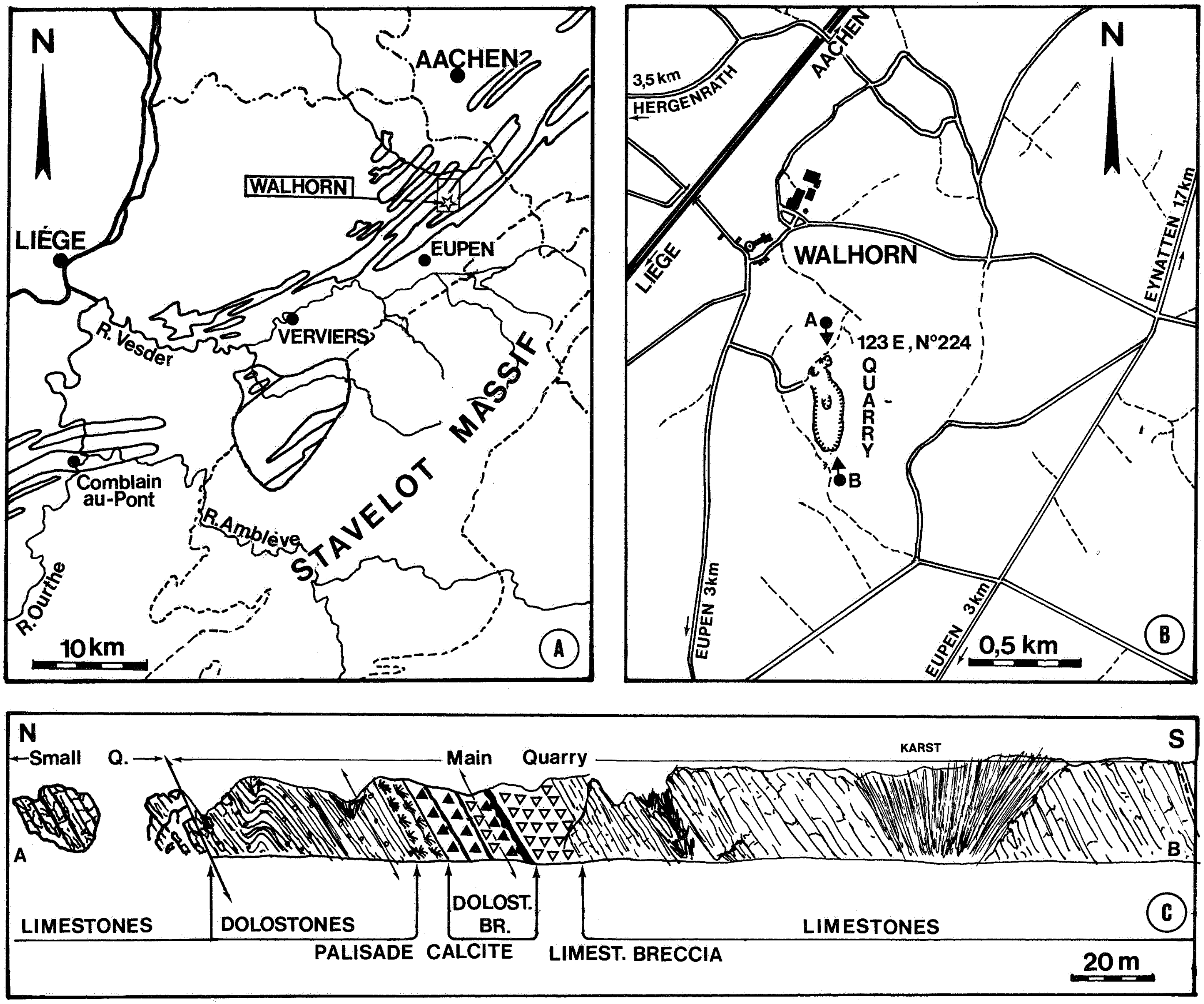


Fig. 1. Geographical position and schematic cross-section of the Walhorn quarry (123E n° 224) (Vesder basin, Belgium).

tests can be observed. Near the top of the unit, relicts of birdseyes and fine-laminated dolostones occur.

The dolostones consist of impure dolomicrosparite to dolosparite ($\overline{X} = 60\ \mu$). The grain size distribution is homogeneous. Normally anhedral dolostone grains occur, often characterized by a cloudy central part and a clear rim. However, rhombohedral dolomite crystals developed in clayey beds. Up to 8% of detrital quartz grains may be present. Iron oxides/hydroxides are common in the clay enriched beds.

Dolomite geodes occur in various amounts over the entire unit, while quartz geodes and black chert nodules are restricted to the lower part of the unit. These quartz geodes have an irregular, cauliflower-like outline (Plate A1). They often display a mosaic, chicken-wire structure. The geodes contain quartzine (lenght-slow chalcedony), different forms of megaquartz, with small lath-shaped anhydrite inclusions (Plate A2).

Interpretation.

In the upper part of the unit, the relicts of birdseyes and the finely laminated dolostones, which are similar to dolomitized stromatolites, point to an inter- to supratidal sedimentation environment of the original carbonate phase. The lower part, which is enriched in crinoïds, is sedimented in some deeper sedimentation environment (inter- to low subtidal). This interpretation is also confirmed by the presence of quartz geodes. The occurrence of length-slow chalcedony and small lath-shaped anhydrite inclusions indicates their pseudomorphous character (FOLK and PITTMAN (1971), CHOWNS and ELKINS (1974), MILLIKEN (1979) and others...). These quartz geodes are similar to the anhydrite nodules described from supratidal sediments in the Persian Gulf (SHEARMAN (1966), KINSMAN (1966), BUTLER (1969) and others ...).

Dolomitization probably occurred late-diagenetic. The cloudy centers of the secondary dolomite crystals may be the result of non-dolomite inclusions.

Unit 2 : The banded palisade calcite beds.

About 5 m of grey to blue-grey calcite beds follow concordantly on the dolostones of unit 1. These beds are characterized by coarse-grained, fibrous, radiating calcite crystals (rosettes) which can be up to 4 cm in length (Plate A3). Some beds are conglomeratic to pseudobreccious.

In a detailed sedimentpetrographic description SWENNEN et al. (1981) distinguished several successions of three subunits;

A : an intraformational conglomerate and breccia;
B : a grumelous microsparite-micrite layer;
C : a palisade calcite, with large vertically oriented conical calcite rosettes.

Interpretation.

The palisade calcite crystals are interpreted as pseudomorphs after gypsum. The successions are deposited in an environment ranging from intertidal to supratidal and restricted (SWENNEN et al. 1981).

Unit 3 : The dolostone breccia.

This breccia (thickness : 11 m) is composed of grey to brown dolostone fragments, ranging in size from 1 mm to 30 cm, cemented by a brown-grey fine-grained dolomite. Well-rounded as well as angular fragments occur. Fragments with apparent crumbled edges are typical. This breccia is characterized by the complete absence of fauna.

The grain size distribution within the breccia fragments is homogeneous but varies from fragment to fragment from dolomicrite to dolosparite. Birdseyes with geopetal infillings and up to 5% detrital quartz grains are recognized.

The grain size distribution of the matrix is heterogeneous. Dolosparite grains of different sizes are embedded in a dolomicritic mud. Collapse and slump structures are the most peculiar features.

Several rusty coloured dedolomitization zones occur within and on top of the dolostone breccia. Their thickness ranges from a few decimeters to two meters.

A detailed description of this breccia can be found in JACOBS et al. (1982).

Interpretation.

A supra- to intertidal sedimentation environment of the original carbonate phase is indicated by the occurrence of birdseyes and possibly by the high amount of detrital quartz grains.

Since a late-diagenetic dolomitization would have homogenized the grain size distribution of the breccia fragments and the matrix, an early diagenetic dolomitization is suggested, giving a primary dolostone. Primary dolostone is used here to mean dolomite by penecontemporaneous replacement of a calcareous sediment which is essentially coincident with deposition. The term secondary dolostone is used if a post-depositional replacement of limestones or calcareous sediments occurred. JACOBS et al. (1982) proposed an evaporitic collapse origin of this breccia. Collapse occurred early in the diagenetic history. The same authors interpreted the dedolomitization zones as paleosurfaces.

Unit 4 : The limestone breccia.

On top of the upper dedolomitization zone of the dolostone breccia, a 13 m thick limestone breccia occurs. In the lower part of the unit, fine-grained breccious limestones predominate, while the upper part consists of a limestone breccia without any bedding planes.

The breccia fragments range in size from 1 mm to 20 cm (Plate A4). Rounded as well as sharp-bordered fragments, often fitting into each other, occur. Main sedimentpetrographic features of the fragments are the occurrences of packstones and/or mudstones containing micritic pellets and intraclasts, of concentric pisolites and of mudstones with birdseyes. The matrix is microsparitic to sparitic, with calcispheres.

Calcite pseudomorphs after evaporitic minerals (gypsum, anhydrite and probably halite) occur.

A detailed description of these strata and of the pseudomorphs can be found in JACOBS et al. (1982).

Interpretation.

JACOBS et al. (1982) presume an inter- to supratidal restricted sedimentation environment for the limestones. An evaporitic collapse origin is accepted for the breccia formation.

Unit 5 : The limestones.

Above the limestone breccia, and with a gradual transition, 110 m of blue-grey limestones occur. The lowest 10 m are breccious. The upper limit of the unit is taken at the base of a 30 cm thick brown-yellow bentonite bed, being the Banc d'Or de Bachant.

A detailed sedimentpetrographical examination revealed the occurrence of 4 successive sequences (Fig. 5); each one composed of up to 5 typical lithologies. These are : micrite ("mudstone"); intrapelmicrosparite to intramicrosparite ("packstone"); intrasparite ("packstone"); oöintramicrosparite to intraoösparite ("packstone" to "grainstone"); pelintraoöbiomicrosparite to biosparite ("packstone" to "grainstone").

Each sequence starts with thin bedded bituminous calcilutites (micrites : "mudstones"), often characterized by the occurrence of birdseyes with geopetal infillings, of detritic quartz grains (up to 5%) and of pseudomorphs after evaporitic minerals. Calcispheres, ostracod shell fragments and algal clasts are locally present. This lithology is often red stained in thin sections. It is followed by calcilutites composed of dense packed micritic pellets and intraclasts. A gradual transition to the following lithology, the intrapelmicrosparite to intramicrosparite ("packstone") occurs. Algal clasts, oncolites, algal laminites, as well as lumps are present in variable concentrations. To the top the pelletic amount decreases and an intrasparite ("packstone") starts to develop. An alternation of this lithology with the foregoing intrapel- to intramicrosparite often occurs. Gradually, proto-oölites and oölites occur, which become more and more important to form the fourth lithology, the oömicrosparite to intraoösparite ("packstone" to "grainstone"). The bed thickness also increases. This lithology is often associated with large algal clasts and aggregates of intraclasts and oölites. A bad sorting of the allochems is characteristic. To the top, the concentration of bioclastic material increases, and the fifth lithology becomes apparent (pelintraoöbiomicrosparite to biosparite; "packstone to "grainstone"). Brachiopod and ostracod shell fragments, corals and algal relicts are the most common bioclasts. With the exception of the first sequence, all sequences are characterized by increasing concentrations of crinoid ossicles. The crinoids and brachiopods often possess a syntaxial rim cement. Relative high amounts in foraminifera only occur in the last two sequences. The biosparite lithology is also characterized by the development of coated grains.

Interpretation.

The different lithologies indicate a transgressive character in each of the four sequences, varying from a supra- to intertidal to an inter- to subtidal turbulent sedimentation environment.

An overall transgressive tendency is present in this formation. It is indicated by the increasing proportion of bioclasts in lithology five, by the absence of crinoid ossicles in the lowest sequence, by the low amount of foraminifera in the two lowest sequences in comparison to the overlying sequences, by the decreasing thickness of the sequences, and possibly by the decreasing thickness of the first micritic lithology over the whole formation.

It is to be remarked that at the boundary of sequence 2 and 3 and in the lower part of sequence 3, different bentonite beds occur. Probably they are related to the abrupt facies changes.

III. STRATYGRAPHY.

a. LITHOSTRATIGRAPHY AND CORRELATIONS.

Fig. 2 shows the lithostratigraphical position of the Walhorn section and its correlation with adjacent regions. The following formations are present :

THE VESDER DOLOSTONE FORMATION.

The described brown to brown-grey secondary dolostones form the upper part of the Vesder Dolostone Formation (BOONEN, 1978 : "Formation des Dolomies de la Vesdre"). These dolostones occur in many sections within the Vesder basin, but so far no complete succession is known.

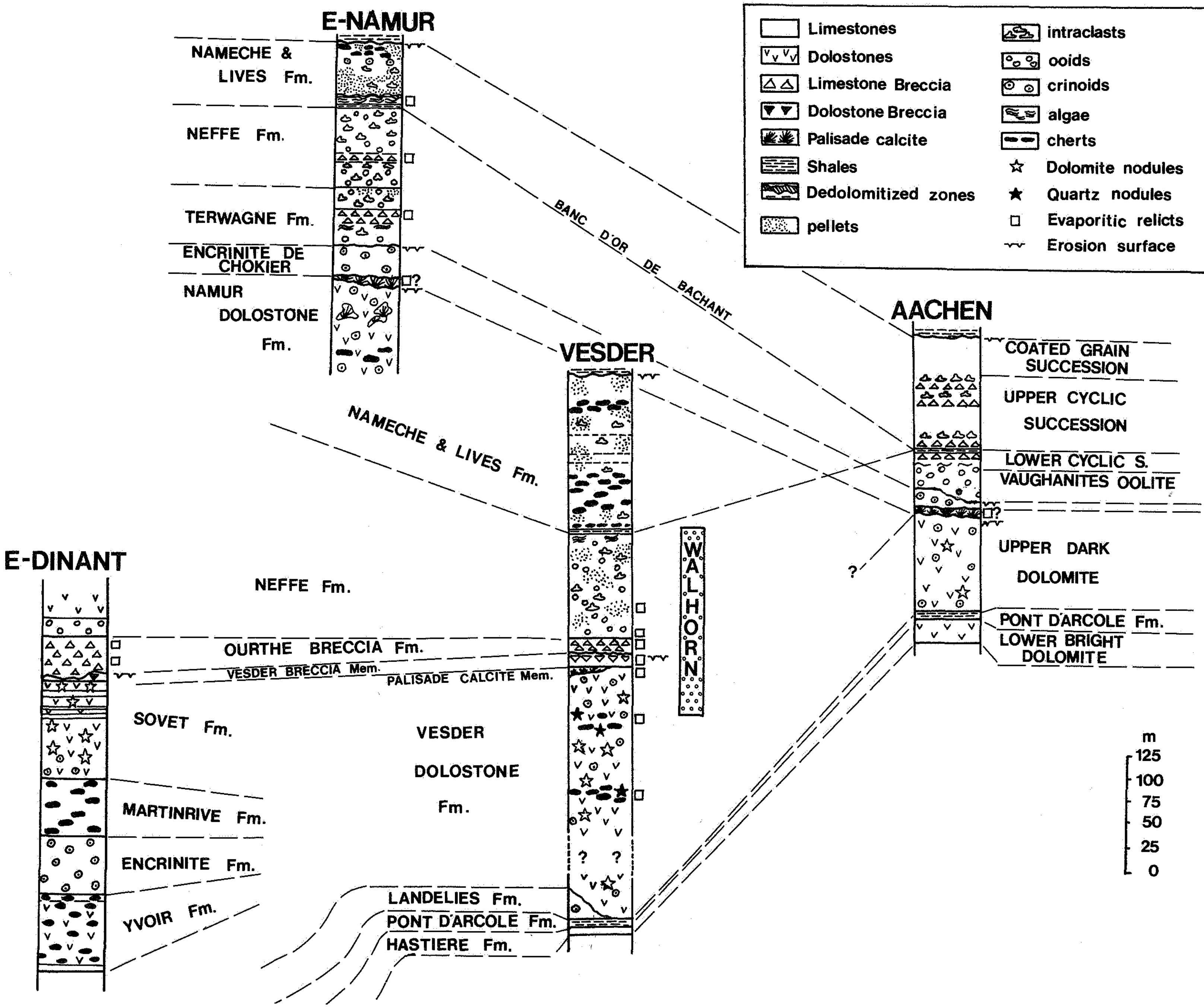
The lower limit of this formation, is best exposed in the Dolhain (136W - 1) and Bilstain sections (136W - 172). Here the contact with the undolomitized crinoidal limestones of the Landelies Formation (Tn2b : Hastarien TI) is exposed. The dolomitization cuts across the bedding of these limestones.

The dolostones are lithologically comparable to the Sovet Formation dolostones (Dinant Basin, CONIL et al. 1967), the Namur Dolostone Formation (Namur Basin; de DORLODOT (1895) "Formation des grandes Dolomies de Namur") and the Upper Dark Dolomite (Aachen area; KASIG (1980). A detailed subdivision of the Vesder Dolostone Formation has not yet been accomplished.

JACOBS et al. (1982) defined two members at the top of this formation : the palisade calcite member and the Vesder breccia member, respectively unit 2 and unit 3 of the Walhorn outcrop. However, the palisade calcite member is only known in the Vesder basin from this quarry and the Vesder breccia member is, if present, very reduced in thickness in other locations (e.g. Dolhain 136W - 272). Nevertheless, in different outcrops, the top of the Vesder Dolostone Formation is often characterized by a dedolomitized surface.

A nearly similar light grey, fibrous (palisade) calcite spar is known on top of the Namur Dolostone Formation in the Namur basin (SWENNEN et al., 1981 appendix) and on

Figure 2. Lithostratigraphy of the Walhorn section and its correlation with adjacent regions.



top of the Upper Dark Dolomite in the Aachen area (KASIG, 1980). A lithological correlation of these units with the palisade calcite member of the Vesder Dolostone Formation may be possible, but has to be verified. No similar palisade calcite spar from the Dinant basin is reported at this stratigraphic level. Here the top of the Sovet Formation is characterized by ripple marks (Belle-Roche quarry).

A dolostone breccia, similar to the Vesder breccia member is only reported from the eastern part of the Dinant basin by LOHEST (1911).

THE OURTHE BRECCIA FORMATION.

The Limestone breccia (unit 4) in the Walhorn section shows identical lithological features as the Ourthe Breccia Formation in the eastern part of the Dinant basin. A lithostratigraphic correlation between both was already suggested by VARLAMOFF (1937). A common origin, namely an evaporitic collapse breccia, is accepted for both breccias (JACOBS et al., 1982).

This limestone breccia is known from several localities in the Vesder basin (Bai-Bonnet 135W - 89, Soiron 135E - 435, Dison 135E - 74,75, Hergenrath 123E - 156, Eynatten 123E - 141, etc...). No similar limestone breccia has been reported neither from the Namur basin, nor from the Aachen area.

THE NEFFE FORMATION.

The blue-grey limestones (unit 5) show similar features to the Neffe Formation of the Dinant basin. The oölitic character is a distinctive common feature.

The correlation of these limestones with the Vaughanites oölites of the Aachen region as suggested by BOONEN and KASIG (1980) has to be verified, since in the Aachen area another lithological succession has been developed. Here, a sometimes crinoidal limestone occurs on top of the fibrous (palisade) calcite spar.

b. BIOSTRATIGRAPHY.

All thin sections and acetate peels have been investigated for foraminifera and algae. Several samples of the dolostone and limestone unit have been dissolved in formic acid in search of conodonts.

- Conodonts

Conodonts have not been discovered from the dolostones of the Vesder Dolostone Formation or from the limestones of the Neffe Formation in the Walhorn quarry. However, a small abandoned quarry at Eynatten (123E - 141) has revealed a few conodonts in the limestones of the Neffe Formation. This small fauna (1 to 2 specimens/kg in only one bioclastic limestone bed) contains Cloghergnathus rhodesi, Cloghergnathus aff., C. globenskii and Spathognathodus scitulus. This indicates a Lower Visean age (Moliniacian). Although, the group of conodont genera with a lateral free blade (Clydagnathus, Cavusgnathus, Cloghergnathus) needs to be studied in more detail.

- Foraminifera

Vesder Dolostone Formation.

Well preserved foraminifera were recognized in thin sections of the chert nodules, occurring in the lower part of this section. Septabrunsiina, Endothyra, Eblanaia, Brunsia and probably Spinoendothyra were recognized (determination by R. CONIL). Pachysphaerina pachysphaerica often occurs. In the dolostones itself, foraminifera occur sporadically but in a very bad state of preservation. Some Endothyroid forms are recognized as well as Tournayellids with a Forshiella-like outline. A Palaeotextularia sp. is to be mentioned with all reserves.

The foregoing foraminifera assemblage is indicative for a Lower Visean (Moliniacian) age. Furthermore a few specimens of Pachysphaerina pachysphaerica also indicates a Visean age for the Palisade Calcite member.

Ourthe Breccia Formation.

From these limestone breccias, only some Pachysphaerinoids are known. Pachysphaerina pachysphaerica is indicative for the Visean.

Neffe Formation.

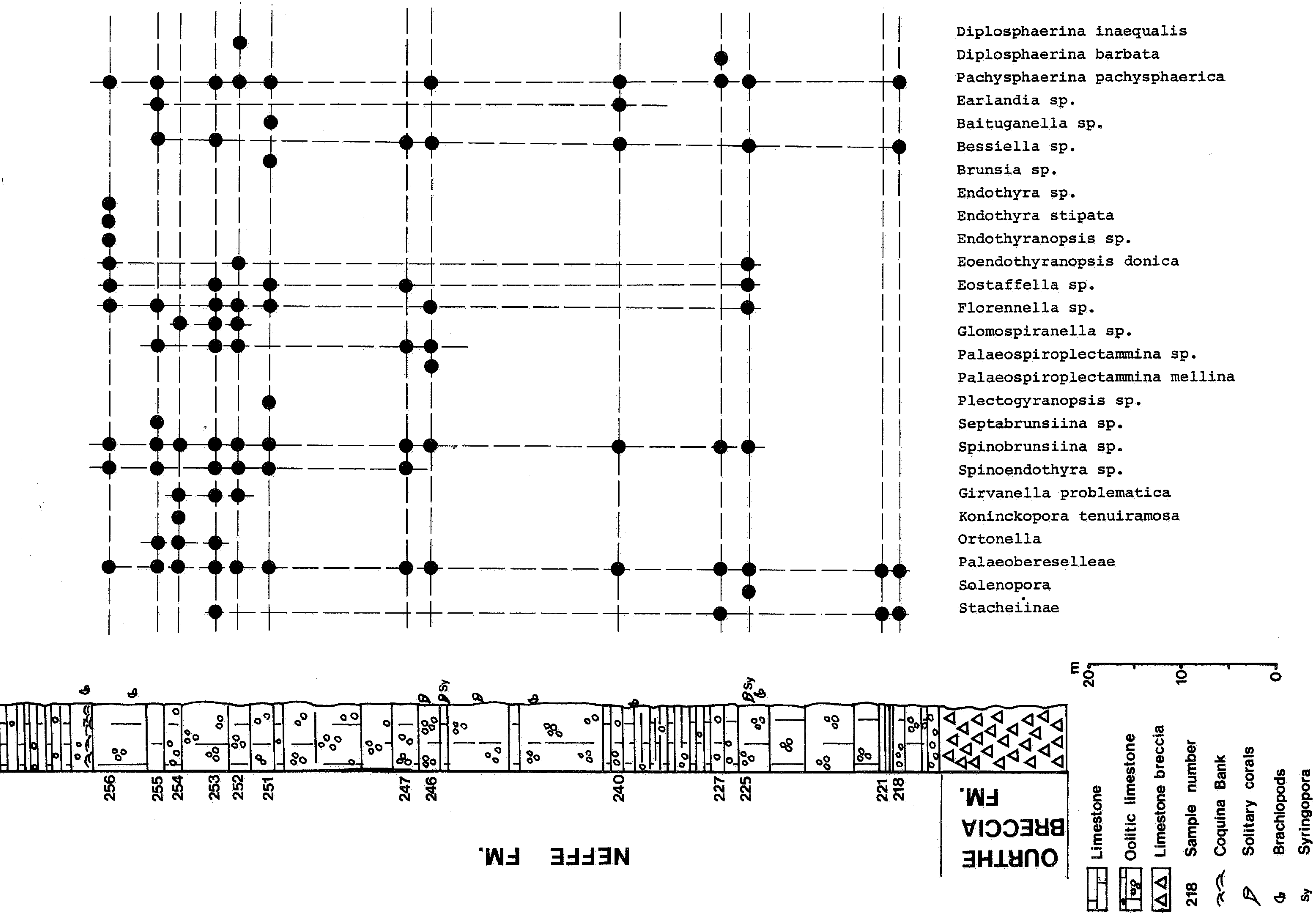
Several bioclastic beds in the Neffe Formation have yielded a foraminifera fauna which allows biostratigraphical interpretations. A fauna list is represented in figure 3.

With Bessiella, Florenella and Eoendothyranopsis the fauna is typical for the Cf 4 (Eoparastaffella)-zone (V1a-V2a or VI-Lower Visean - CONIL et al. 1976). The presence of koninckopora with a differentiated wall, in the top of this unit, places the fauna in the upper part of the Cf 4-zone (V2a).

c. INTERPRETATION.

The litho- and biostratigraphical data of the units with evaporitic features, indicate the development of different evaporitic periods during Lower Visean times. A spatial relationship between the development of evaporites and the primary and secondary dolostones of the Vesder Dolostone Formation is present. Dolomitization within this unit clearly proceeded downwards from its stratigraphical top and took place by hypersaline refluxing brines (SWENNEN et al. 1982, figure 3). Due to the precipitation of gypsum, the Mg/Ca ratio of the residual brine was high enough to dolomitize the calcareous sediments, yielding the primary dolostone. However, the bulk of these brines penetrated downwards, to dolomitize the underlying carbonates, yielding the secondary dolostone. The evaporitic sequence, equivalent to the Vesder (collapse) breccia member, certainly was one of the most important of the Lower Visean. Consequently, it was also an important dolomitization generating unit. However, other evaporitic strata, inducing dolomitization of the underlying strata, are necessary to explain the thick unit of secondary dolostones. At least two of them were already recognized in the Lower Visean, below the Vesder breccia member, in the

Figure 3. Foraminifera assemblages of the Neffe Formation in the Walhorn section.



St-Roch section (Limbourg : research in progress). Similar models have been described by DEFFEYES et al. (1965), SEARS and LUCEA (1980) and others.

NICHOLS and SILBERLING (1980) introduced the term eogenetic, for a similar relationship between primary and secondary dolostones. This term is used when newly deposited sediments are buried at a depth shallow enough to be affected by processes that either operate from the depositional surface or depend upon the proximity of this surface (CHOQUETTE and PRAY, 1970). Later, NICHOLS and SILBERLING (1980) concluded that processes like reflux dolomitization involving surface-derived solutions, show typical eogenetic features. They differentiated five to six main features, which also apply to the studied Tournaisian-Lower Visean dolostones of the Vesder basin.

The main features are :

- Unaltered non-dolomitized limestones which are replaced by eogenetic sugary secondary dolostones. They consist of crinoidal limestones of the Landelies Formation.
- The lower boundary of the secondary dolostone cuts across the bedding of the unaltered crinoidal limestones (figure 2).
- The upper boundary of the secondary dolostones is a well defined stratigraphical surface; in the Walhorn section it corresponds to the palisade calcite member.
- The microcrystalline textures and dessication features often occurring in primary dolostones (NICHOLS and SILBERLING, 1980), are also present in the Vesder breccia member. However, they are partly obliterated by the brecciation process.
- On top of this breccia, different dedolomitization zones, indicating paleosurfaces, were recognized. The occurrence of interbedded calcareous units has not been recognized within the primary dolostone breccia.

After collapse of the Vesder dolostone breccia, and after aereal exposure causing the dedolomitized strata, a new evaporitic sequence developed. Since the evaporitic stage was not sufficient enough to generate dense and high Mg/Ca dolomitizing brines this unit remained unaffected.

The present litho- and biostratigraphical data indicate that the studied formations can be correlated with the eastern part of the Dinant basin. This supports a single sedimentary basin. The correlation with the Namur basin and the Aachen area are less clear since different lithological sequences developed. In both areas, a considerable stratigraphical gap is present on top of the dolostones. Furthermore the overlying (palisade) calcite spar is often followed by a $\sim$ 20 m thick crinoidal limestone unit ("Encrinite de Chokier" in the Namur basin). The Ourthe Breccia Formation is absent. The Visean limestones, which occur on top of the crinoidal limestones, are characterized by several typical sabkha-like conglomerate-breccia units (JACOBS et al. 1982). No similar features have been observed either in the Vesder, or in the eastern part of the Dinant basin.

IV. LITHOGEOCHEMISTRY.

The analytical procedures for the analysis of Mg, Na, Sr, Zn, Pb, Fe, Mn, Ni, K, F, organic matter (Org C) and insoluble residue (IR) are the same as described by VAN ORSMAEL (1980, 1982). The uni- and multivariate statistics of the different lithologies are listed in table 1 respectively table 2. For the multivariate statistical analysis the programme FACTOR from the SPSS package (NIE et al. 1975) was used. The same treatment as described by VAN ORSMAEL (1980) and SWENNEN and VIAENE (1981) has been followed.

The geochemical profile, given in two parts, is shown in figure 4 and 5. For illustration purposes, different concentration scales are used.

- Univariate statistics.

THE VESDER DOLOSTONE FORMATION.

The upper part (51 m) of this formation, as exposed in the Walhorn quarry, is considered. The secondary dolostones are characterized by an irregular and variable distribution of most elements (figure 4). Relatively high Sr, Na, Fe, Zn and Org C concentrations occur (table 1). A positive correlation is clear between Zn, Fe, Mn, Ni, Na and IR. Furthermore a constant increase of Sr towards the overlying evaporitic strata is very characteristic. The Pb concentrations are very low. In the overlying palisade calcite member, only Sr displays an irregular variation, with a mean of 271 ppm (figure 4). Very low Na, Pb, Mn, Org C and F values (table 1) occur in this unit. The primary dolostones are characterized by very high and variable Na concentrations (figure 4). Also high Sr, Fe and Org C concentrations occur (table 1); they are comparable with the values of the secondary dolostones. The dedolomitized strata are characterized by low Sr, Na and by high Zn, Fe, Mn and Pb concentrations. Zn often reaches 1000 ppm. Therefore, a negative correlation between Mg, Sr, Na and Zn, Fe, Mn, Pb (Ni) is apparent (figure 4).

THE OURTHE BRECCIA FORMATION.

These limestone breccias are characterized by a high Sr content which constantly decreases towards younger lithologies (figure 4). A positive correlation between Zn and Fe occurs. High and variable Na, Zn, Fe, Mn and (IR) concentrations are present.

THE NEFFE FORMATION.

The general lithogeochemical distribution (figure 5) displays a normal, rather constant behaviour. A constant decrease, for Sr and Na occurs towards younger lithologies. This was also observed in the Ourthe Breccia Formation limestones. Three distinct zones are characterized by higher and variable concentrations for most trace elements. They are indicated in figure 5. These zones correspond to the thin - bedded micrites with birdseyes which occur at the base of the described sequences. Compared to the underlying limestone breccia (table 1), all trace element concentrations are lower.

FORMATION		NEFFE Fm.		VESDER DOLOSTONE FORMATION								OURTHE BRECCIA Fm.		NEFFE Fm.	
unit / element		limestones (small quarry)		secondary dolostones		fibrous palisade calcite		primary dolostone breccia		dedolomitization z.		limestone breccia		oolitic limestones	
		$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ
%	Mg	0.2	0.1	10.7	0.8	0.2	0.1	10.6	1.4	2.2	1.9	0.4	0.5	0.2	0.1
ppm	Sr	420	334	167	37	271	157	207	48	112	67	574	292	262	92
ppm	Na	81	25	206	97	47	8	427	165	92	59	126	56	67	41
ppm	Zn	53	50	86	83	44	19	66	85	852	382	211	253	43	80
ppm	Pb	9	12	3	3	2	2	3	3	52	38	18	20	18	26
ppm	Fe	861	796	2362	1991	1261	712	3099	1955	6551	3960	2019	2196	557	632
ppm	Mn	98	41	124	68	56	30	152	86	945	669	298	207	110	107
ppm	Ni	4	3	8	6	6	3	4	3	11	7	4	3	2	2
%	Org C	.05	.01	0.23	.19	.02	.01	.16	.05	.06	.06	.08	.04	.04	.02
%	IR	3.0	1.3	6.0	3.9	4.1	1.2	6.1	4.5	5.9	3.1	5.6	2.7	3.1	1.3
ppm	K	130	140	/	/	256	133	843	704	603	477	387	415	/	/
ppm	F	/	/	490	116	85	35	640	218	/	/	300	150	170	130
	270	n=21		n=73		n=10		n=24		n=11		n=24		n=107	

Table 1. Univariate statistics of different lithologies of the Walhorn quarry (X=mean, σ=standard deviation).

Figure 4. Geochemical profile of the Neffe Formation (small quarry), Vesder-Dolostone Fm and Ourthe Fm (main quarry) in the Walhorn section (H= Hiatus in outcrop).

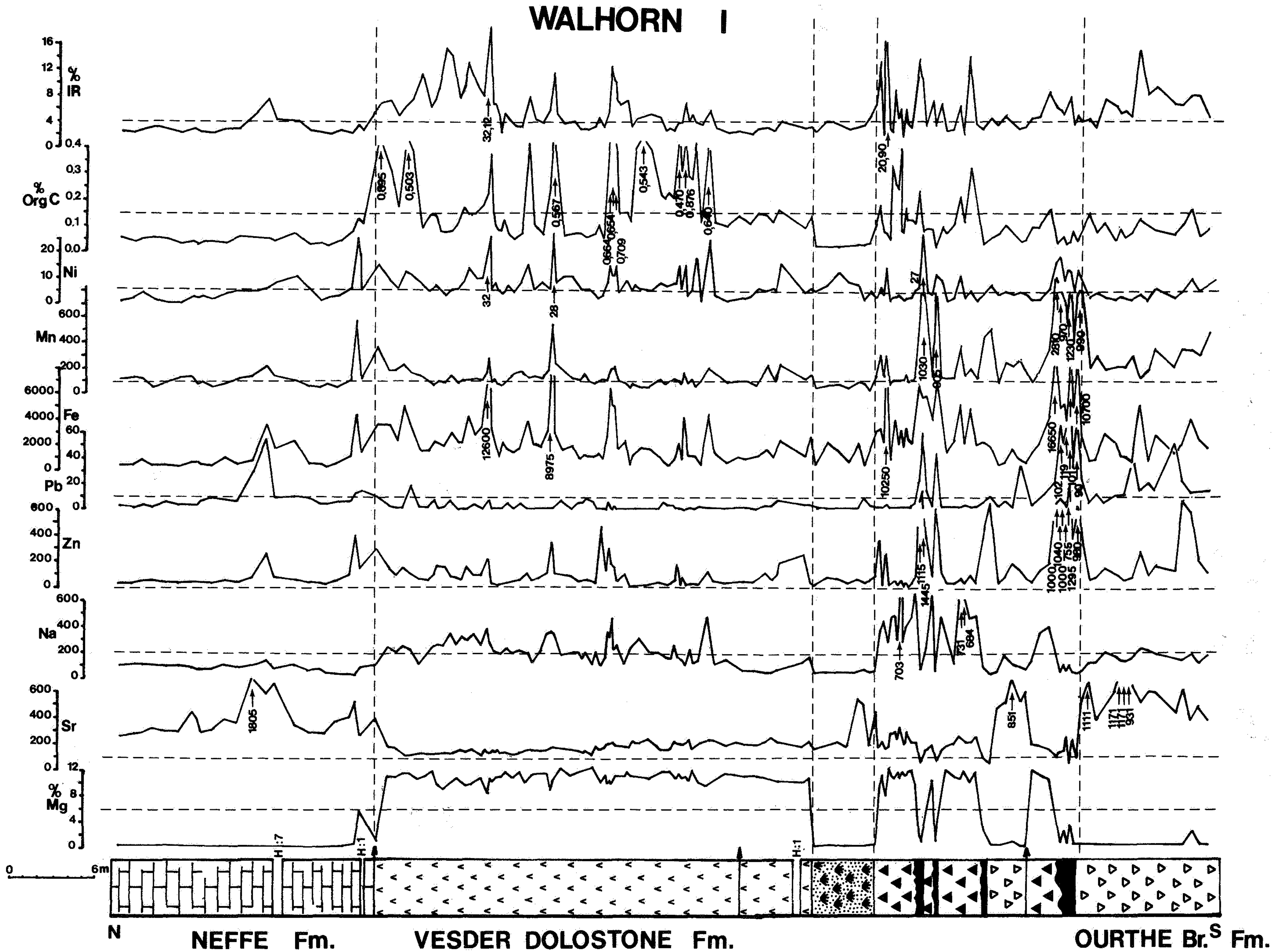
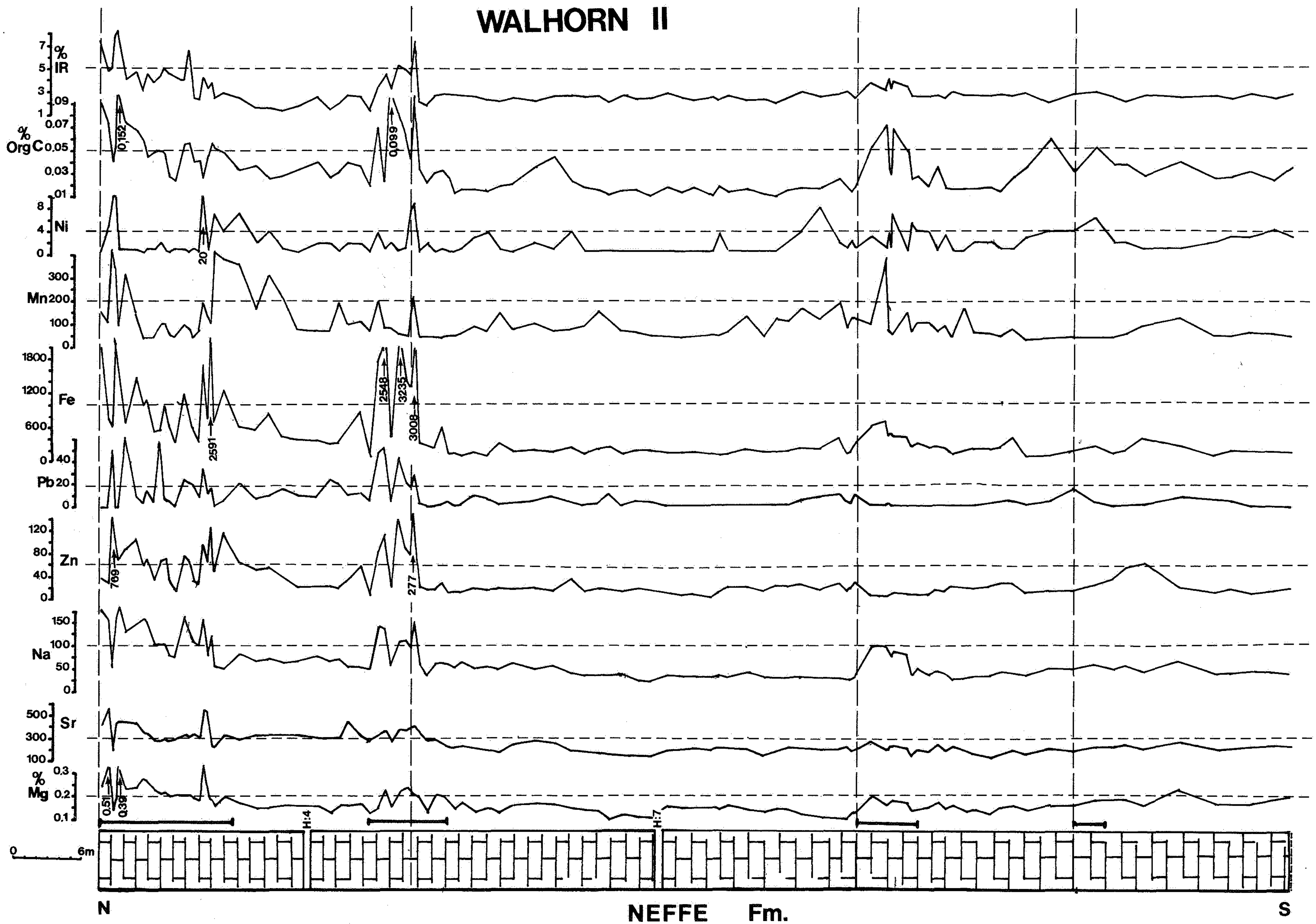


Figure 5. Geochemical profile of the Neffe Formation (main quarry) in the Walhorn section.



A part of the Neffe Formation is repeated in the smaller quarry, north of the dolostones. These limestones are characterized by a similar distribution (figure 4). Only north of the hiatus (H = 7 m), high Sr, Zn, Fe, Mn, Ni and IR concentrations occur.

FAULTS.

Different faults have been recognized in the Walhorn quarry (Figs. 1, 4). An important fault between the limestones of the smaller quarry and the dolostones of the main quarry, and two less important faults, one in the dolostones and one in the dolostone breccia are present (figure 4).

The first fault is filled up by coarse-grained brown coloured calcite. These calcites are characterized by high Zn ($\bar{X}$ = 667 ppm) and Pb ($\bar{X}$ = 128 ppm) concentrations. Very low concentrations occur for Sr ($\bar{X}$ = 32 ppm), Na ($\bar{X}$ = 16 ppm) and Mn ($\bar{X}$ = 124 ppm) (not given in figure 4). Whether the surrounding strata are influenced or not is difficult to evaluate. In the dolostones next to this fault, the higher Zn, Mn, (Fe and Pb) concentrations can be related to higher Org C contents.

Around the two other faults, an influence on the geochemical distribution has not been observed.

- Multivariate statistics.

THE VESDER DOLOSTONE FORMATION.

The multivariate analysis of this Formation was performed only on the eogenetic secondary and primary dolostones. The palisade calcite samples (N = 10), and the dedolomitized beds (N = 11) are excluded, since they have a calcitic mineralogy. Moreover, the last data disturbed the total factor analysis, since they caused a strong dedolomitization factor characterized by the association of Zn, Pb, Fe, Mn, (Ni) and Mg, Sr (both negative).

The factor analysis of the dolomitic strata shows a clear association of IR, -Mg, Fe, Zn, (Mn, Ni). This association is produced by the effect of the IR on the Mg content, and by the adsorption of metals on clay particles and possibly on Fe Mn oxides/hydroxides. It could be called a residue-adsorption factor. Since this factor shows high scores on the clay enriched thin - bedded dolostone samples, it is related to the lithology. The second factor (Org C, Ni, (Fe)) reflects the adsorption of Ni (Fe) by the organic matter. The third factor (Na, Sr) is related to the primary dolostones since highest positive factor scores occurred in these strata. This factor indicates the most hypersaline sequences. The last factor (Pb) possibly reflects the independent behaviour of Pb, as the low Pb concentrations are often near or below the detection limit.

THE OURTHE BRECCIA FORMATION.

The first factor (Zn, Fe, Ni, Mn, Pb) is interpreted as a coprecipitation/adsorption factor, where metals like Zn, Ni, Pb are fixed by Fe Mn oxides/hydroxides. This factor is similar to the mineralization factor in the Poppelsberg section (SWENNEN and VIAENE, 1981). However, the situation is different. In the Walhorn area no mineralizations are known, this being in contrast to the Poppelsberg area. Furthermore, highest factor scores occurred in the Poppelsberg section next to the faults, which were influenced by mineralization related solutions. In the Walhorn section, the factor scores, which are much lower than in Poppelsberg, do not show a control by faults.

The second factor (IR, Na, Org C) is a residue factor, since it is related to the limestone breccia samples with the highest insoluble residue content. The third factor (Sr, Org C) possibly reflects the shielding effect of Org C, inhibiting the loss of Sr during diagenesis. The last factor indicates the independant behaviour of Mg.

THE NEFFE FORMATION.

Only the limestones of the main quarry are considered. The first factor (Mg, Sr, Na, Org C (IR, Fe)) is controlled by the sedimentary environment. High factor scores occur for the micritic strata with birdseyes. Also the second factor (Zn, Pb, Fe, (Na, IR) shows high factor scores for these micritic strata. Here coprecipitation on Fe oxides/hydroxides and partly adsorption on clays play a role. The third factor (Ni (IR)) reflects the independent character of Ni and partly its adsorption on clays. Due to high and irregular concentrations of Mn, especially in the lower part of the formation, Mn plots as an independent fourth factor. Without those exceptional values, a covariant behaviour of Mn with Fe is apparent.

V. DISCUSSION OF THE LITHOGEOCHEMICAL RESULTS.

The data of the Walhorn quarry can be compared with published data of the Vesder syncline (SWENNEN and VIAENE, 1981) and of the Dinant Synclinorium (VAN ORSMAEL et al., 1980; VAN ORSMAEL, 1982). At Walhorn, most trace elements, except Sr, are higher in the dolostones than in the limestones. This feature is in contrast to the data of the Dinant synclinorium, where dolostones generally have lower trace element contents. In comparison with literature data about averages in carbonate rocks (e. g. GRAF 1960, WOLF et al. 1967) the high Zn content is striking. In the following paragraphs, the different formations will be treated separately.

THE VESDER DOLOSTONE FORMATION.

The Sr content or the calculated 1000 Sr/Ca ratio was proposed by VEIZER and DEMOVIČ (1974), KRANZ (1976), and others as a diagenetic indicator for dolostones and as a facies indicator in limestones.

In our case, a differentiation in Sr content between the primary dolostone breccia, and the secondary dolostones (respectively 207 ppm and 167 ppm) is possible. The 1000 Sr/Ca ratio confirms this observation; 0,91 (σ = 0,20) in the primary dolostones and 0,73 (σ = 0,15) in the secondary dolostones. However, the differentiation is weak, and can be explained by their eogenetic relation. The 1000 Sr/Ca ratio of the dolostone breccia fits well in the early

	VESDER DOLOSTONE FORM. (N = 97) (without palisade without dedolom.)					OURTHE BRECCIA FORM. (N = 23)					NEFFE FORMATION (N = 104)				
FA	F1	F2	F3	F4	comm.	F1	F2	F3	F4	comm.	F1	F2	F3	F4	comm.
eigenv.	4.00	1.69	1.12	0.99		4.33	2.11	1.01	0.79		5.26	1.34	0.99	0.76	
%	40.0	16.9	11.2	9.9		43.3	21.1	10.1	7.9		52.6	13.4	9.9	7.6	
Σ	40.0	56.8	68.0	77.9		43.3	64.4	74.5	82.4		52.6	66.0	75.9	83.5	
Mg	-0.89	0.00	-0.11	0.17	0.82	-0.05	-0.12	0.01	0.98	0.98	0.93	0.05	0.02	-0.09	0.87
Sr	-0.32	0.26	0.74	-0.19	0.75	-0.42	-0.04	0.77	0.10	0.78	0.81	0.32	-0.06	0.23	0.82
Na	0.35	-0.08	0.81	0.03	0.79	-0.37	0.83	0.07	-0.04	0.84	0.80	0.49	0.06	0.04	0.89
Zn	0.70	0.20	-0.21	0.16	0.59	0.93	0.00	-0.10	0.05	0.87	0.30	0.82	0.26	0.15	0.86
Pb	0.02	-0.07	-0.11	0.93	0.89	0.71	-0.17	-0.30	-0.27	0.69	0.14	0.79	-0.29	0.25	0.80
Fe	0.80	0.33	0.25	0.19	0.85	0.90	0.20	-0.22	0.08	0.91	0.42	0.79	0.26	0.02	0.87
Mn	0.50	0.21	0.32	0.39	0.55	0.79	-0.31	0.06	-0.09	0.73	0.07	0.17	0.23	0.90	0.90
Ni	0.51	0.68	-0.19	0.27	0.83	0.82	-0.10	-0.29	-0.05	0.77	0.04	0.07	0.88	0.24	0.83
Org C	0.10	0.91	0.19	-0.16	0.90	-0.02	0.63	0.62	-0.18	0.81	0.71	0.36	0.24	0.18	0.72
IR	0.90	0.09	0.01	0.05	0.81	0.12	0.93	-0.02	-0.06	0.88	0.55	0.53	0.40	-0.21	0.80

Table 2. Factor analysis results of the different Formations of the Walhorn section

diagenetic field, deduced by VEIZER and DEMOVIČ (1974, fig. 3).

The Sr values, present in the secondary dolostones of the Walhorn section are high in comparison to the data of the Poppelsberg section ($\bar{X}$ = 96 ppm; σ = 10 ppm). Low values, similar to the ones in the last section, were reported from secondary dolostones of the Sovet Formation of the E-Dinant basin. Furthermore, a constant increase in Sr content towards the overlying strata, with highest values in the evaporitic collapse breccia is apparent in the Walhorn dolostones (figure 4). This behaviour is confirmed by research in progress. Since the dolomitization process is uniform for all these strata, (dolomitization by refluxing hypersaline brines) this feature is in relation to the Sr concentration of the original limestone strata. Since highest concentrations occur near and in the evaporitic equivalents, the increase in Sr reflects an increase in paleosalinity, which is even preserved after dolomitization.

VEIZER et al. (1978) proposed the soluble Na content as a mesure of paleosalinity for Paleozoic rocks. Moreover, the Na content was used as a diagenetic indicator in dolostones by WEBER (1964) and FRITZ and KATZ (1972).

For the secondary dolostones of the Walhorn section relatively high Na contents were found ($\bar{X}$ = 206 ppm, σ = 97 ppm). Similar high concentrations are found in the Tournaisian 2b equivalents of the Vesder Dolostone Formation ($\bar{X}$ = 181 ppm; σ = 38 ppm : SWENNEN and VIAENE 1981) and are also confirmed by recent data (unpublished). Since, the limestones are characterized by lower Na concentrations than the dolostones (e.g. table 1), and since the dolomitization process was of the same type over the whole unit, the constant high Na contents are related to the dolomitizing solution itself, rather than to the paleosalinity of the original carbonate phase. Otherwise an increase in Na content towards the dolostones breccias, as found for the Sr distribution, could be expected. The relatively high Na concentration of these dolostones is in agreement with the dolomitization by refluxing hypersaline brines.

The primary evaporitic dolostone breccia possesses very high Na contents ($\bar{X}$ = 427 ppm; σ = 165 ppm). This high Na content confirms the evaporitic nature of this breccia, and its associated hypersaline sedimentation environment. The relation with the hypersaline facies is also confirmed by the covariant behaviour of Na and Sr (factor 3, table 2).

In comparison with the data of the Poppelsberg section, the dolostones of the Walhorn section show higher but variable Fe content, comparable Zn and Mn content, but lower Pb content. There are also differences in the association of the elements as demonstrated by the factor analyses. In Poppelsberg we have the association Zn, Fe, Mn (Ni, Pb) which is controlled by the development of irregular halos around faults. In Walhorn these elements are lithologically controlled, and therefore associated by IR, -Mg. Here adsorption on clays and possibly coprecipitation with Fe Mn oxide/hydroxides groups the variables. This factor explains 40 % of the total variance. This fact, and the low Pb concentrations suggest that there is no influence of nearby mineralizations.

The high Org C content in the dolostone strata probably indicates an oxygen deficiency of the sedimentary environment, corresponding to a restricted nearshore environment with hypersaline tendencies.

The dedolomitization zones are characterized by very high Fe, Mn, Zn, Pb and Ni concentrations. Since dedolomitization occurred on the dolostone breccia itself, a comparison between the mean concentrations (table 1) of both lithologies may help us to characterize the dedolomitization process. Dedolomitization removes Mg, Sr, Na, (K and Org C), but increases the concentration of Zn, Pb, Fe and Mn. Zn and Pb are concentrated by a factor 15. These high concentrations are probably linked to the Fe oxide/hydroxide coatings, found around the dedolomitized crystals. Low Sr concentrations for dedolomites were also published by SHEARMAN and SHIRMOHAMMADI (1969) and MAGARITZ and KAFRI (1981) indicating the loss of Sr during dedolomitization.

The factors for the Walhorn dolostones are mostly representative for the Vesder Dolostone Formation at least if the dolostones are not influenced by mineralization. Factor 1 (IR, -Mg, Fe, Zn, (Mn, Ni)) reflects the influence of clay adsorption and possibly coprecipitation phenomena; Na and K are often added to this factor. This factor is not restricted to the dolostones, it often occurs in limestones too. In sections where influences of nearby mineralizations are present, this factor is lacking. Instead a mineralization factor (Zn, Pb, Fe, Mn) developed, characterized by high concentrations of these elements and high factor scores near the mineralization or fault, and by its independency from lithological features (e. g. Poppelsberg and Schmalgraf section, SWENNEN and VIAENE, 1981). Factor 2 (Org C, Ni, (Fe, Zn, Pb)) often occurs in dolostone sections. Normally a typical dolomitization factor occurs (Mg, -Sr, Na). However, this factor is lacking in the Walhorn section due to the strong Na-Sr correlation in the primary dolostones.

THE OURTHE BRECCIA FORMATION AND THE NEFFE FORMATION.

The evaporitic limestone breccia possesses high Sr and Na contents compared to the overlying limestones of the Neffe Formation. In these breccias also a higher 1000 Sr/Ca ratio occur ($\bar{X}$ = 1,69; σ = 0,67) than in the limestones ($\bar{X}$ = 0,67; σ = 0,23). These data are confirmed by the unpublished data of the Vesder basin (research in progress).

A decrease in the contents of both elements away from the evaporitic strata is apparent (figure 4 and 5), suggesting a facies control for both distributions. However, Na data must be treated carefully, since in the factor analysis an association of Na with the clays is clear. The facies control was already suggested by VEIZER and DEMOVIČ (1974), VEIZER et al. (1978) and others. Discussing the usefulness of Na distribution in discriminating between depositional environments of ancient carbonate rocks, the former concluded that the approximate boundary between normal marine and hypersaline environments can be placed at ≈ 230 ppm Na, with this limitation that the values in the 150-300 ppm range may not be diagnostic of either environment. The present data suggest that this approximate value must be lowered for the Dinant-Namur basin.

The inter- to supratidal micrites with birdseyes of the Neffe Formation show higher Na and Sr contents. This facies is characterized by higher contents for almost all trace elements.

Concerning the high Zn, Pb, Fe and Mn contents of the limestone breccia two interpretations may be involved : a possible influence by nearby mineralizations or a lithological control (e. g. Fe Mn oxide/hydroxide precipitation phenomena). The lack of any influence by mineralization related phenomena on the lithogeochemistry of the porous dolostones of the Vesder Dolostone Formation, the absence of any clear influence on the geochemical distribution around the faults and the lack of known mineralizations in this area favors the second interpretation. However, in the E-Dinant basin, which is barren in mineralizations, distinct lower contents for these elements were found (VAN ORSMAEL, 1982).

The factor analysis results of the Ourthe Breccia Formation in the Walhorn section mostly agree with the results of other sections of the Vesder basin. Only factor 3 (Sr, Org C) of the Walhorn section is different. This factor, which probably reflects the shielding effect of Org C, often occurs in different lithologies and stratigraphical levels (Plombières section, SWENNEN and VIAENE, 1981). It was also recognized in strata enriched in organic matter by VEIZER and DEMOVIČ (1974) and KRANZ (1976).

The first factor of the Neffe Formation (Mg, Sr, Na, Org C, (IR, F)) frequently occurs in limestones (Schmalgraf and Plombières section, SWENNEN and VIAENE, 1981). It is related to the sedimentary environment. Factor 2 (Zn, Pb, Fe (Na, IR)) is similar to the residue adsorption factor as found in the dolostones. Normally Mn is present in this factor.

CONCLUSIONS.

Five distinct lithological units are recognized in the Walhorn quarry. The first three units belong to the Vesder Dolostone Formation. In each of them features related to evaporites were found, indicating a shallow sedimentation environment (inter- to supratidal and restricted). These features are quartz pseudomorphs after anhydrite nodules in the dolostones, calcite pseudomorphs after gypsum in the palisade calcite member, and collapse-slump structures in the primary dolostone breccia of the Vesder breccia member. In and on top of the last unit, dedolomitization zones occur, indicating paleosurfaces. These units are overlain by the evaporitic limestone collapse breccia of the Ourthe Breccia Formation. A gradual transition to the overlying supra- to inter and inter- to subtidal limestones of the Neffe Formation occurs. On top of those, the Banc d'Or de Bachant was recognized.

Biostratigraphical and lithostratigraphical data indicate that the Walhorn strata can well be correlated with the eastern part of the Dinant basin, suggesting a single sedimentary basin. In analogy with the Sovet Formation and the Ourthe Breccia Formation of the eastern part of the Dinant basin, a Lower Visean age (Moliniacian age VI) is proved for the uppermost part of the Vesder Dolostone Formation and the Ourthe Breccia Formation. The overlying Neffe Formation belongs to the upper part of the Cf 4 (Eoparastaffella) zone (Moliniacian (upper part) VI).

The correlation with the Namur basin and the Aachen area is less clear. In these areas, a sometimes crinoidal limestone occurs on top of the fibrous (palisade) calcite spar ("Encrinite de Chokier" in the Namur basin).

The development of the Lower Visean evaporitic basin explains the underlying secondary dolostones. A dolomitization by refluxing hypersaline solutions occurred. An eogenetic relationship between the primary dolostone breccias and the underlying secondary dolostones was recognized.

A detailed lithogeochemical study revealed high trace element contents in several lithologies. The secondary dolostones and primary dolostone breccia are characterized by relatively high Sr and Zn contents, and by high to very high Na, Fe and Org C contents. The Pb concentration is very low. The high Fe and Zn concentrations are lithologically controlled, as confirmed by the factor analysis results. No relation with mineralizations could be observed. The high Org C content confirms the deduced restricted nearshore sedimentation environment.

Very high Fe, Mn, Zn, Pb and Ni concentrations and low Sr and Na contents are present in the dedolomitization zones. These high values are probably related to the Fe oxides/hydroxides coatings which developed around the dedolomitized crystals. The geochemical characteristics can be explained by weathering processes.

Relatively high Na, and high Sr, Zn, Fe and Mn concentrations occur in the limestone breccia compared to the overlying limestones. These high trace metal contents are probably controlled by Fe Mn coprecipitation adsorption phenomena as it is suggested by geological and geochemical criteria.

In the Neffe Formation limestones a rather constant distribution is present. Higher trace element concentrations are found only in the supra- to intertidal micrites.

The geochemical distribution and the lack of influences around faults suggests an absence of nearby mineralizations next to the Walhorn quarry.

Since high Sr and Na values occur in the strata with evaporitic origin, the use of both elements as paleosalinity and/or diagenetic indicators, as proposed by several authors, was checked.

A differentiation between primary and secondary dolostones is possible by Sr content. However the Sr distribution in the studied dolostones remains also related to the original carbonate phase. Highest Sr contents were found in the evaporitic limestones, and the contents decrease towards younger lithologies. This confirms the use of Sr as a possible paleosalinity indicator, and as a diagenetic indicator in dolostones.

A differentiation in Na content between primary and secondary dolostones is possible. However, the Na distribution is related to the nature of the hypersaline dolomitizing brines. A differentiation on the basis of the Na content between hypersaline and normal saline limestones is possible. However, the Na data must be treated with care, since part of the Na may be fixed by clays, as shown in the covariant behaviour of Na and IR. For the Na content, VEIZER et al. (1978) placed the division between hypersaline and normal saline environments near 230 ppm. The data of the Walhorn section suggest that this value must be lowered for the studied paleozoic strata.

Since a differentiation on the basis of the Sr and/or Na concentration between sub- and intertidal limestones is less clear we suggest that, in our case, both elements are only hypersalinity indicators rather than paleosalinity indicators.

The present data clearly shows that a detailed knowledge of geological, paleoenvironmental and sedimentpetrographical data is needed for an exact interpretation of the lithogeochemical distributions.

The multivariate analysis confirms that this geochemical distribution is determined by lithological features such as the adsorption by clay and/or by organic matter, coprecipitation with Fe Mn oxides/hydroxides and by the sedimentary environment.

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PLATE A1	Quartz geodes, occurring in the lower part of the exposed brown to brown-grey dolostones (unit 1). Typical feature is the irregular, cauliflower-like outline.
PLATE A2	Radiating calcite crystals (rosettes, pseudomorphous after gypsum) from the banded palisade calcite beds (unit 2). Bar = .3 cm.
PLATE A3	Megaquartz cristal, with some small lath-shaped anhydrite inclusions (arrow). Bar = .1 mm.
PLATE A4	Upper part of the limestone breccia (unit 4). Scale diameter = 6 cm.

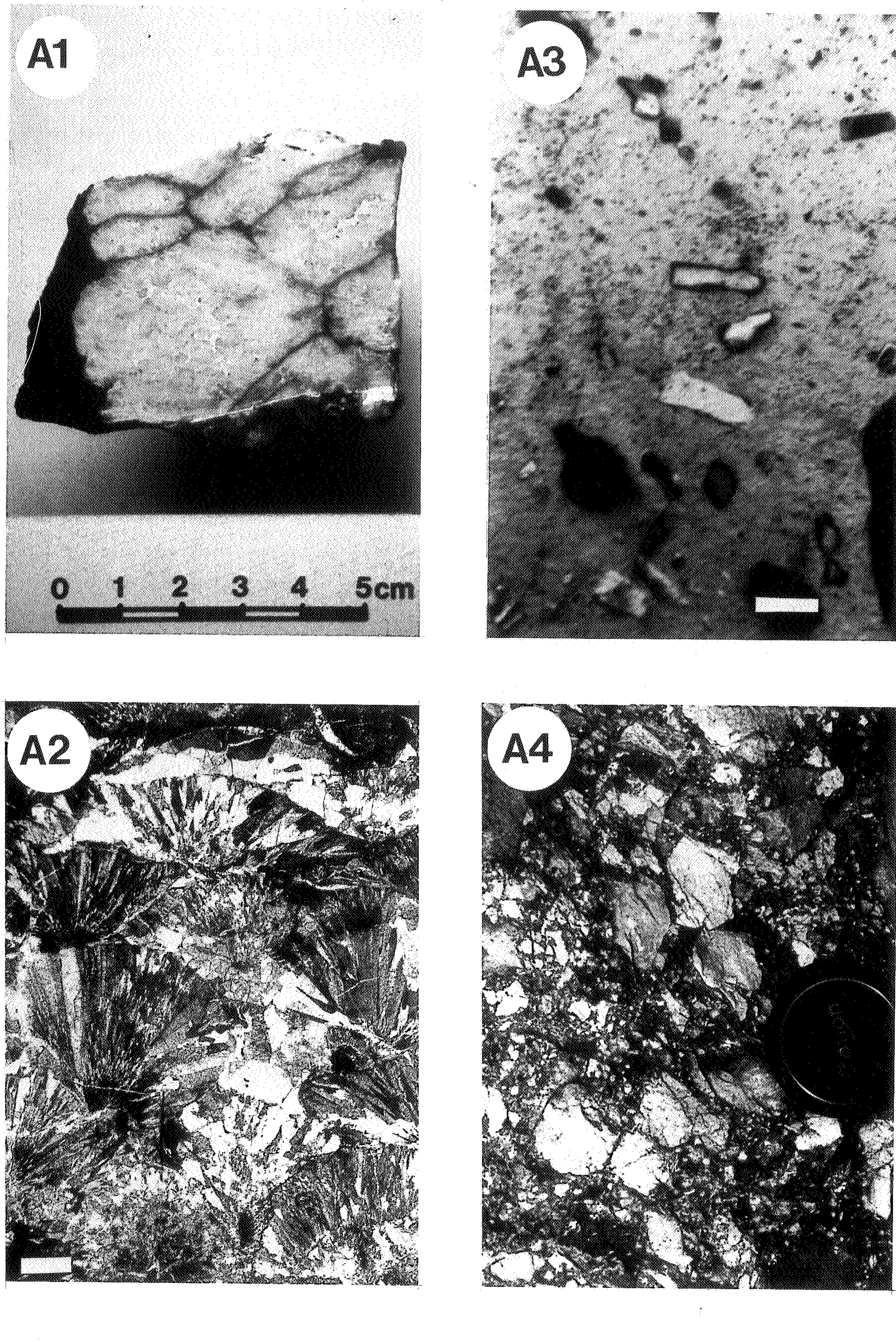
A1
0 1 2 3 4 5cm
A3
A2
A4

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TABLE DES AUTEURS - INHOUD

Tome 90 — Volume 90

ASSEMBLEE GENERALE du 23.2.1982 — ALGEMENE VERGADERING VAN 23.2.1982

1. Rapport du Président — 1. Verslag van de Voorzitter . . 3
2. Rapport du Trésorier — 1. Verslag van de Schatbewaarder . 6

BOCK, L. et MATHIEU, L. - La genèse des accumulations calcaires vue sous l'angle de l'approche géo-morpho-pédologique 19

CASIER, J.-G. - Les ostracodes du Frasnien et de la base du Famennien de la coupe du km 30 (Saoura, Sahara algérien) 195

DEJONGHE, L., GUILHAUMOU, N., et TOURAY, J. C. - Les inclusions fluides de la barite du gisement sédimentaire de Chaudfontaine (Province de Liège, Belgique) 79

DELMER, A. - André AMSTUTZ, notice nécrologique 237

GOOSSENS, D. - A pliocene river deposit in Mid-Belgium 61

GROESSENS, E., HANCE, L. et POTY, E. -

Le Moliniacien supérieur de Vinalmont.

GROESSENS, E. - Le calcaire de Vinalmont 127

HANCE, L. - Le Moliniacien supérieur de Vinalmont, sédimentologie, paléontologie, stratigraphie 135

POTY, E. - Les Tétracoralliaires du Calcaire de Vinalmont 153

GROESSENS-VAN DYCK, M.-Cl. - Note sur les chéloniens et les crocodiles du gisement paléocène de Vinalmont (Province de Liège, Belgique 163

GULINCK, M. (†) - Concrétions gréso-calcaires dans les dépôts tongriens . 235

HANGANU, E. N. et PAPAIANOPOL, I. - Associations significatives du Pontien du bassin dacique (Roumanie) 51

HECK, J. P. et HANOTIAUX, G. - Deux exemples de pédologie appliquée . . . 70

JACOBS, L., SWENNEN, R., VAN ORSMAEL, J., NOTEBAERT, L. and VIAENE, W. - Occurrences of pseudomorphs after evaporitic minerals in the Dinantian carbonate rocks of the eastern part of Belgium 105

JEDWAB, J. et DEJONGHE, L. - Contribution à l'étude minéralogique de l'indice radioactif de Daverdisse 217

MAMET, B. et PREAT, A. - *Givetianella tsienii*, une Dasycladacée nouvelle du Givétien de la Belgique 209

MINERALOGIE DE BELGIQUE (courtes notes rassemblées par UMIBEL)

- VAN TASSEL, R. - Mitridatite 50

- FRANSOLET, A.-M. - Ardennite 50

SWENNEN, R., BOONEN, P. and VIAENE, W. - Stratigraphy and lithogeochemistry of the Walhorn section (Lower Visean; Vesder basin, E-Belgium) and its implications 239

TOURNEUR, F. - Conodontes des trois "récifs de marbre rouge F2J". Stratigraphie et écologie 91

VAN RANST, E., DE CONINCK, F., TAVERNIER, R. and LANGHOR, R. - Mineralogy in silty to loamy soils of Central and High Belgium in respect to autochtonous and allochtonous materials 27

VAN RANST, E. and DECONINCK, F. - Composition and genesis of the ferruginous sandstones of the Diest and the Poederlee formations (Belgium) 45

COMPTES-RENDUS 187

Notice nécrologique : WEGMAN, Eug. (1896-1982) 161

SESSION EXTRAORDINAIRE - Biedenkopf, 17-21 octobre 1980 Compte-rendu par Eric GROESSENS, avec la collaboration de R. CONIL et de M. STREEL 9

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